Tuning of nanoantenna resonances in the mid-infrared spectral range using phase-change materials

Von der Fakultät für Mathematik, Informatik und Naturwissenschaften der RWTH Aachen University zur Erlangung des akademischen Grades einer Doktorin der Naturwissenschaften genehmigte Dissertation

vorgelegt von

Materialwissenschaftlerin, M.Sc.
Ann-Katrin Ursula Michel
aus Plauen im Vogtland

Berichter: Universitätsprofessor Dr. rer. nat. Thomas Taubner
Universitätsprofessor Dr. rer. nat. Matthias Wuttig


Diese Dissertation ist auf den Internetseiten der Universitätsbibliothek online verfügbar.
Tuning of nanoantenna resonances in the mid-infrared spectral range using phase-change materials

To the Faculty of Mathematics, Computer Science and Natural Sciences of RWTH Aachen University for the degree of Doctor of Natural Sciences in the subject of Physics

presented by
Ann-Katrin U. Michel
Master of Science in Materials Science from Plauen, Vogtland

Supervisors: Univ.-Prof. Dr. rer.-nat. Thomas Taubner
Univ.-Prof. Dr. rer.-nat. Matthias Wuttig
In nano-optics, the field of metamaterials (MMs) is emerging. Its focus lies on the effective optical properties of resonant subwavelength metal nanoparticles, which allow for a variety of artificial effects, such as negative refraction, nanofocusing of light or sensing and imaging.

This thesis investigates hybrid nanophotonic structures, which combine passive noble metal nanostructures, so-called nanoantennas, with tunable phase-change materials (PCMs) to obtain novel functionalities. This combination allows for a flexible post-fabrication control of the resonant properties of these nanoantennas, which can be understood as the building blocks of MMs. The control of their optical properties is based on the fact that the spectral resonance position of the antennas can, among other parameters, be influenced by the refractive index of its surrounding.

A large change in the refractive index of the antenna surrounding is directly linked to a large shift of the antenna resonance frequency position. This can be achieved by an external stimulus, such as the insulator-to-metal transition of vanadium dioxide (VO$_2$), the change of the carrier concentration in graphene, as well as the amorphous to crystalline structural transition in PCMs. Furthermore, these tunable materials should not introduce additional dielectric losses to the hybrid nanophotonic structures.

In the mid-infrared (MIR) spectral range, the dielectric losses introduced by various PCMs, which are related to the imaginary part of their complex permittivity, are close to zero. Moreover, PCMs offer a non-volatile structural transition, which can be triggered reversibly. In comparison, VO$_2$ and graphene lack of this non-volatility, since the switched state (and thus, the refractive index change) vanishes after the external stimulus is turned off. As a consequence, PCMs are one of the most promising candidates for applications in tunable (active) plasmonics and photonics.

In this thesis, arrays of nanoantennas are designed for the MIR spectral range, while PCMs with a dielectric function best-suited for the MIR spectral range are investigated. The crystallization of the PCMs by annealing changes the dielectric surrounding of the nanoantennas and thus, the resonance frequency position of the nanoantennas is shifted by up to nearly 20%. A reversible shift of the resonance position is realized by applying laser pulses to re-crystallize and re-amorphize the used PCM.

To do so, laser pulses on the femtosecond, as well as on the nanosecond timescale are applied. The first allows for a large-area change of the structural state of the PCM, while the latter is applied to address single nanoantennas. This can allow for a multistep gradual change of the dielectric surrounding of the antennas and thus, of a gradual shift of the resonance position, pushing the controllability of the resonance shifting.

The presented concept is promising regarding a flexible post-fabrication tuning of the nanoantenna resonance position. Further applications to more complex nanostructures, e.g. a chiral metamaterial, show the reproducibility. Besides, demonstrated polarization control can bridge the gap of optical devices for the MIR spectral range. By understanding the physics of the PCMs the best-suited materials can be chosen to optimize the functionality of the nanostructure-PCM hybrids and thus, it leads towards programmable metamaterials.
Kurzfassung


Diese Arbeit beschäftigt sich mit hybriden nanophotonischen Strukturen, welche passive metallische Edelmetall-Nanostrukturen, sogenannte Nanoantennen, mit einstellbaren Phasenwechselmaterialien kombinieren, um neue Funktionalitäten zu erzielen. Diese Kombination ermöglicht eine flexible Kontrolle der resonanten Eigenschaften dieser Antennen, die als Metamaterial-Bausteine interpretiert werden können, auch nach deren Herstellung. Die Kontrolle ihrer optischen Eigenschaften basiert auf der Tatsache, dass die spektrale Resonanzposition der Antennen unter anderem durch den Brechungsindex ihrer Umgebung beeinflusst werden kann.


In dieser Arbeit sind die Nanoantennen für den mittleren infraroten Spektralbereich designt, wobei PWMs mit einer dielektrischen Funktion, die am besten für diesen Spektralbereich geeignet ist, untersucht wurden. Die Kristallisation der Phasenwechselmaterialien mittels Heizen verändert die dielektrische Umgebung der Nanoantennen und verschieben die Antennenresonanzposition um bis zu 20%. Eine reversible Verschiebung der Resonanzposition wird realisiert, indem Laserpulse auf angewandt werden, um das verwendete PWM zu rekristallisieren und zu reamorphisieren. Dafür werden Laserpulse auf der Femtosekunden-, als auch auf der Nanosekunden-Zeitskala verwendet. Das Erstgenannte erlaubt eine großflächige Veränderung des strukturellen Zustands des Phasenwechselmaterials, wobei das Letztgenannte zur Adressierung einzelner Antennen angewandt wird. Dies kann eine vielschrittige graduelle Veränderung der dielektrischen Umgebung der Antenne und damit eine graduelle Verschiebung der Resonanzposition erlauben und damit die Entwicklung der Steuerbarkeit der Resonanzverschiebung vorantreiben.

Das vorgestellte Konzept ist vielversprechend im Hinblick auf eine flexible Post-
L’important dans la vie ce n’est point le triomphe mais le combat;
l’essentiel ce n’est pas d’avoir vaincu mais de s’être bien battu.

Pierre de Coubertin, founder of the International Olympic Committee

This work is dedicated to Lothar Michel (Apr 6, 1948 - Sep 28, 2006).
Abstract

Kurzfassung (German abstract)

1 Introduction and thesis outline

2 Fundamentals of metallic nanoantennas in the mid-infrared spectral range
   2.1 Introduction
   2.2 Metal nanoantennas for the mid-infrared spectral range
      2.2.1 Metal nanorods
      2.2.2 Split-ring resonators
      2.2.3 Metasurfaces and metamaterials
   2.3 Tuning and shifting of nanostructure resonance positions
      2.3.1 Variation of the coupling distance of split-ring resonator pairs
      2.3.2 Variation of the refractive index of the nanostructure surrounding
      2.3.3 Further approaches for shifting nanostructure resonance frequency positions
      2.3.4 Summary

3 Fundamentals of phase-change materials
   3.1 Introduction
   3.2 Fundamental properties of phase-change materials
      3.2.1 The ternary phase diagram for Ge, Sb and Te
      3.2.2 Bonding mechanism in phase-change materials
   3.3 The permittivity of selected phase-change materials
      3.3.1 General aspects of the dielectric function
      3.3.2 Oscillator models for phase-change materials in the mid-infrared
      3.3.3 Germanium antimony telluride compounds
      3.3.4 Indium antimony
   3.4 Laser-induced switching and optical memories
      3.4.1 Crystallization and glass formation of phase-change materials
      3.4.2 Laser-induced switching of phase-change materials
      3.4.3 Optical data storage devices
8 Summary and outlook

8.1 Summary of the presented results
8.2 Perspectives for future developments

A Appendix on fundamental chapters

A.1 Comments on the optical properties of metals
A.2 Fit parameters for dielectric functions
A.3 Sample fabrication and characterization
  A.3.1 Electron beam lithography
  A.3.2 Physical vapor deposition
  A.3.3 Comments on FTIR microspectroscopy

B Appendix on experimental results

B.1 Geometric and spectral aspects of the metal antenna arrays
B.2 Comments on the thin film interferences of phase-change material layers
B.3 Determination of the peak width
B.4 Spectral influence of the GST-326 superstrate thickness
B.5 Literature comparison for laser-induced switching
B.6 Comments on the femtosecond laser experiments
B.7 Comments on the nanosecond laser switching

C Appendix on simulations

C.1 Applied software
  C.1.1 CST Microwave Studio
  C.1.2 Comsol Multiphysics software
C.2 Sample model for Microwave Studio calculations
  C.2.1 Parameterized model
  C.2.2 Comparison between experimental and simulated samples

List of Abbreviations
List of Symbols
Bibliography
List of publications
Contents

Acknowledgements 231
CHAPTER 1

Introduction and thesis outline

Around the year 1800 Herschel wanted to measure the temperature of the sunlight by guiding the light through a prism. The highest temperature was detected next to the visible red, which led him to the conclusion that the spectrum continues outside of the visible spectrum. Hence, the infrared light was discovered. As can be seen in table 1.1 the infrared (IR) spectral range is divided into the far, mid- and near IR.

The MIR spectral range roughly lies at a wavelength $\lambda$ between about 3 to 50 $\mu$m and a wavenumber $\tilde{\nu}$ between 200 and 3300 cm$^{-1}$ respectively. In this spectral region, technically important applications can be found, such as free-space optical communication, thermal signature detection and control, as well as optical sensing [1]. The latter refers to the MIR being also known as molecular fingerprint region, since vibrational modes of molecules, which allow for a spectral identification of molecular configuration, as well as functional groups, are resonant in the MIR spectral range. This will be discussed in chapter 2. Since these molecular vibrations lead to very weak resonant signals, which are difficult to detect by spectroscopic techniques, resonant nanostructures, such as metallic nanoantennas with a resonance position matching the position of the molecular vibrational mode can be applied to enhance the molecular signal.

The interaction of the electromagnetic radiation with metals or conductive materials is dominated by the interaction of the photons with the free electron gas in the conductive material. However, the electromagnetic radiation with wavelengths in the IR spectral range does not penetrate into the metal (or only for several nm depth) and is reflected instead. This behavior is caused by the dielectric function $\varepsilon(\tilde{\nu})$ of metals in the MIR spectral range, where the real part of the dielectric function $\varepsilon_1 \to \infty$ as discussed in chapter 2. Therefore, metals in the MIR can be considered as perfect electric conductors. Since the relation between frequency and wavevector at a metal-dielectric interface is the same as in free space in the MIR spectral range, a dipole-like character of metal nanoantennas in the MIR follows. The spectral position of the resonance of the dipole-like nanoantennas, which are also known as $\lambda/2$-antennas, can be approximated by their length, as well as by their dielectric surrounding. The first is defined by the fabrication, while the latter can be influenced after the antennas were fabricated. Therefore, a surrounding medium with a switchable or tunable dielectric function such as phase-change materials (PCMs) can allow for a post-fabrication manipulation of the antenna
PCMs are widely applied in storage media, such as re-writable Blu-ray discs (BD-RE) or phase-change random access memories (PCRAMs). Their pronounced contrast in reflectivity and resistivity between the (meta-)stable solid amorphous and crystalline phase allows for non-volatile data storage. In other words, the amorphous and the crystalline phase of PCMs show a pronounced difference regarding the real part $\varepsilon_1$ of their complex dielectric function in the MIR. This large index change is accompanied by very small imaginary parts $\varepsilon_2$ of their complex dielectric function and thus, the losses introduced by the PCM are expected to be minimized in the MIR. These characteristics of the dielectric function can be found for many compounds based on the elements germanium, antimony and tellurium, such as Ge$_3$Sb$_2$Te$_6$ or Ge$_8$Sb$_2$Te$_{11}$, as well as the "non-standard" compound InSb. The optical, as well as the structural properties of PCMs will be discussed in detail in chapter 3.

Samples of resonant aluminum antennas and PCMs require an advanced fabrication process including electron-beam lithography, which allows for the patterning of the nanoantennas, thermal evaporation and sputter deposition as explained in chapter 4. The precise antenna geometry, sample architecture and the used materials for the antennas and the PCM thin film are chosen carefully based on calculations described in chapter 5. This includes the optimized antenna separation in a square lattice leading to a narrowing of the reflectance peak ascribed to the antenna array resonance. As a result of the theoretical considerations, the nanoantennas investigated here feature a submicron length. The amorphous PCM thin films are deposited with a thickness of several tens of nanometers, which decreases for the transition from the amorphous to the crystalline phase since the density increases due to the change in the bonding situation and the structural re-ordering.

The change of the real part of the dielectric function $\Delta \varepsilon_1$ in PCMs can be triggered by thermal annealing on a hot plate or by laser pulses, which allows for a reversible transition between the amorphous and the crystalline phase. The shifts of the resonance frequency position of different antenna-PCM hybrids based on the change of the dielectric surrounding of the antennas are probed by FTIR spectroscopy and will be discussed in detail in chapters 6 and 7.

<table>
<thead>
<tr>
<th>spectral region</th>
<th>wavelength range $\lambda / \mu m$</th>
<th>wavenumber range $\tilde{\nu} / cm^{-1}$</th>
<th>energy range $E / eV$</th>
</tr>
</thead>
<tbody>
<tr>
<td>far infrared</td>
<td>FIR</td>
<td>50 - 1000</td>
<td>10 - 200</td>
</tr>
<tr>
<td>mid-infrared</td>
<td>MIR</td>
<td>3 - 50</td>
<td>200 - 3300</td>
</tr>
<tr>
<td>near-infrared</td>
<td>NIR</td>
<td>0.78 - 3</td>
<td>3300 - 12800</td>
</tr>
<tr>
<td>visible</td>
<td>VIS</td>
<td>0.38 - 0.78</td>
<td>12800 - 26300</td>
</tr>
</tbody>
</table>

Table 1.1: Different spectral regions of the electromagnetic spectrum are summarized, while the values for the wavenumber range in cm$^{-1}$ and the energy range in eV are rounded. The work in this thesis focuses on the MIR spectral range. The values have been taken from [2].
In chapter 6 different sample layouts and PCM compounds are investigated, while the crystallization is realized by annealing. The corresponding reflectance spectra of the nanoantennas with PCM thin films surrounding them reveal the pronounced shifting of the resonance frequency position, while the direction and the amount of the shift depends on the dielectric properties of the applied PCM.

Reversible shifting due to laser-induced phase transitions in the PCM is discussed in chapter 7. There, pulsed laser beams on the femtosecond and nanosecond timescale are investigated regarding the size of the switched spots in the PCM thin film. The first is used for the switching of large PCM areas, while the latter allows for the addressing of individual antennas. Experimental reflectance spectra show that the resonance position ascribed to antenna arrays can be shifted to lower, as well as to higher wavenumbers. Furthermore, the small spot sizes achieved with nanosecond laser pulses can allow for a stepwise shifting of the antenna resonance frequency position since small spots only partly influence the dielectric surrounding of the antenna.

The presented concept of actively controllable resonance properties of nanoantennas in the MIR spectral range can easily be extended to more complex nanostructures and applied in the fields of polarization filters, infrared absorbers or molecular sensing. Tunable chiroptical responses are described in detail. Future concepts and the related requirements on the used materials and the device architecture will be discussed in chapter 8.
CHAPTER 2

Fundamentals of metallic nanoantennas in the mid-infrared spectral range

"... is it possible, for example, to emit light from a whole set of antennas, like we emit radio waves from an organized set of antennas to beam the radio programs to Europe? The same thing would be to beam the light out in a definite direction with very high intensity..."

R. Feynman, Dec 29 1959 [3]

2.1 Introduction

In an everyday language use, antennas are understood as electromagnetic emitters or receivers, mostly known from rooftop tv-antennas, radio antennas or mobile phone antennas. There, electromagnetic waves with a well-defined radiation pattern are sent out by a radio station for example. Antennas, which are part of radios in homes, capture a part of the power of these electromagnetic waves. At their terminals, a low voltage is produced, which is amplified at the corresponding receiver.

By definition of the Institute of Electrical and Electronics Engineers antennas are: "That part of a transmitting or receiving system that is designed to radiate or to receive electromagnetic waves" [4]. The first experiments regarding wireless transmission and receiving of electromagnetic waves were conducted by the physicists Hertz, Tesla and Marconi at the end of the nineteenth century. The principle of radio antennas can also be transferred to optical antennas, as it was pictured by Feynman in his famous speech held at the Californian Institute of Technology (cf. quotation above).

Following Novotny et al., optical nanoantennas are defined as: "a device designed to efficiently convert free-propagating optical radiation to localized energy and vice versa" [6]. In contrast to radio frequencies (kHz to GHz), the frequencies of optical antennas are higher (hundreds of THz), which means that the wavelengths are smaller (several µm to hundreds of nm). Hence, also the antenna dimensions of optical antennas are much smaller than those of radio antennas.

\footnote{Marconi shared the Nobel prize in Physics in 1909 with Braun. They received it "in recognition of their contributions to the development of wireless telegraphy" [5].}
In section 2.2 the work in the mid-infrared spectral range will be motivated and the fundamentals of metallic dipole nanoantennas, which are the workhorse in the framework of this thesis, will be explained. This includes the influence of the dielectric surrounding of the nanoantennas on the nanoantenna spectral properties. Different concepts for influencing the nanostructures resonance frequency published in the literature will be summarized in section 2.3.

2.2 Metal nanoantennas for the mid-infrared spectral range

The mid-infrared spectral range

The work presented in this thesis focuses on nanoantennas in the mid-infrared (MIR) spectral range, which is important for applications such as thermal imaging or chemical sensing, while the latter will be briefly described in the following.

The MIR spectral range includes the so-called molecular fingerprint region. This describes the wavelength (or wavenumber) range, in which molecules, such as N$_2$O or C$_2$H$_4$, directly absorb incident photons of an energy characteristic for their configuration and thus, can be identified. To understand, what causes these absorption patterns, the vibrational or so-called normal modes of molecules need to be defined. According to Atkins, a normal mode is "an independent, synchronous motion of excited atoms (or groups of atoms) without leading to the excitation of any other normal mode and without involving translation or rotation of the molecule as a whole." [7] Only infrared active modes can be probed by absorption spectroscopy, while infrared activity is only given if one of the dipole moments changes during the course of a motion corresponding to a normal mode. Regarding a CO$_2$ molecule, in which the carbon atom is covalently double bonded to two oxygen atoms (O=C=O), a symmetric stretch of both carbon-oxygen bonds does not lead to a dipole change and is IR inactive. In contrast, an antisymmetric stretch of the two CO double bonds is IR active due to its net change in the dipole moment. An example of absorption bands of selected molecules is depicted in figure 2.1.

![Figure 2.1: Characteristic vibrational absorption bands of various molecular bonds can be found in the MIR spectral range. The energy necessary to excite different stretching and bending vibrations (illustrated by arrows and algebraic signs with "+" means coming forward and "+" means coming backward) defines the characteristic absorption bands (illustrated by rectangles). The fingerprint region, which is covered by complex vibrational bending modes is marked by a white rectangle, while the bands of vibrational stretching modes associated with functional groups are marked by gray rectangles. The figure was adapted from [8].](image)
In the low wavelength range between about 2 and 6 µm, narrow bands of functional groups, such as the hydroxy group, can be found, whereas the fingerprint region lies at higher wavelengths between about 6 and 20 µm (here only depicted up to 13 µm). The associated bending vibrations can be in-plane or out-of-plane. In figure 2.1 rocking, scissoring, twisting and wagging are schematically shown (left to right). The functional groups define physical and chemical molecule properties, while the characteristic bands, which depend on the molecule conformation, allow for an identification of the specific molecule [7].

The characterization method of surface enhanced infrared absorption (SEIRA) spectroscopy uses well-designed metal nanostructures to which the molecules get adsorbed. When resonantly excited, these nanostructures lead to enhanced electromagnetic fields, which in turn increase the MIR absorption of the adsorbed molecules by orders of magnitude [8, 9]. Thus, even monolayers or very small amounts of probed molecules can be detected [10].

The optical properties of the metal nanostructures applied for SEIRA can be described by the Drude model, which will be introduced in the following. Depending on the spectral range, oscillations in the free electron plasma, which are quantized by plasmons, can arise. The related phenomena will be described in the following section as well. Furthermore, the resonance properties of metal nanorods and U-shaped nanoantennas (split-ring resonators), which play an important role for artificial materials with engineered optical properties, such as a negative refractive index (metamaterials), will be discussed.

**Description of resonant modes: Drude model and plasmons**

**The Drude model of the dielectric function** The interaction of metallic structures with electromagnetic waves in the infrared spectral range can be characterized by the dominant interaction of the incident photons with the free-electron gas of the noble metal. Quantitatively, this interaction can be described by the *Drude model* which will be explained in the following according to the description given in [11]. In the Drude model, it is assumed that free electrons move relative to the background of positive ions, while the core electrons are tightly bound to the corresponding nuclei and do not contribute to the free electron flow. Only the interactions of the free electrons with the applied field are taken into account. Free electrons do not experience any restoring forces when they are displaced. Their motion due to an incident electromagnetic field of a light wave $\mathbf{E}(t)$ can be described as follows:

\[
\begin{align*}
m^* \frac{d^2 x}{dt^2} + m^* \gamma_D \frac{dx}{dt} &= -e \mathbf{E}(t) \\
\text{with } \mathbf{E}(t) &= E_0 \text{Re} \left(e^{-i(\omega t + \Phi)}\right) \\
\text{and } x(t) &= x_0 e^{-i\omega t}
\end{align*}
\]

with the effective electron mass $m^*$, the damping rate $\gamma_D$ and the electric charge of the electron $e$. The effective mass $m^*$ takes into account that the electrons in a solid are only nearly free and their band structure (or dispersion relation) departs from the free electron dispersion. The damping rate $\gamma_D$ is inversely proportional to the scattering rate $\tau$ with respect to the scattering of the free electrons (electron-electron scattering, electron-phonon scattering, scattering by lattice defects). The amplitude and phase of the time dependent incident light wave $\mathbf{E}(t)$ are described by $E_0$ and $\Phi$ and the angular frequency is denoted with $\omega$. 
Based on the displacement of the electrons $x$ from their equilibrium positions a time-varying dipole moment $p(t) = -ex(t)$ is produced, which contributes to the macroscopic polarization of the medium. The resonant polarization $P_{\text{res}}$ is then given by $P_{\text{res}} = Np$ with $N$ being the number of electrons per unit volume given in $m^{-3}$. From the equation of motion (equation 2.1) it is obtained:

$$x = \frac{\epsilon_0 \mathcal{E}}{m^* (\omega^2 + i \gamma_D \omega)}$$  (2.2)

Since the electric displacement of an isotropic medium $\mathcal{D}$ is defined by $\mathcal{D} = \epsilon_0 \mathcal{E}$ and $\mathcal{D} = \epsilon_0 \mathcal{E} + \mathcal{P}$, the complex permittivity $\varepsilon$ (the underlined symbol indicates complex quantities) can be calculated as follows:

$$\varepsilon_\mathcal{D}(\nu) = 1 - \frac{\tilde{\nu}_p^2}{\nu \cdot (\nu + i \gamma_D)} \quad \text{with} \quad \tilde{\nu}_p = \frac{1}{2 \pi c} \sqrt{\frac{Ne^2}{\epsilon_0 m^*}}$$  (2.3)

with the plasma wavenumber of the free electrons $\tilde{\nu}_p$ (dominated by the free charge carrier density $N$) and the electric permittivity of free space $\epsilon_0$ [11]. Thereby the dielectric function is given in wavenumbers $\nu$, which is the spectroscopic frequency unit [11] and which will be used throughout this thesis. The wavenumber $\nu$ given in cm$^{-1}$ and the angular frequency $\omega$ given in rad s$^{-1}$ are related via the speed of light in vacuum $c$ as given by $\nu = \omega / 2 \pi c$. The real part of the complex permittivity $\varepsilon(\nu)$ can be associated with the polarization in the free electron gas induced by an external field, such as the incident electromagnetic wave $\mathcal{E}$, while the imaginary part describes losses due to the build-up polarization. These losses can arise from electron scattering processes and are summarized in the damping constant $\gamma_D$. For higher wavenumbers $\nu$ in the VIS and UV spectral range absorption becomes more dominant, e.g. due to interband transitions of bound electrons in the metal. The bound electrons, which can oscillate due to excitation by photons of higher wavenumbers (equivalent to higher energies), experience restoring forces due to the binding between the electrons and the nucleus and thus, additional energy losses can occur. As a result, the measured dielectric function $\varepsilon(\omega)$ can not be described by the Drude model given in equation 2.3, which considers intraband absorption only.

For a simple description, the contributions of the interband transitions at higher wavenumbers (energies) to the complex permittivity can also be taken into account in the MIR spectral range by introducing the constant $\varepsilon_{\text{in}}$ and changing equation 2.3 to the following:

$$\varepsilon_\mathcal{D}'(\nu) = \varepsilon_{\text{in}} - \frac{\tilde{\nu}_p''^2}{\nu \cdot (\nu + i \gamma_D)} \quad \text{with} \quad \tilde{\nu}_p'' = \frac{1}{2 \pi c} \sqrt{\frac{Ne^2}{\epsilon_{\text{in}} \epsilon_0 m^*}}$$  (2.4)

It has to be noted that this description is not valid for the description of the dielectric function in the visible spectral range, where interband transitions occur. In this case the Drude model can be extended by Lorentz oscillators, which will be described in the context of optical properties of phase-change materials (cf. chapter 3).

The complex permittivity of aluminum $\varepsilon_\mathcal{D}_{\text{Al}}(\nu)$ was calculated according to equations 2.3 and by using $\omega_p = 1.78 \cdot 10^{16}$ s$^{-1}$, $\gamma_D = 1.3 \cdot 10^{14}$ s$^{-1}$ [12]. The corresponding spectral behavior in the IR, VIS and UV spectral range is shown as a function of the wavenumber $\nu$ in figure 2.2. In the MIR spectral range, the real part of the dielectric function $\varepsilon_{\text{in}}$ approaches infinity for decreasing wavenumbers $\nu$. Thus, the electric field exponentially decays into the aluminum according to $e^{-z / \delta_k}$ (following Beer’s
law) with the field propagation direction $z$ and the skin depth $\delta_{sk}$. The frequency dependent skin depth is defined as follows [13, 14]:

$$\delta_{sk}(\tilde{\nu}) = \frac{2}{\alpha(\tilde{\nu})} = \frac{1}{2\pi\kappa\tilde{\nu}}$$

with the absorption coefficient $\alpha$, the wavenumber $\tilde{\nu}$ in vacuum and the extinction coefficient $\kappa$. The latter is known as imaginary part of the complex refractive index defined as:

$$n = n + i\kappa = \sqrt{\varepsilon_1 + i\varepsilon_2}$$

The real, as well as the imaginary part of the refractive index $n$ can be calculated from the dielectric function $\varepsilon_0 = \varepsilon_1 + i\varepsilon_2$ as defined in appendix A.1. The evaluation of equation 2.5 leads to a skin depth $\delta_{sk}$ in aluminum of about 17 nm in the MIR and NIR spectral range. Therefore, aluminum films or nanostructures must be thicker than the skin depth of about 17 nm to be highly reflective. The reflectivity $R^3$ is evaluated for aluminum and can be found in appendix A.1 as well. For wavenumbers below the plasma wavenumber $\tilde{\nu}_p$, the reflectivity is nearly 100%, while it drops to zero at the plasma wavenumber.

![Figure 2.2](image)

(a) spectral overview of the Drude model for aluminum

(b) MIR spectral range

Figure 2.2: The evaluation of the Drude model for aluminum $\varepsilon_D$ leads to the shown dielectric function $\varepsilon_D(\tilde{\nu})$, depicted for the MIR, NIR and VIS spectral range. In the MIR spectral range the real part of the dielectric function $\varepsilon_1$ tends towards very large negative values for decreasing wavenumbers, while the imaginary part $\varepsilon_2$ approaches infinity.

In this work metal nanostructures will be considered in the MIR spectral range and therefore, the Drude model $\varepsilon_D$ given by equation 2.3 serves as a well-suited description of the dielectric function.

Dispersion relation of plasmons Regarding the Drude model for the complex permittivity given by equation 2.3 in the case of a small damping constant $\gamma_D$, the complex permittivity $\varepsilon_D$ tends towards zero for $\tilde{\nu}_p$. Thus, $\tilde{\nu}_p$ is the frequency of a longitudinal natural oscillation of the free electron gas. Thereby, the thermal motion of the electrons is neglected. The quasiparticles of these plasma oscillations are called plasmons [15]. Is an interface between a metal and a dielectric material present, the quanta of these collective oscillations localized at the interface are surface plasmon polaritons.

---

2The corresponding plots of the frequency dependent extinction coefficient $\kappa(\tilde{\nu})$ and skin depth $\delta_{sk}(\tilde{\nu})$ can be found in appendix A.1.

3In this thesis, the reflectivity $R$ and the reflectance $R$ are clearly separated. The first is used for the description of bulk properties, while the latter applies to thin films.
(SPPs). The corresponding charge distribution is depicted in figure 2.3, where the longitudinal and transverse components of the electric field can be seen. The transverse field components allow for a direct interaction between photons and plasmons and the coupled electric polarization-photon wave is defined as polariton. Referring to the situation sketched in figure 2.3, the SPP surface waves propagate in x-direction.

By solving Maxwell’s equation, the dispersion of the SPPs can be calculated. For a propagation along the interface, the real part \(k_{x,1}\) and the imaginary part \(k_{x,2}\) of the complex wave vector in x-direction \(k_x = k_{x,1} + ik_{x,2}\) is defined as follows [16, 17]:

\[
k_{x,1} = \frac{\omega}{c} \sqrt{\frac{\varepsilon_{m,1}\varepsilon_d}{\varepsilon_{m,1} + \varepsilon_d}} = 2\pi \tilde{\nu} \cdot \sqrt{\frac{\varepsilon_{m,1}\varepsilon_d}{\varepsilon_{m,1} + \varepsilon_d}}
\]

\[
k_{x,2} = 2\pi \tilde{\nu} \cdot \left(\frac{\varepsilon_d}{\varepsilon_{m,1} + \varepsilon_d}\right)^{1/2} \cdot \frac{\varepsilon_{m,2}}{2\sqrt{\varepsilon_{m,1}}}
\]

with \(c\) referring to the speed of light in vacuum and \(\omega = 2\pi c \tilde{\nu}\). The complex dielectric function of the metal is defined by \(\varepsilon_m(\tilde{\nu}) = \varepsilon_{m,1} + i\varepsilon_{m,2} = \varepsilon_D(\tilde{\nu})\), while the permittivity of the dielectric medium \(\varepsilon_d\) is set as real and independent of the wavenumber \(\tilde{\nu}\) [15]. The real part of the wave vector \(k_{x,1}\) determines the wavelength of the SPPs, while the damping of the SPP propagation along the metal/dielectric interface is given by the imaginary part \(k_{x,2}\). In particular, the propagation length \(L_x\) of the SPPs is defined by [17]:

\[
L_x = \frac{1}{k_{x,2}}
\]

This means that the amplitude of the electric field decays to \(1/e\) of its initial value after propagating for the length \(L_x\). In the MIR spectral range the SPPs propagate more than three orders of magnitude further relative to the electromagnetic excitation (\(L_x\approx 2056 \lambda_0\)), while in the VIS spectral range the electric field decays after about the 175-fold of the incident wavelength (\(L_x \approx 175 \lambda_0\), cf. table 2.1).

The SPPs are confined and the amplitudes of the electric fields \(E_{d,z}\) and \(E_{m,z}\) decay evanescently as shown in figure 2.3 [13].

\[\text{(a) metal/dielectric interface}\]

\[\text{(b) small metal nanoparticle}\]

Figure 2.3: The distribution of the charges and the electric field \(\vec{E}\) at the interface between a metal (gray) with \(\varepsilon_m(\tilde{\nu}) = \varepsilon_{m,1} + i\varepsilon_{m,2}\) and a dielectric with \(\varepsilon_d\) (constant and real) are sketched in figure 2.3a. The interface lies in the xy-plane at \(z = 0\) and the magnetic field \(\vec{H}\) points out of this plane. The SPP propagate in z-direction with \(k_z\) (red arrow) and the amplitude of the electric field \(|E|\) decays exponentially in both half-spaces with the decay length \(L_x\). In figure 2.3b, the time-varying electric field \(\vec{E}\) leads to charge density oscillations in a spherical metal nanoparticle, which is much smaller than the incident wavelength \(\lambda_0\). Hence, a LSP resonance occurs. The figures were adapted from [1, 11].

In the special case of a weak damping with \(\tilde{\nu} \gg \gamma_D\) the simple Drude model \(\varepsilon_D(\tilde{\nu})\) given by equation 2.3 can be expressed by [18]:

\[
\varepsilon_m = 1 - \left(\frac{i\gamma}{\tilde{\nu}}\right)^2
\]

(2.9)
For \( \varepsilon_d = 1 \) (air), the real part of the in-plane wave vector \( k_{x,1} \) yields (inserting equation 2.9 in 2.7a):

\[
k_{x,1} = 2 \pi \tilde{\nu} \cdot \sqrt{\frac{1 - (\tilde{\nu}_p/\tilde{\nu})^2}{2 - (\tilde{\nu}_p/\tilde{\nu})^2}}
\]  

(2.10)

This relationship is shown for an aluminum/air interface for the MIR and NIR spectral range in figure 2.4. The dispersion of photons in air - the light line - and the SPP dispersion relation for the metal/air interface are equal in the IR spectral range. This implies that the wavevectors \( k_x \) of freely propagating electromagnetic waves and SPPs are identical. In contrast, the SPP dispersion behaves non-linearly for the VIS and UV spectral range and for large wavevectors \( k_x \) the SPP dispersion asymptotes to the surface plasmon wavenumber \( \tilde{\nu}_{sp} = \tilde{\nu}_p / \sqrt{1 + \varepsilon_d} \), which is depicted in appendix A.1.

Figure 2.4: The dispersion relation for SPPs \( \tilde{\nu}(k_{x,1}) \) (equation 2.10) is given at the interface between aluminum and air (black solid curve, cf. equation 2.10). The wave vector \( k \) was normalized by \( k_p = \omega_p / c \), while the plasmon frequency \( \omega_p \) can be expressed as plasmon wavenumber \( \omega_p = 2 \pi c \tilde{\nu}_p \). The light line for photons in air is shown by a black dashed line. In the MIR and NIR spectral range, the dispersion relation and the light line are identical, while for increasing wavenumbers, the wave vector increases much faster for SPPs at the aluminum/air interface compared to photons in air.

The spatial extent of the electric field \( E \) in the metal and the dielectric (\( \varepsilon_d = 1 \)) can be determined from the wave vector in \( z \)-direction:

\[
k_{m,z} = 2 \pi \tilde{\nu} \cdot \frac{\varepsilon_{m,1}}{\sqrt{\varepsilon_{m,1} + 1}} \left( 1 + i \frac{\varepsilon_{m,2}}{2 \varepsilon_{m,1}} \right) \]  

(2.11a)

\[
k_{d,z} = 2 \pi \tilde{\nu} \cdot \frac{1}{\sqrt{\varepsilon_{m,1} + 1}} \left( 1 + i \frac{\varepsilon_{m,2}}{2 \varepsilon_{m,1} + 2} \right) \]  

(2.11b)

The electric field amplitude decays to \( 1/e \) of its initial value after length \( L_z \), which is given by the wave vector \( k_z \) via [11]:

\[
L_z = \frac{1}{|k_z|} \]  

(2.12)

The decay length in the metal \( L_{m,z} \) is shorter than the decay length in the dielectric \( L_{d,z} \) by a factor of more than 1700 at 2000 cm\(^{-1}\) (MIR) and by a factor of about 21 at 20000 cm\(^{-1}\) (VIS) as listed in table 2.1. Together with the large SPP propagation length \( L_x \) gold can be considered as perfect electric conductor (PEC) in the MIR spectral range. Furthermore, in the MIR spectral range the wavelength of the SPPs \( \lambda_{SPP} = 2 \pi / k_{x,1} \) is equal to the wavelength of the excitation \( \lambda_0 \), while it changes by more than 10% in the VIS spectral range. This means that the SPPs propagate with the free wavelength \( \lambda_0 \) in the MIR spectral range, which is illustrated in figure 2.4, where the light line and the SPP dispersion are identical.
The description above considers two semi-infinite half-spaces of gold and air, which implies that the SPPs at the metal/air interface can propagate without constraints. The SPP propagation can be hindered in case of the structuring of the semi-infinite metal film down to structures below the size of the excitation wavelength \( \lambda_0 \). Curved surfaces of the nanostructured metal interact with the incident oscillating electromagnetic field and a resonance in the nanostructure can arise [13]. This non-propagating excitation of the free electrons of the metal is coupled to the incident electromagnetic field and defined as localized surface plasmon (LSP). LSPs occur in the VIS and UV spectral range, since the electromagnetic field needs to penetrate into the metal nanostructure to generate a charge separation in the nanostructure leading to the LSP resonance as it is sketched in figure 2.3.

For the MIR, the metal the nanostructures are made of can be considered as PEC and plasmonic phenomena, such as LSPs can be neglected.

<table>
<thead>
<tr>
<th>parameter</th>
<th>( \tilde{\nu}_i = 2000 \text{ cm}^{-1}, \lambda_0 = 5 \mu\text{m} )</th>
<th>( \tilde{\nu}_i = 20000 \text{ cm}^{-1}, \lambda_0 = 0.5 \mu\text{m} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPP propagation length ( L_x = 1/\kappa_x )</td>
<td>( 10.28 \text{ mm} ) ( \approx 2056 \lambda_0 ) ( 87.42 \mu\text{m} ) ( \approx 175 \lambda_0 )</td>
<td>( 10.28 \text{ mm} ) ( \approx 2056 \lambda_0 ) ( 87.42 \mu\text{m} ) ( \approx 175 \lambda_0 )</td>
</tr>
<tr>
<td>SPP wavelength ( \lambda_{SPP} = 2\pi/\kappa_{SPP} )</td>
<td>( 4.99 \mu\text{m} ) ( \approx \lambda_0 ) ( 0.48 \mu\text{m} ) ( \approx 0.96 \lambda_0 )</td>
<td>( 4.99 \mu\text{m} ) ( \approx \lambda_0 ) ( 0.48 \mu\text{m} ) ( \approx 0.96 \lambda_0 )</td>
</tr>
<tr>
<td>SPP field decay length in aluminum ( L_{m,z} = 1/\kappa_{m,z} )</td>
<td>( 17.6 \text{ nm} ) ( \approx 0.004 \lambda_0 ) ( 16.8 \text{ nm} ) ( \approx 0.034 \lambda_0 )</td>
<td>( 17.6 \text{ nm} ) ( \approx 0.004 \lambda_0 ) ( 16.8 \text{ nm} ) ( \approx 0.034 \lambda_0 )</td>
</tr>
<tr>
<td>SPP field decay length in air ( L_{d,z} = 1/\kappa_{d,z} )</td>
<td>( 35.0 \mu\text{m} ) ( \approx 7 \lambda_0 ) ( 358.5 \text{ nm} ) ( \approx 0.717 \lambda_0 )</td>
<td>( 35.0 \mu\text{m} ) ( \approx 7 \lambda_0 ) ( 358.5 \text{ nm} ) ( \approx 0.717 \lambda_0 )</td>
</tr>
</tbody>
</table>

Table 2.1: The decay lengths \( L \) in \( x \)-direction - along the aluminum/air interface - and in \( z \)-direction - into the metal and the dielectric -, as well as the wavelength of the SPPs were calculated for the MIR and VIS spectral range with the incident wavenumber \( \tilde{\nu}_i \) and wavelength \( \lambda_0 \). Each parameter is also given as multiple of the incident wavelength. All equations were taken from [17].

2.2.1 Metal nanorods

Description of the nanorod resonance position

The \( \lambda/2 \)-model Rod-like metal nanostructures - so-called nanoantennas are considered, since their relatively simple shape allows for a straightforward calculation of their resonance frequency. Due to the nearly perfect conduction of noble metals in the MIR spectral range, the antenna length \( L \) can be directly related to the wavelength \( \lambda \) of the incident light as it is known from classical antenna theory. Thereby, a metal cylindrical rod with its length \( L \) being much greater than its diameter is considered. An incident wave with wavelength \( \lambda \) and an electric field parallel to the nanorod polarizes the rod along the rod axis as shown in figure 2.5a. There, the charge distribution of a rod-shaped nanoantenna and the corresponding dipole moments \( \vec{p} \) are sketched for \( m = 1, 2, 3 \) with \( m \) being an integer describing the order of the standing wave pattern on the rod surface. This integer is also called the oscillation mode. The surface charge waves propagate along the rod. Resonances similar to those of an ideal dipole antenna are supported and the resonance of the nanoantenna \( \lambda_{res} \) should occur when the antenna length \( L \) is half a wavelength if \( m = 1 \) [19, 20], while for higher modes \( m \) the resonance wavelength \( \lambda_{res} \) decreases.
The charge accumulation at the antenna ends is an electrostatic effect and known as lightning rod effect. It leads to an increase of the local electromagnetic field $E_{\text{loc}}$ at the points of the greatest curvature. Furthermore, nanoantennas suited for the IR and VIS spectral range allow for an enhancement of the optical near-fields. This means that an incident electromagnetic field $E_i$ is enhanced by a factor $f$ leading to a local antenna field $E_{\text{loc}}$ much larger than $E_i$. Thereby, the enhancement factor can be several orders of magnitude [21]. This property is used for sensing with SEIRA spectroscopy for example [22, 23]. In contrast to the electrostatic charge accumulation, the field enhancement is a material resonance and referred to as plasmonic effect [24].

The so-called $\lambda/2$-model approximates the resonance wavelength $\lambda_{\text{res}}$ of single nanorods and the resonance wavenumber $\tilde{\nu}_{\text{res}}$ respectively as follows:

$$\lambda_{\text{res}} = \frac{2 \cdot n(\lambda) \cdot L}{m} + C \quad \text{with} \quad C = \frac{4 \cdot n(\lambda)}{m} R$$

(2.13a)

$$\tilde{\nu}_{\text{res}} = \lambda_{\text{res}}^{-1} \approx (2 \cdot n(\tilde{\nu}) \cdot L)^{-1} \quad \text{for} \quad m = 1$$

(2.13b)

with $n$ representing the real part of the refractive index of the nanoantenna surrounding, $L$ referring to the length of the antenna rod, $m$ being the oscillation mode and $C$ being the fitting parameter based on the finite width of the nanorods (radius $R$) [19, 25, 26]. This constant $C$ allows for a more precise prediction of the nanorod resonance position. However, $C$ is often neglected for approximations [26] as given in equation 2.13b. The relations 2.13 are only valid for very small imaginary parts of the dielectric function $\varepsilon_2$ of the antenna surrounding with $\varepsilon_2 \ll \varepsilon_1$. Thus, the refractive index is real $n \approx n$ (cf. equation A.1) and the resonance position $\tilde{\nu}_{\text{res}}$ is real as well.

In the picture of nanoantennas the wavelength $\lambda$ is more intuitive than the wavenumber $\tilde{\nu}$. However, the experimental results determined by spectroscopic characterization of the nanoantennas will be given in wavenumbers (cf. chapters 5 - 7). The conversion from wavenumbers in cm$^{-1}$ to wavelengths in $\mu$m is given by $\tilde{\nu} = 10^{-4}/\lambda$.

Experimental deviations from the proportionality between $L$ and $\lambda/2$ can be based on the non-negligible skin depth $\delta_{\text{sk}}$. If the skin depth is in the range of the nanorod diameter the relation can get up to $L \propto \lambda/10$ [27].

![Figure 2.5](image_url)

Figure 2.5: In figure 2.5a, the charge distribution of a metal rod-shaped antenna is sketched for the first three longitudinal modes $m$ with the electric field $\vec{E}$. The dipolar moments $\vec{p}$ are marked by white arrows. For $m = 1$ the electric field $\vec{E}$ (enhanced amplitude for better representation) is shown on the right. Furthermore, it can be seen that $\lambda_{\text{res}}$ is influenced by the antenna environment and increases by embedding the antenna in an homogeneous medium with refractive index $n_{\text{emb}}$ or an effective medium with $n_{\text{eff}} = 1/2(n_{\text{super}} + n_{\text{sub}})$, $n_{\text{eff}} < n_{\text{emb}}$, shown in figure 2.5b.
By increasing the total rod length $L$ the resonance wavelength $\lambda_{\text{res}}$ increases and the resonance wavenumber $\tilde{\nu}_{\text{res}}$ decreases according to the relation given in equation 2.13a. Therefore, the resonance position of the nanoantennas can be controlled by selecting the suited nanorod length.

The influence of the dielectric function of the antenna surrounding on the resonance wavelength $\lambda_{\text{res}}$ is illustrated in figure 2.5b. If the antenna (fixed length $L$) is isolated in air with the real part of the refractive index $n = 1$, the resonance wavelength $\lambda_{\text{res}} \approx L/2$ for the first order mode $m = 1$. In the case of an embedding medium with $n > 1$, the resonance wavelength increases $\lambda_{\text{res}}$ as in the bottom left sketch of figure 2.5b. By placing the antenna on a substrate with the real part of the refractive index $n_{\text{sub}} > 1$ while the sample is in air ($n_{\text{super}} = 1$), the antenna resonance is influenced by an effective refractive index $n'_{\text{eff}}$. This can be approximated by an averaged index $n'_{\text{eff}}$ as follows [28]:

$$n'_{\text{eff}} = \frac{n_{\text{super}} + n_{\text{sub}}}{2}$$  \hspace{1cm} (2.14)

In figure 2.5b the effective index $n'_{\text{eff}}$ is smaller than the real part of the refractive index of the embedding medium $n_{\text{emb}}$. As a consequence the resonance wavelength (wavenumber) decreases (increases) for the effective medium compared to the homogeneous embedding medium. It has to be noted that the averaged effective index $n'_{\text{eff}}$ in equation 2.14 is a strong simplification. In the literature, the effective index $n_{\text{eff}}$ is also given as the slope of the resonance position $\tilde{\nu}_{\text{res}}$ plotted as a function of the nanoantenna length $L$ (according to equation 2.13b), while $n_{\text{eff}}$ includes all contributions of the antenna surrounding [19, 26]. This concept will be applied in the chapters 5 to 7 as well.

**Scattering, absorption and extinction cross-sections** As it was shown above, small nanoparticles or nanoantennas can act as an electric dipole, which resonantly absorb and scatter electromagnetic fields. The efficiencies with which the incident light is scattered and absorbed are quantified by cross-sections $\sigma$. In the following the cross-sections will be derived from the polarizability $\alpha$ of a small metal sphere. This sphere shows plasmonic effects. However, the mathematical description for the metal sphere is simpler compared to an ellipsoid or a nanorod for example.

The field enhancement of a metal nanostructure is based on the polarizability $\alpha$. The polarizability $\alpha$ of a metal sphere is related to the dipole moment $\vec{p}$ and the incident electric field $\vec{E}$ as follows:

$$\vec{p} = \varepsilon_0 \varepsilon_d \cdot \vec{\alpha}(\tilde{\nu}) \cdot \vec{E}$$ \hspace{1cm} (2.15a)

with

$$\vec{\alpha}(\tilde{\nu}) = 4\pi a^3 \frac{\varepsilon_m(\tilde{\nu}) - \varepsilon_d}{\varepsilon_m(\tilde{\nu}) + 2\varepsilon_d}$$ \hspace{1cm} (2.15b)

with $a$ being the radius of a spherical nanoparticle, $\varepsilon_m(\tilde{\nu})$ as the dielectric function of the metal nanoparticle and $\varepsilon_d$ as permittivity of the isotropic, non-absorbing surrounding of the nanoparticle [13]. It should be noted that the absorption coefficient $\alpha(\tilde{\nu})$ known from equation 2.5 and the polarizability are both described by the symbol $\alpha(\tilde{\nu})$. Equation 2.15b describes the complex polarizability of a small sphere with a diameter $2a$ much smaller than the wavelength of the incident radiation $2a \ll \lambda_0$. Therefore the harmonically oscillating electromagnetic field is constant over the particle volume and the field can be assumed as electrostatic (quasi-static approximation). Equation 2.15b shows a resonance at:

$$\text{Re}(\varepsilon_m) = \varepsilon_{m,1} = -2\varepsilon_d$$ \hspace{1cm} (2.16)
under the condition of a small \( \text{Im}(\varepsilon_m) = \varepsilon_m \). This so-called Fröhlich condition leads to the dipole surface plasmon of the considered metal nanoparticle, which acts as an electric dipole resonantly scattering and absorbing electromagnetic fields.

The resonantly enhanced polarization \( \alpha(\tilde{\nu}) \) allows for an enhancement of the efficiency the incident light is absorbed and scattered by the nanoparticle. These efficiencies are quantified by the absorption and scattering cross-sections \( \sigma_{\text{abs}} \) and \( \sigma_{\text{scat}} \) defined by [13]:

\[
\sigma_{\text{abs}}(\tilde{\nu}) = \frac{2\pi}{\lambda} \cdot \text{Im}(\alpha) = 2\pi \tilde{\nu} \cdot \text{Im}(\alpha) \\
\sigma_{\text{scat}}(\tilde{\nu}) = \left(\frac{2\pi}{\lambda}\right)^4 \cdot \frac{|\alpha|^2}{6\pi} = (2\pi \tilde{\nu})^4 \cdot \frac{|\alpha|^2}{6\pi}
\]

The extinction cross-section \( \sigma_{\text{ext}} \) can be calculated by adding the absorption and the scattering cross-section \( \sigma_{\text{ext}} = \sigma_{\text{abs}} + \sigma_{\text{scat}} \). To take different nanoparticle geometries into account, such as ellipsoids and spheroids, the polarizability \( \alpha \) can be adapted [29]. In the case of larger nanoparticles, where \( 2a \ll \lambda_0 \) is not satisfied, the field can not be considered as constant over the entire nanoparticle volume. Instead of the quasi-static approximation, a rigorous electrodynamic approach is necessary then. This expansion is given by the Mie theory and is described in detail in [29].

The absorption cross-section \( \sigma_{\text{abs}} \), the scattering cross-section \( \sigma_{\text{scat}} \) and extinction cross-section \( \sigma_{\text{ext}} \) are shown in figure 2.6a for a single aluminum nanoantenna with length \( L = 600 \text{ nm} \), width \( w = 100 \text{ nm} \) and \( h = 40 \text{ nm} \) placed in air with the refractive index \( n = 1.0 \). The spectra were calculated with the software Comsol (cf. appendix C). The peak in all cross-sections can be associated with the resonance frequency position \( \tilde{\nu}_{\text{res}} \approx 6000 \text{ cm}^{-1} \), which is in the near-infrared (NIR) spectral range. Thereby, the resonance peak of the extinction cross-section shows a peak width (full width at half maximum) of FWHM \( \approx 1770 \text{ cm}^{-1} \). In the shown spectral range and especially at resonance, the aluminum antenna scatters the electromagnetic field much more than it absorbs it. Thus, the extinction cross-section is mainly based on the scattering cross-section.

To determine the field-enhancing properties of the rod-shaped nanoantenna, the extinction cross-section \( \sigma_{\text{ext}} \) is normalized to the geometric cross-section \( \sigma_{\text{geo}} \):

\[
\sigma_{\text{norm}}(\tilde{\nu}) = \frac{\sigma_{\text{ext}}(\tilde{\nu})}{\sigma_{\text{geo}}} = \frac{\sigma_{\text{ext}}(\tilde{\nu})}{w \cdot L}
\]

If the normalized extinction cross-section \( \sigma_{\text{norm}} > 1 \) the extinction is larger as what can be referred to simple shadowing of the nanorod (or nanoparticle). This indicates that the nanorod "confines" the light and the electromagnetic field is locally enhanced in the vicinity of the nanowire [28]. The calculations displayed in figure 2.6b show that the normalized extinction cross-section \( \sigma_{\text{norm}} \) (or so-called extinction efficiency) at resonance is about 20 for an aluminum nanorod with length \( L = 600 \text{ nm} \). This result is compared to two shorter nanorods (width \( w = 100 \text{ nm} \) is kept constant) and it can be seen that the normalized extinction cross-section at resonance \( \sigma_{\text{norm}}(\tilde{\nu}_{\text{res}}) \) decreases with decreasing nanorod length \( L \). This behavior is based on the lightning rod effect, which increases for longer nanorods, since the separation between the dipole charges increases upon elongation of the nanoantenna. As a consequence, the restoring force of the displaced charges decreases and the effective dipole moment increases with increasing length \( L \) [30]. The calculated results are in accordance with the literature.
Variations in antenna design  The resonance properties of nanoantennas can not only be influenced by their size and material, but also by their shape. In the literature different geometries are applied, such as disks [32], triangles [21], dimers of rods or triangles (so-called bowties [33]), V- or Y-shaped antennas [34, 35], as well as U-shaped split-ring resonators (SRRs). These can be coupled to short nanorods or to other SRRs, e.g. in [36]. Furthermore, according to the Babinet’s principle each antenna can also be fabricated as aperture, slit or hole, e.g. in [37, 38]. Thereby, the transmittance (reflectance) of an exemplary disk array is identical to the reflectance (transmittance) of the complementary hole array [39]. Since SRRs are widely applied as building blocks for so-called metamaterials, they will be described in the following section.

2.2.2 Split-ring resonators

The split-ring resonator (SRR) is a nanoantenna structure with a magnetic response applied in metamaterials (MMs). A single-SRR can be understood as a planar, highly conductive ring with a non-conductive cut gap at one side, as shown in figure 2.7a. The physical behavior can be explained by an equivalent circuit. In case of a temporally varying magnetic field, an electric circular current \( \vec{j} \) is induced in the ring which acts as inductance. Furthermore, the gap is a capacitance with charges accumulating across it. In this way, a planar, single SRR is described as a resonator coupling to a perpendicular magnetic field or as a so-called LC circuit as displayed in figure 2.7b. The magnetic resonance frequency \( \omega_{LC} \), the so-called LC resonance, is defined as follows [14]:

\[
\omega_{LC} = \frac{1}{\sqrt{LC}} \tag{2.19a}
\]

\[
L = \mu_0 \cdot \frac{I_{xy}}{I} \tag{2.19b}
\]

\[
C = \varepsilon_0 \varepsilon_r \cdot \frac{w l}{d} \tag{2.19c}
\]
2.2 Metal nanoantennas for the mid-infrared spectral range

\[
\Rightarrow \omega_{LC} = \frac{\sqrt{d}}{\sqrt{\mu_0 \epsilon_0 \epsilon_r \cdot l_x l_y w}} = 2\pi c \cdot \tilde{\nu}_{LC}
\] (2.19d)

with the side lengths \(l_x\) and \(l_y\) of the SRR, the thickness \(t\) of the metal layer, the arm width \(w\) and the gap size \(d\), as marked in figure 2.7c. The magnetic permeability of free space \(\mu_0\), the electric permittivity of free space \(\epsilon_0\), as well as the permittivity of the filling medium \(\epsilon_r\) (here simplified by only taking the real part of the dielectric function into account) are used in the equations above. The effective capacitance of the gap is denoted as \(C\) and the effective inductance of the ring is summarized as \(L\).

SRRs, which are nonmagnetic conducting elements, can behave as having a magnetic dipole moment. The periodic arrangement of SRRs allows for a magnetic coupling of the resonators and the generated "new medium" can be interpreted as having an effective permeability \(\mu_{eff}(\tilde{\nu})\), which can attain negative values [40]. Referring to this, SRRs are applied to generate materials, which scatter the incident electromagnetic waves in an artificial way not known from naturally occurring materials. For example a negative refractive index can be realized for these metamaterials, as will be discussed in the following.

The response of the SRR to the incident electromagnetic wave depends on the configuration of the electric field \(\vec{E}\), the magnetic field \(\vec{H}\) and the wave vector \(\vec{k}\) as illustrated in figure 2.7d. Thus, three different resonances can be observed: the magnetic resonance \(\omega_{LC}\), the magnetic LC resonance due to electric excitation coupling to the magnetic resonance (EEMR) also at \(\omega_{LC}\) and a short-wire-like electric resonance, which is denoted as \(\omega_0\) by Zhou et al. [41].

![Diagram of SRR configuration](image)

Figure 2.7: The time varying incident field induces an electric current \(\vec{j}\) in the SRR and produces a magnetic field that opposes or enhances the incident field as shown in figure 2.7a. The equivalent LC circuit is depicted in 2.7b. In 2.7c, the geometrical parameters of a single SRR are given: arm lengths \(l_x\) and \(l_y\), arm width \(w\), metal thickness \(t\) and gap size \(d\). The inductance \(L\) represents the conductive ring, while the conductance \(C\) corresponds to the SRR gap. Configurations of the incident electric field \(\vec{E}\), the magnetic field \(\vec{H}\), as well as the wave vector \(\vec{k}\) are shown in 2.7d, while the related resonances are denoted. Figure 2.7d was adapted from [41].

2.2.3 Metasurfaces and metamaterials

Following the Greek language, the word metamaterial refers to the term beyond conventional materials [14]. Thus, metamaterials (MMs) enable properties, which are artificial and not available for natural materials. Due to their synthetic structure, the electromagnetic energy can be controlled. The effective permittivity \(\varepsilon_{eff}(\tilde{\nu})\), as well as the effective permeability \(\mu_{eff}(\tilde{\nu})\) may be designed independently and arbitrarily throughout a material, while they can take positive and negative values [40]. The design of these properties is analogous to the reasoning used for conventional materials, where the response of a material to electromagnetic excitation is given by an average of individual responses. Each subwavelength unit cell, such as atoms and molecules, which are so-called meta-atoms, is taken into
account. This concept can be upscaled from the VIS [34] to the GHz [42] spectral range.

With MMs, a negative effective refractive index $n$ can be generated. The refractive index $n$ is below zero, if the permittivity $\varepsilon$ and the permeability $\mu$ below zero has not been found in nature. Simultaneous negative effective permittivity $\varepsilon_{\text{eff}}$ and permeability $\mu_{\text{eff}}$ are achieved by using two types of resonator: one magnetic and one electric, while their resonance must be close to one another [43]. Smith et al. showed that a combination of a SRR (magnetic resonance) with a wire (electric resonance) in between in each unit cell and an arrangement as threedimensional array, as in figure 2.8a, leads to a negative effective refractive index $n_{\text{eff}}$ [42].

The situation of a negative refractive index can be visualized by Snell’s law. It is stated that the ratio of the sine of the angle on incidence $\theta_i$ and of the angle of refraction (transmission) $\theta_t$ equals the ratio of the indices of refraction $n$ of two adjacent media. Equivalently the ratio of the phase velocities $v$ can be applied. For the example given in figure 2.8b Snell’s law is defined as follows:

$$\frac{\sin \theta_i}{\sin \theta_t} = \frac{v_{\text{air}}}{v_{\text{diel.}}} = \frac{n_{\text{diel.}}}{n_{\text{air}}}$$ (2.20)

For a positive refractive index $n_{\text{diel.}}$, the incident electromagnetic wave is refracted closer to the normal with $\theta_t < \theta_i$ if the index of refraction increases upon the transmission through the interface (here from $n_{\text{air}} = 1$ to $n_{\text{diel.}} > 1$). In contrast, in figure 2.8c the negative refractive index $n_{\text{MM}}$ (instead of $n_{\text{diel.}}$) leads to a refraction of the incident ray with a negative angle to the normal $\theta_t$. Metamaterials with a negative refractive index have also been denoted as left-handed materials (LHMs), since the phase velocity of light is directed against the flow of energy [44], which is sketched in figure 2.8c. For a positive refractive index medium, the electromagnetic energy flow is directed forward and in the same direction as the wave vector or phase flow [45]. The left-handedness in this sense refers to the orientation of the electric field vector $\vec{E}$, the magnetic field vector $\vec{H}$ and the wave vector $\vec{k}$ (A right-handed system is shown in figure 2.7d.).

By reducing the thickness of MMs and using alternative plasmonic materials, a new class of ultra-thin optical elements is given: optical metasurfaces (MSs), which allow for a variation of the fields amplitude and phase [46]. Holloway et al. described MSs as follows: "Three-dimensional metamaterials can be extended by arranging electrically small scatterers or holes into a two-dimensional pattern at a surface or interface. This surface version of a metamaterial has been given the name metasurface." [47]. Therefore, complex subwavelength structures are needed. Advanced techniques, such as electron-beam lithography or focused ion beam milling allow for their flexible fabrication. In the literature, many different applications of nanoantenna-array MSs (or so-called metafilms), or MMs were shown [46, 48]. Unconventional optical properties allow for new applications regarding the control of electromagnetic radiation, as for example chemical sensing, superlensing, cloaking, hyperbolic MMs or enhanced emission of quantum emitters [44, 46]. Nevertheless, their proposed functionalities could be improved by adding switching and modulation capabilities [48]. In the following section, examples for the tuning of infrared resonances are shown.

2.3 Tuning and shifting of nanostructure resonance positions

The optical response of nanostructures can be influenced differently: either the resonance amplitude is changed, or the frequency position is shifted. This influence can be realized reversibly and irreversibly.
2.3 Tuning and Shifting of Nanostructure Resonance Positions

Figure 2.8: With the combination of SRRs and wires as in figure 2.8a Smith et al. showed the first negative index metamaterial (MM) here for the GHz spectral range [42]. Snell’s law is well-known for materials with a positive real part of the refractive index n as shown in figure 2.8b. There, the refractive index increases from air to the positive refractive index medium (here: dielectric medium) and thus, the transmitted light is refracted to an angle θi smaller than the angle of incidence θr. For MMs, the light incident from air is refracted under a negative angle with the normal in the MM. Thereby the energy flow (black) and the wave vector or phase flow (gray) are in opposite directions, which led to the name left-handed materials. Figure 2.8c was adapted from [49].

The purpose of so-called tuning or switching⁴ is to broaden the spectral range of possible applications for infrared nanostructure resonances, such as chemical sensing (e.g. for SEIRA) for example, as well as to allow for multi-band sensing to address different vibrational bands with only a single sample design. Another objective can be the concept of ON/OFF switching by shifting the resonance (far) out of the initial frequency range. The application of resonance shifting and tuning could also include nanostructure perfect absorber designs [50]. The spectral availability of many MM and MS concepts, for example for beam shaping, e.g. [34, 51], could be extended by using an active medium.

In the following, individual examples of antenna resonance tuning and shifting, which are not restricted to the MIR spectral range, will be discussed. The shown examples are divided depending on the controlled parameter: either the nanostructure itself can be influenced, or the nanostructure’s dielectric surrounding.

2.3.1 Variation of the Coupling Distance of Split-Ring Resonator Pairs

The manipulation of the nanostructure resonance frequency position can be realized by influencing the geometry of an ensemble of nanostructures. After the fabrication of the nanostructures the resonance frequency position $\tilde{\nu}_{res}$ of each single resonant structure is defined. Therefore, the shift of the resonance frequency $\Delta \tilde{\nu}_{res}$ is based on the change of the "effective (coupled) geometry" of complex SRR nanostructures (e.g. coupled SRRs as in figure 2.9a or SRRs coupled to nanorod antennas). The changed coupling geometry has a direct impact on the resonance of these coupled SRR structures by influencing the capacitance C and the coupling strength of the single resonant elements. As shown by equation 2.19 the LC resonance of the SRR $\tilde{\nu}_{LC}$ is proportional to the square root of the gap size $d$. Pryce et al. investigated coupled gold SRRs (100 nm thick) on a flexible poly(dimethylsiloxane) (PDMS) (1 mm thick) substrate, which was uniaxially elastically strained [36]. Thus the coupled SRRs (CSRRs) were moved apart. This is shown in scanning electron microscopy images in figure 2.9a.

Asymmetrically coupled SRRs (ACSSRs) as shown in figure 2.9a are pairs of SRRs with different arm lengths $l_y$ and coupled at their tips with the coupling distance $d$, called gap. Aydin et al. showed

⁴Here, the term tuning refers to a gradual influence, while switching describes a stepwise process, which mostly refers to a single step.
that these structures allow for a resonance frequency tuning by controlling the coupling distance between the individual SRRs [52]. Pryce et al. stretched the substrate with the axial strain defined as \((L - L_0) / L_0 \cdot 100\%\) with the initial length of the PDMS sample defined as \(L_0\). For increased strain, the SRR coupling distance \(d\) increases and the resonance frequency position \(\tilde{\nu}_{\text{res}}\) is shifted to higher wavenumbers (smaller wavelengths). The resonance position \(\tilde{\nu}_{\text{res}}\) can not be directly identified as the LC resonance \(\tilde{\nu}_{\text{LC}}\). The coupling of two SRRs with individual resonances leads to a coupled mode pair based on hybridization interaction in analogy to molecular orbital theory [52]. A symmetric (bright) and an anti-symmetric (dark) mode appear at higher, as well as at lower energy than the individual resonances (cf. appendix A.1). By varying the distance of the ACSRRs the coupling strength between the two SRRs changes and thus, the spectral positions of the two hybridized resonant modes are shifted [52].

![SEM images of CSRRs, strained and relaxed](image1)

![Experimental reflectance spectra of ACSRR arrays](image2)

Figure 2.9: Arrays of \(2 \times 2\) ACSRRs were characterized with scanning electron microscopy (SEM). The variation of the coupling distance ("gap") due to strain and relaxation is shown in (a). Corresponding reflectance spectra are depicted in (b). A blue-shift of the resonance wavelength due to elastic strain, as well as a red-shift due to relaxation (plastic deformation) can be detected. The resonance corresponding to relaxation after a 10% strain (green) matches with the initial spectrum. Thus, a strain of 10% is purely elastic, while a strain of 50% (blue) leads to strong plastic deformation, which can be seen in the spectral shift (dashed blue versus black). The figures were taken from [36].

In figure 2.9b, experimental FTIR spectra of ACSRR arrays\(^5\) on differently strained substrates are shown. The reflection peak is ascribed to the hybridized antisymmetric (dark) resonant mode, which is at lower frequencies and higher wavelengths respectively than the hybridized symmetric (bright) mode [53]. The initial geometry with a gap size \(d\) of 60 nm shows a reflectance peak at about 3.9 \(\mu\)m. Due to elastic tuning (10% strain), the ACSRR array resonance wavelength \(\lambda_{\text{res}}\) is shifted to smaller wavelength. A strain of 50% results in an increase of the coupling distance \(d\) up to 80 nm. After relaxation of the PDMS substrate, the gap of the ACSRRs is decreased relative to the initial coupling distance, which can be ascribed to inelastic deformation of the substrate, and \(\lambda_{\text{res}}\) increases, as it is shown in figure 2.9a.

2.3.2 Variation of the Refractive Index of the Nanostructure Surrounding

As introduced earlier, the resonance frequency position of a nanorod antenna \(\tilde{\nu}_{\text{res}}\) can be approximated by its length \(L\) and the real part of the refractive index of the antenna surrounding \(n_{\text{eff}}\) (cf. equations

---

\(^5\)The arrangement of nanostructures in periodic arrays can allow for a coupling of the local scattered fields and thus for more pronounced resonances. A shift of the resonance position compared to single nanostructures occurs as well. The coupling of nanorods will be discussed in detail in chapter 5.
2.3 Tuning and shifting of nanostructure resonance positions

Figure 2.10: Depicted is the resistance of VO$_2$ as a function of the temperature $T$. The monoclinic insulating phase (I-VO$_2$) is stable for $T \leq 341$ K. The transition into the high-temperature rutile metal phase (M-VO$_2$) proceeds via coexistence of the insulating and the conductive phases. The strongly correlated metal (SCM) exists in the form of metallic puddles in the insulating matrix. Figures were adapted from [60] (2.10a) and [61] (2.10b).

2.13 and 2.14). Thus, by keeping the antenna geometry constant (including more complex two- or three-dimensional arrangements of antennas) a shift of the antenna resonance frequency position $\tilde{\nu}_{\text{res}}$ can only be realized by changing the dielectric surrounding of the nanorod via $\tilde{\nu}_{\text{res}} \propto n^{-1}$. Therefore, a medium with a tunable refractive index $n_\text{eff}$ needs to be introduced in the vicinity of the antenna.

The closer the medium with the tunable refractive index to the antenna (tips) the more pronounced is the influence on the resonance frequency position $\tilde{\nu}_{\text{res}}$ expected to be (according to the local field enhancement of the antenna).

Using changes of the charge carrier concentration

Insulator-to-metal transition of vanadium dioxide In the literature, the phase transition of vanadium dioxide VO$_2$ was employed to tune nanostructure resonances, e.g. [54, 55, 56]. VO$_2$ undergoes an insulator-to-metal transition (IMT) at about 67°C (340 K). There, the material changes from its low-temperature insulating to its high-temperature metallic phase. Simultaneously, the crystal structure is transformed from a monoclinic structure (space group $P2_1/c$ [58]) into a rutile structure ($P4_2/mnm$ [59]) upon heating as displayed in figure 2.10a. This transition is a gradual process from the insulator via a strongly correlated metal (SCM) in the form of nanoscale puddles to the final metal phase, which is shown in figure 2.10a. The percolative nature of the IMT was investigated with SNOM [60].

The IMT is visible in the resistance and in the dielectric function $\varepsilon_{\text{VO}_2}(\lambda)$ given in figure 2.10. In the VIS and IR spectral range the real part of the dielectric function $\varepsilon_{1,\text{I-VO}_2}$ is positive and increases for an increasing wavelength $\lambda$. At the same time the imaginary part $\varepsilon_{2,\text{I-VO}_2}$ decreases and approximates zero in the MIR spectral range. Upon annealing the permittivity behaves as it was introduced for metals earlier in this chapter (cf. figure 2.2): the real part $\varepsilon_{1,\text{M-VO}_2}$ becomes negative, while the imaginary part increases for an increasing wavelength $\lambda$. The temperature dependent resistance of VO$_2$ depicted in figure 2.10a shows a decrease of the resistance by about four orders of magnitude for the IMT. As a consequence, the pronounced change of the dielectric function $\varepsilon_{\text{VO}_2}(\lambda)$ upon the IMT can be related to the increased free charge carrier concentration in the metal phase.

Recently, Aetukuri et al. showed, that the IMT transition temperature of VO$_2$ thin films itself can be continuously tuned in the broad temperature range between 285 and 345 K by manipulating the conductivity, which is based on the orbital occupancy in the metallic state [57].
It should be noted that the cooling back to room temperature $T_R$ - a metal-to-insulator transition (MIT) - leads to an increase of the resistance to its initial value, while a characteristic hysteresis loop with a temperature offset $\Delta T = T_{\text{IMT}} - T_{\text{MIT}}$ was found [56, 61, 62].

Lei et al. investigated the particle plasmon resonance of a single gold nanoparticle with a diameter of about 100 nm placed on a VO$_2$ thin film as shown in figure 2.11a [63]. In the scanning electron microscopy (SEM) image, a rough surface of the VO$_2$ thin film can be seen. Even this resonance lies in the VIS spectral range and its resonance frequency (or wavelength) position cannot be described by the $\lambda/2$-model, this study is chosen as example from the literature here, since the studied sample system is relatively simple compared to three-dimensional MM structures or such. The localized surface plasmon resonance (LSPR) position $\tilde{\nu}_{\text{LSPR}}$ of the nanoparticle is defined as follows:

$$\tilde{\nu}_{\text{LSPR}} = \frac{1}{2\pi c} \sqrt{\frac{N\epsilon^2}{\epsilon_{\text{eff}}^\infty(\epsilon_\infty + 2\epsilon_{d,1})}}$$

(2.21)

with the free electron concentration in the gold nanoparticle $N$, the optical dielectric constant $\epsilon_\infty$ (contributions of high frequencies) of the gold nanoparticle ($\epsilon_{\infty,\text{Au}} = 9$ [14]) and $\epsilon_{d,1}$ being the real part of the surrounding of the nanoparticle (including VO$_2$) [64]. Equation 2.21 is derived from the classical dipole polarizability $\alpha$ (cf. equation 2.15b), the Fröhlich condition (cf. equation 2.16) and the classical Drude model (cf. equation 2.4) [65]. The classical dipole polarizability can be applied since the particle diameter is much smaller than the wavelength.

For the gold nanoparticle placed on a VO$_2$ thin film, the dielectric surrounding includes air and the VO$_2$. Since the shift of the resonance position $\tilde{\nu}_{\text{LSPR}}$ is dominated by the contribution of VO$_2$, the permittivity of the surrounding $\epsilon_{d,1}$ is approximated by $\epsilon_{1,\text{VO}_2}$. Thus, the direction of the LSPR resonance shift $\Delta\tilde{\nu}_{\text{LSPR}}$ can be estimated via the sign of the difference:

$$\Delta\tilde{\nu}_{\text{LSPR}} = \tilde{\nu}_{\text{LSPR,I-VO}_2} - \tilde{\nu}_{\text{LSPR,M-VO}_2} \sim \frac{1}{\sqrt{\epsilon_\infty + 2\epsilon_{d,1,\text{VO}_2}}} - \frac{1}{\sqrt{\epsilon_\infty + 2\epsilon_{d,1,\text{M-VO}_2}}}$$

(2.22)

with $\epsilon_{1,\text{VO}_2} > 0$ and $\epsilon_{d,1,\text{M-VO}_2} < 0$. For wavelengths $\lambda$ shorter than about 950 nm, $\epsilon_{d,1,\text{M-VO}_2}$ attains small negative values ($\epsilon_{d,1,\text{M-VO}_2} > -5$). As a consequence, $\tilde{\nu}_{\text{LSPR,I-VO}_2} < \tilde{\nu}_{\text{LSPR,M-VO}_2}$ and a shift of the LSPR to larger wavenumbers or shorter wavelength is expected upon the IMT of VO$_2$. Lei et al. showed this behavior experimentally as depicted in figure 2.11b. A stepwise heating was associated with an increasing metal fraction in the VO$_2$ film and thus, led to a stepwise shift of the resonance $\Delta\lambda_{\text{LSPR}}$ with the maximum shift of 25 nm between $T_R$ and the maximum $T$. This means that the final resonance position at the highest temperature $T$ is shifted to shorter wavelengths by about 4% relative to the initial resonance position at room temperature $T_R$. Cooling of the VO$_2$ (metal-to-insulator transition) shows a reversible shift of the LSPR back to its initial position including a hysteresis loop $\Delta T$ of about 10°C.

A more complex system based on the same principle as described for the single particle plasmon resonance tuning was presented by Lei et al. in 2015 [56]. They placed an array of periodic gold nanodisks with a diameter between 80 and 210 nm on top of a VO$_2$ thin film with a thickness of 50 nm and illuminated the sample with UV light pulses to realize a more persistent IMT of the VO$_2$ thin film (the metallic state can last up to several hours). The same temperature dependent tuning of the nanodisks resonance wavelength $\lambda_{\text{res}}$ including the hysteresis loop was found, but here in the NIR.
spectral range as can be seen in figure 2.11c. There, the maximum shift $\Delta \lambda_{\text{LSPR}} = 120 \text{ nm}$ between room temperature $T_R$ and the maximum $T$ was measured, which is a resonance change of about 12.6% relative to the initial resonance wavelength.

![Figure 2.11: A single gold nanoparticle (NP) with a diameter of $d = 100 \text{ nm}$ is placed on a VO$_2$ thin film on a glass substrate] as shown in figure 2.11a. (The marker "(b)" remained from [63].) By heating the sample through the insulator-to-metal transition (IMT), the metallic fraction in the VO$_2$ increases and thus, shifts the LSPR position as depicted in figure 2.11b. The hysteresis with a temperature offset $\Delta T$ between the IMT and the MIT (cooling) is characteristic for VO$_2$. In figure 2.11c similar spectral results for an array of gold nanodisks (diameter of $d = 130 \text{ nm}$) placed on a 50 nm VO$_2$ thin film are shown. The stepwise shifted resonance wavelength for an array of nanodisks is related to the metal fraction in the I-VO$_2$ thin film. The figures were taken from [63] (2.11a,2.11b) and [56] (2.11c).

Dickens et al. investigated split-ring resonators (SRRs) made from a 150 nm silver and a 60 nm VO$_2$ layer, which were placed on an Al$_2$O$_3$ substrate [61]. By using a heating stage, the IMT of VO$_2$ was triggered. Upon heating the VO$_2$ layer above the IMT transition temperature, the effective thickness of the resonator element changes, since the total thickness of the SRR is not only given by the thickness of the silver layer, but also by thickness of the metallic VO$_2$ layer. The authors claimed that the effective inductance $L$ and capacitance $C$ of the SRR increased, which led to an increase in the resonance wavelength $\lambda_{\text{res}}$. The percentual shift of 3.2% is relatively small compared to the other discussed concepts.

Recently, Rensberg et al. showed that the IMT temperature can be decreased down to room temperature $T_R$ by irradiation of the VO$_2$ with an argon ion beam (Ar$^+$), which leads to the creation of structural defects in the VO$_2$ (defect engineering) [62]. The irradiation damage displaces vanadium and oxygen atoms from their lattice sites leading to the formation of interstitial vacancy complexes. Since the IMT is very sensitive to structural defects, the transition temperature was shifted from its initial value down to room temperature $T_R$. A tunable metasurface with a variable degree of optical anisotropy in the MIR spectral range was proposed as application of this selective shift of the IMT temperature. Therefore, a periodic structure of parallel ridges of VO$_2$ non-irradiated and irradiated with ion beams was heated to induce the IMT in the irradiated ridges, which led to a preferential polarization-dependent absorption and reflectance respectively. Thereby the transition temperature can be "engineered" by adapting the necessary ion beam irradiation. A further heating above the generic IMT temperature led to a vanishing of the polarization dependence since also the non-irradiated VO$_2$
2.3 Tuning and shifting of nanostructure resonance positions

ridges were transferred into the metal phase.

Bias-controlled charge carrier concentration in doped GaAs By controlling the free carrier concentration in immediate vicinity of resonant nanostructures, their resonance frequency position can be tuned as well. As exemplary concept for bias-dependent tuning of the resonance frequency position the work of Jun et al. [66] will be discussed. There, gold SRRs are placed on top of a stack with an undoped Al$_{0.3}$Ga$_{0.7}$As layer, a n+ doped GaAs layer, and a semi-insulating (SI) GaAs substrate as illustrated in figure 2.12a. The SRRs and the n+ doped GaAs layer form a metal-semiconductor junction, while the Al$_{0.3}$Ga$_{0.7}$As layer works as a barrier to reduce leakage currents.

Equation 2.4 defines the dependence of the plasma frequency $\omega_p$ and the permittivity $\epsilon$ on the charge carrier density $N$, which is also known as doping level. Furthermore, the damping rate $\gamma_D$ is given by the effective mass $m^*$ and the carrier mobility $\mu$ for n+ doped GaAs:

$$\gamma_D = \frac{e \mu}{m^*}$$

(2.23)

Thus, with known values for the mobility $\mu$ and the effective mass $m^*$ the permittivity $\epsilon$ can be calculated as a function of the charge carrier density $N$. The results of the Drude model for the real part $\epsilon_1$ of GaAs in the MIR spectral range, are shown in figure 2.12b. By applying a negative gate bias, carriers are removed (carrier density $N$ decreases) and the depletion region width $W_{\text{depletion}}$ ("depletion region" in figure 2.12a) can be increased by tens of nm. Due to the decreased doping level, the plasma wavenumber $\tilde{\nu}_p$ decreases and thus, the real part of the permittivity of GaAs $\epsilon_{Ga,As,1}$ increases from about 5.5 to about 11 at 10 $\mu$m (red line in figure 2.12b).

In transmission spectra, which are taken with a Fourier-transform infrared spectrometer, and depicted in figure 2.12c, a dip in the MIR spectral range related to the LC resonance (cf. equation 2.19) of the investigated SRRs can be found. This position is gradually shifted to smaller wavenumbers by applying a varied negative bias voltage. Since the LC resonance wavenumber $\tilde{\nu}_{LC}$ is inversely proportional to the square root of the permittivity of the medium filling the capacitor gap of the SRR ($\epsilon_r$ in equation 2.19), an increase of the real part of the permittivity $\epsilon_{Ga,As,1}$ leads to a decrease of the LC resonance position $\tilde{\nu}_{LC}$. With increasing bias voltage, the permittivity increases due to the removed charge carriers and the shift of the resonance to smaller wavenumbers can be observed. The resulting shift of the frequency position is in the order of several wavenumbers with a maximum of 10 cm$^{-1}$. Relative to the position of the center frequency, this corresponds to a shift of about 1%.

Further concepts Yao et al. loaded antennas with graphene [67]. There, a voltage was applied to inject carriers. Recently, Rodrigo et al. studied graphene nanoribbon arrays, which shows a plasmon resonance in the MIR spectral range [68]. By tuning the voltage applied to the graphene the Fermi level of the graphene was changed and thus, the resonance position of the plasmon resonance was altered and applied to the sensing of the vibrational fingerprints of protein molecules. Asib et al. used gold antenna dimers on an indium tin oxide (ITO) substrate and changed the carrier concentration by optical pumping [69].
Using the refractive index contrast of phase-change materials

Phase-change materials (PCMs) exist in at least two (meta)-stable solids, whereby the amorphous (A) state can be changed into the crystalline (C) solid state by thermal annealing above the crystallization temperature \( T_C \). This crystalline state remains stable after the PCM is cooled down to room temperature \( T_R \). Therefore, the phase change is non-volatile. Fundamentals regarding typical PCM compounds, their atomic structure and bonding situation, optical properties and related data storage media based on PCMs will be described in chapter 3.

In figure 2.13, a metal nanorod antenna is placed on a substrate, e.g. silicon, and covered by a PCM thin film. For temperatures \( T \) above the crystallization temperature \( T_C \), the phase of the PCM changes into its crystalline state. In the schematic spectra the sample reflectance \( R \) is shown as a function of the wavenumber \( \tilde{\nu} \). The antenna resonance causes the pronounced peak\(^7\). Due to the phase change, the initial frequency position of the antenna adjacent to a thin film of A-PCM \( \tilde{\nu}_A \) is shifted to \( \tilde{\nu}_C \). If the refractive index \( n_A \) increases upon crystallization, the resonance frequency position decreases. This shift is illustrated by red lines in figure 2.13.

\(^7\)The measurement of such reflectance spectra with Fourier transform infrared (FTIR) spectroscopy will be discussed in chapter 4.

---

2.3 Tuning and shifting of nanostructure resonance positions
An experimental concept using a PCM to influence the resonance peak wavenumber and wavelength respectively of a nanostructure was demonstrated by GholiPouR et al. [38]. Asymmetric split-ring slits (ASRSs) in gold were brought close to a Ge$_2$Sb$_2$Te$_5$ (GST-225) layer, while a ZnS:SiO$_2$ capping layer should prevent gold diffusion into the PCM. On top of the stack, a relatively thick layer of ZnS:SiO$_2$ or SiO$_2$ was chosen to prevent the PCM layer from degradation. The corresponding experimental reflection spectra are shown in figure 2.14b. A resonance peak shift of about 9% upon the amorphous to crystalline phase transition was detected. The phase change was introduced by a single nanosecond laser pulse as follows: $A \rightarrow C$ with 100 ns at 0.1 mW/$\mu$m$^2$ and $C \rightarrow A$ with 50 ns at 0.25 mW/$\mu$m$^2$. Thereby, no results for switching beyond a single transition $A \rightarrow C$ were shown.

Another experimentally demonstrated concept for the use of PCMs was described by Chen et al. [32], who investigated partly crystallization of GST-225 below gold nanodisks leading to a stepwise tuning of the resonance position. The crystallization behavior of the PCM layer itself was not discussed separately, neither was the gold diffusion considered.

In 2013, Hira et al. studied single gold nanoparticles placed on a GST-225 thin film, which were illuminated either by femtosecond laser pulses ($C \rightarrow A$ phase transition) or by continuous wave operation of a laser diode ($A \rightarrow C$ phase transition) [70]. It was assumed that only the GST volume in contact to the gold nanoparticle underwent a phase transition due to the spatially confined field enhancement there. A wavelength shift in the scattering spectra of about 3% was found. Thereby, experimental results for reversible shifting were inconsistent.

Besides, the non-typical PCM compound gallium lanthanum sulphide (GLS)$^9$ was applied by SåMson et al. [71]. ASRSs in gold were covered with a GLS thin film and annealed, which led to a shift of the ASRS resonance position by about 11% in the NIR spectral range.

Cao et al. calculated the shifting of the resonance wavelength of elliptical nanohole arrays (ENAs) with commercial finite difference time domain (FDTD) code [72, 73, 74]. The nanoholes were placed in a layer stack of gold, the PCM Ge$_2$Sb$_2$Te$_5$ (GST-124) or Ge$_2$Sb$_2$Te$_5$ (GST-225) and gold, surrounded by vacumm. The described metal-dielectric multilayer with a periodic array of holes was proven to act as negative-index MM [75]. By changing the phase of the used PCM, shifts of the negative index resonance by about 43% [72, 73] or 40% [74] were calculated. However, all these concepts were only theoretically studied.

![Layer stack design with ASRSs](image)

![Experimental spectrum](image)

Figure 2.14: GholiPouR et al. studied asymmetric split-ring slots (ASRSs) in a gold/ZnS:SiO$_2$/Ge$_2$Sb$_2$Te$_5$/SiO$_2$ layer stack, shown in figure 2.14a. In the measured reflection spectra, a clear shift of the spectrum for crystalline relative to amorphous Ge$_2$Sb$_2$Te$_5$ is visible. Furthermore damping of the crystalline relative to the amorphous reflection upon phase transition of the PCM layer can be detected. The figures were adapted from [38].

$^9$GLS was described as PCM in [71]. An identification as PCM according to the definitions, which will be given in chapter 3, was not possible due to a lack of information about GLS.
2.3 Tuning and shifting of nanostructure resonance positions

2.3.3 Further approaches for shifting nanostructure resonance frequency positions

Additional to the presented approaches, many concepts for the tuning of nanoantenna resonance frequency positions were described in the literature. To round out the literature review, a brief summary of these concepts will be given.

So-called liquid crystals (LCs) behave like a liquid regarding their viscosity, but act as a crystal in respect to their anisotropy of the oriented molecules at the same time. Their different so-called mesophases distinguish between various types of ordering, e.g. nematic [76]. LCs are an example of an electrooptically active dielectric medium, which has found its major application in displays (LCD - liquid crystal display). Recently, frequency tunability of optical metamaterials was realized by changing the dielectric environment of the resonators with LCs: in the visible spectral range Kosyrev et al. reported on voltage-controlled tuning of the plasmonic response of a simple arrayed gold nanodot-liquid crystal composite [77]. Decker et al. used nematic LCs to switch between electric and magnetic resonances of a SRR-metasurface in the near-infrared spectral range [78]. LCs were also used in the near-infrared by Werner et al. [79], where calculations of the reconfigurable index of refraction for a LC metamaterial design were demonstrated. In the visible spectral range, Berthelot et al. studied antenna dimers with LC loaded gaps [80].

Chen et al. presented frequency-agile metamaterials for the terahertz spectral range, which were realized by incorporating semiconductors in metallic SRRs [81]. The design of the metamaterials refers to gold SRRs with Si capacitor plates on a sapphire substrate. The silicon regions of the MM were photoexcited by 30 fs NIR laser pulses with a center wavelength of 800 nm and a repetition rate of 1 kHz. Thus, the charge carriers were excited across the band gap of Si (1.12 eV). By increasing the power of the pump laser and with it the excited charge carrier density, the frequency position of the structure’s resonance was shifted to lower frequencies.

2.3.4 Summary

In the literature, it was shown that the post-fabrication control of coupled SRR resonator geometries and the variation of the refractive index of the surrounding of resonant nanostructures allow for a shifting of the resonance frequency position $\Delta \tilde{\nu}_{\text{res}}$. Thereby, the refractive index was altered by applying the IMT of VO$_2$, by changing the charge carrier concentration in semiconductors due to an applied bias voltage, as well as by using the refractive index change upon crystallization of PCMs. The latter is the focus of this thesis. PCMs are advantageous compared to the other approaches regarding the non-volatility of the structural state. In contrast to PCMs, VO$_2$ can not be stabilized in two different states at room temperature. As soon as the necessary thermal energy is removed, VO$_2$ transforms back into its low-temperature insulating phase. Thus, the VO$_2$ phase change is volatile, while for PCMs this phase change is non-volatile. The same applies to the voltage controlled charge carrier injection or depletion respectively in semiconductors. Furthermore, the structural change from the amorphous to the crystalline phase in PCMs is reversible, since re-amorphization can be triggered by optical or electrical pulses. On the contrary, Pryce et al. showed that the post-fabrication change of the coupling geometry in SRRs led to irreversible plastic deformation of the substrate and thus, the initial resonance position could not be detected again.

Based on these advantages of PCMs regarding the resonance position shifting $\Delta \tilde{\nu}_{\text{res}}$, many related
experimental and theoretical studies were published recently. However, these investigations lack of a particular choice of a suited PCM compound. Instead, most publications applied the well-known GST-225, which can be replaced by compounds leading to much larger shifts $\Delta \tilde{\nu}_{\text{res}}$ as shown in this work (cf. chapters 5 and 6). The published concepts for nanostructure resonance tuning will be compared quantitatively to the experimental results of this thesis regarding the realized resonance shift $\Delta \tilde{\nu}_{\text{res}}$ and resonance peak width FWHM in the end of chapter 6.

Moreover, reversible shifting, which was claimed by Gholipour et al. [38] for example, was not documented by experimental spectra yet. This aspect is taken up by this work and reversible shifting of the nanoantenna resonance positions will be studied in chapter 7. Especially individual addressing of nanostructures can be beneficial regarding MMs, since this could lead to a gradual manipulation of the MM optical functionalities (e.g. polarization, beam shaping).
CHAPTER 3

Fundamentals of phase-change materials

3.1 Introduction

So-called *phase-change materials* (PCMs) are binary, ternary or quaternary compounds containing chalcogens, primarily tellurium (Te), pnictogens, such as antimony (Sb), as well as elements of the carbon group, e.g. germanium (Ge) or tin (Sn). Additionally, indium (In) or silver (Ag) can be used to alloy PCMs. These PCMs offer at least two (meta-)stable solid states, which are the meta-stable amorphous and the long-term stable crystalline state. Metastability refers to the fact, that the phase is in equilibrium as far as no disturbance occurs. Only due to slight interactions, e.g. annealing, the metastable state is susceptible to fall into another state (of lower energy) \[82\]. The amorphous state lacks a short-range order and shows some degree of long-range order, while the crystalline state is characterized by a strong short-range, as well as long-range order. Between the different solid states, a strong contrast of the electrical resistivity and optical reflectivity occurs. Since PCMs can be switched from one state to the other on timescales down to the femtosecond regime \[83, 84\], they are often applied for memory concepts, which was already proposed by Ovshinsky in 1986 \[85\]. The pronounced electrical and optical contrasts between the different phases allow for the application in so-called *Phase-change Random Access Memories* (PCRAMs) or *Blu-ray Disc Recordable Erasable* (BD-RE).

In this thesis, PCMs will be used to influence the surrounding of metallic nanoantennas with resonance frequency positions $\tilde{\nu}_{\text{res}}$ in the MIR spectral range. The contrast in the refractive index $\Delta n$ between different solid phases of PCMs can shift the resonance frequency position of nanoantennas strongly. To understand the origin of this contrast, structural and optical characteristics of PCMs will be discussed in this chapter. In section 3.2 typical compounds, the structure and bonding mechanism of PCMs will be introduced. The permittivities of selected PCMs, which are investigated in this thesis ($\text{Ge}_3\text{Sb}_2\text{Te}_6$, $\text{InSb}$, $\text{GeSb}_2\text{Te}_{11}$, $\text{Ge}_2\text{Sb}_2\text{Te}_5$) will be explained in section 3.3. There, the focus lies on the strong optical contrast between the amorphous and crystalline compounds and its origin. Furthermore, a brief summary of laser-induced switching and the application of PCMs in storage devices will be given in section 3.4.
3.2 Fundamental properties of phase-change materials

Fundamental properties of PCMs, such as density, absorption or resistivity, rely on the phase of the PCM. The structural transition between the amorphous and crystalline phase, is sketched in figure 3.1. The structural transition of each PCM is accompanied by a pronounced change of its electrical and optical properties. PCMs are semiconductors (SCs) with a change in the position of the Fermi energy $E_F$ upon phase transition: in the amorphous phase $E_F$ lies within the bandgap, while $E_F$ is shifted to the valence band due to crystallization. Hence, amorphous PCMs can be classified as non-degenerated SCs and crystalline PCMs as degenerated SCs. The easily accessible contrast in electrical resistivity $\rho$ is fundamental for the applicability of PCMs, e.g. as storage media. The resistivity of GeSb$_2$Te$_4$ changes by about four orders of magnitude upon the phase transitions from an amorphous to a metastable crystalline and to a stable crystalline phase at elevated temperatures [86] for example. Furthermore, a strong contrast in optical reflectance $R$ between the amorphous and crystalline phase can be detected. By evaluating the crystallization upon laser irradiation of a Ge$_2$Sb$_2$Te$_5$ thin film, a relative reflectivity change of more than 20% upon annealing can be determined [87]. In addition to the phase related property contrast, the optical properties of each structure are a function of the energy $E$ (or wavenumber $\tilde{\nu}$) as well. This allows for tailored usage of PCMs depending on the selected spectral range. An elaborate description of the wavenumber dependent permittivity $\varepsilon(\tilde{\nu})$ of different GST compounds is given later in this chapter.

Phase transitions in PCMs are thermally induced. The necessary energy for reversible phase changes is generated by short optical or electrical pulses, whereas the pulse intensity and duration has to be varied either to amorphize or crystallize a PCM film. Since amorphization is a melt-quenching process, the PCM has to be molten and quickly cooled. In contrast, during crystallization the lattice needs sufficient time to relax into a (meta)stable structure. Thus, crystallization limits the operation speed of storage applications. Irreversible phase changes can be realized by a simple heating of the sample on a hot plate (crystallization) - as in figure 3.1 - or by induced pressure (amorphization) [89, 90].

The reversibility of the described structural transition, which can be realized in less than 1 ns [91], and the non-volatility of the phases have great significance for the technological applicability of PCMs. Their states are stable without the necessity of an energy input to retain the structural phase. This behavior is in contrast to vanadium dioxide (VO$_2$), which was elucidated in the previous chapter. VO$_2$ shows an insulator-to-metal transition, whereas the metallic phase requires a constant input of heat.

The difference in the atomic arrangement between an amorphous and a crystalline PCM was schematically shown in figure 3.1. While amorphous phases are "glassy" and refuse a description according
to standard crystallographic classes, crystalline PCMs attain different space groups depending on the annealing temperature, as well as on their stoichiometry. However, similarities can be found for PCM compounds with GeTe or Sb$_2$Te$_3$ subunits. GeTe consists of alternating Te and Ge layers, while Sb$_2$Te$_3$ crystallizes in layered structural units in sequences of Te-Sb-Te-Sb… with Te planes terminating each stack [86]. These are bound by Te-Te bonds, which can be classified as so-called van-der-Waals forces. Thereby Sb$_2$Te$_3$ dictates the stacking in metastable, as well as in stable crystalline Ge-Sb-Te (GST) phases [92]. As a consequence, crystalline GST compounds can be interpreted as superlattices, which are composed of GeTe units inside a Sb$_2$Te$_3$ unit and single Sb$_2$Te$_3$ blocks [92].

In this framework vacancies play an important role, since vacancy concentrations in crystalline PCMs can be as high as 25% [93]. In rocksalt structures (face-centered cubic), which are typical for metastable crystalline GST phases, Te atoms occupy anion sites, while Sb, Ge and intrinsic vacancies occupy cation sites [94]. Density functional theory (DFT) calculations indicate that vacancies can order intrinsically [95] or arrange to completely formed vacancy layers leading to a large reduction in energy [96].

3.2.1 The ternary phase diagram for Ge, Sb and Te

In figure 3.2, a ternary phase diagram with the three elements germanium Ge, tellurium Te and antimony Sb is shown. Each element is located at the apex, while binary compounds can be found at the sides and ternary compounds are located in the triangle. In the depicted phase diagram, different classes of Ge-Sb-Te based PCMs are marked. In particular, the pseudo-binary tie line between GeTe and Sb$_2$Te$_3$, the region around Sb$_2$Te, as well as the area around Sb occupy three of the technologically most important classes of PCMs discovered so far. The fourth class, which is defined by the compound In$_3$SbTe$_3$, will be briefly introduced in chapter 8. The pronounced optical contrast and the fast switching properties of these PCMs are applied for optical data storage [97, 98].

Following the pseudo-binary line (GeTe)$_x$-(Sb$_2$Te$_3$)$_{1-x}$ in figure 3.2 from lower to higher Te concentration several trends can be identified. From GeTe ($x = 1$) to Sb$_2$Te$_3$ ($x = 0$) the molar mass increases, whereas the crystallization temperature $T_C$, which marks the thermally induced amorphous-to-crystalline phase transition, decreases. For the GST compounds Ge$_8$Sb$_2$Te$_{11}$, Ge$_3$Sb$_2$Te$_6$ and Ge$_2$Sb$_2$Te$_5$, as well as for GeTe, structural and transport parameters are compared in table 3.1. The pseudo-binary compositions Ge$_3$Sb$_2$Te$_6$, Ge$_2$Sb$_2$Te$_5$, Ge$_1$Sb$_2$Te$_4$ and Ge$_1$Sb$_4$Te$_7$ ($b$ to $e$ on the marked line in figure 3.2), undergo not only a reversible crystallization process, but also an irreversible crystalline phase transition. The amorphous compound crystallizes into a metastable rocksalt structure (face-centered cubic). In a narrow temperature range, an intermediate phase with coexisting face-centered cubic (fcc) and rhombohedral structures exists. At elevated temperatures, it finally crystallizes into the stable rhombohedral structure [99]. In contrast, the compounds GeTe and Ge$_8$Sb$_2$Te$_{11}$ undergo a reversible crystalline phase transition from a rhombohedrally distorted to a high-temperature cubic phase at about 670 K [100, 101].

It is worth noting that due to the stacking in the crystalline structure an increase in the GeTe content (increasing $x$) is accompanied by a decrease of the vacancy concentration $n_{vac}$ [102]. In turn the atomic diffusion at moderate temperatures is hampered and the structural order takes more time, which leads to an increase of the crystallization temperature $T_C$ for (GeTe)$_x$-(Sb$_2$Te$_3$)$_{1-x}$ compounds with a higher GeTe content. The vacancy concentration $n_{vac}$ and the crystallization temperature $T_C$ can be found in table 3.1.

Associated with the structural change of PCMs, the density increases upon crystallization up to 10%
(amorphous to stable crystalline). Exemplary density values for different GST compounds are listed in table 3.1 as well.

Figure 3.2: Two dimensional representation of the ternary system Ge-Sb-Te. Each corner represents an element. Technologically important PCM classes based on Ge, Te and Sb are marked by three white areas. On the quasibinary line (GeTe)\(_x\)-(Sb\(_2\)Te\(_3\))\(_{1-x}\), the following GeSbTe compounds can be found - a: Ge\(_8\)Sb\(_2\)Te\(_{11}\) \((x = 8/9)\), b: Ge\(_3\)Sb\(_2\)Te\(_6\) \((x = 3/4)\), c: Ge\(_5\)Sb\(_2\)Te\(_5\) \((x = 2/3)\), d: GeSb\(_2\)Te\(_4\) and e: GeSb\(_3\)Te\(_6\). In this thesis, especially Ge\(_3\)Sb\(_2\)Te\(_6\), as well as Ge\(_8\)Sb\(_2\)Te\(_{11}\) and Ge\(_2\)Sb\(_2\)Te\(_5\) are investigated for infrared applications.

### 3.2.2 Bonding mechanism in phase-change materials

The electric susceptibility \(\chi\), which is a measure for the polarizability of a dielectric medium, can be expressed as follows [11]:

\[
\chi = \varepsilon_\infty - 1
\]  

with the optical dielectric constant \(\varepsilon_\infty\) defined at the energy \(E = 0.05\) eV following Shportko et al. [103]. This energy lies above the highest phonon frequencies reported for PCMs (below 20 meV for A-GST-225 [104] and C-GeTe [101], cf. page 44), but below the electronic transitions. (In section 3.3, the optical dielectric constant \(\varepsilon_\infty\) will be discussed in detail. However, in the framework of the bonding mechanism in PCMs, only a phenomenological description will be used here.) According to equation 3.1, large values of \(\varepsilon_\infty\) indicate a strong electric polarizability. Shportko et al. reported that PCMs show a pronounced increase of \(\varepsilon_\infty\) upon crystallization [103]. Depending on the stoichiometry of the PCM, an increase between 106 and 222% has been measured for \(\varepsilon_\infty,C\) relative to \(\varepsilon_\infty,A\). For example regarding the compound GST-225 the optical dielectric constant increased from \(\varepsilon_\infty,A = 16.0\) to \(\varepsilon_\infty,C = 33.3\). These findings lead to conclusions on the bonding nature of PCMs.

The low energy-limit of the real part of the dielectric function \(\varepsilon_1\), \(\varepsilon_\infty\) was analyzed by the so-called Clausius-Mossotti model with constant polarizabilities \(\alpha_i\) for each element \(i\), for instance Ge, Sb or Te:

\[
\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} = \frac{\rho}{3\varepsilon_0} \sum_i n_i \cdot m_i \cdot \alpha_i
\]  

with \(\rho\) being the density, \(m_i\) is the atomic weight of element \(i\), \(n_i\) represents the atomic density for each element and \(\varepsilon_0\) is the vacuum permittivity [105]. For the amorphous phase, this model is in very good agreement with the measured values for \(\varepsilon_\infty,A\). For the crystalline phase, the experimental data has been analyzed including the increased density of the crystalline phase relative to the amorphous phase. However, the Clausius-Mosotti model with constant \(\alpha_i\) (equation 3.2) under-estimates the
optical dielectric constant by about 20 to 38%, depending on the specific PCM. Even another model, which includes polarizability for covalent bonds [106], has been used, the same trend as for the Clausius-Mossotti model has been found: the amorphous data can be fitted, the crystalline cannot.

Thus, the enhanced polarizability of the crystalline bonds does not agree with the covalent bonding model, which follows the so-called 8-N rule with $N$ being the number of the main group in the periodic system. It states, that elements of the $N$-th main group tend to form 8-$N$ saturated covalent (electron pair) bonds [107]. The atomic structure of amorphous PCMs can be described by a covalent bonding model. However, Kolobov et al. showed, that a considerable difference between the local structure of the amorphous and the crystalline phase of the PCM compound Ge$_2$Sb$_2$Te$_5$ exists [94].

Indeed, the bonding situation for the crystalline case can be described by the so-called resonant bonding model by Pauling [107]. For benzene (cyclohexa-1,3,5-triene, C$_6$H$_6$), which is a classic example for resonance bonding, the delocalized electrons involved in the bonds are often pictured as a ring inside a carbon hexagon. In the case of PCMs, the resonance bonding occurs on a three-dimensional scale. Considering that, the resonant bonding can be schematically described with the example of an antimony lattice. Sb is a good example, since its distorted, six-fold coordinated rhombohedral structure is also known from GeTe, an extensively studied PCM. The electron configuration of Sb is [Kr]4d$^{10}$5s$^2$5p$^3$, which indicates, that three valence electrons (half filled p-orbital: p$^3$) are available for chemical bonding. For a covalent bond, three electrons can only bind to three of the six nearest neighbours. Two possible cases are depicted in schemes 1 and 3, in which the electron pair bonds are marked. The resonant bonding is shown in scheme 2. The description following Lewis [108] with localized covalent bonds (as in 1 and 3) can not be given in this case. Instead, the electrons are delocalized. This situation shown in scheme 2, is an energetically favorable state.

![Figure 3.3](image_url)

Figure 3.3: Schematically displayed is an un-distorted, six-fold coordinated rhombohedral structure as known from antimony. The central atom is marked in black, while its six nearest neighbours are marked in gray. In schemes 1 and 3, the three electrons of the outer shell of the central Sb atom bind to three of the six nearest neighbours (electron pair bonds - gray). In 2, the resonant bonding is shown, where the delocalized electrons (gray ellipses) lower the energy of the solid compared to the covalent bonds (schemes 1 and 3). Scheme 2 can be interpreted as a superposition of 1 and 3. It has to be noted, that only bonds for the marked atoms are considered and the distortion of the lattice is not taken into account here. The scheme has been adapted from [103].

Regarding the atomic structure, the difference in the ordering level of the amorphous and the crystalline phase illustrates the contrast in the bonding character. In amorphous phases the high level of ordering of the neighbouring atoms, which is required for resonant bonding, is missing. Only the nearest neighbours need to be aligned for covalent bonding, which refers to an existing short-range order of the atoms. In contrast, the alignment of the higher neighbours, a medium- and long-range order, in the crystalline phase allows for the resonant bonds [109].
Table 3.1: This table summarizes properties of GST compounds of the pseudo-binary (GeTe)\(_x\)-(Sb\(_2\)Te\(_3\))\(_{1-x}\). The crystallization temperature \(T_C\) refers to the phase transition from disordered amorphous (A) to meta-stable crystalline (C), while \(T_C^\ast\) refers to the second solid-solid phase transition, which appears either as a reversible transition from a rhombohedral distorted to cubic phase (\(x = 8/9, 1\)), or as a reversible cubic-to-hexagonal transition (\(x = 1/3, 1/2, 2/3, 3/4\)). It has to be noted that the crystallization temperature, which was determined via differential scanning calorimetry measurements, depends on the heating rate used during the experiments. The term “reversible” refers to the crystallization transition. Without references were determined by re-fitting (cf. appendix A.2).

<table>
<thead>
<tr>
<th>(x)</th>
<th>(T_C)</th>
<th>(T_C^\ast)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0/9</td>
<td>250°C</td>
<td>327°C</td>
</tr>
<tr>
<td>0/8</td>
<td>250°C</td>
<td>327°C</td>
</tr>
<tr>
<td>0/7</td>
<td>250°C</td>
<td>327°C</td>
</tr>
<tr>
<td>0/6</td>
<td>250°C</td>
<td>327°C</td>
</tr>
<tr>
<td>0/5</td>
<td>250°C</td>
<td>327°C</td>
</tr>
<tr>
<td>0/4</td>
<td>250°C</td>
<td>327°C</td>
</tr>
<tr>
<td>0/3</td>
<td>250°C</td>
<td>327°C</td>
</tr>
<tr>
<td>1/2</td>
<td>250°C</td>
<td>327°C</td>
</tr>
<tr>
<td>1/1</td>
<td>250°C</td>
<td>327°C</td>
</tr>
<tr>
<td>1/0</td>
<td>250°C</td>
<td>327°C</td>
</tr>
</tbody>
</table>

Note:
- \(A\) transition temperature \(T_C^\ast\) between 327 and 427°C. The value for the second solid-solid phase transition, which appears either as a reversible transition from a rhombohedral distorted to cubic phase (\(x = 8/9, 1\)), or as a reversible cubic-to-hexagonal transition (\(x = 1/3, 1/2, 2/3, 3/4\)). It has to be noted that the crystallization temperature, which was determined via differential scanning calorimetry measurements, depends on the heating rate used during the experiments. The term “reversible” refers to the crystallization transition. Without references were determined by re-fitting (cf. appendix A.2).
- \(B\) transition temperature \(T_C^\ast\) between 327 and 427°C. The value for the second solid-solid phase transition, which appears either as a reversible transition from a rhombohedral distorted to cubic phase (\(x = 8/9, 1\)), or as a reversible cubic-to-hexagonal transition (\(x = 1/3, 1/2, 2/3, 3/4\)). It has to be noted that the crystallization temperature, which was determined via differential scanning calorimetry measurements, depends on the heating rate used during the experiments. The term “reversible” refers to the crystallization transition. Without references were determined by re-fitting (cf. appendix A.2).
- \(C\) transition temperature \(T_C^\ast\) between 327 and 427°C. The value for the second solid-solid phase transition, which appears either as a reversible transition from a rhombohedral distorted to cubic phase (\(x = 8/9, 1\)), or as a reversible cubic-to-hexagonal transition (\(x = 1/3, 1/2, 2/3, 3/4\)). It has to be noted that the crystallization temperature, which was determined via differential scanning calorimetry measurements, depends on the heating rate used during the experiments. The term “reversible” refers to the crystallization transition. Without references were determined by re-fitting (cf. appendix A.2).
- \(D\) transition temperature \(T_C^\ast\) between 327 and 427°C. The value for the second solid-solid phase transition, which appears either as a reversible transition from a rhombohedral distorted to cubic phase (\(x = 8/9, 1\)), or as a reversible cubic-to-hexagonal transition (\(x = 1/3, 1/2, 2/3, 3/4\)). It has to be noted that the crystallization temperature, which was determined via differential scanning calorimetry measurements, depends on the heating rate used during the experiments. The term “reversible” refers to the crystallization transition. Without references were determined by re-fitting (cf. appendix A.2).
- \(E\) transition temperature \(T_C^\ast\) between 327 and 427°C. The value for the second solid-solid phase transition, which appears either as a reversible transition from a rhombohedral distorted to cubic phase (\(x = 8/9, 1\)), or as a reversible cubic-to-hexagonal transition (\(x = 1/3, 1/2, 2/3, 3/4\)). It has to be noted that the crystallization temperature, which was determined via differential scanning calorimetry measurements, depends on the heating rate used during the experiments. The term “reversible” refers to the crystallization transition. Without references were determined by re-fitting (cf. appendix A.2).
- \(F\) transition temperature \(T_C^\ast\) between 327 and 427°C. The value for the second solid-solid phase transition, which appears either as a reversible transition from a rhombohedral distorted to cubic phase (\(x = 8/9, 1\)), or as a reversible cubic-to-hexagonal transition (\(x = 1/3, 1/2, 2/3, 3/4\)). It has to be noted that the crystallization temperature, which was determined via differential scanning calorimetry measurements, depends on the heating rate used during the experiments. The term “reversible” refers to the crystallization transition. Without references were determined by re-fitting (cf. appendix A.2).
- \(G\) transition temperature \(T_C^\ast\) between 327 and 427°C. The value for the second solid-solid phase transition, which appears either as a reversible transition from a rhombohedral distorted to cubic phase (\(x = 8/9, 1\)), or as a reversible cubic-to-hexagonal transition (\(x = 1/3, 1/2, 2/3, 3/4\)). It has to be noted that the crystallization temperature, which was determined via differential scanning calorimetry measurements, depends on the heating rate used during the experiments. The term “reversible” refers to the crystallization transition. Without references were determined by re-fitting (cf. appendix A.2).
- \(H\) transition temperature \(T_C^\ast\) between 327 and 427°C. The value for the second solid-solid phase transition, which appears either as a reversible transition from a rhombohedral distorted to cubic phase (\(x = 8/9, 1\)), or as a reversible cubic-to-hexagonal transition (\(x = 1/3, 1/2, 2/3, 3/4\)). It has to be noted that the crystallization temperature, which was determined via differential scanning calorimetry measurements, depends on the heating rate used during the experiments. The term “reversible” refers to the crystallization transition. Without references were determined by re-fitting (cf. appendix A.2).
- \(I\) transition temperature \(T_C^\ast\) between 327 and 427°C. The value for the second solid-solid phase transition, which appears either as a reversible transition from a rhombohedral distorted to cubic phase (\(x = 8/9, 1\)), or as a reversible cubic-to-hexagonal transition (\(x = 1/3, 1/2, 2/3, 3/4\)). It has to be noted that the crystallization temperature, which was determined via differential scanning calorimetry measurements, depends on the heating rate used during the experiments. The term “reversible” refers to the crystallization transition. Without references were determined by re-fitting (cf. appendix A.2).
- \(J\) transition temperature \(T_C^\ast\) between 327 and 427°C. The value for the second solid-solid phase transition, which appears either as a reversible transition from a rhombohedral distorted to cubic phase (\(x = 8/9, 1\)), or as a reversible cubic-to-hexagonal transition (\(x = 1/3, 1/2, 2/3, 3/4\)). It has to be noted that the crystallization temperature, which was determined via differential scanning calorimetry measurements, depends on the heating rate used during the experiments. The term “reversible” refers to the crystallization transition. Without references were determined by re-fitting (cf. appendix A.2).
The enhanced polarization of the crystalline compared to the amorphous phase can be explained with the concept of the resonant bonding and its pronounced electron delocalization. However, this delocalization is weakened by the distortion of the crystalline structures in PCMs, which has not been taken into account in figure 3.3. This so-called Peierls-like distortion, which is also denoted as strong electron-phonon-coupling [119], localizes the electrons [93]. The atoms are shifted out of the symmetry positions of the crystal structures. An unequal superposition of wavefunctions describes these displacements [112]. Due to the local distortions the energy gap $E_G$ increases and thus, reduces the resonant bonding [103].

As already mentioned, the large values for $\varepsilon_{\infty}$ respectively $\Delta \varepsilon_{\infty}$ indicate resonant bonding. This parameter is the most direct experimental evidence. It has been shown, that resonance bonding can be observed by further criteria: the transverse effective charge $Z^*_{\text{T}}$, which measures the induced polarization produced by a relative displacement of the crystal sublattices [120], the transverse optical phonon frequency $\Omega_{\text{TO}}$, as well as the band gap $E_G$ [109, 121]. These three criteria will be discussed in the following.

**Dynamical atomic charge** The dynamical charge $Z^*$ (or $e^*$) corresponds to the change of polarization or dipole moment due to an atomic displacement in a solid. It depends on the atomic bonding and thus, on the rate, charges are transferred, as well as on the macroscopic electric field. Since a crystal structure is a periodic system, a generalized dynamical charge tensor can be defined. The *transverse or Born effective charge* (BEC) $Z^{*(T)}_{\kappa,\alpha\beta}$ monitors long-range Coulomb interaction and the BEC determines the splitting between LO and TO phonon modes at $\Gamma$, which is the center of the first Brillouin zone [15]. The BEC tensor is defined as follows:

$$Z^{*(T)}_{\kappa,\alpha\beta} = V_0 \left. \frac{\partial P_{\beta}}{\partial \tau_{\kappa,\alpha}} \right|_{E=0}$$

with the unit cell volume $V_0$ and the macroscopic polarization per unit cell $P$ created in direction $\beta$ and the displacement of the sublattice $\tau$ of atoms $\kappa$ in direction $\alpha$ (linearly independent Cartesian directions) [122]. The change of the polarization upon displacement is observed under zero macroscopic electric field $E$. Hereby, $V_0 P$ is the dipole moment per unit cell. Thereby the BEC $Z^{*(T)}_{\kappa,\alpha\beta}$ is proportional to $Z^{*(L)}_{\kappa,\alpha\beta}$, which is the *longitudinal or Callen effective charge* (CEC), via the optical dielectric tensor $\varepsilon_{\infty}$. The CEC is defined similar to equation 3.3, but under the condition of a zero macroscopic displacement field $D$. For isotropic materials, this leads to: $Z^{*(T)}_{\kappa} = \varepsilon_{\infty} Z^{*(L)}_{\kappa}$ [122].

Anomalously large values for BECs, which are caused by pronounced coupling between electronic states and phonons, are associated with resonantly bonded materials and can be find for the crystalline phase of GeTe for example [121, 123]. Upon decreasing rhombohedral distortion of the crystalline GeTe, the high $Z^{*(T)}$ increases even further [124]. This relaxation towards the undistorted rocksalt phase of crystalline GeTe concurs with a strong softening of the optical phonon modes $\Omega_{\text{TO}}$ [101]. Thereby *mode softening* refers to a shift of the mode to lower energies compared to the initial state.

---

1Following Peierls, a one-dimensional metal with filled conduction band orbitals to the wavevector $k_F$ at $T = 0 \text{ K}$ is unstable in terms of the static lattice deformation vector $G = 2 K_F$ [117]. The deformation opens up a energy gap. This effect can be also seen in polyacetylene [118] for example.
Transverse optical phonon  The softening of the optical phonon modes $\Omega_{TO}$ is another criterion for resonance bonding in PCMs. For PCMs, this vibrational softening can be observed upon crystallization, e.g. for amorphous to metastable C-GST-124, as it has been shown for the Te and Sb element-specific density of phonon states. For both density functions, the optical modes shift to lower energies and the center of mass of optical modes is lowered simultaneously [124].

For the high-temperature crystalline transition from rhombohedral to cubic GeTe, a further softening of $\Omega_{TO}$ can be determined. Following Littlewood, cubic GeTe shows $\Omega_{2TO}^2 < 0$ (at $T = 0$ K) and as a result of $\Omega_{2TO}^2$ being negative, the cubic phase is instable to TO-phonon distortions and in the rhombohedral phase frozen-in displacements of Ge and Te sublattices along the (111)-direction are present [121].

Band gap  The decrease of the band gap $E_G$ upon crystallization is one of the criteria relevant for resonance bonding. For semiconductors, the band gap $E_G$ can be related to the optical dielectric constant $\varepsilon_\infty$ as follows [109]:

$$\varepsilon_\infty = 1 + \frac{\hbar \omega_p^2}{E_G}$$

(3.4)

with the reduced Planck constant $\hbar$ and the plasma frequency $\omega_p$. It has to be noted, that Lucovsky et al. have used this equation to predict the BEC by $(Z^{*}(T))^2 \sim (\varepsilon_\infty - 1)$, which in turn allows for an indication of the presence of resonance bonding just by $\varepsilon_\infty$ [109].

The relation between the optical dielectric constants $\varepsilon_{\infty, A} < \varepsilon_{\infty, C}$ described earlier can be associated with the following relation between the band gaps (cf. equation 3.4):

$$E_{G,A} > E_{G,C}$$

(3.5)

Hence, in crystalline PCMs the band gap $E_G$ is smaller than the band gap of the amorphous phase. For conventional semiconductors, this increase of the electronic bandgap on amorphization is unknown, but it seems to be fundamental for PCMs [125]. The situation of smaller average bandgaps compared to covalent bonding due to resonant bonding is more extensively discussed in [126]. Also Lencer et al. [123] defined the two ratios $\zeta$ and $\gamma$, which indicate resonant bonding in the crystalline state and hence, need to be large for PCMs. These are given in table 3.2.

<table>
<thead>
<tr>
<th>$\frac{\varepsilon_{\infty,A}}{\varepsilon_{\infty,C}} - 1 = \zeta$</th>
<th>$\frac{E_{G,A}}{E_{G,C}} = \gamma$</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCM: GST-225</td>
<td>$\frac{33}{16} - 1 \approx 1.08$</td>
<td>$\frac{0.77}{1.60} \approx 1.60$</td>
</tr>
<tr>
<td>SC: GeSe</td>
<td>$\frac{8.0}{6.8} - 1 \approx 0.18$</td>
<td>$\frac{1.50}{1.29} \approx 1.16$</td>
</tr>
</tbody>
</table>

Table 3.2: The ratios $\zeta$ and $\gamma$ were defined by Lencer et al. [123]. By comparing these ratios for an examplary crystalline PCM and SC, it can be seen that both ratios are much larger for PCMs, which indicates resonance bonding of PCMs.

The occurrence of lattice defects influences $E_G$. In the crystalline phase, a shift of the Fermi level into the valence band leads to a slightly exceeded optical band gap, which is known as Burstein-Moss effect.
3.2 Fundamental properties of phase-change materials

The Burstein-Moss effect describes the increasing optical band gap due to additional energy levels (impurities) near the conduction band edge, which is known from degenerately doped semiconductors. Thus, the number of available states near the band edge, to which an electron can be excited, decreases [129]. In the amorphous phase, defects can be accommodated in the (sufficiently flexible) structure and the Fermi level stays pinned at the middle of the band gap [130]. More information on the effects of lattice defects can be found in [86, 93, 115] and [131].

Matrix element for optical transition  Aside from that, significant changes in the transition matrix element are necessary to explain resonance bonding respectively the large $\Delta \varepsilon_\infty$ [93, 132]. The transition matrix elements originate from Fermi’s golden rule, which describes the transition from one electronic state to another due to absorption of a photon with energy $\hbar \omega$. The transition rate from an initial quantum state $\psi_i$ (consisting of an electronic system in its ground state and a photon) to a final state $\psi_f$ (described by the same atomic structure with an ionized atom and a photo electron [112]) is given as:

$$W_{i \rightarrow f} = \frac{2\pi}{\hbar} |M|^2 g(\hbar \omega) \quad \text{with} \quad M = \langle f | H' | i \rangle$$

(3.6)

with the matrix element $M$, the joint density of states (JDOS) $g(\hbar \omega)$ and the perturbation associated with a light wave $H'$ [11]. In general, JDOS describes the number of electronic states in the valence and the conduction band, which are separated by a given photon energy. Welnic et al. determined (the velocity form of) the transition matrix element $M$ and the JDOS $g(\hbar \omega)$ for GeTe, as well as GST-124 and showed, that the optical contrast $\Delta \varepsilon_2$ upon crystallization is dominated by an increase of the (velocity form) of the transition matrix elements $\Delta M$ [132]. On the contrary, for semiconductors, such as Si or GaAs, the change in absorption $\varepsilon_2$ (upon amorphization) has been found to be caused by a change in the JDOS $\Delta g(\hbar \omega)$ due to a loss of long-range order [133].

In PCMs, the change in the bonding upon the structural phase transition leads to an increase in the matrix elements of the optical transition respectively in their amplitude. This amplitude of the transition matrix elements $M$ can be interpreted as oscillator strength of the optical transitions [132]. The larger the overlap of the quantum states $|\langle f | i \rangle|$ [134], the larger is $M$. Thus, distorted structures show a reduced transition matrix element $M$ compared to structures with aligned orbitals, such as octahedrally coordinated resonant structures with aligned $p$-orbitals [88].

To summarize, the unique crystalline phase is a fingerprint characteristic of PCMs. The resonant bonding in this state allows for a narrowing of the band gap $E_G$ and a strong increase of the optical dielectric constant $\varepsilon_\infty$ upon crystallization. Large transition matrix elements $M$, as well as very large values for the BEC $Z_{(T)}^{*}$, which mirrors the sensitivity of the crystalline structure to distortion, are a consequence of the resonant bonding as well.

As it was pointed out, depending on their structure and bonding situation a material can be identified as PCM. Thus, with a detailed understanding of the atomic arrangement and fundamental atomic parameters, a prediction of new PCMs should be possible. Lencer et al. presented a two-dimensional map classifying already known and perspective PCMs [123]. The tendency towards hybridization (or covalency) and ionicity organize the different compounds. The term ionicity is comparable with the difference in electronegativity, which is a rule of thumb regarding the type of chemical bond two elements form. It is calculated by subtracting the electronegativities of the involved atoms. PCMs can
be found for a low degree of ionicity and hybridization, which is crucial for resonant bonding. Larger values for these parameters are characteristic for covalent or ionic bonds.

### 3.3 The permittivity of selected phase-change materials

Here, PCMs are used to shift the resonance frequency position of nanoantennas $\tilde{\nu}_{res}$ to lower and higher wavenumbers. This is enabled by the large difference in the refractive index of the applied PCMs $\Delta n$ in the MIR spectral range. Furthermore, absorption, which dampens the nanostructure resonance, is undesired regarding applications in MMs or sensing applications, such as surface enhanced infrared absorption spectroscopy (SEIRA) [135]. Hence, PCMs need to exhibit a strong difference in the refractive index, while the absorption introduced by the PCM should be relatively low.

A detailed analysis of the dielectric function $\varepsilon_{PCM}$ will be given in this section. Therefore, oscillator models describing the interaction of the electromagnetic waves with bound and free electrons of PCMs, will be discussed in detail. The dielectric functions of amorphous and crystalline GST-8211, GST-326, GST-225 and InSb will be shown. The corresponding description of $\varepsilon(\omega)$ is based on the work of Shportko et al. [103].

#### 3.3.1 General aspects of the dielectric function

By the end of the nineteenth century Lorentz proposed a fully classical picture of the interactions between light and matter. Thereby, Maxwell’s equations are applied to model the light wave while the atoms are considered as oscillating dipoles described by a mechanical system. The nucleus and the bound electron are understood as a heavy and a much lighter mass connected by a spring with a natural frequency $\omega_0$. Due to the electric driving field the spring is set in motion and dependent on the attraction or repulsion of the electron the spring is compressed or stretched. The corresponding dipole oscillator model is well-known as Lorentz oscillator and will be described briefly in the following. A more elaborate mathematical description can be found in [11].

The incident light wave $E$ interacts with the bound atoms of a considered material, while the displacement of the atomic dipoles is modeled as damped harmonic oscillator. Since the nuclei are much heavier than the electrons with the effective mass $m^*$, the nuclei motion is neglected and only the electron displacement $x$ is considered:

$$m^* \frac{d^2 x}{dt^2} + m^* \gamma \frac{dx}{dt} + m^* \omega_0^2 x = -eE(t)$$

with

$$\varepsilon(t) = \varepsilon_0 \text{Re} \left( e^{-i(\omega t + \Phi)} \right)$$

The resonant polarization $P_{res}$ is then given by:

$$P_{res} = N p = \frac{Ne^2}{m^* \left( \omega_0^2 - \omega^2 - i\gamma\omega \right)} E$$
with the electron density $N$ given in m$^{-3}$. It can be seen that the polarization $P_{\text{res}}$ becomes large at the natural resonance frequency $\omega_0$. If many electronic oscillators at different frequencies occur (such as lattice vibrations and electronic contributions), the total polarization $\vec{P}$ of the medium can be calculated as follows:

$$\vec{P} = \left( \frac{Ne^2}{m^*} \sum_j \frac{1}{\left( \omega_j^2 - \omega^2 - i\gamma_j\omega \right)} \right) \vec{E}$$  \hspace{1cm} (3.9)$$

with the angular frequency $\omega_j$ and the damping coefficient $\gamma_j$ referring to a particular resonance. Since the electric displacement of the medium $\vec{D}$ is defined by $\vec{D} = \varepsilon_0 \vec{E} + \vec{P}$ and $\vec{D} = \varepsilon_0 \varepsilon \vec{E}$, the complex permittivity $\varepsilon$ can be calculated as follows:

$$\varepsilon(\omega) = 1 + \frac{Ne^2}{\varepsilon_0 m^*} \sum_j \frac{1}{\left( \omega_j^2 - \omega^2 - i\gamma_j\omega \right)}$$  \hspace{1cm} (3.10)$$

with the electric permittivity of free space $\varepsilon_0$. All transitions in the medium are described by equation 3.10 and the full spectral range of the complex permittivity $\varepsilon(\omega)$ can be evaluated. The strong dependency of the complex permittivity $\varepsilon$ on the energy $E$ range$^2$ of the driving electric field $\vec{E}$ is schematically depicted in figure 3.4. The spectral features of $\varepsilon_1$ - a "wiggle" (or highly dispersive line shape) - and $\varepsilon_2$ - a sharp peak - around the resonance positions marked by vertical dotted lines are called Lorentzians [11]. In between each Lorentzian the medium is transparent without any absorption and an almost constant real part of the complex dielectric function $\varepsilon_1$.

By increasing the energy $E$ of the driving electric field $\vec{E}$, particular contributions to the total polarization of the considered medium vanish. This implies that the medium shows no polarization at very high energies and the real part of the complex permittivity $\varepsilon_1$ becomes unity since the electrons are too "slow" to respond to the incident light waves. In the UV spectral range the inner electrons of the atoms contribute to the materials polarization, while the polarization of the dielectric due to outer electrons is restricted up to energies of the VIS spectral range. With an incident field in the THz and far-infrared (FIR) spectral range the phonon contributions to the polarization of the medium have to be taken into account.

---

$^2$The description as a function of the energy $E$ is equivalent to a description based on the angular frequency $\omega$ via $E = \hbar \omega$ with the reduced Planck constant $\hbar$. 

Figure 3.4: The real and the imaginary part of the dielectric function $\varepsilon_1$ and $\varepsilon_2$ of a hypothetical dielectric solid are schematically displayed as a function of the energy $E$. Three separated resonances occur due to lattice vibrations and the oscillations of the bound inner and outer electrons within the atoms. With increasing energy $E$ the real part $\varepsilon_1$ decreases, while at resonance a peak in the imaginary part $\varepsilon_2$ can be detected. Between the resonances, the medium is transparent and $\varepsilon_1$ is almost constant. The shaded energy range corresponds to the spectral range, which is investigated in this thesis: between about 0.19 eV (1500 cm$^{-1}$) and about 0.50 eV (4000 cm$^{-1}$). As a point of reference the spectral regions are denoted in the scheme. This figure was adapted from [11] and [105].
The static dielectric constant $\varepsilon_{\text{st}}$ represents the low-energy (or low-frequency) limit, while the optical dielectric constant $\varepsilon_{\infty}$ is the high-energy limit of the particular resonance (here $E \approx 0.02 \text{ eV}$). This position matches the highest phonon contributions reported for PCMs (between about 13 and 20 meV, cf. page 36). In the investigated MIR spectral range (light red area in figure 3.4), the dielectric function $\varepsilon$ shows only a very weak dispersion and the absorption is close to zero, which will be shown for particular PCMs in the following section.

The contributions of free electrons can be described by applying the Lorentz dipole oscillator model to the free electron system, which is called Drude-Lorentz model. Regarding the classical description by Lorentz the stiffness of the spring vanishes and leads to a natural resonance frequency $\omega_0 = 0$ (compare to the equation of motion of the Drude model in equation 2.1). It has to be noted that the high frequency limit of the real part of the complex permittivity $\varepsilon_1$ being unity accounts only for dielectrics described by equation 3.10, but not for metals.

### 3.3.2 Oscillator models for phase-change materials

The optical properties of PCMs can be described with two different oscillator models depending on the structural state the PCM is in. The described models are valid between the MIR and the UV spectral range, which corresponds to the energy range between 0.05 eV and 4 eV [110]. To extract the model parameters and thus, predict $\varepsilon$ over a large energy (frequency) range the dielectric data set given in [136] was re-fitted (cf. appendix A.2).

As it was mentioned earlier, phonon contributions can be neglected in this energy range. The frequencies of optical phonon modes, which are higher than the acoustic modes [124], can be calculated by $\sqrt{K/\mu}$ with the restoring constant $K$ (in the framework of an atomic chain) and the reduced mass $\mu$ [11]. The lightest element in GST compounds, Ge shows the highest optical phonon mode below 40 meV for a homopolar Ge-Ge bond (323 cm$^{-1}$) [137]. Thus, phonon contributions of the introduced PCMs should lie at smaller energies. Density functional theory calculations, nuclear inelastic scattering experiments, as well as Raman measurements proved vibrational contributions below 25 meV for GST-225 [94, 124, 138, 139]. Thus, the definition of $\varepsilon_{\infty} = \varepsilon_1(E = 50 \text{ meV})$ mentioned earlier has been chosen as a low-energy limit, since it is just above the highest phonon frequencies $\Omega_{\text{TO}}$.

In case of a crystalline structure, contributions of free charge carriers have to be considered as well. In amorphous PCMs, free charge carriers do not have to be included. They can be rather described as a semiconductor with a relatively small band gap $E_{G, A}$: typical values for PCMs are $E_{G, A} = 0.8 \text{ eV}$, $E_{G, C} = 0.5 \text{ eV}$, while exemplary semiconductors show $E_{G}(\text{SiC}) = 2.9 \text{ eV}$, $E_{G}(\text{GaN}) = 3.44 \text{ eV}$, $E_{G}(\text{ZnS}) = 3.8 \text{ eV}$ [11]. Also interband transitions for $E > E_G$ need to be included. Excitons, which are not expected to occur in PCMs, and defect-related intraband transitions for energies below the band gap $E < E_G$ are not part of the discussed models [140], which are well-established for the description of the permittivity of PCMs. For further reading regarding the influence of defect states the recent work of Rüttten et al. [141] is recommended.
3.3 The permittivity of selected phase-change materials

Jellison et al. modeled the optical function $\varepsilon$ of amorphous semiconductors and insulators based on the semi-classical Lorentz oscillator and the Tauc joint density of state (JDOS) by using five fitting parameters [140].

**Semi-classical Lorentz oscillator** The complex permittivity $\varepsilon(\omega)$ described by the classical Lorentz oscillator model has been defined in equation 3.10. There, each oscillator contributes to the polarization as given by equation 3.8. In contrast, experimental results reveal that different atomic transitions vary regarding their absorption strength due to the variation of the quantum mechanical transition probability (cf. transition rate $W_{i\rightarrow f}$ in equation 3.6) [11]. In a semi-classical description only a phenomenological oscillator strength $f_{ij}$ is introduced and the dielectric function known from equation 3.10 is modified as follows:

$$\varepsilon(\omega) = 1 + \frac{N_{e}^{2}}{\varepsilon_{0}m_{0}} \sum_{j} \frac{f_{ij}}{\left(\omega_{j}^{2} - \omega^{2} - i\gamma_{j}\omega\right)} \quad (3.11)$$

The equations for the oscillator strength for transitions between degenerate, as well as non-degenerate discrete atomic levels can be found in [11].

However, the Lorentz oscillator is not sufficient to predict the dielectric function of the PCMs in the spectral range of the interband transitions of the valence electrons, which occur above the band gap $E_{G}$ (around 0.8 eV for A-GST and around 0.5 eV for C-GST, cf. table 3.1). To be able to describe interband transitions in a broad spectral range and to correct errors (unphysical results, not-incorporated time-reversal symmetry, etc.), which appear in earlier formalisms [142, 143], Jellison et al. developed a new model [140, 144]. There, they used the described semi-classical Lorentz oscillator and the JDOS presented by Tauc et al. [145].

**Tauc joint density of states** To describe the absorption edge, Tauc et al. related the imaginary part of the permittivity $\varepsilon_2$ to the band gap $E_{G}$ in the following way [145]:

$$\varepsilon_{2,T}(\omega) \propto \frac{(\hbar\omega - E_{G})^{2}}{\omega^{2}} \quad (3.12)$$

The expression $(\hbar\omega - E_{G})$ is related to the JDOS of the valence and the conduction band of the considered PCM. (The valence and the conduction band retain their meaning in the amorphous phase [145].) The index $T$ refers to Tauc and thus, relation 3.12 is called Tauc joint density of states. Furthermore, Tauc et al. found indications that only the energy but not the wavevector $\vec{k}$ is conserved, which describes indirect band transitions [145].

**Tauc-Lorentz model** The parameterized imaginary part of the dielectric function $\varepsilon_{2,TL}$ applied to model the dielectric data of amorphous PCMs is composed of the imaginary part of a Lorentz oscillator (equation 3.11) and the Tauc joint density of states (equation 3.12). Furthermore, the real part of the permittivity $\varepsilon_{1,TL}$ is derived from $\varepsilon_{2,TL}$ by using the Kramers-Kronig integration [140, 144]. The expressions for the real $\varepsilon_{1,TL}$ and the imaginary part of the permittivity $\varepsilon_{2,TL}$ are given in appendix.
3.3 The permittivity of selected phase-change materials

A.2. Finally, the dielectric function of amorphous PCMs can be calculated by the following equation:

\[ \varepsilon_A(\omega) = \varepsilon_{\text{const}} + \varepsilon_{\text{TL}}(\omega) \]  \hspace{1cm} (3.13a)
\[ \varepsilon_{\text{TL}}(\omega) = \varepsilon_{1,\text{TL}}(\omega) + i \cdot \varepsilon_{2,\text{TL}}(\omega) \] \hspace{1cm} (3.13b)

with the constant \( \varepsilon_{\text{const}} \) referring to polarizabilities at higher energies, such as contributions of core electrons for example [103]. However, this contribution is very small compared to the real part of the dielectric function described by \( \varepsilon_{1,\text{TL}} \).

Tauc-Lorentz oscillator with Drude term for crystalline phase-change materials

In the crystalline phase, free charge carriers need to be considered. The Drude model describes free electrons, which experience no restoring forces in case of exciting electromagnetic waves. Unoccupied states at the valence band edge due to vacancies lead to metallic p-type conductivity inducing the Drude peak for low energies in the crystalline phase (cf. figure A.6) [146]. Thus, the permittivity of crystalline PCMs can be calculated as follows:

\[ \varepsilon_C(\omega) = \varepsilon_{\text{const}} + \varepsilon_{\text{TL}}(\omega) + \varepsilon_D(\omega) \] \hspace{1cm} (3.14a)
\[ \varepsilon_D(\omega) = -\frac{\omega_p^2}{\omega^2 + i \gamma_D \omega} \] \hspace{1cm} (3.14b)

with the plasma frequency \( \omega_p \) and the damping constant \( \gamma_D \) [11, 103]. The index \( D \) denotes the Drude model. The contribution of interband transitions described by \( \varepsilon_{\text{TL}}(\omega) \) is already known from equation 3.13. The same holds for \( \varepsilon_{\text{const}} \). Altogether, seven parameters need to be fitted for crystalline PCMs: the oscillator strength \( A \), the broadening term \( C \), \( E_G \) associated with the band gap, the peak transition energy \( E_0 \), \( \varepsilon_{\text{const}} \), the plasma frequency \( \omega_p \) and the damping rate \( \gamma_D \) (cf. appendix A.2).

In the following, dielectric data of several PCMs will be discussed focussing on the spectral range between 1000 and 6000 cm\(^{-1}\) (0.12 - 0.74 eV), which includes the MIR spectral range. The experimental data has been collected by Kremers by using ellipsometry and spectrometry [110], as mentioned in appendix A.2. The optical models introduced in this section have been applied to fit these measured spectra with the software SCOUT by W. Theiss. Thus, lists of \( \varepsilon_1 \) and \( \varepsilon_2 \) as a function of energy \( E \) given in eV with a step size of about 10 meV for each phase and PCM compound were generated and are available to the author of this thesis. For further calculations, these data sets were re-fitted by the introduced oscillator models (equations 3.13a and 3.14a) within the investigated spectral range. The resulting fitting parameters are summarized in appendix A.2, table A.1. The dielectric data of InSb was collected by Herpers [147] and is discussed in [110] as well.

3.3.3 Germanium antimony telluride compounds

In figure 3.5, dielectric functions of GST compounds, which were used for the presented experiments, are displayed in the MIR and NIR spectral range. In general, the real part of the dielectric function of A-PCM \( \varepsilon_{1,A} \) is relative constant over the shown spectral range and between about 12 and about 22, depending on the considered compound. The imaginary part \( \varepsilon_{2,A} \) is close to zero and almost constant as well. Upon crystallization the real and imaginary parts \( \varepsilon_{1,C} \) and \( \varepsilon_{2,C} \) increase (GST compounds).
and decrease (InSb) respectively. Besides the dielectric function of C-GST compounds are much more dispersive than what was found for A-GST compounds.

In more detail, the real part of the permittivity $\varepsilon_1$ is relatively constant below the bandgap $E_G$, which is above the depicted energy range for amorphous GST compounds and between about 0.33 and 0.55 eV for the crystalline GST compounds discussed here. The band gap energy explains the behavior of the imaginary part of the dielectric function $\varepsilon_2$ as well. The imaginary part of the dielectric function of the amorphous phases A-GST $\varepsilon_{2,A}$ is zero or very close to zero in the entire spectral range discussed here, which is below the band gap energy $E_{G,A}$. Upon crystallization the imaginary part $\varepsilon_{2,C}$ increases compared to $\varepsilon_{2,A}$. Thereby, the imaginary part of the permittivity $\varepsilon_{2,C}$ shows a convex behavior, which is least pronounced for GST-326. The increase of the imaginary part $\varepsilon_{2,C}$ at a low energy $E$ can be assigned to the Drude contribution. This becomes clear in the comparison of the dielectric function of C-GST-8211 and without the Drude contribution depicted in figure A.6. The density of the free carriers $N$ of crystalline GST compounds is in the range of $10^{20}$ cm$^{-3}$ (cf. table 3.1). The imaginary part $\varepsilon_{2,C}$ increases again for energies above the band gap $E_{G,C}$. The bonding-antibonding transitions$^3$ for resonant bonding of crystalline PCMs can be found for energies above the bandgap $E_{G,C}$ and lead to a pronounced peak in the complex permittivity. This is visible for higher energies as presented in [103], as well as for GST-8211 in figure A.6.

$\text{Ge}_3\text{Sb}_2\text{Te}_6$ In figure 3.5a, the complex permittivity $\varepsilon$ is shown as a function of energy $E$ and wavenumber $\tilde{v}$ for the amorphous and crystalline phase of GST-326. In the MIR spectral range $\varepsilon_{1,C}$ increases with increasing energy $E$, while $\varepsilon_{1,A}$ only shows an moderate increase from 12 to 14. The imaginary part of the dielectric function for A-GST-326 $\varepsilon_{2,A}$ is close to zero in the MIR, since the absorption below the band gap $E_{G,A} = 0.87$ eV is negligible. For energies above the band gap $E_{G,C}$, which is at about 0.55 eV (cf. table 3.1), $\varepsilon_2$ of the crystalline phase increases from zero to about 15. For the depicted low-energy limit, a small Drude contribution leads to a non-zero imaginary part $\varepsilon_{2,C}$.

$\text{Ge}_5\text{Sb}_2\text{Te}_11$ The compound GST-8211 shows a behavior similar to GST-326 regarding the qualitative behavior of the dielectric function in the depicted spectral range, which can be seen in figure 3.5b. As already known from GST-326, $\varepsilon_{1,A}$ increases steadily for increasing $E$ with a very small slope from about 14 to 16. In contrast, upon crystallization $\varepsilon_{1,C}$ shows a much larger increase than $\varepsilon_{1,A}$. Due to the band gap in the amorphous phase $E_{G,A}$ at about 0.81 eV, the imaginary part of the permittivity $\varepsilon_{2,A}$ is zero. However, the contribution of free carriers visible in the low energy regime $\varepsilon_{2,C}$ is higher than for GST-326. In table 3.1 it can be found that the carrier density $N$ is 20% larger compared to GST-326 ($1.2 \cdot 10^{20}$ cm$^{-3}$ versus $1.0 \cdot 10^{20}$ cm$^{-3}$). For increasing energy $E$ the imaginary part $\varepsilon_{2,C}$ decreases up to an energy of about $E = 0.50$ eV and increases again, which can be associated with the band gap energy $E_{G,C} = 0.54$ eV (cf. table 3.1).

$\text{Ge}_3\text{Sb}_2\text{Te}_9$ The compound GST-225 is well-known from applications in phase-change memories and optical storage media. Its complex permittivity is displayed in figure 3.5c. The qualitative behavior of the complex dielectric function of the amorphous phase $\varepsilon_{A}$ is similar to the dielectric functions of A-GST-326 and A-GST-8211 depicted in figures 3.5a and 3.5b. Upon crystallization the real, as well as the imaginary part of the permittivity $\varepsilon_{C}$ increase as it has been observed for the other GST compounds. However, the behavior of the real part $\varepsilon_{1,C}(E)$ is concave with a maximum at about 0.68 eV. This can

---

$^3$The valence band and the conduction band are formed by unshared p-electrons and antibonding states respectively [148].
be related to the small band gap energy \( E_{G,CST} = 0.33 \text{ eV} \) \[111\]. At this point, it has to be noted that the available data for the permittivity of C-GST-225 differs from the complex permittivity shown by Shportko et al. \[103\] and Kremers \[110\] especially regarding the curvature of \( \varepsilon_{1,C}(E) \) (concave versus convex). This is ascribed to the annealing conditions, which are given as about \( 170^\circ \text{C} \) for \[103\] and \[110\], whereas the available data set was related to annealing at \( 350^\circ \text{C} \) (available data set was named as \textit{gst225_350C.txt}). Therefore, it is assumed that the dielectric function shown in \[103\] and \[110\] can be ascribed to the metastable C-GST-225, while \( \varepsilon_{1,C}(E) \) in figure 3.5c refers to the stable \( C^*\)-GST-225 with a transition temperature of \( T_{C^*} = 326^\circ \text{C} \) (cf. table 3.1). According to the band gap \( E_{G,CST} = 0.33 \text{ eV} \) the imaginary part \( \varepsilon_{2,C} \) increases for increasing energies \( E \) above the band gap.

Similar to the description for GST-326 and GST-8211, the Drude contribution to the polarizability of C-GST-225 (or \( C^*\)-GST-225) leads to a large value for \( \varepsilon_{2,C} \) at the low-energy limit displayed in figure 3.5c.

Figure 3.5: The complex permittivity \( \varepsilon \) of GST-326 and GST-8211 is plotted as a function of the energy \( E \) and wavenumber \( \tilde{\nu} \), respectively, in 3.5a and 3.5b, while \( \varepsilon(E) \) of GST-225 and InSb is depicted in 3.5c and 3.5d. The amorphous permittivity is given by dashed lines, while the permittivity of the crystalline phase is marked by solid lines, which is in accordance to the experimental data presented in this work (chapters 5 to 7). The real parts \( \varepsilon_1 \) are represented by black lines, while the imaginary parts \( \varepsilon_2 \) are given by gray lines. The direction and the magnitude of the change of the dielectric parameters \( \Delta \varepsilon_1 \) and \( \Delta \varepsilon_2 \) is emphasized by black and gray arrows. The band gap of the crystalline phase of each GST compound \( E_{G,CST} \) is marked by a red tick. The red \('\) in figure 3.5c marks the band gap of the hexagonal phase of C-GST-8211. The red \('\) in figure 3.5d marks the band gap of A-InSb. The dielectric data was taken from \[136\].

\[\begin{align*}
\text{(a) dielectric function of GST-326} & \\
\text{(b) dielectric function of GST-8211} & \\
\text{(c) dielectric function of GST-225} & \\
\text{(d) dielectric function of InSb} & 
\end{align*}\]
3.3.4 Indium antimony

Indium antimony is a III-V compound semiconductor exhibiting a so-called Zincblende structure in its crystalline phase. It consists to 50% of the element Sb, which is typical for PCMs. However, the fingerprint characteristics described for PCMs (cf. page 41) are not observed for InSb. As discussed earlier, $\varepsilon_{\infty,A} < \varepsilon_{\infty,C}$ is crucial for the resonant bonding in crystalline PCMs. InSb shows the opposite trend with $\varepsilon_{\infty,A} \approx 22 > \varepsilon_{\infty,C} \approx 14$. Hence, the relation of the band gaps is also contrary relative to what has been shown for PCMs: for InSb $E_{G,A} \approx 0.50 < E_{G,C} \approx 0.57$ [147], while the opposite behavior has been stated for PCMs (cf. equation 3.5). Furthermore, the resistivity of both InSb phases contradicts the trends described for PCMs, although amorphous and crystalline InSb show different resistivities.

Since the behavior of $\varepsilon_{\infty,C}$ and $E_{G,C}$ observed for InSb disagrees with the properties of resonance bonding, InSb cannot be classified as PCM. Nevertheless, in the MIR and NIR spectral range, InSb offers a pronounced contrast in $\varepsilon_1$ between the amorphous and the crystalline phase as it can be seen in figure 3.5d. Furthermore, $\varepsilon_2$ is close to zero for both phases, while $\varepsilon_{2,C} < \varepsilon_{2,A}$. No subgap free carrier contributions can be observed for small energies.

Interestingly, the difference between the amorphous and the crystalline phase is inverted compared to the shown GST compounds, which is based on the lack of resonance bonding in crystalline InSb. Thus, according to the inverse proportionality between $\Delta \tilde{\nu}_{\text{res}}$ and $\Delta \varepsilon_1$, $\varepsilon_{1,C} < \varepsilon_{1,A}$ should lead to a shift of the antenna resonance position to the opposite direction as it can be expected from $\varepsilon_{1,C} > \varepsilon_{1,A}$. According to the shown dielectric function, as well as to the reversible switchability [148, 149], InSb seems to be well-suited for the application as active medium for antenna resonance tuning.

3.4 Laser-induced switching and optical memories

Many requirements for PCMs are derived from the expectations towards the (optical) PC memory device. Thereby, PCMs are applied in optical memories, such as CD-RW (compact disc rewritable), DVD-RW (digital versatile disc rewritable) and DVD-RAM (DVD random access memory), as well as in phase-change random access memories (PCRAMs) [97].

To be generally suited for memory devices, the material has to exhibit a clear property difference in at least two states, which applies to the amorphous and the crystalline phase of PCMs. These states can be assigned as logical "0" and "1", which refers to low ("0") and high reflectivity ("1") in case of PC optical storage. The necessary read access depends on an easy assignability of these properties. Furthermore, the respecting states must be stable for a very long time at room temperature to ensure for a long lifetime of the disc. Thus, the necessary temperature for the SET operation (crystallization - "0" to "1") must be much higher than the room temperature to avoid random erasure. In contrast, the temperature for the RESET operation (amorphization - "1" to "0") should be limited, since it defines the maximum power necessary for a PC memory device. For a fast operation speed, the time for SET and RESET must be minimized, while the SET operation is the much slower operation, since the structure "relaxes" in the crystalline phase.

In this section on PC optical memories and their laser-induced reversible switching, crystallization and amorphization kinetics will be discussed first, followed by an introduction to switching of PCMs via pulsed laser irradiation. Finally, fundamentals of optical data storage with PCMs will be summarized.
3.4.1 Crystallization and glass formation of phase-change materials

As mentioned above, time and temperature restrictions need to be considered to realize reversible switching. These kinetics are generally valid for PCM switching processes, independent of the storage concept (electrical or optical). The dynamics of the phase transition will only be briefly discussed here. A deeper insight is given in [150].

Time-temperature-transformation diagram

In figure 3.6, a so-called time-temperature-transformation (TTT) diagram is shown. Depending on the temperature and time scale, the existing PCM phases are marked, while the contours represent the degree of crystallization. Nucleation rates and growth of the crystalline phase, nucleation site density and distribution determine the shape of these curves [151]. The glass transition temperature \( T_g \) and the liquidus temperature \( T_L \) are limits for the molten and amorphous state of the considered PCM. The liquidus temperature \( T_L \) separates the fully liquid medium from the equilibrium between the solid and the liquid phase. Thereby the medium is an alloy of different elements, such as a PCM, whereas the melting temperature \( T_m \) is only defined for an element [152]. However, the parameter melting temperature \( T_m \) is used in the literature, e.g. in [153, 154], which is assumed to be related to the re-amorphization process, which is based on melt-quenching of the liquid phase. The glass transition temperature \( T_g \) is defined according to the viscosity of the undercooled liquid PCM being on the order of \( 10^{12} \) Pa·s [155] and depends on the heating or cooling rate [156]. At the glass transition temperature \( T_g \) the time scale for atomic rearrangement becomes larger than the experimentally imposed time window and the undercooled liquid is configurationally frozen [157]. It has to be noted that the crystallization temperature \( T_C \) will be used instead of the glass transition temperature \( T_g \), since both temperatures are within \( 10^\circ \)C [155]. The preference is given to the crystallization temperature \( T_C \), since it was used in PCM-related literature e.g. on nano-optics or metamaterials (cf. section 2.3.2).

Figure 3.6: Displayed is a schematic TTT diagram for a PCM including the room \( T_R \), crystallization \( T_C \) and liquidus temperature \( T_L \), as well as the following processes: melt-quenching \( \circled{1} \), \( \circled{2} \) (gray) and annealing \( \circled{3} \), \( \circled{4} \) (red), which differ in cooling and heating rate. The amorphous, crystalline and liquid phase of the investigated PCM are marked. The solid curves refer to 1%, 50% (middle) and 99% crystallization. Following the isotherm of \( \circled{3} \), the amorphous PCM is crystallized to about 50% after \( t_{min} \). This figure was adapted from [86, 151].

In the TTT diagram in figure 3.6, melt-quenching and annealing processes are illustrated by gray lines. To realize amorphization of the molten PCM, a very fast melt-quenching (steep gray line \( \circled{1} \)) is necessary. So-called quenching rates of about \( 10^9\)-\( 10^{11} \) K/s are necessary for amorphization [153]. In case of a slower process with a low quenching rate, the atomic mobility is relatively high and can lead to relaxation of the atoms into the crystalline lattice. Thus, a partial crystallization is achieved (the more shallow line \( \circled{2} \)). On very short timescales, the atomic mobility is finite. Structural rearrangement, which is necessary for reaching thermal equilibrium, is disabled. Thus, the amorphous
state is frozen. This very low atomic mobility guarantees the stability of the amorphous phase at room temperature, which is crucial for the application as data storage. The atomic mobility is higher for increased temperatures and enables the atomic movement. The crystallization of an amorphous PCM is based on a temperature between \( T_g \) and \( T_L \) and sufficient time for the atoms to arrange in the crystal lattice. A higher temperature leads to faster crystallization, which can be seen by comparison of the two annealing processes (faster \( \S \) and slower process \( \S \)) in the TTT diagram.

Since the amorphous, or so-called glassy state is not in thermal equilibrium at room temperature \( T_R \), it is a meta-stable state. Thus, so-called aging effects can be observed. The molar volume, the enthalpy, as well as the entropy decreases and the solid compacts [150]. Furthermore, the amorphous local structure evolves towards the crystalline one upon aging and thus aging can be understood as structural relaxation [158].

**Nucleation and growth-dominated crystallization**

Crystallization can be realized by nucleation and by crystal growth. The nucleation - the formation of a crystalline nucleus in an amorphous matrix - is described by the so-called classical nucleation theory by Volmer, Weber, Becker, Döring, Turnbull and Fisher. Their proposed concepts can be found in [159], [160] and [161].

For nucleation a crystal cluster is necessary. In case the cluster is stable, it can grow to a macroscopic size. The nucleation, as well as the growth rate depend on the temperature. Depending on the ratio between these rates, the PCMs can be classified: for a nucleation rate higher than the growth rate, the PCM is called nucleation-dominated as for e.g. GST compounds. If the rates behave inversely, the PCM is called growth-dominated as for e.g. AgInSbTe (AIST) compounds [150]. The different principles are visualized in figure 3.7. There, the starting point is a crystalline PCM film with an amorphous mark, which has been generated by a laser pulse. To induce re-crystallization of the amorphous mark, the PCM can be annealed on a hot plate. According to the dominant effect - nucleation or growth - the re-crystallization starts at several different spots (scheme (1)) or at the crystalline rim (scheme (2)). For the nucleation-dominated PCMs, the size of stable crystalline nuclei increases by crystal growth too. In case of a fully amorphous PCM film, crystallization starts always with nucleation. Then, the dominant effect determines, whether many nuclei are generated, or if relatively fewer nuclei grow. Thus, a first crystallization event of an as-deposited amorphous PCM requires a single nucleation event, which occurs after an incubation time on a microsecond timescale. Consequently, the first crystallization of an as-deposited amorphous mark (diameter about 500 nm) takes several microseconds, while re-crystallization of a growth-dominated amorphous mark with crystalline grains present (as given in figure 3.7, scheme (2)) is concluded after a few nanoseconds [162].

The growth of a crystalline nucleus of radius \( r \) within a glassy phase or undercooled melt is classically defined by the interplay between surface and volume effects. This can be analytically analyzed by the expression for the difference of the free energy \( \Delta G \), which is also known from the solid state nucleation in molten metals [152]. The nucleus formation depends on the interplay between the energetic cost of the formation of an interface (crystalline - amorphous interface) \( A(r) \) and the energetic gain due to

\[ A(r) \] for melt-quenched Ag\(_{4}\)In\(_{3}\)Sb\(_{7}\)Te\(_{26}\) a maximum growth velocity of about 100 m/s has been estimated [153].
3.4 Laser-induced switching and optical memories

Figure 3.7: Displayed is a scheme of nucleation- (1), as well as of growth-dominated crystallization (2) of PCMs. An amorphous mark (gray, A) is generated in a crystalline background (white, C) by a laser pulse. The PCM is then heated above the glass transition temperature $T_g$, e.g. on a hot plate. In case of a higher nucleation-rate compared to the growth-rate, the amorphous material re-crystallizes by nucleation. As soon as the nuclei are stable, the crystallization continues by crystal growth. If the growth-rate is higher, the PCM re-crystallizes by growth starting at the crystalline rim toward the center of the mark.

the nucleus volume $V(r)$. The interface energy scales with $r^2$, the volume energy with $r^3$. Thus, the driving force $\Delta G(r)$ can be expressed as follows:

$$\Delta G(r) = V(r) \cdot \Delta G_V + A(r) \cdot \sigma$$

$$= \frac{4}{3} \pi r^3 \cdot \Delta G_V + 4 \pi r^2 \cdot \sigma$$

with $\sigma$ representing the interfacial energy per unit surface area, $A(r)$ and $V(r)$ being the surface and volume of the crystalline nucleus [150]. The driving force for crystallization is maximized with $r$ at its critical value $r_C$. Thus the growth of a nucleus in an undercooled melt is restricted to nuclei with radius $r$ exceeding a critical value $r_C$. For a nucleus with $r < r_C$ (subcritical), the nucleus dissolves in the melt again, for $r > r_C$ (supercritical) the nucleus grows. Nucleation is a stochastic process, which can be experimentally revealed by a variation of the nucleation time obtained under similar conditions (e.g. sample, laser power) from 5 to 60 $\mu$s for AIST for example [163]. A shift of the distribution to short nucleation times can be observed in case of pre-annealing in a furnace with $T < T_g$, laser priming in [163] or a suited distribution of subcritical nuclei, which may occur during sputter deposition of the amorphous phase [163].

3.4.2 Laser-induced switching of phase-change materials

The reversible switching from the amorphous to the crystalline state and vice versa can be triggered either by an electrical or by an optical pulse. Here, only the laser-induced optical switching will be described, since its applied in chapter 6.

Amorphous PCMs can only crystallize, if the temperature in the PCM is elevated. The sample temperature needs to be increased above the glass transition temperature $T_g$. Furthermore, a minimum time for the atoms to relax from the amorphous phase into the energetically favorable crystalline structure is a necessary condition for crystallization. These requirements are fulfilled by a single laser pulse of relatively low energy and long duration as shown in figure 3.8. Depending on the laser setup, these parameters vary and an overview can be found in chapter 6. Exemplary values for the PCM AIST are as follows: an initial crystallization was realized with a laser pulse of 1.1 ms duration and 25.1 mW

---

5 In case of laser priming, the sample is illuminated by a laser pulse of an energy below the power necessary for laser-induced crystallization - comparable to pre-annealing below $T_g$ - and of short duration, e.g. 1 $\mu$s. Thus, nucleation seems more likely after a short time, e.g. 5 $\mu$s, and the crystallization time is reduced as well [163].

6 It has to be noted, that for PCM nanoparticles or extremely thin PCM films, the kinetic parameters differ from the ones known for bulk samples and thin films above 10 nm [164].
power [154].

As already described in the TTT diagram, amorphization is based on melt-quenching. Therefore, a crystalline PCM layer needs to be heated above the liquidus temperature \( T_L \) (for AIST about 534°C [112]). The frozen glassy state can only be achieved, if the melt, which exhibits a high atomic mobility, is rapidly cooled down with rates of \( 10^9-10^{11} \text{ K·s}^{-1} \) [153]. This avoids the relaxation of the material into its crystalline structure. Thus, a single laser pulse of relatively high energy and very short duration as shown in figure 3.8 is used for amorphization. Exemplary values for AIST are given as follows: melt-quenching of a circular area with a diameter of about 500 nm was realized with a laser pulse of 29 ns duration and 80.5 mW power [154].

![Diagram of temperature and laser power profiles for optical induced crystallization and amorphization](image)

Figure 3.8: Schematic temperature \( T \) (black) and laser power \( P \) profiles (gray) for optically induced crystallization and amorphization are given as a function of time \( t \). Denoted are the glass transition \( T_g \), the liquidus temperature \( T_L \), the laser pulse power for crystallization \( P_c \) and amorphization \( P_A \) and the corresponding pulse duration \( t_c \) and \( t_A \). In PCM storage devices the depicted operations are called SET and RESET. The amorphization process involves a molten phase, which is not displayed.

The laser pulse parameters necessary to realize amorphization and crystallization can be determined by recording a so-called power-time-effect (PTE) diagram. The laser pulse power \( P \) is plotted as a function of the pulse duration \( \tau \), while for each combination \((P, \tau)\) the "effect" on the investigated PCM film is shown, e.g. the reflectance change \( \Delta R \). This change in reflectance \( \Delta R \) is accessible by a pump-probe setup. Salinga et al. developed the so-called Phase-change optical electrical tester (POET), which includes a pump-probe laser system, which has been used for the study of the crystal growth velocity for example [87, 153, 154]. Depending on the achieved reflectivity contrast, the phase of the PCM can be evaluated and parameter regimes for crystallization or amorphization can be defined. Regimes of \((P, \tau)\) leading to ablation or to no change in the PCM can be determined as well.

### 3.4.3 Optical data storage devices

Optical storage devices are a typical external or so-called secondary memory. These are non-volatile memories, which are not directly connected to the central processing unit of a computer. Optical storage devices are removable and much cheaper compared to primary memories. Three generations of optical media can be distinguished: so-called compact discs (CDs), digital versatile discs (DVDs) and blu-ray discs (BDs), which are available as read only (ROM), write once read many (R), re-writable (RW, RAM) or recordable erasable (RE) media. Some of these differences are "historical" (RE is newer than RW), while some formats are only supported by distinct manufacturers. The development of the different storage devices depended particularly on the availability of suited lasers. If one compares all three generations, the storage density increased from 0.65 GB for CDs to 25 GB for BDs by a factor of about 40 while maintaining the physical size of the optical disc, which is 120 mm in diameter.

---

\(^1\)In memory hierarchy, fast accessible memory levels, which are of small capacity and expensive per byte, are close to the central processing unit, while slower, larger and cheaper memories are placed further away [165].
Thereby the available wavelength of the applied laser diodes decreased from 780 nm for CDs (AlGaAs laser diode) to 405 nm for BDs (InGaN laser diode) [150]. A further increase in storage density has been realized by using both sides of each disc, as well as by multilayer storage. Thus, the BDXL (BD with three or four data layers) format allows for more than 100 GB [105], while the new Archival Disc concept is planned with 1 TB capacity [166]. The multilevel recording allows for a higher data transfer rate as well.

**Architecture of optical storage discs**

Optical storage relies on a rotating optical disc, which contains binary information ("0" and "1") stored as a reflectivity contrast. This information is read out in an optical disc drive by a reflected laser beam. Pre-formatted so-called grooves and lands, which is the open space between the grooves, allow for a positioning of the so-called pick-up head including laser and focus lens [150].

Read-only (non-writable) optical discs, such as the CD-ROM, consist of bottom and top polycarbonate disc layers with a reflective layer of aluminum and a label layer, e.g., artwork. The top polycarbonate layer shows indentations, so-called pits, which are pressed grooves reflecting the laser beam differently compared to the elevated areas (lands). This can be detected with a photodiode. The binary information is encoded with a digital-to-analog converter. The write-once read-many discs, such as the CD-R, include an additional organic dye layer of phthalocyanine or azo compounds, as well as a protective layer against UV radiation. During the irreversible writing procedure, the dye is heated by a laser beam leading to breakage of unsaturated chemical bonds, which in turn leads to a change in absorption. This difference in reflectivity, or absorption respectively, contains the binary information. Rewritable discs, such as the CD-RW, include more complex storage layers of a PCM layer (15 - 20 nm [150]) and protective dielectric layers, an aluminum reflective layer, as well as a UV resin. The layer stack is embedded in polycarbonate layers.

PCMs for optical discs need to satisfy the following merits: a large optical contrast in the wavelength range of the reading laser for a clear distinction between "0" and "1", a stable amorphous phase at room temperature to avoid an unintentional SET operation, a large cyclability (jeopardizing: risk of segregation, micro-cracks, buildup stress due to repeated switching), fast crystallization for fast data transfer rates, a relatively low liquidus temperature to reduce the maximum laser power by ensuring data retention and a compatibility to semiconductor fabrication processes [86, 150, 168]. Compounds on the pseudo-binary line as shown in figure 3.2 offer a large reflectance contrast $\Delta R$ between the amorphous and crystalline phase of more than 30% in the applied wavelength range (405 to 780 nm) and a very fast phase transition. The latter is attributed to the crystallization process in compounds, such as GST-124 or GST-225. The phase transformation from the low-temperature metastable crystalline (fcc) to the amorphous phase occurs without a phase separation and thus, the re-organization of the atoms proceeds on short spatial scales. This allows for switching on ns time scales. GST compounds on the GeTe-Sb$_2$Te$_3$ pseudobinary line, as well as AIST are applied in RW optical discs [169, 170]. AIST offers a high controllability of written marks, which is ascribed to the nucleation-dominated crystallization. Compared to the growth-dominated GST compounds, marks written in AIST layers have a better defined shape with sharp edges [171]. Furthermore, In$_2$SbTe$_2$ (IST) and compounds near this alloy

---

\*In the literature, "0" and "1" are ascribed differently - for example Deringer et al. denoted the amorphous state as "0" [88], while Fulay identified the crystalline state as "0" [167]. Also Lencer et al. described a stored "bit" as amorphous [86]. Here, the first concept with amorphous "0" and crystalline "1" is followed.\*
3.4 Laser-induced switching and optical memories

respectively, have been investigated for optical storage. Stable repetition of write and erase operations above $10^5$ cycles, a long-term retention due to a crystallization temperature of about $280^\circ$C, no phase separation upon crystallization, as well as a crystallization time (the time to erase the amorphous mark) between 50 and 100 ns show a high potential for application in optical storage discs [98, 172].

Principles of optical recording

To write or erase information stored in the PCM layer of an optical disc a focused laser beam is used. The power of the laser beam to read the optical storage medium is small to avoid unintentional influences on the structure of the PCM marks (in the PTE diagram, a parameter range, which does not influence the PCM, needs to be chosen). Write and erase operations are triggered by a laser beam with higher power introducing heat into the PCM layer. Depending on the pulse power and duration, the PCM crystallizes or melt-quenches into the amorphous state. The density of the stored information depends on the size of the written marks and the available optics, such as laser wavelength $\lambda$ and numerical aperture $NA$ of the focus lens. The smaller the laser wavelength $\lambda$, the smaller is the spot area $A$ written in the material. In contrast, the smaller the numerical aperture $NA$, the larger gets the spot area $A$. Since the areal density $D$ is inversely proportional to the spot area $A$ [150], the correlation can be formulated as follows:

$$D \propto \left( \frac{NA}{\lambda} \right)^2$$  \hspace{1cm} (3.16)

However, a high $NA$ leads to a strong increase of spherical abberation, which can be overcome by using a low-$NA$ lens as solid immersion lens leading to a high effective-$NA$ lens without the cost of stronger abberation [173]. An increase in areal density $D$ due to even shorter wavelengths of the laser beam is rather difficult due to the use of polycarbonate discs, which can not transmit UV radiation.

Additionally, the storage density $D$ can be increased by so-called land-groove-recording. Historically, marks were only written in grooves, while lands served as tracking guides and heat sinks for adjacent grooves. The writing on grooves and lands leads to a gain of area density. However, the track pitch (separation between adjacent tracks) had to be increased to avoid optical cross-talk or thermal cross-erasure [174]. Thus, the writing on grooves and lands did not lead to a doubling of the area density $D$. Dual-side or multilayer storage concepts (e.g. BDXL [105]) leading to a huge increase of $D$ will not be discussed here.

Besides the discussed relation between the storage density $D$, the spot area $A$ and the numerical aperture $NA$, so-called super-resolution near-field structure (super-RENS) disks [176] are used to increase $D$. With super-RENS, the readout of feature sizes below the diffraction limit can be realized by using evanescent fields to carrier the information. The applied stack is based on a layer, in which a small near-field aperture is generated due to optical nonlinearity of the material, a dielectric separation layers and a recording layer. In the thin layer of an optically nonlinear material - the super-RENS layer, a reversible subwavelength optical aperture is induced by a laser beam [177]. The first super-RENS system presented by Tominaga et al. used antimony (Sb) as mask or super-RENS layer, silicon mononitride (SiN) as oxidation and heat shock protection and GST-225 as recording layer [178].

In figure 3.9 a schematic representation of the super-RENS effect is given. A focussed laser spot passes through the layer stack composed of a super-RENS layer embedded in two (ZnS)$_{85}$-(SiO$_2$)$_{15}$ layers, e.g. for oxidization protection, and a data layer. If the beam intensity is above the threshold
Table 3.3: This table summarizes system parameters of different optical storage devices including PCMs. The parameters have been taken from [97] (CD, DVD) and [175] (BD, super-RENS).

value to trigger the nonlinear effect of the super-RENS layer material (e.g. Sb₂Te), a local change in its optical properties occurs.

Due to the nonlinear absorption characteristic of Sb-based PCMs [179], a much smaller area than the focused laser spot diameter shows the super-RENS effect: the crystalline Sb₂Te becomes temporary highly transmissive upon laser irradiation (here for 1 μs at a power of 100 μW) [180]. The transmissivity decreases rapidly after the heat source is removed, since no permanent phase change (amorphization) has been conducted. SIMPSON et al. assumed that a weakening of the resonant bonding [179] occurs, which recovers after the laser is switched off. An increase of the transmissivity can be associated with a weakening of the resonant bonding and thus parts of the incident laser beam can be transmitted temporary through the layer stack to the data layer.

Further literature on super-RENS structures based on data storage layers of metal oxides, such as silver oxide AgOₓ or platinum oxide PtOₓ can be found in [176, 182] and [183] respectively. The scatterer-type super-RENS layer stacks are described in [177, 182, 184]. Silver oxide AgOₓ has been applied as mask or super-RENS layer as well, while the recording layer is made of GST-225 [185].
CHAPTER 4

Experimental techniques

Rod-shaped nanoantennas with resonances in the mid-infrared spectral range require their length and width to be in the sub-micron range. For the fabrication of these nanostructures, electron beam lithography (EBL) was used. This method will be discussed in section 4.1. Two methods for the material deposition - thermal evaporation, as well as sputter deposition - will be briefly described in the appendix A.3. For optical characterization of the fabricated nanostructures, infrared reflectance spectra were collected by using Fourier-transform infrared (FTIR) microspectroscopy. This method will be discussed in section 4.2. Furthermore, images of the nanostructures were taken by scanning electron microscopy (SEM) using the EBL system.

4.1 Electron beam lithography

The fabrication of the used nanoantennas arranged in an array of a well-defined periodicity requires a technique, which allows for reproducibility and precision. Electron beam lithography (EBL) is a well-established method, which was used for the fabrication of resonant nanostructures in different studies, e.g. [186], [187] or [26]. With EBL, a beam of accelerated electrons is deflected either electromagnetically or electrostatically to pattern a radiation sensitive polymeric material, the so-called resist, which is deposited on a substrate. The main process steps of EBL will be summarized in the first part. This description should allow for a replication of the general procedure. Based on the detailed process description, the setup and the limiting parameters for the resolution of electron beam lithography will be explained in detail.

4.1.1 Process steps of electron beam lithography

EBL is a physical technique, which allows for the patterning of nanometer size structures of desired shape and arrangement. To achieve this very high resolution, the EBL technique depends strongly on the precise performance of each process steps in a cleanroom environment. In this work, a so-called positive tone resist strategy, as depicted in figure 4.1, was applied.

---

1In general, an EBL system closely resembles a SEM. For EBL the beam is scanned according to the instructions coming from a pattern generator, while in a SEM the beam is raster-scanned over the sample in order to collect secondary electrons to form an image.
4.1 Electron beam lithography

The supplier of the EBL resist recommends a pre-treatment, which was conducted for the sample fabrication related to this work:

- **Warming of resists** The EBL resists need to be removed from the refrigerator, where they need to be stored at about 4°C, and warmed to room temperature. This takes several hours. A cold resist leads to precipitations of air moisture on the resist.

- **Opening of the resist** Loosening of the resist bottle lid ensures for less air bubbles in the resist. Thus, a better resist film quality can be achieved, which in turn ensures for sharp structures written by the electron beam.

The EBL process itself can be described by the following tasks, while the applied experimental parameters are mentioned as well (a detailed list of all applied materials can be found in table A.2):

1. **Cleaning of the substrate** For the shown experiments, purchased silicon wafer pieces (area: $1 \times 1 \text{cm}^2$, thickness: 500 $\mu$m) terminated with a native oxide were used. The surface roughness and with it the resolution of the EBL depends on the cleanliness of the substrate. The adhesion strength between resist and substrate determines the quality of the patterned nanostructures. An ultrasonic bath is used to clean the samples with acetone and isopropanol (here: each for about 30 min). Additionally, the substrate need to be dried on a hot plate for several minutes to remove condensed moisture, e.g. due to the use of acetone, which evaporates and thus cools the sample.

2. **Deposition and baking of the resist** With a pipet a drop of resist is set on the sample surface (here: AR-P 679.04, cf. table A.2). The amount of resist, which can be dropped on the sample is limited by the surface tension of the resist drop, since the liquid resist flows off the sample, as soon as the resist drop collapses. Afterwards, the sample is rotated by a spin coater (here: 6000 rpm). Subsequently, a tempering at a well-defined temperature (here: 2 - 3 min at 145°C) is performed to harden and dry the resist films. The resulting resist thickness achievable with one execution of this process step is limited (here: to about 220 nm according to the resist manufacturer) and depends the velocity of the spin coater. With a repetition of the resist deposition, the resist thickness can be increased. By experience the resist is chosen to be at least three times as thick as the designed height of the nanostructures to ensure a successful lift-off (cf. step 6).

3. **Exposure to the electron beam** A computer-aided design (CAD), which was realized beforehand, is transferred into the resist by a controlled deflection of the electron beam. Depending on the electron beam exposure, the positive tone resist changes its solubility. In case of a positive resist, the solubility of the exposed resist increases (marked in gray in figure 4.1). For the samples investigated in this thesis, the following parameters were applied: 20 kV acceleration voltage, 10 $\mu$m aperture, about 40 pA beam current, 100 $\mu$C·cm$^{-2}$ dose for patterned areas, 1000 pC·cm$^{-1}$ dose for patterned lines, $(200 \times 200) \mu$m$^2$ writefield size and 5 nm stepsize.

4. **Development of the resist and rinse** After the sample is unloaded from the EBL system, the sample is dipped into a developer bath and the resist, which was exposed to the electron beam, is removed from the sample. Here, a positive tone mask of the design was achieved by applying a developer solution (here: AR 600-55). The development process proceeds fast (here: 60 s) and needs to be stopped immediately, which can be realized with isopropanol (here: 30 s) or with specific stopper solutions.
4.1 Electron beam lithography

5. **Metal deposition** After the development of the pattern in the resist, the material the nanostructures will be made of, is deposited. In the case of the presented nanostructures, a very thin layer (here: about 3 nm) of the adhesion layer chromium (Cr) and between 30 and 35 nm aluminum (Al) were thermally evaporated.

6. **Lift-off of the excess resist and metal** The samples are brought into a remover solution (here: AR 300-70), while its effectiveness can be enhanced by heating. Furthermore an ultrasonic bath can be used, although this needs to be watched carefully to avoid the removal of all metal (and not only the excess metal).

7. **Cleaning of the final nanostructures** The lift-off process needs to be stopped by dipping the sample into acetone. Furthermore, the sample needs to be cleaned by using acetone, as well as isopropanol.

All steps, except of step 5, are conducted in a cleanroom environment. The repetition of the described process steps enables more complex, three-dimensional nanostructures, e.g. multi-layer structures.

---

**Figure 4.1:** Depicted is a scheme of an EBL process with positive tone resist. Thus, nanostructures are fabricated at the areas, where the resist was exposed to the electron beam. The numbers in the right corner of five of the schemes relate to the number of the listed process steps.

**Comments on EBL resists**

**Positive tone resist** For positive resists, the area exposed to the electron beam is removed, since polymer backbone bonds are broken by the electron irradiation [188]. This results in fragments of lower molecular weight. The corresponding developer washes away only areas with relatively low molecular weight. The pattern in the resist has a so-called **positive tone** then. Polymethylmethacrylate, which is well-known as PMMA, is the standard positive EBL resist. A relatively new positive resist is called ZEP and consists of the two copolymers \(\alpha\)-chloromethacrylate and \(\alpha\)-methylstyrene. ZEP has a resolution very close to PMMA, but its sensitivity is up to about one order of magnitude higher. However, the applicable dose window for each exposure voltage is smaller for ZEP than for PMMA, which results in a less robust process [189].

**Double layer resist** For the fabrication of well-defined metal structures, including sharp edges and very closely placed structures, a strong undercut of the positive tone resist is needed. This can be realized by two resist layers. The difference of the two layers in their molecular weight results in a different sensitivity of the resist. The undercut of the resist is achieved by the deposition of the more sensitive below the less sensitive resist layer. Thus, the top layer is characterized by a higher molecular weight compared to the bottom layer. If both layers are sensitive to electron exposure,
the same solution can be used for the development of both layers and the undercut profile is only a function of the sensitivity difference. In figure 4.2 the different effect on the metal deposition for a single and a double layer resist is shown. The double layer ensures a disconnection of the metal layer leading to better resolved nanostructures. As an example, a two-layer resist in combination with a proximity effect correction allows for the fabrication of nanoelectrodes with a separation down to three nm [190]. There, polymethylglutarimide (PMGI), which is a typical so-called undercut layer for double-layer lift-off processes, has been used together with PMMA. It has to be noted, that the left scenario in figure 4.2 with a connected metal layer is more likely for sputter deposition than for thermal evaporation due to the lack of directionality during sputtering [191]. Alternatively, a polymer bottom layer insensitive to the electron beam, a so-called lift-off resist (LOR), can be chosen as bottom layer. Consequently, the patterning procedure is only realized in the top resist layer. After exposure and development, a mask for dissolution of the bottom layer is built. Controlled dissolution of the LOR leads to a well-defined undercut profile, which is independent from the e-beam process. However, removers of LORs can attack metal films, such as Al, which can be disadvantageous for some sample systems [192]. An example are Al bottom layers, which can allow for EBL on insulating substrates [193].

Figure 4.2: For a single layer positive tone resist (1), the deposited metal can form a continuous layer. Hence, sharp metal edges may remain after the lift-off or the lift-off may be disabled even. In case of a more sensitive resist (1) below a less sensitive one (2), this can be avoided [194]. Typically, (2) is much thinner than (1), which allows for a better disconnection of the metal on top and in the gap.

4.1.2 Setup for electron beam lithography

For the fabrication of the nanoantennas presented in this thesis, the EBL system eLINE, delivered by the company RAITH GmbH is used. This system offers an accelerating voltage of 100 V to 30 kV and six different apertures ranging from 7.5 to 120 µm. To pattern a sample area, a so-called writefield needs to be chosen. The eLine system allows for quadratic writefields with side lengths of 5, 25, 50, 100, 200 and 1.000 µm. Larger patterns are composed of several smaller writefields. The process of combining these writefields is called stitching.

Generally, an EBL system is built of a scanning electron microscope and a pattern generator, which transfers a designed pattern via the electron beam to a sample system. EBL systems have four main units: an electron source, an electron column, which forms the electron beam, a mechanical stage to position the samples, and a control unit. The latter is not only used to control all subunits of the EBL system, but also for transferring the pattern, which is supposed to be written into the resist, to the electron column. The main difference between available EBL systems concern their electron source and the type of lens used for the electron beam deflection.

In figure 4.3 a scheme of an EBL system is given. The electrons are emitted by an high voltage (HV) electron gun. A thermal field emission filament is used as a source. A beam with a narrow energy spread can be compared to monochromatic light. Even the energy spread of the emitted electrons is

60
4.1 Electron beam lithography

Figure 4.3: Displayed is a scheme of an electron beam lithography setup. Electrons are generated and travel through an electron lens (striped), blanking electrodes (white), deflection coils (black), a magnetic lens (gray) and the aperture (black bars). The sample, which is brought in with an air lock, is placed on the movable sample stage (squared). All subunits despite the air lock are constantly under vacuum. To ensure the fabrication of high resolution nanostructures the system needs to be isolated from vibrations. With a computer, the pattern, which is supposed to be written into the electron beam resist on the sample, is transferred to the system. At the same time, an electron detector (not shown) assists with focusing. The figure has been adapted from [195].

narrow at the gun, it increases during the move of the electron beam down the column, which is called Boersch effect [196].

After the beam has been generated, it travels through the column, which focuses and deflects or blanks the electron beam. Either magnetic or electrostatic lenses can be used for focusing. Electrostatic lenses consist of several electrodes, with a ground potential applied to the outer electrode and a different potential applied to the inner one. Electrons can be redirected to the optical axis then. The commonly used type is a so-called einzel lens, which focuses the beam without changing its energy [197]. On the one hand, electron lenses are disadvantageous regarding aberration\(^2\) compared to magnetic lenses. On the other hand, since electrostatic lenses are applicable for ultrahigh vacuum and high-temperature compatible, they are used close to the electron gun. Thus, the first lens in the column in figure 4.3 (striped) is an electrostatic lens.

To turn the beam on and off, blanking electrodes are used. The working principle is based on electrostatic deflection. With an applied voltage, the electron beam is deflected off the optical axis. The blanking must be realized as fast as possible to avoid leaving streaks at the sample surface due to the beam deflection. This is also supported by an optimized positioning of the blanks, e.g. centering at an intermediate focal point [195].

Since the goal of EBL is the writing of a pattern into a resist layer, the electron beam needs to be deflected. This scanning with deflection coils can be done electrostatically or magnetically. As already discussed for lenses, magnetic deflection is advantageous regarding aberrations relative to electrostatic deflection. At the same time, due to inductance of the magnetic deflection coils, electrostatic deflection is faster.

To form the beam before finally hitting the sample surface, a beam limiting aperture is used. The small hole, which is available in different sizes (diameters are 7, 10 or 30 \(\mu\)m) through which the electron beam passes, defines the beam convergence angle. The aperture can be aligned manually before every EBL writing procedure if necessary. To avoid contamination, apertures are either heated or have to be cleaned regularly.

\(^2\)In the sense of imaging with electrons, spherical aberration describes the stronger focusing of the lens in its outer zone relative to its inner zone. Chromatic aberration refers to the fact that electrons of different energies get focused at different image planes [196].
The final lens, which is the crucial lens for the system performance regarding aberrations, is commonly a magnetic lens. These lenses are built from two circularly symmetric polepieces (e.g. iron) with a winding (e.g. copper) in-between. Magnetic lenses are often liquid-cooled to ensure a stable operation of the system, which would be disturbed by an increased temperature of the lens.

The sample stage can be moved in all three spatial directions. The control in $x$- and $y$-direction is necessary to position the sample in the optical axis of the electron beam and to pick a suited sample area, which is clean and not to close to the sample edge, to write the pattern. The movement in $z$-direction allows for the focusing of the electron beam on the sample surface.

To compensate imperfections in the alignment of all column components, a stigmator is used. Furthermore, the beam cross section becomes elongated instead of circular while travelling through the EBL column. To correct this astigmatism, magnetic coils in quadruple orientation are used. Additionally, a Faraday cage is used to measure the beam current. With this, the optimized dose for the resist exposed to the beam is calculated. The Faraday cage, which is below the final aperture, as well as the stigmator are not depicted in figure 4.3.

The sample itself is brought into the EBL setup by an air lock. The electron gun and the column need to be under ultra-high vacuum (UHV) and are only vented in the case of repair or replacement of elements. The air lock allows for loading the sample without the time-consuming and component-damaging venting of the entire EBL system. As soon as the vacuum in the small air lock is comparable to the vacuum of the chamber, the sample is transferred into the chamber. Afterwards, the valves are closed and the air lock is isolated from the EBL system again. The unloading of the samples follows the same principle. During the load and the unload procedure, the gun and the column are separated from the sample chamber by closed valves. UHV is advantageous for a high resolution of the generated sample images, as well as of the written nanostructures, since in UHV conditions electron scattering is minimized.

### 4.1.3 Resolution limits of electron beam lithography

Even EBL allows for the fabrication of nanostructures with feature sizes down to only a few nm, its resolution is limited. Different contributions restrict the minimum feature size, which can be realized with EBL. The physical limit of diffraction, the scattering of the electrons and several process parameters, as the chosen EBL chemicals (resist and developer), the exposure dose and the baking conditions are limiting factors. These contributions will be discussed in the following.

#### Diffraction

The limit of the resolution in conventional light microscopy has been described by Ernst Abbe. There, the resolution limit is defined as the distance $d_{\text{min}}$, which is the smallest distance between two distinguishable features visible in the microscope:

$$d_{\text{min}} = \frac{\lambda_{\text{vac}}}{n \cdot \sin(\theta_{\text{max}})}$$ (4.1)

with $\lambda_{\text{vac}}$ being the illumination wavelength in vacuum, $n$ is the refractive index of the medium the light travels trough (for air $n = 1$ or for an immersion oil e.g. $n = 1.5$) and $\theta_{\text{max}}$ representing the maximum diffraction angle. The denominator is called the numerical aperture (NA) [198].

\[3\]This includes scattering of the electron beam before hitting the sample and scattering of the particles back-reflected from the sample surface. The back-reflected particles are necessary for the generation of the electron image.
For electrons, the wavelength $\lambda$ is given by the de Broglie equation:

$$\lambda = \frac{h}{m_0 \cdot v} = \frac{h}{\sqrt{2m_0 \cdot e \cdot U}}$$  \hspace{1cm} (4.2)

with $h$ being Planck’s constant, $m_0$ representing the electron mass, $e$ being the elementary charge and $U$ is the electric potential for electron acceleration. In the electron beam setup eLine, an acceleration voltage of $UL = 20$ kV is used for the patterning process since this acceleration voltage and a 10 µm aperture have allowed for fabricated nanostructures with feature sizes below 100 nm before [199]. Furthermore, the applied InLens detector of the eLINE system can only be used for acceleration voltages $\leq 20$ kV. For higher voltages the conventional secondary electron (SE) detector has to be used. The latter is placed laterally of the investigated object, while the InLens detector is positioned on top of the sample and allows for a much better resolution.

With equation 4.2 and $UL = 20$ kV, the electron wavelength can be calculated to $\lambda \approx 8.67$ pm. Due to this, diffraction is not the factor limiting the structural resolution of electron beam lithography. Instead, the electron beam column, the electron scattering and the process chemicals limit the resolution of the structures and will be described in the following.

**Electron beam column** The electron beam diameter $d$ is a function of the demagnification of the column and the spherical and chromatic aberrations. Hence, $d$ can be described as a square root of the sum of all contributions:

$$d = \sqrt{d^2_0 + d^2_S + d^2_C}$$  \hspace{1cm} (4.3)

with $d^2_0$ being directly proportional to the beam current and inversely proportional to the brightness of the beam (current density per unit solid angle), $d_S$ referring to the diameter of the circle of least confusion\footnote{The so-called circle of confusion is also known as blur circle or circle of indistinctness. The circle of least confusion is defined as the smallest cross-section of the blur circle between two focal lines formed by an astigmatic lens [200].} caused by spherical aberration and $d_C$ is the diameter of the circle of least confusion of the final lens, which is proportional to the effective energy spread of the electron beam. This energy spread depends on the interaction between the electron beam currents, the fluctuations in the current of the magnetic lens and in the accelerating potential of the electron gun, as well as on the initial energy spread of the gun (Boersch effect). All contributions are discussed in [195].

**Electron scattering** In contrast to photolithography, where photons are absorbed at once, electrons deposit their energy gradually and scatter within the resist. Thus, the limitation of the resolution is also based on scattering. Electrons are forward scattered in the resist (typically small angle deflection), as well as back scattered (wide angle scattering) from the substrate. Elastic collisions of electrons entering the resist lead to a change of the electron direction. Inelastic collisions result in a loss of energy. Due to these scattering events, the electron beam is broadened. Resist areas, which are not in the region of the incident electron beam, are exposed to electrons. Consequently the developed resist shows much wider patterns than expected by design. This scattering effect is called *proximity effect* [190, 201].

The relevant parameters for the electron scattering in the resist need to be discussed individually:

- **Beam energy** The higher the electron beam energy, the lower the energy loss per unit path length leading to a decreasing scattering cross-section. As a consequence, the lateral expansion of the
forward scattered electrons is decreased, whereas the lateral extent of the backscattered electrons is increased [202].

- **Resist film thickness** With increasing resist film thickness, the forward scattering increases. This relies on the accumulation of forward scattering events in the resist. Consequently, a broader area at the interface between substrate and resist contributes to the resist exposure [196].

- **Substrate** The heavier the substrate elements, the higher the electron reflection coefficient. Consequently, the backscattering is increased. In case the layer underneath the resist is a relatively heavy metal film, the backscattering increases significantly [203].

**Process chemicals** For each nanostructure (array) an optimized system of EBL resist, corresponding developer and their process parameters, such as exposure dose, development time, developer temperature and baking conditions needs to be developed. Furthermore, a so-called *exposure function* can be calculated, which allows for a corrected dose distribution including the parasitic exposure of unwritten areas due to scattered electrons, already introduced as proximity effect. For the investigated simply shaped nanorods with relatively large separation distances, no dose correction was necessary.

## 4.2 Fourier transform infrared microspectroscopy

In this thesis, the samples were spectrally characterized by *Fourier transform infrared (FTIR) microspectroscopy*, which is the combination of FTIR spectroscopy and optical microscopy. Thereby, infrared spectroscopy is the measurement of wavelength or frequency dependent absorption of infrared light by a sample [204]. Moreover, FTIR microspectroscopy allows for the visualization and infrared analysis of a specific local region of interest on the sample (referring to the microscopic character of this method), while it is noninvasive, highly sensitive and in many operation modes easy to handle.

The introduction of the Fourier transform principle revolutionized the infrared spectroscopy, which was a dispersive technique up to this point, and led to the FTIR spectroscopy. The FTIR microspectrometer and its components will be described in the beginning of this section and will be followed by a description of the Fourier transform principle. In the last part, vibrational spectroscopy, which enables the detection of spectral signatures of molecules, will be discussed briefly.

### 4.2.1 FTIR microspectrometer

A general scheme of the FTIR microspectrometer is shown in figure 4.4. These instruments are built from an infrared spectrometer - infrared light source, Michelson interferometer and a suited detector - and a microscope optical system. The latter can be operated in several different modes and with different objectives, such as a *Schwarzschild-type Cassegrain objective*, *grazing angle objective* (GAO) or *attenuated total reflectance* (ATR) objective. Following figure 4.4, a source emits infrared light, which travels through the Michelson interferometer and a Schwarzschild-type Cassegrain objective in the microscope. The light is focused onto the sample on a xyz-sample stage, which is also part of the microscope. After the light hits the sample, it is either reflected back in the same objective (*reflectance mode*) or it is transmitted to another condenser (*transmission mode*). The radiation is collected, for example with a mercury cadmium telluride (MCT) detector, where the irradiance is
4.2 Fourier transform infrared microspectroscopy

determined. Irradiance is defined as the power of electromagnetic radiation per unit area incident on a surface [205]. The irradiance is detected as a function of the path difference $\delta$ between the two arms of the Michelson interferometer: one arm is defined by the beamsplitter and the moving mirror and the other arm is defined by the beamsplitter and the stationary mirror. This interference pattern - the irradiance (or intensity $I$) as a function of the path difference $\delta$ - is called an interferogram. Fourier transformation leads to the infrared spectrum.

For the work presented in this thesis a FTIR microspectrometer from the company Bruker Optik GmbH was used. The FTIR spectrometer Vertex 70 and the attached microscope Hyperion 2000 with two Schwarzschild-type Cassegrain objectives (15-fold and 36-fold magnification) were available. In appendix A.3.3, the detailed FTIR parameters for all reflectance spectra depicted in chapters 5 to 7, as well as the detailed optical beam path of the Hyperion 2000 microscope are given. A very detailed characterization of the entire FTIR microspectrometer setup is presented in [206].

The infrared light source, the Michelson interferometer, the optical microscope as well as the detector will be described in more detail in the following.

![Diagram of a FTIR microspectrometer](image)

Figure 4.4: A scheme of a FTIR microspectrometer is displayed. Infrared light (IR) travels through a Michelson interferometer (beamsplitter BS, stationary mirror SM and moving mirror MM) and is focused on the sample by using an optical microscope (MIC). With a detector (D) for infrared light an interferogram is generated. Fourier transformation (FT) leads to the spectrum. At the beamsplitter (BS, gray) light is reflected to the stationary mirror and transmitted to the moving mirror. After the light has been backreflected from the two plane mirrors (SM, MM) to the beamsplitter, the beams are recombined. Their path difference $\delta$ is given as a difference of the two arms (BS-MM) and (BS-SM), which are marked with dashed arrows. Depending on the path difference $\delta$, the recombined beam is guided to the detector (D) and back to the source (IR). The measured signal $S(\delta)$ (including $I(\delta)$) and the intensity spectrum $B(\tilde{\nu})$ will be discussed in the framework of the Fourier transformation principle.

**Infrared light source** Typically, a high-temperature blackbody is used as a mid-infrared source. A glowing silicon carbide (SiC) rod heated to a temperature above 1.000°C, a so-called Globar, or a high-pressure mercury (Hg) lamp are examples for these types of sources [207]. The spectrometer Vertex 70 is equipped with an external Globar, which allows for a higher intensity compared to the internal source. The intensity is given by the analog-to-digital converter (ADC) count. The ratio between the ADC counts of the external to the internal MIR source is about 1.5 [206]. The source is water cooled.

**Michelson interferometer** The Michelson interferometer was invented by Michelson in 1891\(^5\) and is the simplest two-beam interferometer type. Two-beam interferometers applied in FTIR spectrometers

---

\(^5\)Micelston received the Nobel prize in physics in 1907 *"for his optical precision instruments and the spectroscopic and metrological investigations carried out with their aid"* [208].
4.2 Fourier transform infrared microspectroscopy

nowadays are based on the principle of the Michelson type. The setup is schematically shown in figure 4.4. A collimated beam of a light source is guided to a beamsplitter, which splits the beam into two arms. The beamsplitter is set at an angle bisecting two plane mirrors with an angle of 90° or 60° between the mirrors while an angle of 60° between the mirrors allows for a size reduction of the interferometer compared to an angle of 90° [209]. The beam is partially reflected to a stationary mirror and partially transmitted to a moving mirror. Both beams are reflected back to the beamsplitter, where they interfere and are partially reflected and transmitted again. Thus, the beams travel partially to the detector and back to source. The position of the moving mirror is determined by using a HeNe laser with a defined wavelength, which is coupled in the beam path of the interferometer.

Whether the beams interfere constructively or destructively depends on the optical path difference $\delta$ between the two interferometer arms and the wavelength of light (considered monochromatic for the following description). In case of zero path difference (both mirrors are placed with the same distance to the beamsplitter), both beams recombine without phase difference$^6$ at the beamsplitter. This leads to a maximum amplitude of the recombined beam. Hence, for this so-called constructive interference a maximum irradiance can be measured at the detector, since all light travels to the detector. In contrast, no light travels back to the source. For an optical path difference of a quarter of the incident wavelength $\lambda_0/4$, the total path difference at the beamsplitter would be $\lambda_0/2$ (It is $\lambda_0/4$ for the light traveling to the mirror and $\lambda_0/4$ for the back-reflected light.). Therefore, the two beams interfere destructively and at the detector zero irradiance is generated. In case of a path difference of half of the incident wavelength, the same situation as described for zero path difference occurs. Thus, for a constant movement of the mirror a sinusoidal detector signal follows, whereas the distance between the maximum amplitude is $\lambda_0$. The resolution of the FTIR spectrometer is limited by the moving mirror and its maximum achievable path difference $\delta_{\max}$.

In practice, the infrared light source emits a broad continuous spectrum. A constructive interference of all wavelengths only occurs, if all individual beams travel the same distance, which is only the case for $\delta = 0$ as depicted in figure 4.4. This peak is called centerburst. In contrast, destructive interference can be observed for $\delta \neq 0$. The interferogram shows the intensity (ADC signal) as a function of the optical path difference. With suited software, the resulting complex interferogram, which is in the time domain, is Fourier transformed to the frequency domain. Deconvolution leads to the final spectrum.

Elements of the optical microscope The use of an optical microscope for spectroscopy allows for the investigation of local sample areas. Several elements of the microscope - visible illumination, charge-coupled device (CCD) camera, aperture, polarizer and objectives - will be briefly discussed here. They can also be seen in figure A.8. The sample can be observed by using visible illumination and a CCD camera system. To avoid an unwanted source for external thermal radiation, the implemented light bulb of the used Hyperion 2000 was removed and a self-built light-emitting diode illumination system was installed instead. With the CCD image on the LCD screen, which is part of the microscope, binoculars or via the FTIR software$^7$ the sample region of interest can be located. With two transparent knife-edge apertures, it is possible to define the area of the sample. CCD sample images including

$^6$For normal incidence, a beam reflected by a mirror undergoes a phase change of 180°. A beam reflected by an ideal beamsplitter undergoes a phase change of 90°. A beam transmitted by an ideal beamsplitter undergoes no phase change.

$^7$The Opus software by Bruker is used for visualization of the sample and the spectra, as well as for the control of the setup.
apertures can be seen in appendix, figure B.3. In principle, areas down to about 65 µm² can be probed [206]. The alignment is done with the optical microscope image. By using a polarizer the light illuminates the sample area only with the chosen polarization direction. The polarizer element is brought into the beam path just before the objective.

In the infrared spectral range, most of the available optical components are not transparent or if, only in a narrow spectral range. To circumvent this restriction, reflective optical components are used for infrared microscopy. Simultaneously, chromatic aberration, a failure in imaging with optical lenses, is avoided for reflective optics [210]. FTIR microscopes use a Schwarzschild-type Cassegrain objective, which is schematically shown in figure 4.5a [207]. Collimated light is guided by a convex to a concave mirror to the sample. The primary, concave mirror is larger than the secondary, convex mirror. The sample is illuminated under the polar and azimuthal angles \( \theta_i \) and \( \phi_i \) illustrated in figure 4.5b. The described principle is known from the Cassegrain telescope developed by L. Cassegrain (1629 - 1693), whereas K. Schwarzschild (1873 - 1916) adapted it for microscope objectives.

In the available setup, the samples can be investigated either by reflection or by transmission measurements. For reflection measurements, the upper Cassegrain objective (above the sample, 15- or 36-fold) is used as objective as well as condensor, since the light is reflected back into the objective. In contrast, in transmission mode the light is guided into the Cassegrain condensor below the sample. This is displayed in figure A.8. In reflection mode, only a half-space of the objective mirrors is illuminated for each direction the light is traveling along, as it is shown in figure 4.5a.

Figure 4.5: In 4.5a is a scheme of the optical path in a reflecting Schwartzschild-type Cassegrain objective with its first (A) and second (B) mirror depicted. The incident light is illustrated with black arrows, whereas the reflected light is marked in gray. For reflectance measurements, only one halfspace of the objective is illuminated by the incident light. The scheme was taken from [211]. In 4.5b the the polar and azimuthal angles \( \theta_i \) and \( \phi_i \) of the incident light are depicted.

**MCT detector** Generally the FTIR detector converts the infrared light from the sample into an electrical signal. So-called quantum detector types are based on the excitation of electrons in a semiconductor from a lower (valence) to a higher (conduction) band due to the influence of the infrared radiation on the electrons of the solid\(^8\) [212]. In case of electrons promoted from the valence to the conduction band, a current will be passed by the detector material. The MCT detectors described here belong to the quantum detector type. They are based on the variable band gap \( \text{Hg}_{1-x}\text{Cd}_x\text{Te} \) alloy, which has been discovered by Lawson et al. in 1959 [213]. These alloys exhibit a bandgap from 0.05

---

\(^8\)The term "quantum" is based on quantum nature of the radiation.
to 1.77 eV (400 to about 14.300 cm$^{-1}$) [214] and enable the infrared detection over the entire infrared spectral range.

MCT detectors are available as photoconductors, photodiodes, and Avalanche photodiodes. In the *Hyperion 2000* a photodiode is used. The two doped semiconductors HgTe and CdTe are joined. The electrons and holes in them migrate to the other side, which leads to a built up charge across the interface. Any more diffusion is impeded. If a photon with $E > E_g$ (bandgap) hits the detector, holes are generated in the valence band, since electrons are excited to the conduction band. This leads to a current, since the recombination of electrons and holes is hindered by an applied potential [209]. Since the energy of the photons, which needs to be probed, is rather low, thermal leakage is an issue. In practice, MCTs are vacuum-sealed and need to be cooled to about 77 K with liquid nitrogen. Otherwise the thermally excited carriers would disturb the detection of the infrared radiation and lead to a high noise level. Even MCT detectors need the described cooling to very low temperatures and are relatively heavy or bulky due to the Dewar flask, the very high detection speed and sensitivity is advantageous.

**Thermal stage** The available FTIR microspectrometer is equipped with a *Linkam* thermal stage, which allows for the heating (up to about 600°C [215]), as well as for the cooling (down to about -200°C [215]) of the sample. This thermal sample treatment can be conducted while spectra are taken, which allows for temperature dependent FTIR spectra. However, focusing of the sample surface during thermal treatment is difficult.

### 4.2.2 Normalization to background spectra

Before taking a spectrum of the sample, a background spectrum is measured. The subsequently collected spectrum of the sample will be divided by this background spectrum. The background spectrum includes all information of the infrared light source, the interferometer, the optical elements of the microscope and the detector. As a consequence, these contributions are excluded from the sample spectrum due to normalization and only the spectral information of the investigated sample is detected. Besides, spectral contribution of ambient water and carbon dioxide will be seen in the reference spectrum. The modes due to stretching vibrations of the OH bond (water) lie in the range between 3000 and 3650 cm$^{-1}$ [216]. For the CO double bond (CO$_2$) the stretching vibrations can be found in the range between 1680 and 1820 cm$^{-1}$ [216]. Since the described parameters can vary with time and ambient conditions (temperature, atmospheric pressure), the background spectrum should be collected in a timely manner to the sample measurement. Furthermore, the microscope aperture, the objective and the polarization (if the incident light is polarized) need to be similar for the background, as well as the sample spectrum for an accurate normalization.

To validate the stability of the background, a reference spectrum is taken. As a reference either a mirror (e.g. gold) or the substrate, which has been chosen for the sample, can be used. In case of an accurate background measurement the reference spectrum is expected to be a nearly flat line at a normalized reflectance of about 1.0. Usually, the mode of the stretching vibrations of the CO double bond, which is characteristic for carbon dioxide, is still clearly visible. This could only be avoided by purging the measurement area with dry CO$_2$ free air or nitrogen.
4.2 Fourier transform infrared microspectroscopy

4.2.3 Fourier transformation principle

Fourier transformation is a mathematical way to transpose from a spatial or time domain to a frequency domain and vice versa is given. This is implemented by the fact that every signal can be decomposed as a sum of sinusoidal curves (Fourier decomposition), which in turn is described with phase, magnitude and spatial frequency. In Fourier transform spectroscopy, the Fourier transformation is used to get a frequency dependent spectrum out of a detected interferogram. The interferogram is the modulated component of the probed beam intensity at the detector as a function of the path difference, \( I(\delta) \). The Fourier transformation is automatically realized by the spectrometer software.

The following equations are based on the book of Griffiths and de Haseth [209] to a great extent. The description here focuses on the general principle of Fourier transformation for spectroscopy, which results in a reduced extent of the presented equations relative to the cited literature.

Interferogram and spectrum For a monochromatic incident wave, the probed beam intensity \( I \) at the detector is the square of the absolute value of the electric field \( \mathcal{E} \) at the detector:

\[
I(\delta) = |\mathcal{E}(x,t)|^2
\]  
(4.4)

with \( \delta \) being the optical path difference between the beams that travel to the fixed and the movable mirrors and back to the beamsplitter as described in the previous paragraph. The spatial coordinate and the time are given by \( x \) and \( t \) respectively. Due to the path difference between both beams of the Michelson interferometer, the electric field has two components:

\[
\mathcal{E}(x,t) = \frac{\mathcal{E}_0}{2} e^{i(k_0 x - \omega t)} + \frac{\mathcal{E}_0}{2} e^{i(k_0 |x+\delta| - \omega t)}
\]  
(4.5)

Here, \( k_0 \) stands for the wavenumber, which is typically used in the field of infrared spectroscopy. It equals \( 2\pi/\lambda_0 \) with \( \lambda_0 \) being the wavelength of the incident wave. The unit of the wavenumber is \( \text{cm}^{-1} \). Referring to experimental descriptions, the wavenumber is given as \( \tilde{\nu} \). In equation 4.5, the wave’s angular frequency is given as \( \omega \). Equation 4.5 can be simplified as follows:

\[
\mathcal{E}(x,t) = \frac{\mathcal{E}_0}{2} e^{i(k_0 x - \omega t)} \cdot \left( 1 + e^{i k_0 \delta} \right)
\]  
(4.6)

With Euler’s formula the square of the absolute value of \( \mathcal{E}(x,t) \) can be calculated:

\[
e^{i k_0 \delta} = \cos(k_0 \cdot \delta) + i \cdot \sin(k_0 \cdot \delta)
\]

\[
|\mathcal{E}(x,t)|^2 = \frac{\mathcal{E}_0^2}{4} \cdot 2 \cdot [1 + \cos(k_0 \cdot \delta)] = \frac{\mathcal{E}_0^2}{2} \cdot [1 + \cos(k_0 \cdot \delta)]
\]  
(4.7)

By applying equation 4.4 the intensity can be expressed as a function of the path difference:

\[
I(\delta) = \frac{I_0}{2} \cdot [1 + \cos(k \cdot \delta)]
\]  
(4.8)

\( I_0 = I(k_0) \) is the intensity of the source. The interference record \( I(\delta) \) consists of two summands: a constant and a modulated component with only the latter being considered for spectroscopic measurements. Thus, the following descriptions focus on the modulated component.
4.2 Fourier transform infrared microspectroscopy

The FTIR spectrometer detects the intensity given by an analog-to-digital converter (ADC) count. The measured signal $S(\delta)$ from the setup amplifier includes

$$S(\delta) = \frac{1}{2} \cdot B(k_0) \cdot \cos(k_0 \cdot \delta)$$

with $B(k_0) = H(k_0) \cdot G(k_0) \cdot I(k_0)$ (4.9)

The factors can be described as follows: $H(k_0)$ is a correction factor including the beamsplitter efficiency and $G(k_0)$ is the responsivity of the detector, as well as of the signal amplifier. $B(k_0)$ gives the intensity of the source modified by instrumental characteristics.

In case of a broad infrared source, the entire range of incident $k_i$ instead of a single $k_0$ needs to be considered. Equation 4.9 must be replaced by an integral over infinity. Then, the cosine Fourier transform pair can be calculated by:

$$S(\delta) = \int_{-\infty}^{+\infty} B(\lambda_0) \cdot \cos(k_0 \cdot \delta) \, dk$$

$$B(k) = \int_{-\infty}^{+\infty} S(\delta) \cdot \cos(k_0 \cdot \delta) \, d\delta$$

(4.10)

The necessary Fourier transformation causes the name of the spectrometry method.

**Apodization** Since the optical path length is finite, the integration over infinite boundaries $[-\infty, \infty]$ is not useful. Instead, the integration needs to be done over finite boundaries $[-\delta, \delta]$. As an effect, not only the spectral lines, but also side minima or maxima occur. These secondary weak lines can be circumvented by multiplying a weight function $A(\delta)$ (e.g. a boxcar or triangular function) to the interferogram in advance to the Fourier transformation:

$$B(k) = \int_{-\delta}^{+\delta} S(\delta) \cdot A(\delta) \cdot \cos(k \cdot \delta) \, d\delta$$

(4.11)

The procedure is called *apodization*, which is advisable in case of features narrower than the nominal resolution. If the resolution is narrower than the bandwidths of the spectral lines, apodization smoothens the spectrum, but lowers the spectral quality due to a loss in resolution [207].

A simple triangular apodization function would be given by:

$$A_T(\delta) = \begin{cases} 1 - \frac{|\delta|}{\Delta} & \text{for } -\Delta \leq \delta \leq \Delta \\ 0 & \text{for } |\delta| > |\Delta| \end{cases}$$

(4.12)

with $1/\Delta$ being the nominal resolution [209]. For the experimental data presented in this thesis, a so-called exact three term Blackman-Harris (BH) window has been used. This apodization function is advantageous regarding a smooth and strong asymptotic side lobe decay, but not best suited for the resolution of very sharp absorption peaks [217]. Since the investigated antenna resonance peaks show...
a peak width of more than 100 cm$^{-1}$ and the apodization is used to surpress noise, the BH window is well-suited. The exact three term BH function is defined as follows [218]:

$$A_{BH}(\delta) = \frac{7938}{18608} - \frac{9240}{18608} \cdot \cos \left(2\pi \frac{\delta}{\Delta} \right) + \frac{1430}{18608} \cdot \cos \left(4\pi \frac{\delta}{\Delta} \right)$$

(4.13)
CHAPTER 5

General considerations concerning the sample design

5.1 Introduction

This chapter investigates the influence of the surrounding medium, e.g. phase-change materials (PCMs), on the antenna array resonance frequency position \( \lambda_{\text{res}} \). In chapter 2 it was introduced that the PCM in the vicinity of an antenna can affect the antenna resonance by its dielectric function \( \varepsilon_{\text{PCM}} \), which is a function of the structural phase of the PCM (A and C), as well as of the wavelength \( \nu \), as it was discussed in chapter 3. The attainable shifts of the antenna resonances are influenced by various parameters, such as materials and sample layout as sketched in figure 5.1. First, the sample materials, which are suited for the proposed concept of resonance frequency shifting, will be discussed in section 5.2. Hereafter, the influence of the sample layout on the resonance frequency shift \( \Delta\nu_{\text{res}} \) will be illustrated in section 5.3. This includes effects of the antenna length, the PCM film thickness as well as the position of the antenna arrays relative to the PCM layers. In section 5.4, the antenna array and its spectral properties will be described, which involves also the interference between the antenna array and the PCM thin films.

Figure 5.1: In chapter 5, sample parameters, such as materials, sample layout (deposited PCM film thickness \( t_A \), antenna geometry including \( w, h \) and \( L \) - not to scale - and positioning of the antenna relative to the PCM thin film) and arrangement of antennas in an array are discussed regarding their influence on antenna resonance frequency shifting. Their practical influence on the experimental results will be described in the following chapter 6.
5.2 Considerations on sample materials

To realize large resonance frequency shifts $\Delta \tilde{\nu}_{\text{res}}$ accompanied by low losses the investigated sample system is composed of a flat substrate, nanoantennas and a PCM thin film. The used materials are suited for the MIR spectral range regarding their reflectivity and their refractive index contrast (referring to PCMs). Furthermore, several aspects, such as requirements concerning sample fabrication and characterization, as well as stability regarding sample treatment (annealing on a hot plate or optical laser pulses) need to be taken into account to choose materials for the sample components. To maximize the desired effect of resonance frequency shifting the best suited materials, as well as the best configuration needs to be found.

5.2.1 Substrates

For the fabrication by electron beam lithography (EBL), the substrate has to be planar and sturdy, as well as insoluble in water or aqueous solutions. Regarding safety aspects, a nontoxic sample is much easier to be handled compared to a toxic substrate material. Cost is another factor of the substrate that needs to be considered.

To crystallize the PCM thin films by heating on a hot plate, the substrate material has to be thermally stable at the annealing temperature $T_{AN} \geq T_C$. Additionally, a substrate with a high thermal conductivity $\kappa_T$ is needed to realize laser induced reversible switching of the PCM. For the optically triggered phase transitions, the sample is heated by an optical pulse. Especially for re-amorphization, this heat has to drain off as fast as possible, which is related to the quenching of the molten state of the PCM. However, PCMs offer a very low thermal conductivity $\kappa_T$, for example $\kappa_T \approx 1 \text{mW} \cdot \text{cm}^{-1} \cdot \text{K}^{-1}$ for amorphous and $\kappa_T \approx 4 \text{mW} \cdot \text{cm}^{-1} \cdot \text{K}^{-1}$ for crystalline GST-225 [219]. Silicon with a thermal conductivity $\kappa_T \approx 1.42 \text{W} \cdot \text{cm}^{-1} \cdot \text{K}^{-1}$ at 300 K [220] is an ideal candidate to serve as a heat sink. It has to be noted that the thermal conductivity is denoted as $\kappa_T$ to distinguish between the extinction coefficient $\kappa$ and $\kappa_T$.

Besides offering the relatively high value for $\kappa_T$, Si substrates are insoluble in water or aqueous solutions, electrically conductive as well as thermally stable. Furthermore, silicon shows a very low absorption in the MIR spectral range [221] and its real part of the refractive index $n$ in the MIR is about 3.43 [222]. This is much higher than typical substrate materials with a low absorption in the MIR spectral range, such as calcium fluoride $\text{CaF}_2$ with $n = 1.4$ and zinc selenide $\text{ZnSe}$ with $n = 2.4$ [21]. Thus, the relatively high refractive index $n$ of silicon leads to a shift of the antenna resonance position $\tilde{\nu}_{\text{res}}$ to lower wavenumbers compared to the case where antennas are placed on a substrate with a smaller refractive index (cf. equation 2.13).

5.2.2 Nanoantennas

Rod-shaped nanoantennas are a model system for resonant nanostructures. Their resonance frequency position $\tilde{\nu}_{\text{res}}$ can be described by using an analytical model instead of numerical simulations as discussed in chapter 2. Furthermore, the fabrication of nanorod arrays is relatively simple compared to more complex nanostructures with small gaps or three-dimensionally arranged as known from some MMs, e.g. in [223].

To ensure for a direct influence of the change in the refractive index of the PCM $\Delta n_{\text{PCM}}$ on the
nanoantenna resonance frequency $\tilde{\nu}_{\text{res}}$, the antennas should be brought in direct contact with the PCM. In the literature, gold (Au) is often used as antenna material, e.g. in [26, 32, 38]. However, a negative bonding enthalpy was found for AuX$_2$ compounds (X = In, Sb, e.g.) [224] and the diffusion of gold into GST-326 and Ge$_{15}$Sb$_{85}$ was observed for an annealing temperature of 210°C [110, 147, 225]. Therefore, GholiPour et al. applied a diffusion barrier of (ZnS)$_{80}$-(SiO$_2$)$_{20}$ between gold ASRSs and GST-225 [38]. Thus, no direct contact between the resonant nanostructure and the PCM is given, which is assumed to lead to smaller resonance shifts $\tilde{\nu}_{\text{res}}$. In this work, aluminum is used as an alternative nanoantenna material. Thereby, it is assumed that the native aluminum oxide layer, which is built immediately after the deposition of aluminum, acts as a diffusion barrier.

Despite the avoidance of diffusion, aluminum offers the advantage of integrability into industry relevant complementary metal-oxide-semiconductor (CMOS) fabrication. Furthermore, the low costs, the low electric field screening and the high electron density of aluminum compared to gold make aluminum a promising candidate for applications in the field of plasmonics [187].

The metallic nanoantennas need to show pronounced resonance peaks. Therefore, the scattering and the absorption cross sections $\sigma_{\text{scat}}$ and $\sigma_{\text{abs}}$ of a single antenna made of the typical antenna material gold and of the alternative metal aluminum were compared and these numerical results computed with the software Comsol are given in figure 5.2. To observe the resonance frequency in the MIR spectral range while the antenna is surrounded by vacuum, the antenna length $L$ was chosen as 1.2 μm. The pronounced resonance frequency peaks for a gold and an aluminum antenna were calculated as $\tilde{\nu}_{\text{res,Au}} = 2935$ cm$^{-1}$ and as $\tilde{\nu}_{\text{res,Al}} = 3202$ cm$^{-1}$ respectively. Besides the shift of the resonance position by 267 cm$^{-1}$, the maximum scattering cross section $\sigma_{\text{scat}}$ increases from about 3.24·10$^6$ nm$^2$ to about 3.44·10$^6$ nm$^2$ by replacing gold with aluminum. Furthermore, the resonance peak is less narrow for aluminum compared to gold with FWHM$_{\text{Al}} = 888$ cm$^{-1}$ and with the full width at half maximum FWHM$_{\text{Au}} = 673$ cm$^{-1}$. Both the calculated absorption cross section $\sigma_{\text{abs}}$ the extinction cross section, which is the sum of the scattering and the absorption cross section, are higher for gold compared to aluminum. Since the absorption cross section $\sigma_{\text{abs}}$ of an aluminum antenna is smaller, while the scattering cross section $\sigma_{\text{scat}}$ at resonance is slightly larger for aluminum compared to gold, aluminum is better suited as nanoantenna material in the MIR spectral range than gold. To measure pronounced resonance peaks in the antenna reflectance spectra, the absorption should be minimized and the scattering should be maximized.

Figure 5.2: The scattering and absorption cross sections $\sigma_{\text{scat}}$ (circles) and $\sigma_{\text{abs}}$ (triangles) of a single antenna embedded in vacuum ($n = 1.0$) were calculated with the Comsol (cf. appendix C). The antenna materials aluminum (black) and gold (gray) were compared and the geometry was defined as follows: width $w = 100$ nm, height $h = 40$ nm and length $L = 1.2$ μm. The edges of the antenna were smoothed. The dielectric functions of the metals $\tilde{\varepsilon}_m$ were determined by piecewise cubic interpolation of dielectric data sets given in [226] (Al) and [227] (Au).
Metal nanostructures can be fabricated by EBL. A successful lift-off step during the EBL process requires an adhesion layer between the structured metal and the substrate (cf. chapter 4). A nanostructure fabrication test without an adhesion layer showed an unsuccessful lift-off, during which nearly all nanostructures were washed from the sample surface, for five out of six samples. As a consequence, all following nanoantennas were fabricated by using an adhesion layer. The standard adhesion layer metals are titanium (Ti) and chromium (Cr) [187]. Since titanium was reported to show resonance damping [228] and is not well suited for thermal evaporation, which is the fabrication technique of choice\(^2\), chromium has been chosen as adhesion layer.

### 5.2.3 Phase-change materials

As introduced in chapter 2, the resonance frequency of a nanorod antenna \(\tilde{\nu}_{\text{res}}\) can be approximated by its length \(L\) and the real part of the refractive index of the nanoantenna surrounding \(n\) (equation 2.13). The surrounding medium includes a PCM thin film, a silicon substrate and air. Thus, the effective refractive index \(n_{\text{eff}}\) is suited for the approximation of the resonance frequency position of the nanoantennas \(\tilde{\nu}_{\text{res}}\). In contrast to air and the silicon substrate, the dielectric properties of the PCM \(\varepsilon_{\text{PCM}}\) are not only a function of the spectral range, but change strongly by a phase transition from the amorphous to the crystalline phase as presented in chapter 3.

Taking into account that upon crystallization only \(n_{\text{PCM}}\) changes, while \(n_{\text{air}}\) and \(n_{\text{Si}}\) remain constant, equation 2.13 is modified as follows:

\[
\tilde{\nu}_{\text{res}} \approx \frac{1}{2 \cdot n_{\text{PCM}} \cdot L} \quad (5.1)
\]

According to this equation and by assuming a constant antenna length \(L\), a large shift of the antenna array resonance frequency position \(\Delta \tilde{\nu}_{\text{res}}\), which is one of the main goals in this thesis, is proportional to the change of the refractive index of the PCM \(\Delta n_{\text{PCM}}\):

\[
\Delta \tilde{\nu}_{\text{res}} = \tilde{\nu}_C - \tilde{\nu}_A \sim \frac{1}{n_C} - \frac{1}{n_A} \quad (5.2)
\]

As a consequence, a large contrast between the real parts of the refractive indices of the amorphous and the crystalline phase of the PCM \(n_A\) and \(n_C\) is the fundamental material requisition for a maximized shift \(\Delta \tilde{\nu}_{\text{res}}\). Furthermore, losses introduced by the PCM, which might dampen the maximum reflectance of the antenna, should be minimized. To identify the PCM best suited for antenna resonance frequency shifting, different compounds were compared regarding their dielectric function \(\varepsilon_{\text{PCM}}\) introduced in chapter 3. This comparison will be discussed in the following paragraph.

#### Study of permittivity ratios of different PCMs

To quantify the dielectric parameters influencing the nanoantenna resonance frequencies \(\Delta \tilde{\nu}_{\text{res}}\), the difference of the square root of the dielectric functions:

\[
\Delta \tilde{\nu}_{\text{res}} \sim \frac{1}{n_C} - \frac{1}{n_A} = \frac{1}{\sqrt{\varepsilon_{1C}}} - \frac{1}{\sqrt{\varepsilon_{1A}}} := \Delta \varepsilon_{\text{PCM}}^{1/2} \quad (5.3)
\]

\(^{2}\)For metal deposition, sputter deposition, as well as thermal evaporation were available. However, the latter has allowed for a faster and more frequent access (own evaporator in the group, less users).
with the real part of the permittivity of the crystalline and the amorphous phase $\varepsilon_{1,c}$ and $\varepsilon_{1,a}$ is discussed here. The difference $\Delta\varepsilon_{\text{PCM}}^{-1/2}$ was calculated for a spectral range between 1000 and 6000 cm$^{-1}$ in steps of 500 cm$^{-1}$ using Mathematica. In figure 5.3 $\Delta\varepsilon_{\text{PCM}}^{-1/2}$ is shown for nine exemplary PCMs.

![Graph showing $\Delta\varepsilon_{\text{PCM}}^{-1/2}$ vs. wavenumber for various PCMs.](image)

**Figure 5.3:** For exemplary PCMs, the difference $\Delta\varepsilon_{\text{PCM}}^{-1/2}$ is plotted as a function of the wavenumber $\tilde{\nu}$ in the MIR and NIR spectral range. This difference is directly related to the shift of the antenna resonance position $\Delta\tilde{\nu}_\text{res}$. Each color represents a different PCM. The data points were calculated, while the interpolated lines serve as a guide to the eye. The dielectric data $\varepsilon(\tilde{\nu})$ for the shown PCMs was taken from [136] and treated as explained in appendix A.2. For comparison, the absolute values $\varepsilon_1$ and $\varepsilon_2$ of GST-326, GST-225, GST-8211, and InSb (marked by +) can be found in chapter 3.

According to the difference $\Delta\varepsilon_{\text{PCM}}^{-1/2}$ and considering the entire investigated spectral range, the largest shift of the resonance frequency position $\Delta\tilde{\nu}_\text{res}$ is expected for GST-326. The PCMs GST-348, GST-8211, and GST-225 offer large values of the difference $\Delta\varepsilon_{\text{PCM}}^{-1/2}$ as well, while the maximum calculated value $\Delta\varepsilon_{\text{PCM}}^{-1/2}$ for all PCM was found for GeTe at low wavenumbers.

InSb shows a positive difference $\Delta\varepsilon_{\text{PCM}}^{-1/2}$, which is in contrast to all other compounds investigated here. The sign indicates the direction of the antenna array resonance frequency position shift $\Delta\tilde{\nu}_\text{res}$ and thus, for InSb a shift to higher wavenumbers upon crystallization is expected, while all other compounds...
are expected to lead to a resonance position shift to lower wavenumbers after crystallization. Besides, InSb is expected to allow only for relatively small shifts of the resonance frequency position compared to all other compounds shown in figure 5.3.

Since dielectric losses additional to the ones associated with the metallic nanoantennas itself have been supposed to be avoided as far as possible, a deeper look is given into the imaginary part of the dielectric function $\varepsilon_{PCM}$ evaluated by the ratios:

$$\frac{\varepsilon_{2,a}}{\varepsilon_{1,a}} \quad \text{and} \quad \frac{\varepsilon_{2,c}}{\varepsilon_{1,c}}$$

(5.4)

which in general describe the energy dissipation of a dielectric material [229] and are considered as a measure for resonance damping due to losses. The evaluation is shown in figure 5.4. There, a ratio $\frac{\varepsilon_{2,a}}{\varepsilon_{1,a}}$ very close to zero can be seen for all investigated GST compounds and GeTe. Only for wavenumbers above 5000 cm$^{-1}$, the ratio $\frac{\varepsilon_{2,a}}{\varepsilon_{1,a}}$ increases slowly. In contrast, for InSb and GIST $\frac{\varepsilon_{2,a}}{\varepsilon_{1,a}}$ of up to about 0.24 was calculated. Upon crystallization, the ratio $\frac{\varepsilon_{2}}{\varepsilon_{1}}$ behaves very differently for the investigated compounds. For GeTe, GIST and GST-225 relatively large areas of the circles, which refer to $\frac{\varepsilon_{2,c}}{\varepsilon_{1,c}}$, can be seen in figure 5.4, while the areas remain small for GST-326, GST-124 and GST-8211 throughout the entire spectral range depicted in figure 5.4. Regarding InSb, small values for $\frac{\varepsilon_{2,c}}{\varepsilon_{1,c}}$ were calculated, while in the amorphous phase InSb shows the largest values of $\frac{\varepsilon_{2,a}}{\varepsilon_{1,a}}$ compared to all other evaluated PCMs.

As a result, the large $\Delta\varepsilon_{PCM}$ depicted in figure 5.3, as well as the small ratios $\frac{\varepsilon_{2}}{\varepsilon_{1}}$ indicate that GST-326 is well-suited for the proposed resonance shifting. Potentially, relatively "lossy" PCMs, such as GIST or GeTe (in the range of low wavenumbers) could be candidates for applications regarding the damping of antenna resonance peaks. GIST and GeTe would be favorable due to their large increase of the ratio $\frac{\varepsilon_{2}}{\varepsilon_{1}}$ upon crystallization.

Figure 5.4: For exemplary PCMs, the ratios of the real and imaginary parts of the permittivity for both phases $\frac{\varepsilon_{2,a}}{\varepsilon_{1,a}}$ and $\frac{\varepsilon_{2,c}}{\varepsilon_{1,c}}$ are plotted as a function of the wavenumber $\tilde{\nu}$ in the MIR and NIR spectral range. Each color represents a different PCM (as in figure 5.3). The position of the circles represents the ratio $\frac{\varepsilon_{2,c}}{\varepsilon_{1,c}}$, while the area of the circles scales with the ratio $\frac{\varepsilon_{2,a}}{\varepsilon_{1,a}}$. The largest circle (GeTe at 1000 cm$^{-1}$) equals $\frac{\varepsilon_{2,c}}{\varepsilon_{1,c}} \approx 0.25$, while the smallest circle (GST-326 at 3500 cm$^{-1}$) equals $\frac{\varepsilon_{2,c}}{\varepsilon_{1,c}} \approx 0.02$. The small striped dummy visualizes $\frac{\varepsilon_{2,c}}{\varepsilon_{1,c}} \approx 0.25$. This number is equal to the maximum of the y-axis and allows for a comparison between both ratios $\frac{\varepsilon_{2,a}}{\varepsilon_{1,a}}$ and $\frac{\varepsilon_{2,a}}{\varepsilon_{1,a}}$. For comparison, the absolute values $\varepsilon_{1}$ and $\varepsilon_{2}$ of GST-326, GST-225, GST-8211 and InSb (marked by *) can be found in chapter 3.
5.2.4 Summary

In this section, the sample materials were chosen due to their suitability regarding sample fabrication, but especially regarding the proposed concept of the antenna resonance frequency position shift $\Delta \tilde{\nu}_{\text{res}}$. By calculating the scattering cross section, it was found that aluminum is as suited as gold for nanoantennas in the mid-infrared spectral range. Besides, aluminum has not been reported to diffuse into PCMs, which is in contrast to gold. By evaluation of the dielectric functions $\varepsilon_{\text{PCM}}$, GST-326 was found to be the most promising PCM regarding a maximized resonance shift $\Delta \tilde{\nu}_{\text{res}}$, while InSb was identified as the only PCM, which allows for a shift to higher wavenumbers upon crystallization. Thus, InSb and GST-326 have been selected for the following considerations and initial experiments.

Figure 5.5: The list of the sample materials given in the introduction of this chapter was updated due to the findings discussed in this section. Silicon was determined to be a well-suited substrate, while aluminum was chosen as antenna material. Due to the antenna fabrication with EBL, a chromium adhesion layer was chosen as well. Based on their dielectric properties, GST-326 and InSb were initially selected as PCMs, while GST-8211 and GST-225 were added later on. It has to be noted that for simplicity, the chromium layer will not be included into the following sample schemes.

5.3 Considerations on the sample layout

In the following, three different aspects of the sample design will be discussed. The geometric parameters length $L$, width $w$ and height $h$ of the rodshaped aluminum nanoantennas can be chosen, which determine the antenna resonance frequency $\tilde{\nu}_{\text{res}}$. Corresponding theoretical studies will be discussed in section 5.3.1. Furthermore, the thickness of the PCM thin films $t$ can be varied to change the influence of the dielectric function $\varepsilon_{\text{PCM}}$ on the resonance frequency position $\tilde{\nu}_{\text{res}}$, which will be presented in section 5.3.2. Finally, the arrangement of multiple antennas in an array influences the antenna (array) resonance peak strongly. Based on simulations, the spectral properties of the antenna separation in the array will be shown.

5.3.1 Geometry of rodshaped nanoantennas

The resonance position $\tilde{\nu}_{\text{res}}$ of a nanoantenna following the $\lambda/2$-model can be approximated by the antenna length $L$ and the real part of the effective refractive index of the surrounding medium of the antenna $n_{\text{eff}}$ (cf. equation 5.1). Thereby, the change of the refractive index $\Delta n_{\text{eff}}$ is given by the change of the dielectric function $\Delta \varepsilon_{\text{PCM}}$ upon phase transition. PCMs provide large contrasts of the real part of their dielectric function $\Delta \varepsilon_{1,\text{PCM}}$ in the MIR spectral range. Furthermore, the imaginary part of their dielectric function $\varepsilon_{2,\text{PCM}}$, which can be associated with the dissipation in the medium, is very low in this spectral range. To exploit the low losses and the large contrast of PCMs $\Delta \varepsilon_{1,\text{PCM}}$ in the MIR spectral range, the antennas need to be tailored to show resonances $\tilde{\nu}_A$ and $\tilde{\nu}_C$ in the MIR spectral range.

In figure 5.6, the calculated scattering cross section $\sigma_{\text{scat}}$ of a single aluminum antenna with length $L$ is depicted. The antenna is embedded in vacuum with $n = 1.0$ and in a medium with the real part of the refractive index $n = 3.55$ ($n_{\text{A-GST}}$ at 3300 cm$^{-1}$). A pronounced resonance peak appears...
Figure 5.6: The scattering cross section $\sigma_{\text{scat}}$ (filled marks) of a single aluminum antenna fully embedded in vacuum ($n = 1.0$, black) and a medium with $n = 3.55$ (gray) were calculated with Comsol. Each calculated wavenumber is represented by a mark. The antenna geometry was defined as follows: width $w = 100$ nm, height $h = 40$ nm and length $L = 600$ nm. The dielectric functions of the metals $\varepsilon_n$ were determined by piecewise cubic interpolation of dielectric data sets given in [226] (Al) and [227] (Au). The increase of the real part of the refractive index $n$ leads to a strong red-shift of the antenna resonance peak while its amplitude decreases.

for both antennas ($\bar{\nu}_{\text{res},1} = 6004 \text{ cm}^{-1}$ and $\bar{\nu}_{\text{res},3.55} = 1735 \text{ cm}^{-1}$), while for the antenna in $n = 3.55$, a second much weaker resonance peak at about $\bar{\nu}_{\text{res},3.55} = 5337 \text{ cm}^{-1}$ occurs. This peak can be associated with the third resonance order $m = 3$, since $\bar{\nu}_{\text{res},3.55} \approx 3 \cdot \bar{\nu}_{\text{res},3.55}$. The shift of the antenna resonance peak $\Delta\bar{\nu}_{\text{res}}$ from $6004 \text{ cm}^{-1}$ to $1735 \text{ cm}^{-1}$ is linked to the increase of the real part of the refractive index from $n = 1.0$ to $n = 3.55$. The antenna in the experiments was not fully embedded in the PCM and was influenced by the air surrounding the sample as well. Thus, in the real part of the (experimental) effective refractive index $n_{\text{eff}}$ is smaller than 3.55, but much higher than 1.0. Consequently, the experimentally determined resonance frequency position $\bar{\nu}_{\text{res}, A-PCM}$ is expected to be between the approximated extreme values shown in figure 5.6. Since the refractive index of the PCM increases upon crystallization, the experimentally determined resonance frequency position $\bar{\nu}_{C}$ was expected to be red-shifted relative to $\bar{\nu}_{A}$. As a result, an antenna length $L$ of $600$ nm is well-suited for the application as resonant nanostructure adjacent to PCMs, which show a high refractive index in the MIR and NIR spectral range. Accordingly, antennas with lengths $L = 600, 500$ and $400$ nm will be studied in chapters 6 and 7 to cover the wavenumber range between about $1000$ and $4000 \text{ cm}^{-1}$.

Furthermore, the antenna height $h$ and width $w$ were chosen as based on restrictions due to the antenna fabrication process, as well as on the optical properties of the nanoantennas. The lower limit of the width $w$ was given by the antenna fabrication process electron beam lithography (EBL). Linewidths of about $50$ nm and less were experienced to be not reproducible due to the chosen electron beam process (positive tone resist), as well as due to the limited accelerating voltage of the electron beam (cf. chapter 4). Moreover, AIZPURUA et al. found, that in the NIR spectral range an increase in the rod diameter (cylindrical gold nanorod antennas were considered) led to a pronounced increase in the farfield intensity of the considered antennas, which is based on the increase of the induced dipole moment [30]. However, an elongated rod shape had to be maintained and thus, the width $w$ was limited given by this rod shape, for which the ratio between length and width $L/w$ has to be much larger than one, e.g. $L/w \geq 4$. According to the shortest chosen investigated antenna length $L = 400$ nm, the antenna (design) width was defined as $w = 100$ nm. It has to be noted that the fabricated width can deviate from the design width due to variations of the electron beam parameters during the EBL process. The antennas investigated in this thesis showed mainly a width $w \approx 110$ nm (including the resolution of the scanning electron microscope, which was used to characterize the antennas).
5.3 Considerations on the sample layout

Concerning the antenna fabrication, limitations of the height $h$ were given by thermal evaporation of aluminum. There, about 80 to 100 nm were the maximum reproducible aluminum layer thickness which can be fabricated during one evaporation process (cf. appendix, page 180). Nevertheless, the height $h$ was strongly related to the sample layout and thus, to the PCM layer thickness $t$. This is illustrated in figure 5.7. In case of a PCM thin film covering the nanoantenna, the antenna should be more shallow than the PCM layer thickness $t$ to ensure the coverage of the antenna tips (area of field enhancement) with the PCM (medium with the tunable refractive index). Therefore, the density increase upon crystallization (e.g. 8% for GST-326) needed to be taken into account. Since the PCM layer thickness $t$ will be discussed in the following section, the determination of a well-suited antenna height $h$ will be postponed to section 5.3.2.

Throughout all experiments and simulations, the height $h$ and width $w$ of the antennas are chosen to be constant and independent of the antenna length $L$. The constant height $h$ was based on the fabrication process, since all nanostructures on one sample were fabricated by the same thermal evaporation process.

**Figure 5.7:** A PCM thin films covers the Al nanorod antenna placed on a Si substrate. If the height $h$ of the nanoantenna is larger than the PCM film thickness $t$, the antenna tips are not covered by the PCM entirely. Thus, the antenna height $h$ was adapted to the PCM film in this thesis. In this figure the sample geometry is sketched to scale relatively $(L/w, h/t, \ldots)$.

### 5.3.2 Phase-change material layer thickness

The following considerations were conducted for the PCM GST-326, which has been selected as the favorite compound in the previous section, since it offers the most promising dielectric data in the investigated spectral range (large $\Delta \varepsilon^{-1/2}_{\text{PCMs}}$, small $\varepsilon_2 / \varepsilon_1$). Most GST compounds behave very similar in the NIR and MIR spectral range, and thus general insights in the optical properties of PCM thin-film can be given by the description of the optical properties of GST-326 thin films.

**Calculated thin-film interferences**

To determine a well-suited thickness $t$ of the PCMs, the reflectance and transmittance of electromagnetic waves at the boundaries air / PCM and substrate (Si) / PCM were studied while the PCM thickness was varied to a thickness in the range of several to hundreds of nanometers. The incident light is transmitted or reflected by the thin film and thus, can interfere constructively and destructively at both boundaries leading to thin film interferences (TFIs). The transmittance and reflectance of the incident light were calculated by using Fresnel equations given in appendix B.2.

The reflectance $R$ is displayed as a function of the wavenumber $\tilde{\nu}$ both for the amorphous and crystalline phase in figure 5.8. In general, for increasing layer thickness $t$ more interference fringes occur in the spectrum between 1000 and 7000 cm$^{-1}$. Upon crystallization, both the number of fringes increases, and the maximum reflectance is shifted to lower wavenumbers.
The PCM film thickness chosen for the experiments, is a compromise between a maximal influence of the PCM on the effective refractive index of the antenna array’s surrounding $n_{\text{eff}}$ and a minimal influence of the interference fringes on the antenna resonance characteristics. The first requirement ensures for a large antenna array resonance frequency shift $\Delta \tilde{\nu}_{\text{res}}$. The latter requisite is based on the interplay between the antennas resonances and the interference fringes. The corresponding optimization of the thickness $t$ towards a narrow antenna resonance peak (small FWHM), was put aside by choosing a layer thickness without pronounced interference fringes. For A-GST-326, $t_A = 50 \text{ nm}$ is the largest thickness without pronounced interference fringes and thus, the experiments on antenna array resonance shifting due to a phase transition of different PCMs shown in this thesis were conducted with $t_A = 50 \text{ nm}$ unless otherwise stated.

In figure 5.9 experimental reflectance spectra of GST-326 thin films with two different thicknesses $t_A = 50 \text{ nm}$ and $t_A = 25 \text{ nm}$ prior and after crystallization are shown. Additionally, calculated spectra with $t_A = 50 \text{ nm}/t_C = 46.12 \text{ nm}$ and $t_A = 25 \text{ nm}/t_C = 23.06 \text{ nm}$ (including the density change upon crystallization) are depicted. The calculations match the experimentally determined reflectance spectra very well. The strong difference between the reflectance of A- and C-GST-326, which is based on the strong contrast of the dielectric functions of both PCM phases $\varepsilon_A$ and $\varepsilon_C$, allows for a spectral identification of the phase of the investigated PCM.

### Quantitative comparison between measured and calculated thin film interferences

The calculated and the experimental data of GST-326 displayed in figure 5.9 match well qualitatively, especially for the thicker GST-326 film in figure 5.9b. Quantitatively, the reflectance differs slightly, while the mismatch is pronounced for the lower wavenumber range of the 23 nm C-GST-326 film (gray: solid line/filled marks) and the higher wavenumber range of the 50 nm A-GST-326 film (black: dashed line/empty marks). These deviations of the reflectance could be ascribed to the potential reasons: the sample design used for the determination of the dielectric data [136], the FTIR light source and detector geometry, as well as variations in deposited PCM film thickness $t_A$.

The sample layer stack studied here and by KREEMERS [110] show considerable differences regarding the PCM layer thickness (GST-326: $t_A = 590 \text{ nm}$ versus 50 nm and Al/Si versus Si substrate). This aspect is discussed in detail in appendix B.2.

Regarding the FTIR light source and detector geometry, the experimental setting can not be fully reproduced by the applied analytical calculation model. The experimentally used 36-fold Cassegrain objective of the FTIR microspectrometer illuminates and collects light under an angular range $15^\circ \leq \theta_i \leq 29^\circ$ with its maximum intensity at about $27^\circ$ [230]. In contrast, a fixed angle of incidence $\theta_i = 27^\circ$ (highest intensity for all angles of the total $\theta_i$ distribution) was used for the TFI calculations. In figure 5.10, the reflectance $R$ is displayed as a function of the wavenumber $\tilde{\nu}$ and the angle of incidence $\theta_i$ for the GST-326 layer. It can be seen that for an increasing angle $\theta_i$ between $0^\circ \leq \theta_i \leq 50^\circ$ the reflectance is independent of $\theta_i$.

Only for large angles above about $50^\circ$ an angular dependence of $R$ can be found. Thus, for the experimental angle distribution $15^\circ \leq \theta_i \leq 29^\circ$ the reflectance $R$ of the PCM film is not influenced by the angle or angular distribution of the incident light.

Besides, the possibility of a variation in sputtered film thickness $t$ as reason for a quantitative mismatch of $R$ was illuminated and can be excluded as well. This aspect is discussed in detail in appendix B.2.
5.3 Considerations on the Sample Layout

Figure 5.8: The shown plots for the reflectance $R$ (color gradient) and variable layer thickness $t$ of amorphous (a) and crystalline (b) GST-326 were calculated as a function of the wavenumber $\tilde{\nu}$ by using Fresnel equations. In both figures, the film thickness relevant for the shown experiments is marked by a horizontal line: $t_A = 50\,\text{nm}$ in (a) and $t_C = 46\,\text{nm}$ in (b) due to the increased density upon crystallization. The minimum of the color scale was chosen according to the experimental and calculated spectra given in figure 5.9.
In summary, the light source and detector geometry, as well as variations in deposited PCM film thickness \( t \) were excluded as reasons for the deviations of the reflectance. Instead, \( \Delta R \) was ascribed to the differences in the compared PCM films, such as differences in the sample stack as mentioned above or slight deviations in the stoichiometry of the sputtered PCM thin films.

![Graphs showing reflectance vs. wavenumber for GST-326 films with different thicknesses](image)

(a) GST-326 thin film with \( t_A = 25 \text{ nm} \), \( t_C = 23.1 \text{ nm} \)  
(b) GST-326 thin film with \( t_A = 50 \text{ nm} \), \( t_C = 46.1 \text{ nm} \)

Figure 5.9: Calculated (lines) and experimental (markers) reflectance spectra of A-GST-326 (dashed line/triangles) and C-GST-326 (solid/circles) are compared. In figure 5.9a, the as-deposited film thickness \( t_A \) is 25 nm (red/light red), while in 5.9b \( t_A \) is 50 nm (black/gray). The thin film interferences were calculated by using dielectric data from [110].

![Graphs showing reflectance vs. wavenumber for amorphous and crystalline GST-326](image)

(a) reflectance for amorphous GST-326  
(b) reflectance for crystalline GST-326

Figure 5.10: The shown plots for the reflectance \( R \) (color gradient) and variable angle of incidence \( \theta_i \) of amorphous (a) and crystalline (b) GST-326 were calculated as a function of the wavenumber \( \tilde{\nu} \) by using Fresnel equations. The color codes in (a) and (b) are similar. In both figures, the strongest angle (highest intensity for all angles of the total \( \theta_i \) distribution [230]) of the 36-fold FTIR microspectrometer objective is marked by a horizontal line: \( \theta_i = 27^\circ \).
Decay length of the antenna field

If the antenna is resonantly excited, its field penetrates far into its surrounding while the penetration depth is defined by the dielectric properties of the media around the metallic antenna. To roughly approximate the field decay length in \(z\)-direction \(L_z\), the simplified system of an interface between a semi-infinite dielectric medium with its real part of the complex permittivity \(\varepsilon_{1,d}\) and a semi-infinite metal with \(\varepsilon_{1,m}\) was considered. This model was introduced in chapter 2 (cf. figure 2.3). Here, the GST-326 thin film was chosen as the dielectric medium. For frequencies \(0 < \omega < \omega_p/\sqrt{1 + \varepsilon_d}\), the wavevector in \(x\)-direction \(k_x\) is real and \(|\varepsilon_m|\) is large, as it is the case in the MIR spectral range, where aluminum can be considered as perfect electric conductor \((|\varepsilon_m| \rightarrow \infty)\). For small wavevectors \(k_x\) the plasmon dispersion curve approaches the light line and the spatial extent of the fields in the \(z\)-direction can be derived from the wavevector \(k_z\) \([11]\). The field decay length in \(z\)-direction into the GST-326 film can be calculated as follows:

\[
L_{GST,z} = \frac{1}{|k_{GST,z}|} = \frac{2\pi \tilde{\nu} \cdot \sqrt{-\varepsilon_{1,GST}^2}}{\varepsilon_{1,Al} + \varepsilon_{1,GST}} \tag{5.5}
\]

with the real part of the dielectric function of A-GST-326 \(\varepsilon_{1,GST}\) and the real part of the dielectric function of aluminum \(\varepsilon_{1,Al}\) (cf. equation 2.12).

![Graph showing decay length as a function of wavenumber](image)

(a) spectrally dependent decay length in PCM for semi-infinite Al/PCM halfspaces
(b) semi-infinite halfspaces
(c) antenna on substrate

Figure 5.11: The decay length \(L_{z,GST}\) is plotted as a function of the wavenumber \(\tilde{\nu}\) and the phase of the GST-326 thin film. The field penetrates further in A-GST-326 than in C-GST-326, which is caused by the larger real part of the dielectric function \(\varepsilon_1\) in case of C-GST-326. The A-GST-326 film thickness \(t_A = 50\, \text{nm}\) is marked (gray, dashed). In the inset, \(L_{z,GST}\) is displayed for thinner PCM films. It is visible that in the MIR spectral range the field penetrates to a depth of more than the chosen film thickness. For the calculation of the displayed decay length, two semi-infinite halfspaces were assumed as shown in figure 5.11c, while the experimentally investigated sample was designed as shown in figure 5.11c.

The decay length in GST-326 \(L_{z,GST,z}\) was calculated for the amorphous as well as for the crystalline phase of the GST-326 by applying the corresponding permittivity. The resulting calculated \(L_{z,A,GST}\) and \(L_{z,C,GST}\) are displayed in figure 5.11 and suggest that the field decays far into the GST-326 surrounding the antenna. For \(\tilde{\nu} = 3000\, \text{cm}^{-1}\), which is in the range of the resonance frequency position of the experimentally investigated nanoantennas, the decay length is about \(L_{z,A,GST} \approx 1.4\, \mu\text{m}\) and \(L_{z,C,GST} = \ldots\)
400 nm. At $\tilde{\nu} = 6000 \text{ cm}^{-1}$, the decay length is $L_{z,A,GST} = 300 \text{ nm}$ and $L_{z,C,GST} = 70 \text{ nm}$. Therefore, the GST-326 thin film with $t_A = 50 \text{ nm}$ is assumed to be fully penetrated by the field. Furthermore, it is assumed that a maximized influence of the GST-326 thin film on the refractive index $n_{\text{eff}}$ could be achieved by a film thickness in the range of the field decay length $L_{GST,z}$, which would be more than 100 nm for A-GST and more than about 70 nm in the spectral range investigated here.

However, it has to be noted that this approximation does neither include the influence of a thin film (instead of semi-infinite GST-326) on the dispersion relation, nor the influence of the nanoantenna (instead of semi-infinite Al) on the dispersion relation [231], which is illustrated in figures 5.11b and 5.11c. Nevertheless, the description given by equation 5.5 served as a first approximation, which allowed for the assumption that the GST-326 thin films with $t_A = 50 \text{ nm}$ were fully penetrated by the field of the resonantly excited antenna.

### 5.3.3 Positioning of the antenna arrays relative to the phase-change material

#### An antenna fully embedded in a PCM

For nanoantennas fully embedded in the PCM, the influence of the PCM on the nanoantenna resonance $\tilde{\nu}_\text{res}$ would be maximized. Thus, the resonance position $\tilde{\nu}_A$ is only influenced by the refractive index of the as-deposited PCM. Upon crystallization, the refractive index of the PCM changes strongly and the resonance position is shifted by $\Delta\tilde{\nu}_\text{res} = \tilde{\nu}_C - \tilde{\nu}_A$. For GST-326 and InSb, the resonance positions $\tilde{\nu}_A$ and $\tilde{\nu}_C$, as well as the resonance position shift $\Delta\tilde{\nu}_\text{res}$ were calculated by using the relation $\Delta\tilde{\nu}_\text{res} = (2 \cdot \Delta n_{\text{PCM}} \cdot L)^{-1}$ with $L = 600 \text{ nm}$. By using GST-326 as antenna surrounding, the resonance position shifts by about $1000 \text{ cm}^{-1}$ to lower wavenumbers upon crystallization. In contrast InSb allows for a shift of about $400 \text{ cm}^{-1}$ to higher wavenumbers.

These calculated values for the resonance shift $\Delta\tilde{\nu}_\text{res}$ can be interpreted as upper limit for an achievable shift. Concerning the presented experiments, all antennas were placed on a substrate and hence, the surrounding includes different materials (air, PCM thin film, substrate) summarized in the effective refractive index $n_{\text{eff}}$. Consequently, the percentual influence of the PCM on the effective refractive index is below 100% and the measured resonance shift will be smaller than $1000 \text{ cm}^{-1}$ and $400 \text{ cm}^{-1}$ respectively.

#### Variation of the antenna position relative to a substrate

The spectral influence of the PCM thin film on the effective refractive index $n_{\text{eff}}$ of the antenna can be studied by changing the position of the antenna relative to the PCM thin film. Therefore, three different sample geometries are considered. The antenna arrays were placed below and on top of a PCM thin film with thickness $t_A$. Furthermore, a PCM film with thickness $t_A/2$ was sputtered as substrate. Subsequent to the antenna array fabrication on this layer, another PCM film with thickness $t_A/2$ was deposited as superstrate. This leads to an antenna array embedded in a PCM film. Consequently, the antenna is either covered by a PCM film of thickness $t_A$ or $t_A/2$ or not covered at all as displayed in figures 5.12a to 5.12c. By applying this strategy, the effective dielectric function of the antenna array surrounding $n_{\text{eff}}$ should be different for each case.
5.3 Considerations on the sample layout

Figure 5.12: Displayed is a scheme of different sample geometries (cross section along the long antenna axis with length \( L \)). The PCM thin film is used as antenna superstrate with thickness \( t \) as in 5.12a or as substrate layer with thickness \( t \) as well, shown in 5.12c. In 5.12b, the nanoantenna is placed between two PCM thin films with bisected thickness \( t_A/2 \). In the following, the thickness of the deposited film \( t_A \) is chosen to be 50 nm unless otherwise stated.

5.3.4 Summary

Based on the materials selected in section 5.2, the sample layout was chosen in this section. First, the antenna geometry was theoretically determined with the objective to achieve a resonance peak position \( \tilde{\nu}_{\text{res}} \) between about 2000 and 4000 cm\(^{-1}\). Furthermore, restrictions due to the antenna fabrication (ratio between antenna height \( h \) and PCM film thickness \( t \)) were taken into account. The calculated optical properties of GST-326 thin films allowed for a selection of a 50 nm thick as-deposited A-GST-326 layer which is a compromise between less pronounced TFIs and significant influence of the PCM’s refractive index on the antenna surrounding. Finally, three different sample layouts were considered to study the influence of the refractive index on the antenna resonance position \( \tilde{\nu}_{\text{res}} \).

Figure 5.13: According to the scheme given in the introduction of this chapter, the specifications of the sample layout were updated due to the findings discussed in this section. The antenna geometry was defined to show a resonance peak between about 2000 and 4000 cm\(^{-1}\). The as-deposited PCM thin film was selected to be 50 nm thick. Furthermore, the antenna was chosen to be varied regarding its position relative to the PCM thin film by investigating different sample layouts.
5.4 Theoretical Considerations of the Antenna Array

Up to this point, single antennas were considered. To be able to measure pronounced and narrow reflectance signals with FTIR microspectroscopy later, it is beneficial to collect the reflected signal of many beneficially coupled antennas at once.

5.4.1 Arrays of Metal Nanorods

Nanoantennas arranged in large arrays as illustrated in figure 5.14 can exhibit a much stronger field enhancement and much narrower far-field spectral responses compared to single nanorods if the separation distance is chosen accordingly [19]. The far-field response of a single nanorod antenna to an incident field can be described with an induced point dipole as long as the frequency of the incident field is close to the dipole mode ($m = 1$). In contrast, each nanorod of an antenna array experiences a local field composed of the incident electric field and the scattered field from the other nanorods (cf. [19, 26]). Following [19], this sum strongly depends on the phase delay which is experienced by the retarded dipolar interactions among the nanoantennas. The collectively enhanced local fields can become extremely large and the far-field spectral response very narrow, if the induced dipolar fields of the antennas add in phase and the radiation damping is suppressed [232]. In [26], it was reported that the critical distance of antennas in an array with equal separation in $x$- and $y$-direction is given by $d_c$:

$$d_c \approx \lambda_{inc} \frac{\sqrt{i^2 + j^2}}{n_{sub}}$$

(5.6)

where $n_{sub}$ refers to the refractive index of the substrate and the grating order is defined by the integers $i$ and $j$, which refer to the reciprocal lattice vetors $\vec{G}_{i,j}$. By considering the first order with $(i, j) = (1, 0)$ and the resonance wavelength $\lambda_{res} = 2L \cdot n_{sub}$ with the antenna length $L$ (cf. equation 2.13), the critical separation is given by:

$$d_c \approx 2L$$

(5.7)

For $d < d_c$ the field is evanescent and the linewidth of the resonances is small, which means that the resonance peaks are narrow. As soon as the periodicity increases to $d > d_c$, the coupling becomes radiative [19]. Thus, the collective resonances are dampened and the linewidth broadens. The appearance of a new grating order leads to a pronounced increase of the power radiated from the antenna array. This is associated with the so-called Rayleigh anomaly, which will be discussed in the following section.

Figure 5.14: A scanning electron microscopy image of an array of aluminum nanoantennas (measured length $L \approx 600 \text{ nm}$, width $w \approx 115 \text{ nm}$ according to SEM images) including a chromium adhesion layer is displayed. The separations in $x$- and $y$-direction are marked by white arrows. The squared array, where $d_x = d_y = d_c$ with $d_c = 2L = 1 \mu\text{m}$, was fabricated by electron beam lithography.
A normalized reflectance spectrum of an aluminum antenna array with the calculated spacing $d_x$ was calculated and is shown in figure 5.15. The normalization of the spectrum was realized by division of the antenna spectrum by a spectrum of the Si substrate. The settings of the numerical simulation are given in appendix C. The resonance position of the antenna array is $\tilde{\nu}_{\text{res}} = 2457 \text{ cm}^{-1}$. The approximation of the resonance position given by equation 2.13 and with $n_{\text{sub}} = n_{\text{Si}} = 3.44$ leads to $\tilde{\nu}_{\text{res}} = 2423 \text{ cm}^{-1}$, which matches the resonance position of the calculated spectrum very well. In contrast, the resonance position of the antenna array differs by about 745 cm$^{-1}$ from the resonance position of a single nanorod surrounded by air as it is marked by $\tilde{\nu}_{\text{single}}$ in figure 5.15. The geometry of the compared nanorods is similar, while the placement on a silicon substrate, as well as the arrangement in an array, led to this pronounced shift of the resonance position.

Figure 5.15: The depicted normalized reflectance spectrum of an Al antenna array (without Cr adhesive layers) on a Si substrate was calculated with CST Microwave Studio. Only every 5th data point is shown. The antenna geometry was chosen as follows: length $l = 600 \text{ nm}$, height $h = 30 \text{ nm}$, width $w = 110 \text{ nm}$ and antenna periodicity $d = d_x = 1.2 \mu \text{m}$ in $x$- and $y$-direction. The resonance position of a single antenna (cf. figure 5.2) is marked.

5.4.2 Rayleigh anomaly and Fano interference

Due to the periodic arrangement of the resonant nanoantennas, a so-called Wood or Rayleigh anomaly (RA) as non-resonant spectral feature occurs [233, 234]. RAs and individual antenna resonances can couple to lattice surface modes (LSMs), which can be tailored to generate an interaction of a broad resonance and a much narrower one [235]. Therefore, the RA has to be in the spectral range of the antenna array resonances to create this Fano-type resonance [236]. Fano-type resonances exhibit an asymmetric shape due to the constructive and destructive interference of a broad spectral feature or continuum and a narrow resonance [237]. Following the Bragg coupling condition for a two-dimensional grating at an air/substrate interface, the spectral position of the RA is defined as follows [238]:

$$\lambda_{\text{RA},(i,j)} = -A + \sqrt{A^2 - B}$$

$$A = \frac{\sin(\theta_i)}{\left( \frac{i}{d_x} \right)^2 + \left( \frac{i}{d_y} \right)^2} \cdot \left( \frac{i \cdot \sin(\phi_i)}{d_x} + j \cdot \cos(\phi_i) \cdot \frac{j}{d_y} \right)$$

$$B = \frac{\sin^2(\theta_i) - n_{\text{sub}}^2}{\left( \frac{i}{d_x} \right)^2 + \left( \frac{i}{d_y} \right)^2}$$

with the grating order $(i, j)$, the antenna separations $d_x$ and $d_y$, the real part of the refractive index of the substrate $n_{\text{sub}}$, and the polar and azimuthal angles of incidence $\theta_i$ and $\phi_i$. These angles are related to the configuration of the Schwartzschild-type Cassegrain objective used in the FTIR microspectrometer (cf. figure 4.5). By considering the first grating order $(i, j) = (1,0)$ and taking into account that a
5.4 Theoretical considerations of the antenna array

A square lattice of nanoantennas with \( d_x = d_y \) has been chosen and, equation 5.8 can be simplified. Since the 36-fold Cassegrain objective was used for the measurements of the antenna array reflectance spectra, the polar angle \( \theta_i \) can be approximated by 27°, which is associated with the maximum intensity of the incident light. In reflectance mode, the light impinges from the 180° azimuthal angular range (from -90° to 90°) and, therefore, \( \phi_i \) can not be approximated. In the investigated spectral range, the incident wavelength is much longer than the thickness \( t \) of the PCM thin film. Thus, the PCM thin-films can be neglected regarding the wavelength (or frequency) position of the RA and as a consequence \( n_{\text{sub}} = n_{\text{Si}} = 3.44 \). In summary, the spectral position of the RA can be calculated by:

\[
\lambda_{\text{RA},(1,0)} \approx d \cdot \left( \sqrt{0.206 \cdot \sin^2(\phi_i) + 11.628 - 0.454 \cdot \sin(\phi_i)} \right)
\] (5.9)

The evaluation of equation 5.9 for different antenna array separations \( d \) and a broad distribution of \( \phi_i \) is illustrated in figure 5.16. It can be seen that an antenna separation of \( d = 0.8 \mu m \) leads to RAs in a spectral range between about 2.39 and 3.11 \( \mu m \). For an increasing distance \( d \), the spectral width of the RAs increases. It has to be noted that the broad range of \( \phi_i \) does not result in a single broad RA, but rather in many sharp RAs between the lowest and the largest spectral position of \( \lambda_{\text{RA},(1,0)} \). This is visualized by the dashed ticks in the bottom left corner of figure 5.16. The larger the antenna separation \( d \), the broader is the distribution of the sharp RAs.

However, the average of the sinusoidal characteristic of the RA wavelength is given by the following approximation:

\[
\lambda'_{\text{RA},(1,0),d} = \lambda'_{\text{RA},d} = 3.44 \cdot d
\] (5.10)

with \( n_{\text{sub}} = 3.44 \) for Si, which can be seen by the colored horizontal solid lines in figure 5.16. These averaged positions can also be found in the calculated reflectance spectra of an antenna arrays with antenna length \( L \) and varied antenna separation \( d \) depicted in figure 5.17. For these calculations, the polar angle \( \theta_i \) was defined as 27°, while the azimuthal angle \( \phi_i \) was defined as 0°. The position of the Rayleigh anomaly at this angle is almost equal to the averaged position \( \lambda'_{\text{RA},(1,0),d} \).

In figure 5.17, the antenna array resonance peak narrows as the antenna separation \( d \) increases, since the RA \( \lambda'_{\text{RA},(1,0)} \) moves towards the antenna array resonance frequency position \( \tilde{\nu}_{\text{res}} \). The narrowing of the resonance peak can be quantified by the strong decrease of FWHM, which is shown in the inset of figure 5.17. Since a narrow peak or a high so-called quality factor \( Q = \tilde{\nu}_{\text{res}} / \text{FWHM} \), which rates the damping of a resonator’s oscillation, is advantageous for sensing applications, the peak width FWHM should be as small as possible [135]. According to a minimized FWHM, the experimentally realized antenna distance is chosen as \( d = d_c = 1.2 \mu m \).

Besides, in figure 5.17, a decreased resonance peak reflectance can be observed for an increasing distance \( d \), which is based on an increase of the antenna sample coverage (Al antennas cover about 12.25% of the array for \( d = 0.7 \mu m \), but only 4.17% for \( d = 1.2 \mu m \)).

Considering an antenna array with \( L = 600 \text{ nm} \) and \( d = 1.2 \mu m \), the Rayleigh anomaly position associated with air, which occupies (the majority) of the upper halfspace of each antenna array, can be approximated by \( \lambda_{\text{RA},1.2} = d = 1.2 \mu m (\approx 8333 \text{ cm}^{-1}) \). This is far from the resonance position \( \tilde{\nu}_{\text{res}} \) and out of the spectral range covered in the presented experiments and thus, can be neglected in the following.
5.4 Theoretical considerations of the antenna array

Figure 5.16: The wavelength of the RA with respect to the first grating order $\lambda_{RA/(1,0)}$ can be visualized as a function of the azimuthal angle $\phi$, as well as of the separation distance $d$ between 0.8 and 1.3 $\mu$m (color coded), cf. equation 5.9. For $d = 0.8 \mu$m, exemplary positions of $\lambda_{RA/(1,0)}$ are marked by dots. Each angle $\phi$ (here: steps of 30°) leads to a RA $\lambda_{RA/(1,0)}$, which is represented by short horizontal black dashed lines (bottom left). The colored horizontal solid lines represent the approximation $\lambda_{RA/(1,0)} = d \cdot n_{Si}$, which is equal to the average of the angular distribution given by equation 5.9. It has to be noted that the data is represented in wavelengths instead of wavenumbers.

Figure 5.17: The shown reflectance spectra were calculated for an Al antenna array on an A-GST-326 substrate layer ($h_A = 50 \text{ nm}$) on a Si substrate. The antennas were designed as follows: length $l = 600 \text{ nm}$, width $w = 100 \text{ nm}$ and height $h = 35 \text{ nm}$, while the distance is varied with $0.8 \mu$m < $d$ < 1.8 $\mu$m. The entire data set including the spectra for the separation $1.4 \mu$m < $d$ < 1.8 $\mu$m is shown in the appendix, figure B.9. The spectral positions of the RAs $\lambda_{RA/(1,0),d}$ are marked by colored ticks in the top (only $\lambda_{RA/d}$ is marked due to the limited space). The closer the RA is relative to the antenna array resonance position, the narrower is the resonance peak or the smaller is the FWHM$_A$ respectively. The latter is depicted in the inset$^a$.

The calculations were conducted with CST Microwave Studio (cf. appendix C). The increase of $d$ from $0.8 \mu$m < $d$ < 1.2 $\mu$m leads to a strong decay of FWHM$_A$, while it increases again for larger separations $d$. The smallest FWHM$_A$ is found for $d = d_c = 2L$, which has been chosen for the experimental investigations shown in the following.

$^a$To determine the width FWHM$_A$ of the asymmetric resonance peaks the low wavenumber minimum of the reflectance peak ($R \approx 0.26$) was used.

91
5.4.3 Summary

Based on the antenna material and geometry, as well as on the PCM with a defined thickness \( t \), the antenna separation in an array was discussed in this section. The arrangement in arrays has been chosen to design a sharp and pronounced resonance peak, which would have not been possible by using single isolated antennas. The beneficial use of the interference between the Rayleigh anomaly, which originates from the array, and the antenna resonance peak, allowed for an optimization of the peak width quantified by the full width at half maximum FWHM.

Finally, the experimental investigations can be based on the sample specifications selected throughout this chapter. In the following chapter, it will be described, how the chosen sample materials and layouts were applied to realize the tuning of the nanoantenna array resonance position \( \tilde{\nu}_{\text{res}} \) upon crystallization of PCM thin films. In chapter 7, laser pulses will be applied to present reversible switching of the resonance position \( \tilde{\nu}_{\text{res}} \).

Figure 5.18: According to the scheme given in the introduction of this chapter, the specifications of the antenna arrays were updated due to the findings discussed in this section. A squared arrangement with a separation distance \( d_c = 2L \) with \( L \) being the antenna length led to the narrowest resonance peak.
CHAPTER 6

Tuning of mid-infrared nanoantenna resonance frequencies

6.1 Introduction

The phase of exemplary PCMs has been changed either by heating the sample on a hot plate or by optical laser pulses. The first is related to a (potentially gradual) tuning process, while the latter refers to (binary) switching as it was introduced in chapter 2. The thermal treatment leading to the tuning process, which is the matter of this chapter, does not allow for a re-amorphization of the crystallized sample, while the switching process, which allows for repeated re-amorphization and re-crystallization, will be elucidated in the following chapter.

In the beginning of this chapter reflectance spectra of antenna arrays without the influence of a PCM thin film will be presented in section 6.2, which will be followed by reflectance spectra of antenna arrays with GST-326 and InSb in section 6.3. Large resonance frequency shifts $\Delta \bar{\nu}_{\text{res}}$ to lower, as well as to higher wavenumbers will be demonstrated. The reflectance spectra will be analyzed according to the sample parameters introduced in chapter 5, such as antenna material, antenna geometry, GST-326 film thickness, sample layout and antenna separation in an array to identify parameters leading to the largest resonance shifts $\Delta \bar{\nu}_{\text{res}}$. The comparison between calculated and experimental spectra concludes this section. Thereafter, the considerations on PCMs suited for large shifts of antenna array resonances given in chapter 5 will be applied and as a result, reflectance spectra of antenna arrays with GST-225 and GST-8211 will be presented in section 6.4. Based on the experimental results discussed in this chapter, all sample parameters will be ordered according their influence on the spectral properties and summarized in section 6.5. This chapter will conclude with a comparison between the results in the literature and the experimental investigations evaluated here in section 6.6 showing the much larger so-called tuning figure of merit realized in this work. Parts of these results were published in [239].

6.2 Reflectance spectra of aluminum antenna arrays

The spectral range between about 2000 and 4000 cm$^{-1}$ has been shown to be well-suited concerning the real and the imaginary part of the dielectric function $\varepsilon_{\text{PCM}}$ of the investigated PCMs. As it was theoretically considered in chapter 5, the imaginary part of the dielectric function of amorphous GST-326 and InSb $\varepsilon_{2,A}$ is very close to zero with a relatively small increase upon crystallization ($\varepsilon_{2,C}$)
in the investigated spectral range, while the difference of the real parts between the amorphous and the crystalline phase $\Delta \varepsilon_1$ is large. In order to achieve antenna resonances between about 2000 and 4000 cm$^{-1}$, antennas with a length $L$ between about 400 and 600 nm, a width $w$ of about 100 nm and a height $h$ of about 35 nm including a chromium adhesive layer ($h_{\text{Cr}} \approx 3 \text{nm}$) were fabricated with electron beam lithography (EBL) and thermal evaporation. An optimized separation of the antennas in the array has been calculated to be $d = 2L$ in $x$-, as well as in $y$-direction.

Regarding EBL, a single layer resist procedure has ensured for reproducible rod shaped nanoantennas. If advanced features, such as very narrow gaps (below 100 nm) between two antennas, were required, a double layer resist had to be applied\(^1\). Nevertheless, the lift-off, which is a task of the EBL process, was observed to be more successful by using a two resist layer compared to a single layer strategy, even for the relatively simple nanorods presented in this chapter. The bottom resist layer of the double layer process requires a baking temperature much higher than the crystallization temperature $T_C$ of the investigated PCMs. Thus, nanoantenna fabrication by using a double layer resist process on top of an amorphous PCM substrate was impossible, since it would have led to a crystallization of the PCM thin film during the EBL process. Therefore, the single resist process was advantageous regarding fabrication effort and especially regarding the baking temperature of the resists recommended by the supplier (cf. appendix A.3).

Reflectance spectra of the nanoantenna arrays were collected with incident light polarized along the antenna axis and are shown in figure 6.1. For the normalization a reflectance spectrum of the silicon substrate was determined (background spectrum). With increasing antenna length $L$, the resonance frequency position is shifted to shorter wavenumbers $\tilde{\nu}$, while the peak width FWHM decreases (cf. table 6.1). Furthermore, it can be seen, that the Rayleigh anomaly (RA) moves closer to the resonance frequency position $\tilde{\nu}_\text{res}$ for increasing antenna length $L$. Besides, an asymmetric peak shape was found with a higher reflectance for the highest investigated wavenumbers ($6000 \text{ cm}^{-1}$) compared to the reflectance for the lowest detected wavenumbers ($1000 \text{ cm}^{-1}$). The difference between the minima is about 10%, while it increases for decreasing antenna length.

In figure 6.1b, the calculated and the experimental spectrum for $L = 600 \text{ nm}$ are compared. Both were normalized to silicon and the calculated spectrum has already been introduced in figure 5.15.

The asymmetric peak shape, which was found for the measured spectra, was confirmed by the calculation. Furthermore, the difference in the maximum reflectance of the calculated and the measured resonance peaks is large (2.17 versus 1.34), while the resonance frequency position $\tilde{\nu}_\text{res}$ is shifted as well (2457 cm$^{-1}$ versus 2702 cm$^{-1}$). The width of the calculated peak FWHM is 468 cm$^{-1}$, which is about half as broad as the measured reflectance peak.

The differences have been ascribed to the large difference between the perfectly smooth aluminum antennas in the calculations and the experimentally evaporated aluminum with a pronounced surface roughness. Exemplary sample images are given in appendix B.1. Furthermore, in the calculations the native aluminum oxide has not been considered. Aluminum oxide is a dielectric and thus, can dampen the resonance of the metal nanoantennas. The differences between the sample design used for the simulations and the fabricated samples is discussed in detail in appendix C.

\(^1\)The antenna dimers presented in the Master’s thesis of De Rose and briefly in chapter 7 were fabricated by applying a double layer resist: AR-P 639.04 and AR-P 679.02 [240]. A SEM image of an antenna dimer is shown in figure B.27.
6.2 Reflectance spectra of aluminum antenna arrays

Table 6.1: The resonance frequency positions $\tilde{\nu}_{\text{res}}$ and peak widths FWHM of antenna arrays with different length $L$ were detected. The FWHM was determined by using the low wavenumber reflectance (about 1.0 at 1000 cm$^{-1}$) as minimum value. Based on the resonance positions $\tilde{\nu}_{\text{res}}$ (cf. equation 2.13b), an effective refractive index $n'_{\text{eff}}$ was calculated. Furthermore, the averaged refractive index $n''_{\text{eff}}$ was calculated according to equation 2.14.

The resonance positions, which were measured for the fabricated antenna arrays, were approximated by using equation 2.13 with an effective refractive index $n_{\text{eff}}$ by $n_{\text{eff}} = (2L\tilde{\nu}_{\text{res}})^{-1}$. To model an averaged $n'_{\text{eff}}$ as introduced by equation 2.14, the following values were set: $n_{\text{sub}} = 3.44$ (Si) and $n_{\text{super}} = 1.0$ (air), which led to a calculated average effective refractive index of $n''_{\text{eff}} = 2.22$ (cf. table 6.1). This averaged effective index was applied to calculate the resonance frequency position $\tilde{\nu}_{\text{res}}$ and led to values about 39% larger than the measured resonance frequency position. This deviation can be based on the complex layer system investigated in the experiments (oxide layers and small deviations in the length $L$ of 400 nm (dotted), 500 nm (dashed) and 600 nm (solid) and with an antenna separation of $d = 2L$ were investigated. The positions of the Rayleigh anomaly $\tilde{\nu}_{\text{RA}}$ (for the first grating order (1,0)) are marked in the top. The small reflectance dip at around 2350 cm$^{-1}$ is due to atmospheric CO$_2$ absorption. In 6.1b, the experimental (black) and the calculated resonance peak (gray) are compared for $L = 600$ nm.

In table 6.1, a refractive index derived from the measured resonance frequency positions $n_{\text{calc}} = 3.08$ is given. This value, which was found to be nearly equal for all different samples, differs strongly from the calculated averaged effective refractive index $n_{\text{average}} = 2.22$. Thus, the refractive index, which influences $\tilde{\nu}_{\text{res}}$, seems to have been dominated by the halfspace with the larger refractive index (here: 1.25)}.
6.3 Tuning of resonance frequencies by using Ge₃Sb₂Te₆ and InSb

Si). This dominance was found in the work of Hoffmann as well [21]. There, antenna resonance wavelengths were compared for different substrate materials with air as upper halfspace. The resonance positions are very close to \( \lambda_{\text{res}} = 2 \cdot n_{\text{subs}} \cdot L \). Furthermore, Adato et al. determined the resonance wavelength \( \lambda_{\text{res}} \) for Au nanorods with \( L = 0.8 - 1.2 \mu m \) on a Si substrate and fitted the results with the dipole antenna relation given in equation 2.13a, which lead to \( n_{\text{eff,ap}} = 3.11 \) [19]. This is in very good agreement with \( n_{\text{calc}} = 3.08 \), which was calculated here.

6.3 Tuning of resonance frequencies by using Ge₃Sb₂Te₆ and InSb

In this section, the results for annealing of GST-326 and InSb (both \( t_A = 50 \text{ nm} \)) adjacent to aluminum antenna arrays (lengths \( L = 400, 500 \) and \( 600 \text{ nm} \)) will be described. The corresponding normalized reflectance spectra of antenna arrays are shown in figure 6.2. The spectra were collected by FTIR microspectroscopy, while for normalization spectra of PCM thin films on silicon substrates were measured on the same sample at a position next to the arrays. Thus, only the spectral contribution of the antenna arrays was measured in the final normalized spectra. Illustrative sample images taken with the camera attached to the FTIR microspectrometer are shown in appendix B.1. The incident light was polarized along the long antenna axis (y-direction). The samples were annealed for 30 min at 180° C on a hot plate in a cleanroom environment.

In figure 6.2, the normalized reflectance spectra of the antenna arrays with amorphous GST-326 and InSb thin films are displayed as dashed lines. The resonance peaks are very pronounced and shift upon crystallization (solid lines). The black arrows correspond to these shifts \( \Delta \tilde{\nu}_{\text{res}} \). As expected in chapter 5, the antenna array resonance positions shift to lower wavenumbers for GST-326 and to higher wavenumbers for InSb, while the shift upon crystallization of GST-326 is much larger compared to the results achieved with InSb.

In the following section, these experimental results will be discussed in detail. The spectra will be evaluated regarding the influences of the antenna materials and the PCM thin films.

6.3.1 Spectral influence of sample materials

The annealing of the samples could have influenced the aluminum antennas as well, leading to shifts of the antenna array resonance frequency positions. In turn, these could have contributed to the resonance shifts \( \Delta \tilde{\nu}_{\text{res}} \) between antenna arrays covered with GST-326 or with InSb thin films. To investigate this influence, the spectral effects of the annealing procedure on the antenna arrays will be discussed in the following. Furthermore, the thin films of GST-326 and InSb will be evaluated in detail regarding their influence on the antenna array reflectance spectra.

Spectral influence of the annealing procedure on aluminum nanoantennas

Figure 6.3 shows normalized reflectance spectra of aluminum antenna arrays with different length \( L \) and a separation \( d = 2L \) prior and after the annealing procedure, which was applied for PCM thin films. No PCM thin film was present. In the spectra, the resonance frequency shifts to higher wavenumbers due to annealing by 16 to 96 cm⁻¹ (cf. table 6.2), which corresponds to a percentual shift \( \Delta \tilde{\nu}_{\text{ann}}/\% = \Delta \tilde{\nu}_{\text{ann}}/\tilde{\nu}_{\text{RT}} \) of about 0.49% to about 2.37%. The shift \( \Delta \tilde{\nu}_{\text{ann}} \) is defined as the difference \( |\tilde{\nu}_{180} - \tilde{\nu}_{\text{RT}}| \) with the antenna array resonance position prior to and after annealing \( \tilde{\nu}_{\text{RT}} \) and
\( \nu_{180} \) respectively. The room temperature is denoted as "TR". Compared to the resonance frequency shifts \( \Delta \tilde{\nu}_{\text{res}} \) visible in the spectra of the antenna arrays with GST-326 and InSb thin films, the shift \( \Delta \tilde{\nu}_{\text{ann}} \) is very small. According to the shown results, the antennas were stable regarding the annealing procedure, which was used for the crystallization of the PCM thin films. However, possible explanations for the determined shifts of the resonance frequency positions \( \Delta \tilde{\nu}_{\text{ann}} \) were investigated.

Figure 6.2: The shown reflectance spectra of Al antenna arrays covered by GST-326 (left) and InSb (right) thin films were normalized to bare PCM thin films (next to the investigated arrays) on Si substrates. The incident light has been polarized along the long nanorod axis. A 36-fold Cassegrain objective and an aperture of \((40 \times 27) \mu m^2\) was used, while additional FTIR parameters are listed in appendix A.3. Figures 6.5a illustrates the design of the investigated samples. In the spectra of figures 6.2b and 6.2c, the rows correspond to different antenna lengths \( L \) (gray antenna sketch). The shift \( \Delta \tilde{\nu}_{\text{res}} \) (black arrows) of the antenna array resonance peak is caused by the change from the amorphous (dashed) to the crystalline (solid) phase of the PCM. For GST-326 the resonance position \( \tilde{\nu}_C < \tilde{\nu}_A \), while for InSb \( \tilde{\nu}_C > \tilde{\nu}_A \) can be seen. The following parameters are marked by colored ticks: the atmospheric CO\(_2\) absorption at about 2350 cm\(^{-1}\) (gray) and the position of the Rayleigh anomaly (red). The depth of the CO\(_2\) absorption varies strongly, which has been based on the variation of the CO\(_2\) in the atmosphere during the measurements. This contribution might have been minimized by detecting the background spectrum prior to each antenna array spectrum instead of prior to the entire set of spectra, as it was done here.
6.3 Tuning of resonance frequencies by using Ge$_3$Sb$_2$Te$_6$ and InSb

Figure 6.3: Displayed are reflectance spectra of Al antenna arrays (normalization to Si substrate). The incident light is polarized along the rod axis. Antennas which have not been annealed (dashed) are compared to antennas after the thermal treatment (solid) used for crystallization of the PCM thin films (30 min at 180°C). Different antenna length $L$ were investigated: 600 nm (black), 500 nm (gray) and 400 nm (red). The small reflectance dip at around 2350 cm$^{-1}$ is due to atmospheric CO$_2$ absorption. The spectra shown for untreated arrays have already been displayed in figure 6.1.

Taking a geometric change of the antennas into account, the shifts due to annealing $\Delta\tilde{\nu}_{\text{ann}}$ between 17 and 96 cm$^{-1}$ would correspond to a shortening of the antennas between 4 and 9 nm. Since this is much smaller than the resolution limit of the scanning electron microscope (±20 nm), a decrease of the antenna length $L$ upon annealing can not be excluded. In figure B.4, SEM images of antennas prior and after annealing are compared. No change of the antenna geometry was detected according to the resolution limit of the SEM.

Furthermore, the antenna "quality" could have changed upon annealing. Deposited aluminum passivates spontaneously, as soon as it is in contact with air and thus, further corrosion is inhibited. Kim et al. reported a Al$_2$O$_3$ layer thickness of at least 10 nm, depending on the sample fabrication and storage (under high vacuum or exposure to air) [242]. For aluminum oxide, a densification can lead to a very rough or even fissured surface. Cimalla et al. reported a strong density contrast $\Delta \rho$ from about 3.0 g/cm$^3$ to about 3.5 g/cm$^3$ upon annealing, but this was only observed for much higher temperatures (about 1000°C) than the chosen annealing temperature (180°C) [243] and thus can be excluded as explanation of the resonance position shift $\Delta\tilde{\nu}_{\text{ann}}$ visualized in figure 6.3.

In summary, neither shortening, nor densification of the aluminum was found as explanation for the small shifts of the resonance frequency position upon annealing $\Delta\tilde{\nu}_{\text{ann}}$. Hence, a minor change of the antenna quality due to the thermal treatment and sample handling is assumed to cause $\Delta\tilde{\nu}_{\text{ann}}$.

It has to be noted that a change of the peak reflectance was measured as well. However, this change of ±0.8% has been rated as negligible.

<table>
<thead>
<tr>
<th>length /nm</th>
<th>RT $\tilde{\nu}_{\text{RT}}$/cm$^{-1}$</th>
<th>180°C $\tilde{\nu}_{180}$/cm$^{-1}$</th>
<th>$\Delta\tilde{\nu}_{\text{res}}$/cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>2702</td>
<td>2719</td>
<td>17</td>
</tr>
<tr>
<td>500</td>
<td>3276</td>
<td>3292</td>
<td>16</td>
</tr>
<tr>
<td>400</td>
<td>4055</td>
<td>4151</td>
<td>96</td>
</tr>
</tbody>
</table>

Table 6.2: This table summarizes the resonance frequency positions of aluminum antenna arrays with and without heating. The annealing at 180°C has been used for crystallization of PCM thin films. The total shifts of the resonance frequency position $\Delta\tilde{\nu}_{\text{ann}}$ / cm$^{-1}$ = $|\tilde{\nu}_{180} - \tilde{\nu}_{\text{RT}}|$ are listed. RT denotes the room temperature.
6.3 Tuning of resonance frequencies by using Ge$_3$Sb$_2$Te$_6$ and InSb

Spectral influence of the PCM thin films

Modelling introduced in chapter 5 suggests that the change in the dielectric function of the PCMs $\Delta \varepsilon_{\text{PCM}}^{-1/2}$ is inversely proportional to the shift of the resonance frequency position $\Delta \tilde{v}_{\text{res}}$. The evaluation of the dielectric functions of GST-326 and InSb in the investigated spectral range has led to the following relations:

$$\Delta \varepsilon_{\text{GST}}^{-1/2} < 0 \quad \implies \quad \tilde{v}_{A,\text{GST}} > \tilde{v}_{C,\text{GST}}$$

$$\Delta \varepsilon_{\text{InSb}}^{-1/2} > 0 \quad \implies \quad \tilde{v}_{A,\text{InSb}} < \tilde{v}_{C,\text{InSb}}$$

$$|\Delta \varepsilon_{\text{GST}}^{-1/2}| > |\Delta \varepsilon_{\text{InSb}}^{-1/2}| \quad \implies \quad |\tilde{v}_{A} - \tilde{v}_{C}|_{\text{GST}} > |\tilde{v}_{A} - \tilde{v}_{C}|_{\text{InSb}}$$

with the antenna array resonance frequency positions $\tilde{v}_{A}$ and $\tilde{v}_{C}$ referring to the amorphous and the crystalline phase of the considered PCM. With the FTIR spectra in figure 6.2, these theoretical expectations were confirmed experimentally. The measured spectra were quantified further by introducing total shift $\Delta \tilde{v}/\text{cm}^{-1}$ and the percental shift $\Delta \tilde{v}/\%$:

$$\Delta \tilde{v}_{\text{res}}/\text{cm}^{-1} = |\tilde{v}_{A} - \tilde{v}_{C}|$$  \hspace{1cm} (6.1a)

$$\Delta \tilde{v}_{\text{res}}/\% = |\tilde{v}_{A} - \tilde{v}_{C}| / \tilde{v}_{A}$$  \hspace{1cm} (6.1b)

These parameters are listed in table 6.3. The resonance frequency position of antenna arrays in contact with GST-326 has been shifted to shorter wavenumbers upon crystallization by a total shift $\Delta \tilde{v}_{\text{res}}$ between about 220 and 400 cm$^{-1}$. In case of InSb, the resonance frequency position shifts to longer wavenumbers by between about 110 and 170 cm$^{-1}$ due to annealing above $T_C$. The difference in direction, as well as in the absolute value of $\Delta \tilde{v}_{\text{res}}$ between GST-326 and InSb matches the assumptions given earlier.

In chapter 5, the averaged values for $\Delta \varepsilon_{\text{PCM}}^{-1/2}$ for GST-326 and InSb were calculated to about -0.13 and 0.025 respectively, which corresponds to a difference by a factor of about 5.2 (neglecting the sign flip). As it has been described earlier, the parameter $\Delta \varepsilon_{\text{PCM}}^{-1/2}$ has been associated with the shift of the resonance frequency position $\Delta \tilde{v}_{\text{res}}$. However, the experimentally determined shifts $\Delta \tilde{v}_{\text{res}}$ differ only by a factor up to 2.3 (neglecting the sign flip again). This means that no direct prediction of the resonance position and the resonance position shift can be given by $\Delta \varepsilon_{\text{PCM}}^{-1/2}$. Nevertheless, the direction can be predicted by the sign of this parameter, while the relative magnitude of the shifts of different PCMs can be predicted by the comparison of the value $\Delta \varepsilon_{\text{PCM}}^{-1/2}$ for the considered compounds.

The reflectance spectra presented in figure 6.2 were also evaluated regarding the peak width quantified by the full width at half maximum FWHM, which is listed in table 6.3 and visualized in figure 6.4. In this diagram, the peak broadening (narrowing) is visualized by an upwards (downwards) arrow, while the resonance shift is marked by the length and direction (rightwards/leftwards) of these arrows. The calculation of the peak width was much easier for InSb compared to GST-326, since for the latter the antenna array resonance peak is much more asymmetrical. Especially for C-GST-326 the minimal reflectance of the spectra at low wavenumbers ($R = 1.05$ at 1000 cm$^{-1}$) has been found to be much different compared to the minimum of the spectrum at high wavenumbers ($R = 0.95$ at about 3500 cm$^{-1}$). This behavior can not be associated with the bare aluminum arrays, since the corresponding reflectance spectra showed a contrary behavior (cf. figure 6.1), as well as since the...
asymmetry varies for the peaks with GST-326 compared to InSb. The determination of the peak width FWHM for the spectra of the antenna arrays with GST-326 superstrates has been explained in appendix B.3 in detail.

Figure 6.4: The plot shows the peak widths FWHM$_A$ and FWHM$_C$ of the antenna array resonance peaks as a function of the resonance frequencies $\tilde{\nu}_A$ and $\tilde{\nu}_C$. The data is based on the evaluation of the reflectance spectra of antenna arrays with a GST-326 and an InSb superstrate, as given in figure 6.2. The superstrate materials are color coded (GST-326 black, InSb gray), while different antenna length $L$ are marked by different lines. The shift of the antenna array resonance position $\Delta \tilde{\nu}_{\text{res}}$, as well as the increase of the peak width $\text{FWHM}_C > \text{FWHM}_A$ (peak broadening upon crystallization) are marked as well.

antenna arrays with PCM thin film superstrates, $t_A = 50 \text{ nm}$

<table>
<thead>
<tr>
<th>length $L$/nm</th>
<th>amorphous $\tilde{\nu}_A$/cm$^{-1}$</th>
<th>crystalline $\tilde{\nu}_C$/cm$^{-1}$</th>
<th>shift $\Delta \tilde{\nu}_{\text{res}}$/cm$^{-1}$</th>
<th>$\Delta \tilde{\nu}_{\text{res}}$/%</th>
<th>FWHM$_A$/cm$^{-1}$</th>
<th>TFOM$_A$</th>
<th>FWHM$_C$/cm$^{-1}$</th>
<th>TFOM$_C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GST-326 600</td>
<td>2096</td>
<td>1869</td>
<td>223</td>
<td>10.6</td>
<td>501</td>
<td>0.45</td>
<td>594</td>
<td>0.38</td>
</tr>
<tr>
<td>500</td>
<td>2490</td>
<td>2164</td>
<td>326</td>
<td>13.1</td>
<td>598</td>
<td>0.55</td>
<td>757</td>
<td>0.43</td>
</tr>
<tr>
<td>400</td>
<td>3006</td>
<td>2605</td>
<td>401</td>
<td>13.3</td>
<td>775</td>
<td>0.52</td>
<td>1028</td>
<td>0.39</td>
</tr>
<tr>
<td>InSb 600</td>
<td>2093</td>
<td>2203</td>
<td>110</td>
<td>5.3</td>
<td>424</td>
<td>0.26</td>
<td>455</td>
<td>0.24</td>
</tr>
<tr>
<td>500</td>
<td>2414</td>
<td>2564</td>
<td>150</td>
<td>6.2</td>
<td>509</td>
<td>0.30</td>
<td>544</td>
<td>0.28</td>
</tr>
<tr>
<td>400</td>
<td>2938</td>
<td>3110</td>
<td>172</td>
<td>5.9</td>
<td>667</td>
<td>0.26</td>
<td>686</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Table 6.3: These antenna array resonance frequency positions $\tilde{\nu}_{\text{res}}$, the total, as well as the percental shift of the resonance position $\Delta \tilde{\nu}_{\text{res}}$, the resonance peak widths FWHM$_A$ and FWHM$_C$, as well as the tuning figures of merit TFOM$_A$ and TFOM$_C$ were extracted from figure 6.2. The parameters are listed as a function of the antenna length $L$.

The evaluation showed, that the peak width of antenna arrays covered with InSb is smaller than the peak width of arrays with similar $L$ and a GST-326 superstrate. Furthermore, the peak width has increased upon crystallization, which means, that FWHM$_C >$ FWHM$_A$ except for the antenna array with $L = 400$ nm and the InSb superstrate. Moreover, the resonance peaks of the antenna arrays with InSb are more narrow compared to GST-326 with FWHM$_{A, \text{InSb}} \approx 0.88 \cdot$ FWHM$_{A, \text{GST}}$ and FWHM$_{C, \text{InSb}} \approx 0.69 \cdot$ FWHM$_{C, \text{GST}}$. 

100
6.3 Tuning of resonance frequencies by using Ge$_2$Sb$_2$Te$_5$ and InSb

Since the imaginary part of the dielectric function $\varepsilon_2$ is associated with energy dissipation in a material [11], the dielectric properties of GST-326 and InSb can explain this peak broadening visible in figure 6.4. In figure 3.5, the imaginary parts $\varepsilon_{2,A}$ and $\varepsilon_{2,C}$ were shown. Only for wavenumbers higher than about 4000 cm$^{-1}$ the imaginary part $\varepsilon_{2,C}$ of C-GST-326 increases above values close to zero, while for A-GST-326 $\varepsilon_{2,A}$ sticks to the zero line. In case of A-InSb, the imaginary part $\varepsilon_{2,A}$ is close to zero as well, while it increases slowly for wavenumbers higher than about 3700 cm$^{-1}$. In contrast, $\varepsilon_{2,C}$ sticks to the zero line upon crystallization. Consequently, the imaginary parts of the dielectric function can not cause the broadening of the resonance peaks for GST-326 superstrates compared to InSb superstrates.

The so-called tuning figure of merit TFOM can be calculated as follows [36, 61]:

$$\text{TFOM}_j = \frac{\Delta \tilde{\nu}/\text{cm}^{-1}}{\text{FWHM}_j} \quad \text{with} \quad j = A, C$$

(6.2)

while a tuning figure of merit larger than one is related to a shift of the resonance frequency position greater than the peak width FWHM. The tuning figures of merit TFOM$_{A\text{-GST}}$ and TFOM$_{C\text{-GST}}$ are about 1.9 and 1.5 times as large as the tuning figures of merit of InSb TFOM$_{A\text{-InSb}}$ and TFOM$_{C\text{-InSb}}$ respectively. On the one hand, this is based on the much smaller resonance shifts $\Delta \tilde{\nu}_{\text{res}}$ achieved with InSb compared to GST-326. On the other hand, the resonance peak widths FWHM for the antenna arrays covered with InSb are only slightly narrower than the ones associated with GST-326.

Besides the aspect of the resonance frequency shift, clear changes in the normalized peak reflectance were found. While for GST-326 the reflectance at the particular resonance frequency position has decreased strongly upon crystallization, the peak reflectance has even increased for the crystallization of InSb. The same has been also found in the calculated reflectance spectra, which will be discussed in detail later in this section. Experimental reflectance spectra of bare aluminum antenna arrays (cf. figure 6.3) only show a change of the peak reflectance of $\pm 0.8\%$. Thus, the damping of the nanoantenna resonances introduced by the PCM has been considered to explain the decrease (increase) of the peak reflectance for GST-326 (InSb) upon crystallization. Regarding the imaginary part of the dielectric function of the PCMs $\varepsilon_2$, it has been found, that it attains very low values in the spectral range, where the resonance frequency positions were measured (between about 2000 and 4000 cm$^{-1}$). Thus, it was assumed that the PCMs can only contribute small losses to the nanostructure resonance and therefore, can not explain the detected changes in the normalized peak reflectance. Oxidation of the PCM layer has been excluded as major reason for the reflectance peak damping as well, since the simulated spectra show a similar reflectance decrease, even no oxidization of the PCM was considered.

6.3.2 Spectral influence of the sample layout

Both the antenna length $L$ and the position of the antennas relative to the PCM thin film were varied throughout the experiments. While antenna arrays with nanorods of lengths $L = 400$, 500 and 600 nm were fabricated, these arrays were also placed below a GST-326 thin film of thickness $t_A$, as well as embedded between two layers each of thickness $t_A/2$ and on top of the thin film. This geometric variation has been motivated to study the influence of the effective refractive index $n_{\text{eff}}$ on the resonance
6.3 Tuning of resonance frequencies by using Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} and InSb

frequency position. Thereby, it was assumed, that the refractive index of the upper and lower halfspace of the antennas surrounding has been changed due to the varied position of the antennas relative to the GST-326. The influence of the antenna length on the measured reflectance spectra will be discussed regarding the spectra displayed in figure 6.2, where GST-326 and InSb were deposited as superstrate film. Later, additional reflectance spectra of antenna arrays with GST-326 and varied antenna array placement will be displayed and discussed.

Spectral influence of the antenna length

In the reflectance spectra shown in figure 6.2 a resonance position shift $\Delta \tilde{\nu}_{\text{res}} = |\tilde{\nu}_A - \tilde{\nu}_C|$ dependent on the antenna length $L$ can be seen. For decreasing length, an increase of the resonance frequency position $\tilde{\nu}_A$ (and in turn an increase of $\tilde{\nu}_C$), as well as of the total resonance shift $\Delta \tilde{\nu}_{\text{res}}$ was determined. Referring to the inverse proportionality between resonance frequency position $\tilde{\nu}_{\text{res}}$ and antenna length $L$ introduced in chapter 2, this behavior was expected.

Furthermore, the proportionality between the resonance frequency position $\tilde{\nu}_{\text{res}}$ and the effective refractive index of the antenna surrounding $n_{\text{eff}}$ has been described in chapter 2 as well. Upon deposition of GST-326 and InSb, a large total shift between the resonance frequency position of the bare aluminum arrays $\tilde{\nu}_{\text{res}}$ (cf. section 6.2) and the resonance frequency position of the arrays covered with the PCM thin film $\tilde{\nu}_A$ has been determined. For decreasing antenna length $L$, this shift $\tilde{\nu}_{\text{res}} - \tilde{\nu}_A$ increases from about 600 cm$^{-1}$ to about 1050 cm$^{-1}$ upon A-GST-326 layer deposition and from about 600 to about 1110 cm$^{-1}$ upon A-InSb layer deposition. Therefore, the shift $\tilde{\nu}_{\text{res}} - \tilde{\nu}_A$ is based on the introduction of the PCM superstrate. Thus, the dielectric properties of the upper halfspace of the antenna change from air with the real part of the dielectric function $\varepsilon_1 \approx 1.0$ to GST-326 with $\varepsilon_{1,A} \approx 12$ and to InSb with $\varepsilon_{1,A} \approx 25$ respectively (cf. figure 3.5). Furthermore, the difference of the real parts of the dielectric functions $\varepsilon_{1,A,\text{PCM}} - \varepsilon_{1,\text{air}}$ increases for increasing wavenumbers, which can explain the increasing shift $\tilde{\nu}_{\text{res}}$ for decreasing antenna length $L$ (increasing resonance frequency positions). Interestingly, the shift between the resonance position of the bare aluminum antenna arrays and the arrays with as-deposited amorphous PCM superstrates $\tilde{\nu}_{\text{res}} - \tilde{\nu}_A$ shows only small differences for A-GST-326 and A-InSb, even the real part of the dielectric function of InSb is about twice as large as $\varepsilon_{1,A}$ of GST-326.

Upon crystallization the same relation between the resonance position shift $\Delta \tilde{\nu}_{\text{res}}$ and the antenna length $L$ has been found as it has already been described for the samples with the amorphous PCM layers: the shorter the antennas in an array, the larger is the shift of the antenna array resonance peak position. Again, this can be associated with the increase of the difference between the real parts of the dielectric function for amorphous and crystalline PCMs $\Delta \varepsilon_1$ or referring to the difference $\Delta \varepsilon_{\text{PCM}}^{-1/2}$, which has been introduced in chapter 5 as follows:

$$\Delta \varepsilon_{\text{PCM}}^{-1/2} = \frac{1}{\sqrt{\varepsilon_C}} - \frac{1}{\sqrt{\varepsilon_A}}$$

At the resonance positions $\tilde{\nu}_A$ and $\tilde{\nu}_C$, the difference $\Delta \varepsilon_{\text{PCM}}^{-1/2}$ decreases from about -0.124 to -0.130 for GST-326 and increases from about 0.047 to 0.054 for InSb. The shift of the resonance frequency position $\Delta \tilde{\nu}_{\text{res}}$ increases from 223 to 401 cm$^{-1}$ upon crystallization of GST-326, while only an increase from 110 to 172 cm$^{-1}$ has been determined for the crystallization of InSb. This means that the higher magnitude of the change in $\Delta \varepsilon_{\text{PCM}}^{-1/2}$ for GST-326 matches with the higher antenna array resonance frequency position shift $\Delta \tilde{\nu}_{\text{res}}$, while the sign of $\Delta \varepsilon_{\text{PCM}}^{-1/2}$ matches with the direction of the resonance
shift $\Delta \tilde{\nu}_{\text{res}}$.

In summary, the inverse proportionality between the antenna length $L$ and the resonance frequency $\tilde{\nu}_{\text{res}}$, as well the increase in $|\Delta \epsilon_{\text{PCM}}^{-\frac{1}{2}}|$ explain the increase of the resonance position shift $\Delta \tilde{\nu}_{\text{res}}$ for decreasing antenna length $L$.

The peak widths FWHM for antenna arrays on GST-326 and InSb superstrates both increase for decreasing antenna length $L$. This behavior is similar to the trend found for bare aluminum antenna arrays without a PCM thin film (cf. table 6.1). There, FWHM for an antenna array with length $L = 400 \text{ nm}$ is about 1.5 as broad as the resonance peak for antennas with length $L = 600 \text{ nm}$. A similar comparison conducted for the reflectance spectra of the antenna arrays ($L = 600 \text{ nm}$ and $400 \text{ nm}$) with GST-326 and InSb has led to a broadening of the peaks by a factor between about 1.4 and 1.7. Thus, the increase of the peak width FWHM for decreasing antenna length $L$ can be found for antenna array spectra with and without PCMs.

Moreover, a change in the normalized peak reflectance can be seen. In the previous section a dependence on the superstrate material was discussed (cf. page 101), while the dependency on the antenna length $L$ will be considered here. For A-InSb, as well as C-InSb, the peak reflectance decreases for decreasing antenna length $L$. This behavior is similar for C-GST-326, while in contrast for A-GST-326 the peak reflectance even slightly increases for decreasing antenna length. Since the peak reflectance for bare aluminum antenna arrays has only shown small changes (1.34 for $L = 600 \text{ nm}$ and 1.32 for $L = 500$ and 400 nm), the pronounced differences in the peak reflectance found for the antenna arrays covered with GST-326 and InSb can be related to the PCMs only.

Spectral influence of the antenna position relative to the PCM

For GST-326, three different sample designs were investigated with the normalized reflectance spectra displayed in figure 6.5a: GST-326 as superstrate, as embedding medium and as substrate. Thereby, A-GST-326 has been deposited with a film thickness $t_A = 50 \text{ nm}$ for all investigated layouts. The spectra related to the GST-326 superstrate were already shown in figure 6.2. For a better comparison of all three sample layouts, these spectra are displayed again in figure 6.5. The representation of the normalized reflectance spectra resembles the spectra for the GST-326 and InSb superstrates: the normalized reflectance spectra of the antenna arrays with amorphous PCM thin films are displayed as dashed lines, while the resonance peaks are very pronounced and shift upon crystallization (solid lines). The black arrows correspond to the shift $\Delta \tilde{\nu}_{\text{res}}$. Here, three different antenna lengths $L$ were investigated for the three sample layouts as well. A general trend has been expected prior to the measurements: the influence of the refractive index of the PCM on the antenna array resonance position was expected to increase from the arrays with GST-326 substrate to the GST-326 superstrate. This assumption was based on the volume the PCM takes up in the upper halfspace above the antennas. For a GST-326 substrate, the upper halfspace is filled with air, while for the embedding GST-326 and the GST-326 substrate it is filled with the PCM. Due to the large real part of the dielectric function $\epsilon_1$ associated with the shift of the antenna array resonance position $\Delta \tilde{\nu}_{\text{res}}$, this shift was expected to be the largest for the GST-326 superstrate compared to the embedding medium and the substrate. Thereby, the shifts were expected to increase for decreasing antenna length $L$ as it was found for the antenna arrays with InSb and GST-326 superstrates.

In table 6.4, the values, which quantify the antenna array resonance peaks, are listed and the param-
6.3 Tuning of resonance frequencies by using GeSbTe and InSb

Parameters resonance frequency position shift $\tilde{\nu}_{\text{res}}$ and peak widths FWHM$_A$ and FWHM$_C$ are visualized in figure 6.6. On the one hand, the GST-326 substrate has led to the largest shifts $\Delta\tilde{\nu}_{\text{res}}$. This is in contrast to the expectations described above. The total shifts, which have been achieved by the GST-326 superstrates, are slightly smaller than the shifts associated with the embedded layout (except of $L = 500$ nm), while the percental shifts showed an opposite trend. On the other hand, the assumed dependency of the resonance shift $\Delta\tilde{\nu}_{\text{res}}$ on the antenna length $L$ was confirmed by the experimental results for the GST-326 thin film as embedding medium and substrate.

Furthermore, the peak width of the antenna array resonance peaks FWHM narrows strongly upon crystallization of the GST-326 substrate. In case of the embedding GST-326, FWHM decreases by less than 100 cm$^{-1}$ after crystallization. The broadening of the resonance peaks related to the GST-326 superstrates was discussed earlier.

In summary, the GST-326 substrate has led to the largest shifts $\tilde{\nu}_{\text{res}}$ compared to the other layouts, which has exceeded even the peak width associated with an antenna array of antenna length $L = 400$ nm on a C-GST-326 substrate. This is quantified by the tuning figure of merit TFOM$_C$.

For the purpose of a maximized TFOM with PCM thin films, a sample layout with a PCM substrate should be chosen for further experiments.

The increasing shift of the resonance frequency position $\Delta\tilde{\nu}_{\text{res}}$ for a decreasing antenna length $L$ was expected due to the results, which were found for the GST-326 and InSb superstrates earlier. For an explanation of the dependency of $\Delta\tilde{\nu}_{\text{res}}$ on the sample layout, the scattered near field of the first resonant antenna mode was calculated for the three investigated sample designs. Thereby, the scattered near field is the difference of the total near field and the incident near field at every point\(^2\). The results are displayed in figure 6.7 and it can be seen how the field penetrated into the A-GST-326 thin films adjacent to the antennas. In contrast, the amplitude of the scattered field in the silicon substrate is relatively small.

\(^2\)It should be noted that this is not identical with the total field/scattered field formalism known from FDTD calculations.
6.3 Tuning of resonance frequencies by using Ge\(_3\)Sb\(_2\)Te\(_6\) and InSb antennas

(a) PCM superstrate, embedding medium and substrate, \(t_A = 50\) nm

(b) GST-326/antenna array spectra with different antenna lengths \(L\).

Figure 6.5: The shown reflectance spectra of Al antenna arrays adjacent to GST-326 thin films are normalized to bare PCM thin films (next to the investigated arrays) on Si substrates. The incident light has been polarized along the long nanorod axis. Figure 6.5a illustrates the design of the investigated samples. In the spectra of figure 6.2b, the rows correspond to different antenna lengths \(L\) (gray antenna sketch), while the columns refer to the sample layouts on top. In the spectra, the change of the antenna array resonance peak is caused by the change from an amorphous (dashed) to a crystalline (solid) PCM thin film. In all spectra the following parameters are marked: the atmospheric CO\(_2\) absorption at about 2350 cm\(^{-1}\) (gray tick), the position of the Rayleigh anomaly (red tick) and the shift of the antenna array resonance position upon crystallization \(\Delta\tilde{\nu}_{\text{res}}\) (black arrow).
6.3 Tuning of resonance frequencies by using GeSbTe and InSb

Figure 6.6: The plot shows the peak widths FWHM$_A$ and FWHM$_C$ of the antenna array resonance peaks as a function of the resonance frequencies $\tilde{\nu}_A$ and $\tilde{\nu}_C$. The data is based on the evaluation of the reflectance spectra of antenna arrays given in figure 6.5. Different sample layouts are color coded (superstrate - black, embedding medium - gray, substrate - red), while different antenna lengths $L$ are marked by different lines.

Table 6.4: This table summarizes resonance frequency positions $\tilde{\nu}_{\text{res}}$ of antenna arrays with a GST-326 thin film as superstrate, embedding medium or substrate. The phase of the PCM has been changed by thermal annealing for 30 min at 180°C. Three different antenna lengths $L$ were studied. The total, as well as the percental shift of the resonance position $\Delta \tilde{\nu}_{\text{res}}$, the FWHM$_A$ of the amorphous resonance peak and the TFOM$_A$, as well as the averaged TFOM$_A$ are calculated. The related spectra can be found in figure 6.2b, while the numbers are visualized in figure 6.6.
6.3 Tuning of resonance frequencies by using Ge$_2$Sb$_2$Te$_5$ and InSb

Figure 6.7: Displayed is the absolute value of the difference between the total near field and the incident near field at every point ("scattered field", color coded) at the first resonant mode induced in the nanoantenna array for different sample designs: GST-326 superstrate (top), embedding medium (middle) and substrate (bottom figure). The position of the antenna is marked by a gray rectangle. The largest expansion of the scattered field into the GST-326 thin film has been found for the PCM substrate. Thus, the strongest shift \( \tilde{\nu} \) has been expected for the GST-326 antenna array substrate. The quantification in table 6.4 agrees with this assumption. The shown results were calculated by D. Chigorin.

Regarding the GST-326 superstrate (top in figure 6.7), the electric field penetrated the silicon substrate, the GST-326 substrate and air. Thereby, the field was localized at the antenna surrounding close to the nanorod tips, which matches the description of the field enhancement at the tip ends given in chapter 2. The scattered field in figure 6.7 is the highest in the GST-326 layer, as well as in the silicon substrate, while its expansion is larger into the PCM, as into the silicon. As a consequence, the contributions of the GST-326 superstrate and the silicon substrate to the effective refractive index \( n_{\text{eff}} \) were assumed to be stronger than the contribution of air. In case of an embedded antenna array (middle in figure 6.7), the scattered field is the highest in air, as well as in the GST-326. In the bottom of figure 6.7, the antenna array is placed on a GST-326 substrate and the field penetrates into the GST-326, as well as in air. The scattered field in air is the highest for the three sample designs. Besides, the scattered field has expanded less into silicon substrate compared to the sample design with the GST-326 thin film as superstrate or embedding medium. Moreover, the GST-326 substrate volume, which is penetrated by the scattered field is the largest penetrated GST-326 volume of the three investigated sample layouts. Hence, \( n_{\text{eff}} \) has been expected to be dominated by the PCM, which led to the assumption of the largest antenna array resonance position shifts \( \Delta \tilde{\nu}_{\text{res}} \). The results shown in figure 6.6 and table 6.4 have confirmed this assumption based on the calculated scattered field.

Air influences \( n_{\text{eff}} \) stronger for the GST substrate (bottom) compared to the embedding medium (middle) and superstrate (top). This could have led to a decrease of the effective refractive index \( n_{\text{eff}} \) and thus to a decrease of the resonance frequency position shift \( \tilde{\nu}_{\text{res}} \) for the superstrate relative to the two other designs. Regarding the experimental results, the superstrate allowed for a larger resonance frequency position shift \( \tilde{\nu}_{\text{res}} \) compared to the embedded design only for \( L = 400 \) nm. In case of antenna lengths \( L = 600 \) and 500 nm, the embedded antennas showed a larger shift compared to the GST-326 superstrate.

Interestingly, in figure 6.7 the scattered field does not penetrate the GST-326 directly on top of the antenna, but is rather shifted into the air around the edges of the GST-326 antenna cover. This behavior is likely to be a geometric effect.

6.3.3 Spectral influence of the antenna separation in an array

Previous calculations (cf. figure 5.17) showed that the antenna separation \( d \) has a strong influence on the antenna array resonance frequency position \( \tilde{\nu}_{\text{res}} \). For the exemplary sample with antennas of length \( L = 600 \) nm and a GST-326 superstrate with thickness \( t_A = 50 \) nm, a similar separation in x-,
as well as in y-direction with \((d_x, d_y) = (2L, 2L)\) is preferable regarding the width of the individual antenna array resonance peaks \(\text{FWHM}_A\). Thereby, the narrowing of the resonance peaks is related to the interference between the Rayleigh anomaly position \(\tilde{\nu}_{RA,(i,j),(d_x,d_y)}\), which is defined by the grating order \((i,j)\), as well as the antenna separation in the array \((d_x, d_y)\) and the antenna array resonance peak position \(\tilde{\nu}_{\text{res}}\). However, considering the first grating order \((i,j) = (1,0)\), the spectral position of the Rayleigh anomaly becomes independent on the antenna separation in y-direction \(d_y\). This can be seen by reviewing equation 5.8 for the Rayleigh anomaly position \(\lambda_{RA,(1,0),d_x}\) given in wavelengths, as it has been discussed in chapter 5:

\[
\lambda_{RA,(1,0),2L} = -2L \cdot \sin(\theta) \cdot \sin(\phi) + \sqrt{(2L \cdot \sin(\theta) \cdot \sin(\phi))^2 - (4L^2 \cdot (\sin^2(\theta) - 3.44^2))}
\]

with the antenna separation in x-direction \(d_x = 2L\), the real part of the refractive index of the silicon substrate \(n = 3.44\) and the polar and azimuthal angles \(\theta\) and \(\phi\).

In the following, the measured data presented in sections 6.2 and 6.3 will be evaluated regarding the influence of the interference between the Rayleigh anomaly position and the antenna array resonance frequency on the peak width \(\text{FWHM}\). Therefore, the difference between the averaged lattice resonance frequency \(\tilde{\nu}'_{RA,(1,0),2L}\) (calculated) and the antenna array resonance frequency position \(\tilde{\nu}_{\text{res}}\) (experimental) is displayed as a function of the peak widths \(\text{FWHM}_A\) and \(\text{FWHM}_C\) in figure 6.8. The averaged Rayleigh anomaly frequency has been calculated as follows (cf. equations 5.9 and 5.10):

\[
\tilde{\nu}'_{RA,(1,0),2L} = (3.44 \cdot d_x)^{-1}
\]

with the real part of the refractive index of the silicon substrate in the MIR spectral range given as \(n_{\text{sub}} = 3.44\). It has to be noted, that the averaged lattice resonance frequency is a function of the antenna separation in x-direction \(d_x = 2L\) and thus, of the antenna length \(L\) and in turn, of the resonance frequency position \(\tilde{\nu}_{\text{res}}\). The following frequency positions were calculated: \(\tilde{\nu}'_{RA,(1,0),1.2} = 2422.5 \text{ cm}^{-1}\) for antennas with length \(L = 600 \text{ nm}\), \(\tilde{\nu}'_{RA,(1,0),1.0} = 2907.0 \text{ cm}^{-1}\) for antennas with length \(L = 500 \text{ nm}\) and \(\tilde{\nu}'_{RA,(1,0),0.8} = 3633.7 \text{ cm}^{-1}\) for antennas with length \(L = 400 \text{ nm}\).

Figure 6.8 shows a comparison of the peak width \(\text{FWHM}\) and the frequency difference \(\tilde{\nu}'_{RA,(1,0),2L} - \tilde{\nu}_{\text{res}}\) for the samples discussed so far (InSb superstrate, GST-326 superstrate/embedding medium/substrate). A loose trend can be identified: the peaks are more narrow, if the antenna array resonance position \(\tilde{\nu}_{\text{res}}\) is close to the lattice resonance frequency \(\tilde{\nu}'_{RA,(1,0),2L}\). Furthermore, the peak width \(\text{FWHM}\) increases slower for a decreasing antenna length \(L\), if the antenna array resonance position \(\tilde{\nu}_{\text{res}}\) is smaller than the lattice resonance frequency \(\tilde{\nu}'_{RA,(1,0),2L}\). These data sets can be found right of the vertical line \(\tilde{\nu}'_{RA,(1,0),2L} - \tilde{\nu}_{\text{res}} = 0\). Besides, for all samples the peak broadens for a decreasing antenna length \(L\) (arrows in figure 6.8).

A similar evaluation was conducted for the calculated resonance peaks discussed in section 5.4. There the antenna separation in a squared array with \((d_x, d_y) = (d, d)\) was varied between \(d = 0.8 \mu\text{m}\) and \(d = 1.8 \mu\text{m}\). While in figure 6.8 the antenna length \(L\) and sample layout or material are changed, these parameters are kept constant in figure 6.9 with \(L = 600 \text{ nm}\) and an A-GST-326 superstrate of thickness \(t_s = 50 \text{ nm}\) and only the separation \(d\) varies. Thus, the Rayleigh anomaly position \(\tilde{\nu}'_{RA,(1,0),d}\) (calculated), as well as the resonance frequency position \(\tilde{\nu}_{\text{res}}\) (measured) vary for each shown data point in figure 6.9. The peak width \(\text{FWHM}_A\) is minimal for a minimized difference between the
Rayleigh anomaly position and the antenna array resonance frequency position $\tilde{\nu}_{RA,(1,0),d} - \tilde{\nu}_{res}$. This is the case for an antenna separation of $d = 2L = 1.2 \mu m$. Interestingly, a very strong increase of the peak width FWHM$_{\tilde{\nu}}$ was calculated for a small increase of the difference $\tilde{\nu}_{RA,(1,0),d} - \tilde{\nu}_{res}$ provided that $\tilde{\nu}_{RA,(1,0),d} < \tilde{\nu}_{res}$. In the experimental results shown in figure 6.8, a similar behavior can be seen. There, the broadening of the resonance peaks with $\tilde{\nu}_{RA,(1,0),d} < \tilde{\nu}_{res}$ (left of the vertical line zero line) is much more pronounced than for the resonance peaks with $\tilde{\nu}_{RA,(1,0),d} > \tilde{\nu}_{res}$ (right of the vertical zero line). As a consequence, the antenna arrays should be designed to show a resonance position $\tilde{\nu}_{res}$ smaller than the RA position $\tilde{\nu}_{RA,(1,0),d}$ in order to allow for narrow resonance and a large TFOM.

![Figure 6.8](image)

Figure 6.8: The difference between the averaged Rayleigh anomaly frequency $\tilde{\nu}_{RA,(1,0),2L}$ (calculated) and the antenna array resonance frequency position $\tilde{\nu}_{res}$ (experimental) is displayed. The data set, which corresponds to one sample (PCM thickness and phase are constant, $L$ varies), is color coded. Since three antenna lengths $L$ were investigated for each sample and PCM phase, three data points are displayed for each sample prior and after the crystallization. The arrow heads indicate the decreasing antenna length $L$. All displayed data sets were presented as normalized reflectance spectra and data tables before.

![Figure 6.9](image)

Figure 6.9: The difference between the averaged Rayleigh anomaly frequency $\tilde{\nu}_{RA,(1,0),2L}$ (calculated) and the antenna array resonance frequency position $\tilde{\nu}_{res}$ (experimental) is shown. Samples with antenna length $L = 600$ nm and an A-GST-326 superstrate of thickness $L_{\text{A}}$ with the varied symmetric antenna separation $(d,d)$ between $d = 800$ nm and $d = 1800$ nm has been studied. The arrow indicates the increase of the antenna separation. The minimum peak width FWHM$_{\tilde{\nu}}$ corresponds to $d = 1.2 \mu m$. 

109
6.3.4 Comparison between measured and calculated reflectance spectra

The experimental reflectance spectra of antenna arrays with GST-326 and InSb superstrate thin films (as-deposited thickness $t_A = 50 \text{ nm}$) were complemented by numerical calculations. For the presented results regarding GST-326, the calculations were performed using the so-called finite integration method (FIT), which was realized with the software Microwave Studio by the company Computer Simulation Technology (CST). Regarding InSb, the so-called finite-difference time-domain (FDTD) method using the software FDTD Lumerical Solutions was applied. The calculations are based on the dielectric permittivity data measured on thin film samples as discussed in section 3.3, while the details of the simulation models are given in appendix C.

In figure 6.10, experimental and calculated normalized reflectance spectra are compared for an antenna length $L = 600 \text{ nm}$ and a symmetric antenna separation in the array $(d_x, d_y) = (2L, 2L)$. Both agree qualitatively very well. The direction of the antenna array resonance position shifts $\Delta \tilde{\nu}_{res}$, as well as the direction of the change of the peak reflectance upon crystallization experimentally determined (decrease for GST-326 and increase for InSb) were confirmed by the calculated reflectance spectra. However, quantitative discrepancies can be found regarding the absolute value of the resonance shifts, as well as the absolute value of the peak reflectances. The calculations overestimated the resonance shifts $\Delta \tilde{\nu}_{res}$ for GST-326 by about 94% and for InSb by about 70%. The peak reflectances were overestimated by about 80% for GST-326 and by about 17% for InSb. Regarding the peak width associated with A-PCM FWHM$_A$ the calculations showed a 30% narrower (GST-326) and 18% broader (InSb) resonance peak. Concerning the resonance peak corresponding to the crystalline phase the calculations revealed a 18% (GST-326) and 3% smaller peak width FWHM$_C$. All spectral parameters are listed in table 6.5.

The deviations between the measured and calculated resonance shifts and peak reflectances were supposed to originate from the simplifications of the modeled structure, including simplified shape, neglected adhesive chromium layer, and the neglected oxide layers (natural silicon oxide, natural aluminum dioxide and the natural oxide of the PCM). Broadening of the measured spectra compared to the calculated spectra could be assigned to sample imperfections, which include inhomogeneities in the structure dimensions.

<table>
<thead>
<tr>
<th>method</th>
<th>amorphous $\tilde{\nu}_A / \text{cm}^{-1}$</th>
<th>crystalline $\tilde{\nu}_C / \text{cm}^{-1}$</th>
<th>shift $\Delta \tilde{\nu}_{res} / \text{cm}^{-1}$</th>
<th>$\Delta \tilde{\nu}_{res} / %$</th>
<th>FWHM$_A / \text{cm}^{-1}$</th>
<th>TFOM$_A$</th>
<th>FWHM$_C / \text{cm}^{-1}$</th>
<th>TFOM$_C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GST</td>
<td>exp. 2096</td>
<td>1869</td>
<td>223</td>
<td>10.6</td>
<td>501</td>
<td>0.45</td>
<td>594</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td>calc. 2060</td>
<td>1620</td>
<td>440</td>
<td>21.4</td>
<td>350</td>
<td>1.26</td>
<td>490</td>
<td>0.90</td>
</tr>
<tr>
<td>InSb</td>
<td>exp. 2093</td>
<td>2203</td>
<td>110</td>
<td>5.3</td>
<td>424</td>
<td>0.26</td>
<td>455</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td>calc. 1941</td>
<td>2129</td>
<td>188</td>
<td>9.7</td>
<td>500</td>
<td>0.38</td>
<td>441</td>
<td>0.43</td>
</tr>
</tbody>
</table>

Table 6.5: The spectral parameters are compared for the calculated and experimentally determined spectra shown in figure 6.10. The experimental parameters were presented in tables 6.3 and 6.4 already.
6.4 Tuning of resonance frequencies by using Ge$_2$Sb$_2$Te$_5$ and Ge$_8$Sb$_2$Te$_{11}$

To experimentally verify the theoretical analysis of suited PCMs for nanoantenna resonance tuning, two more GST compounds have been studied. In chapter 5 the parameter $\Delta \varepsilon_{-1/2}^{\text{PCM}}$ has been associated with the shift of the resonance frequency position $\Delta \tilde{\nu}_{\text{res}}$. There, it was found that Ge$_8$Sb$_2$Te$_{11}$ (GST-8211) and Ge$_2$Sb$_2$Te$_5$ (GST-225) show a large difference $\Delta \varepsilon_{-1/2}^{\text{PCM}}$ (cf. figure 5.3), while the imaginary parts - especially of GST-8211 - remain relatively small compared to GST or GST-348 for example (cf. figure 5.4).

An amorphous GST film of about 50nm thickness was sputtered on Si substrates and afterwards aluminum antenna arrays were fabricated on top. For crystallization, all samples were annealed in an oven at 180°C, which is above their crystallization temperature $T_C$ (cf. table 3.1) for about 30 min. With FTIR microspectroscopy and an aperture of about $(40 \times 30)$ µm$^2$, all spectra were taken and normalized to the background. As background, the sample area next to the antenna areas was used, which included a silicon substrate with the corresponding PCM thin film next to the antenna arrays. The spectra are displayed in figure 6.11: the normalized reflectance spectra of the antenna arrays with amorphous PCM thin films are displayed as dashed lines, while the pronounced resonance peaks shift upon crystallization (solid lines). The black arrows correspond to the shift $\Delta \tilde{\nu}_{\text{res}}$. As for the samples before, three different antenna length $L$ were investigated for GST-8211 and GST-225.

In table 6.6, the resonance frequency positions $\tilde{\nu}_{\text{res}}$ for different GST compounds and different antenna lengths are listed, while figure 6.12 visualizes these spectral parameters. According to the difference $\Delta \varepsilon_{-1/2}^{\text{PCM}}$ evaluated in the wavenumber range between 2500 and 3500 cm$^{-1}$, GST-225 and GST-8211 were expected to lead to similar shifts of the resonance frequency position $\Delta \tilde{\nu}_{\text{res}}$. GST-326 was expected to lead to larger shifts $\Delta \tilde{\nu}_{\text{res}}$ compared to GST-225 and GST-8211. However, the experimental results show that the resonance shifts $\Delta \tilde{\nu}_{\text{res}}$ associated with the GST-326 and GST-8211 substrates are nearly similar, while GST-225 has allowed for a much smaller shift (between about 44 and 33% less). This becomes especially clear in figure 6.12. Moreover, GST-326 and GST-8211
led to similar peak widths FWHM \(_A\) for the amorphous substrate, while the peaks associated with A-GST-8211 are slightly narrower than the peaks related to the A-GST-326 substrate. In contrast, the resonance peaks of the antenna arrays on A-GST-225 are much narrower than the resonance peaks associated with A-GST-326 and A-GST-8211. This is the only data set, which is in contrast to the observed trend for the relative spectral position \(\tilde{\nu}_{RA(1,0),d} - \tilde{\nu}_{res}\) and the peak width FWHM. The corresponding diagram can be found in figure B.15.

(a) PCM substrate with antenna array on top, \(t_A = 50\, \text{nm}\)

(b) GST-8211/antenna array spectra

(c) GST-225/antenna array spectra

Figure 6.11: The shown reflectance spectra of aluminum antenna arrays on GST-8211 (left) and GST-225 (right) thin films have been normalized to bare PCM thin films (next to the investigated arrays) on silicon substrates. The incident light has been polarized along the long nanorod axis. Figure 6.11a illustrates the design of the investigated samples. In the spectra of figures 6.11b and 6.11c, the rows correspond to different antenna lengths \(L\) (gray antenna sketch). In the spectra, the change of the antenna array resonance peak is caused by the change from an amorphous (dashed) to a crystalline (solid) PCM thin film. In all spectra the following parameters are marked: the atmospheric CO\(_2\) absorption at about 2350 cm\(^{-1}\) (gray tick), the position of the Rayleigh anomaly (red tick) and the shift of the antenna array resonance position upon crystallization \(\Delta \tilde{\nu}_{res}\) (black arrow).
6.4 Tuning of resonance frequencies by using Ge$_2$Sb$_2$Te$_5$ and Ge$_8$Sb$_2$Te$_{11}$

Tuning of resonance frequencies by using Ge$_2$Sb$_2$Te$_5$ and Ge$_8$Sb$_2$Te$_{11}$

Figure 6.12: The given plot showing the peak widths FWHM$_A$ and FWHM$_C$ of the antenna array resonance peaks as a function of the resonance frequencies $\tilde{\nu}_A$ and $\tilde{\nu}_C$ is based on the evaluation of the reflectance spectra of antenna arrays on PCM substrate films given in figures 6.2 and 6.11. The resonance positions $\tilde{\nu}_A$ and $\tilde{\nu}_C$ are plotted for different antenna length $L$ (coded by the style of the lines) and all investigated GST-compounds: GST-326 (black), GST-8211 (red) and GST-225 (gray). The resonance shift upon crystallization $\Delta\tilde{\nu}_{\text{res}}$ is illustrated by arrows. While the resonance positions and shifts of GST-326 and GST-8211 have been very similar, GST-225 has shown a much smaller shift, which is accompanied by much smaller FWHM$_A$ compared to GST-326 and GST-8211.

Table 6.6: This table summarizes antenna array resonance positions extracted from normalized reflectance spectra of antenna array samples with GST-225 and GST-8211 as substrate layers below the antenna arrays. Furthermore, the shift of the resonance position $\Delta\tilde{\nu}_{\text{res}}$, the peak widths FWHM$_A$ and FWHM$_C$ of the amorphous and crystalline resonance peak and the related TFOM$_A$ and TFOM$_C$ are calculated. The resonance positions are listed as a function of the GST compound and as a function of the antenna length $L$. For comparison, the values for the GST-326 substrate are shown (taken from table 6.4).
6.5 Summary

Upon crystallization the peak width FWHM\(_C\) is similar for all three investigated GST compounds. Thereupon, the peak narrowing after crystallization is much more pronounced for the antenna arrays on the GST-8211 and GST-326 substrate films compared to GST-225.

Regarding the different antenna lengths \(L\), the same trend as seen for the results presented earlier can be found: the shorter the antenna length \(L\), the larger is the shift of the resonance frequency position \(\Delta \tilde{\nu}_{\text{res}}\). This effect is related to the decreasing difference \(\Delta \varepsilon_{\text{PCM}}^{-1/2}\) as discussed earlier as well.

Considering the peak reflectance, GST-8211 allowed for the highest peak reflectance compared to GST-225 and GST-326 (cf. figure 6.5). Upon crystallization the peak reflectances decrease, which was observed for all antenna array reflectance spectra involving thin films of GST compounds. Thereby, the largest decrease was detected for GST-8211, while GST-225 and GST-326 show similar changes for antenna arrays with length \(L = 600\) and \(500\) nm. Considering the shortest antennas with \(L = 400\) nm, the peak reflectance associated with the GST-225 antenna substrate decreases less than what was found for the GST-326 substrate. These findings were compared with the data on the imaginary part \(\varepsilon_2\) of the dielectric functions \(\varepsilon_{\text{PCM}}\). However, no clear correlation to the ratio \(\varepsilon_2/\varepsilon_1\) has been found (cf. figure 5.4). According to the calculated ratio \(\varepsilon_2/\varepsilon_1\), C-GST-326 shows the smallest values, while C-GST-225 reveals the largest ratio \(\varepsilon_2/\varepsilon_1\) in the spectral range the antenna array resonance frequencies were detected in. As a consequence, the dielectric data predicts the resonance shifts \(\Delta \tilde{\nu}_{\text{res}}\) very well and the parameter \(\Delta \varepsilon_{\text{PCM}}^{-1/2}\) allows for a selection of PCMs suited for large resonance frequency shifts \(\Delta \tilde{\nu}_{\text{res}}\). Nevertheless, a quantitative prediction of the peak reflectance from the dielectric properties of the PCMs has not been realized yet.

6.5 Summary

In the experiments discussed here, aluminum nanoantenna arrays were brought in contact with amorphous PCM thin films - different GST compounds, as well as InSb - and thus, the nanoantenna array resonance frequency \(\tilde{\nu}_A\) was shifted to the position \(\tilde{\nu}_C\) upon crystallization of the PCM layer. According to the theoretical considerations conducted in chapter 5, the PCMs used in this thesis were chosen to realize a frequency shift as large as possible. Therefore, the largest values for the difference \(\Delta \varepsilon_{\text{PCM}}^{-1/2}\) in the spectral range of the antenna array resonance frequency positions were identified. Simultaneously, the imaginary parts of the dielectric function of each PCM \(\varepsilon_{2,\text{PCM}}\) were considered as well, since generally, this parameter has been associated with the energy dissipation within a material. The consideration of the imaginary part \(\varepsilon_{2,\text{PCM}}\) has been based on the purpose to keep the absorption due to the PCM as small as possible. As a result, the compounds GST-326, GST-8211 and GST-225 have been selected and investigated for different sample geometries. To do so, the position of the metal nanoantennas relative to the PCM thin film was varied to study the influence of the effective refractive index \(n_{\text{eff}}\) on the spectral parameters, such as resonance frequency position shift \(\Delta \tilde{\nu}_{\text{res}}\) and the peak width FWHM.

The aluminum antenna arrays with different lengths \(L\) (600, 500 and 400 nm) showed pronounced resonance peaks in the measured reflectance spectra in the MIR spectral range. The resonances remained stable upon annealing of the antennas. Moreover, the chromium adhesion layer, which was necessary due to the antenna array fabrication process, did not dampen the antenna array resonances.

The deposition of GST-326 and InSb thin films as superstrate shifted the antenna array resonance
position $\tilde{\nu}_{\text{res}}$ due to the increase of the real part of the refractive index $n$ of the upper halfspace of the antennas surrounding. Upon crystallization, the resonance frequency position shifted again, while InSb allowed for a shift to higher wavenumbers and GST-326 for a shift to smaller wavenumbers. This resonance shift $\Delta \tilde{\nu}_{\text{res}}$ increased for decreasing antenna length $L$, which has been related to the wavenumber dependence of the dielectric function of each PCM. This means that the difference $\Delta \varepsilon^{-1/2}_{\text{PCM}}$ is a function of the wavenumber and increases for higher wavenumbers for the investigated PCMs. For GST-326, as well as for InSb, a broadening of the resonance peaks was determined by evaluation of the peak widths $\text{FWHM}_A$ and $\text{FWHM}_C$.

Additionally, the variation of the antenna array position relative to the position of GST-326 thin films led to larger antenna array resonance shifts $\Delta \tilde{\nu}_{\text{res}}$ upon crystallization than what was detected for samples with the PCM superstrates. The GST-326 arranged as substrate layer did not only lead to the largest resonance shifts $\Delta \tilde{\nu}_{\text{res}}$, but also to the narrowst resonance peaks for the crystalline phase of the GST-326. The increase of the resonance shifts $\Delta \tilde{\nu}_{\text{res}}$ has been related to the calculated penetration of the scattered fields. These fields penetrate the furthest into the GST-326 in case of the antennas placed on top of the PCM.

The compounds GST-8211 and GST-225 were used as antenna array substrates. GST-8211 led to the largest shifts of the antenna array resonance positions $\Delta \tilde{\nu}_{\text{res}}$ determined in this thesis. Besides, the antenna array resonance peak width $\text{FWHM}_A$ associated with A-GST-225 were the smallest, which were detected for amorphous GST compounds applied in this thesis.

The peak widths of all investigated samples have been related to the difference between the Rayleigh anomaly position and the antenna array resonance position $\tilde{\nu}'_{\text{RA},(1,0),2L} - \tilde{\nu}_{\text{res}}$. A loose trend has been identified, where for most samples a small difference $\tilde{\nu}'_{\text{RA},(1,0),2L} - \tilde{\nu}_{\text{res}}$ can be associated with a narrower peak width $\text{FWHM}_A$ or $\text{FWHM}_C$. In contrast, an increase of this difference was accompanied with a broader peak.

These findings were organized regarding the sample parameters, which was already introduced in chapter 5. The spectral parameters resonance frequency position $\tilde{\nu}_{\text{res}}$, the shift of the antenna array resonance frequency position $\Delta \tilde{\nu}_{\text{res}}$, as well as the peak width $\text{FWHM}$ have been related to the sample materials, the sample layout including the PCM thickness, the antenna geometry, as well as the position of the antenna arrays relative to the PCM thin films. Furthermore, the influence of the antenna arrangement in an array on the spectral parameter has been considered. In figure 6.13, the relation between the spectral parameters and these sample specifications is displayed. The chosen sample materials defined the resonance frequency position $\tilde{\nu}_{\text{res}}$ due to their dielectric properties $\varepsilon(\tilde{\nu})$. The variation of the antenna position led to changes in the peak width $\text{FWHM}$, as well as of the resonance frequency shift $\Delta \tilde{\nu}_{\text{res}}$. The PCM thickness, which is discussed in appendix B.4, led to variations in the peak width $\text{FWHM}$ and the resonance frequency shift $\Delta \tilde{\nu}_{\text{res}}$ as well. Finally, a change in the antenna array separation allowed for a variation of the peak width $\text{FWHM}$ and the resonance frequency shift $\Delta \tilde{\nu}_{\text{res}}$. 

115
6.6 Comparison between the shown results and the literature

Since the tuning figure of merit TFOM has been used in the literature [36, 61] to rate the presented concepts, it has been calculated for each experiment presented in the framework of this thesis. Moreover, it has been compared with different published approaches for the shifting of the nanostructure resonance frequency, listed in table 6.7. Only experimental results have been included in this tabular summary. Several theoretical studies by CAO et al., where gold nanostructures surrounded by GST-225 were applied for absorber designs and negative index metamaterials [72, 73, 74, 244, 245], have not been listed in table 6.7.

It can be seen that the concepts, which involve PCMs, have led to the largest tuning figures of merit TFOM. This implies, that the shifts of the nanostructure resonance frequencies $\Delta \tilde{\nu}_{\text{res}}$ have been larger than the peak width.

The tuning figure of merit TFOM of all publications listed in tables 6.7 and 6.8 is visualized in figure 6.14. In figure 6.14a the spectral range, in which the experimental results were shown, is displayed, while in figure 6.14b the realized shift of the antenna array resonance frequency position $\Delta \tilde{\nu}_{\text{res}}$ is depicted. The concepts, which are summarized by one color in figure 6.14 correspond to the grouped publications in tables 6.7 and 6.8: the resonance position shift has either been realized by applying the insulator-to-metal transition (IMT) of VO$_2$, or by the post-fabrication variation of the resonator geometry (coupling distance of coupled resonators), or by the variation of the charge carrier concentration in graphene or semiconductors, such as GaAs, as well as by the use of PCMs. The latter includes publications related to this thesis, which are marked separately in figure 6.14.

In figure 6.14a it can be seen that resonance shifting by the variation of the charge carrier concentration was applied in the FIR and MIR spectral range. The contribution of the released charge carriers to the dielectric function lies in this spectral range (cf. figure 3.4). The post-fabrication variation of the resonator geometry was realized in the same spectral range, which is based on the size of the used resonant nanostructures. The application of PCMs was most beneficial in the MIR and NIR spectral range. The suitability of their dielectric function in the MIR and NIR was discussed in chapter 3 in detail. In contrast to the other concepts, the IMT of VO$_2$ was used from the FIR to the VIS spectral range in the literature. The behavior of the dielectric functions $\varepsilon_I$-VO$_2$ and $\varepsilon_M$-VO$_2$ (figure 2.10) allows for a spectrally broad application of VO$_2$. The achieved resonance shifts $\Delta \tilde{\nu}_{\text{res}}$ are shown in figure 6.14b.
For all concepts a TFOM of up to 0.68 was published, while the studies related to this thesis exceed these results. The large TFOMs were realized by the application of the well-selected PCM GST-326 regarding a large shift of the antenna array resonance position $\Delta \tilde{\nu}_{\text{res}}$ in the MIR/NIR spectral range [50, 83, 223, 239]).

In the future, even larger shifts $\Delta \tilde{\nu}_{\text{res}}$ and TFOMs can be realized by applying even better suited PCMs (such as GST-8211 in the NIR, cf. table 6.6, or GIST and GeTe in the MIR, cf. table 5.3), optimized sample designs (protection layers against PCM aging, cf. section 7.3.5, or resonances with narrower peaks, such as surface phonon polariton modes of silicon carbide [246]). Furthermore, unpublished investigations by the author of this thesis showed that narrower antenna array resonances and larger resonance position shifts $\Delta \tilde{\nu}_{\text{res}}$ can be realized by the beneficial use of an interference between the antenna resonance, the lattice resonance (Rayleigh anomaly) and the thin film interferences (TFIs) of a PCM thin film much thicker than as it has been used in this thesis ($t_A = 250 \text{ nm}$ versus $t_A = 50 \text{ nm}$ applied here).

Figure 6.14: Published concepts for the shifting of nanostructure resonance frequency positions are compared regarding their tuning figure of merit TFOM as a function of the initial resonance frequency position $\tilde{\nu}_i$ of the considered nanostructure (6.14a) and as a function of the achieved resonance position shift $\Delta \tilde{\nu}_{\text{res}}$ (6.14b). Each data point refers to a publication listed in table 6.7 (IMT in VO$_2$ - black, varied resonator geometry - gray, varied charge carrier concentration - blue) and table 6.8 (PCM based concepts - red). The publications related to "this thesis" are marked separately in bright red and show the second-largest TFOM (refers to the results for GST-8211 presented in this chapter, which are not published "$[np]$" yet) and relatively large resonance shifts $\Delta \tilde{\nu}_{\text{res}}$. The largest and the fourth-largest TFOM were achieved in publications, which were based on collaborations with the University of Stuttgart. In the top of figure 6.14a the symbol * marks the FIR spectral range.
Table 6.7: Different publications focusing on the tuning and switching of resonant frequency positions. "yes\(^*\)" marks papers focusing on post-fabrication variation of the resonant nanostructure geometry.

<table>
<thead>
<tr>
<th>Publication</th>
<th>Sample Design</th>
<th>Volatile</th>
<th>Frequency Position</th>
<th>Technique</th>
<th>Frequency Shift Relative to Initial Position</th>
<th>FWHM of Narrower Peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>Driscoll, 2009</td>
<td>SRR on VO(_2)</td>
<td>yes</td>
<td>158</td>
<td>THz</td>
<td>55</td>
<td>46</td>
</tr>
<tr>
<td>Dicken, 2009</td>
<td>SRR on VO(_2)</td>
<td>yes</td>
<td>1257</td>
<td>THz</td>
<td>43</td>
<td>9</td>
</tr>
<tr>
<td>Lei, 2010</td>
<td>Au nanoparticle on VO(_2)</td>
<td>yes</td>
<td>15823</td>
<td>VIS</td>
<td>15474</td>
<td>651</td>
</tr>
<tr>
<td>Kats, 2013</td>
<td>Y antenna on VO(_2)</td>
<td>yes</td>
<td>1064</td>
<td>MIR</td>
<td>962</td>
<td>102</td>
</tr>
<tr>
<td>Pryce, 2010</td>
<td>SRR on flexible substrate</td>
<td>partly yes</td>
<td>3115</td>
<td>MIR</td>
<td>2833</td>
<td>282</td>
</tr>
<tr>
<td>Ou, 2011</td>
<td>SRS on bridges of different α</td>
<td>yes</td>
<td>1300</td>
<td>NIR</td>
<td>1257</td>
<td>43</td>
</tr>
<tr>
<td>Jun, 2012</td>
<td>SRR on doped GaAs</td>
<td>yes</td>
<td>1112</td>
<td>MIR</td>
<td>1102</td>
<td>10</td>
</tr>
<tr>
<td>Yao, 2013</td>
<td>Graphene on antenna array</td>
<td>yes</td>
<td>1538</td>
<td>MIR</td>
<td>1412</td>
<td>126</td>
</tr>
<tr>
<td>Rodrigo, 2015</td>
<td>Graphene on nanoribbon array</td>
<td>yes</td>
<td>1510</td>
<td>MIR</td>
<td>1760</td>
<td>250</td>
</tr>
<tr>
<td>Altug, 2015</td>
<td>Graphene on nanoribbon array</td>
<td>yes</td>
<td>1510</td>
<td>MIR</td>
<td>1760</td>
<td>250</td>
</tr>
</tbody>
</table>

Note: "yes" marks papers focusing on experimental results, while "no" marks theoretical studies. "Volatile" indicates whether the tuning is reversible. "TFOM\(_{\text{max}}\)" is the maximum magnitude of the Tunable Frequency Optical Mode (TFOM). "FWHM\(_{\text{min}}\)" refers to the minimum full width at half maximum (FWHM) of the TFOM. "THz" denotes terahertz frequency range. "NIR" stands for near-infrared range. "VIS" stands for visible range. "MIR" stands for mid-infrared range. "FIR" stands for far-infrared range.
<table>
<thead>
<tr>
<th>lead author, year</th>
<th>ref.</th>
<th>sample design and tuning mechanism</th>
<th>volatile character</th>
<th>spectral range</th>
<th>res. freq. ( \tilde{\nu}_i ) / cm(^{-1} )</th>
<th>res. freq. ( \tilde{\nu}_f ) / cm(^{-1} )</th>
<th>spectral shift ( \Delta \tilde{\nu} ) / cm(^{-1} )</th>
<th>relative spectral shift ((\Delta \tilde{\nu}/\tilde{\nu}_i)) / %</th>
<th>FWHM(_{\text{min}}) / cm(^{-1} )</th>
<th>TFOM(_{\text{max}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gholipour, 2013</td>
<td>[38]</td>
<td>SRSs with GST-225</td>
<td>yes</td>
<td>NIR</td>
<td>6250</td>
<td>5714</td>
<td>536</td>
<td>8.6</td>
<td>887</td>
<td>0.60</td>
</tr>
<tr>
<td>Zheludev</td>
<td></td>
<td>switching by laser pulse</td>
<td>no</td>
<td>MIR</td>
<td>3766</td>
<td>3157</td>
<td>609</td>
<td>16.2</td>
<td>592</td>
<td>1.03</td>
</tr>
<tr>
<td>Michel, 2013</td>
<td>[239]</td>
<td>rod antennas with GST-326 and InSb</td>
<td>no</td>
<td>MIR</td>
<td>2164</td>
<td>2600</td>
<td>436</td>
<td>20.1</td>
<td>463</td>
<td>0.94</td>
</tr>
<tr>
<td>Wuttig/Taubner</td>
<td></td>
<td>tuning on hot plate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Michel, 2014</td>
<td>[83]</td>
<td>rod antennas with GST-326</td>
<td>yes</td>
<td>MIR</td>
<td>3413</td>
<td>2755</td>
<td>658</td>
<td>19.3</td>
<td>696</td>
<td>0.95</td>
</tr>
<tr>
<td>Wuttig/Taubner</td>
<td></td>
<td>tuning by laser pulse</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tittel 2014</td>
<td>[50]</td>
<td>Al squares on GST-326 and Al mirror</td>
<td>no</td>
<td>MIR</td>
<td>4122</td>
<td>4833</td>
<td>711</td>
<td>17.2</td>
<td>445</td>
<td>1.60</td>
</tr>
<tr>
<td>Taubner/Giessen</td>
<td></td>
<td>tuning on hot plate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yin, 2015</td>
<td>[223]</td>
<td>antenna dimer stack with GST-326</td>
<td>yes</td>
<td>MIR</td>
<td>7519</td>
<td>5831</td>
<td>1688</td>
<td>22.4</td>
<td>3209</td>
<td>0.53</td>
</tr>
<tr>
<td>Taubner/Giessen</td>
<td></td>
<td>tuning on hot plate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rudé, 2016</td>
<td>[250]</td>
<td>Au nanoholes covered with GST-225</td>
<td>yes*</td>
<td>NIR</td>
<td>7519</td>
<td>5831</td>
<td>1688</td>
<td>22.4</td>
<td>3209</td>
<td>0.53</td>
</tr>
<tr>
<td>Pruneri</td>
<td></td>
<td>tuning on hot plate ((A \rightarrow C))</td>
<td>no</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>switching by laser pulse ((C \rightarrow A))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6.8: Different publications focusing on the tuning and switching of nanostructure resonance frequency positions \( \tilde{\nu}_{\text{res}} \) with volatile ("yes"), as well as nonvolatile ("no") character are summarized. Only experimentally demonstrated concepts (mostly in the MIR spectral range) are listed, while different general sample designs are separated by a horizontal line. In case of multiple resonance shifts published, the shift of the antenna resonance position leading to the maximum TFOM\(_{\text{max}}\) is chosen. The following definition is used: \( \Delta \tilde{\nu} = |\tilde{\nu}_f - \tilde{\nu}_i| \) with the initial \( i \) and the final \( f \) resonance peak. The FWHM\(_{\text{min}}\) refers to the narrower peak width (initial compared to final peak). "(A)SRR" abbreviates (asymmetric) split-ring resonator, while "SRS" stands for split-ring slits. The abbreviation "rev." refers to demonstrated reversible switching. The reversibility of the switching process demonstrated by Rudé et al. ("rev.: yes") is given in principle, but has not been shown for the optical pumping, as well as for the heating by a DC current.
CHAPTER 7

Laser-induced switching of mid-infrared nanoantenna resonance frequencies

In the previous chapter, the antenna array resonance frequency tuning by thermal annealing has been investigated. However, by using a hot plate or an oven, the re-amorphization of a crystallized phase-change film can not be realized and thus, the antenna array resonance frequency position $\tilde{\nu}_C$ can not be shifted back to the initial position $\tilde{\nu}_A$. In this chapter, femtosecond and nanosecond laser pulse induced switching of GST-326 thin films adjacent to antenna arrays will be discussed. The first has been applied to switch large sample areas, while the later has been used to address single nanostructures. Since optical laser pulses allow for reversible phase transitions, the reversible shift of the resonance frequency positions $\Delta \tilde{\nu}_{\text{res}}$ of antenna arrays covered with GST-326 will be investigated. The related reflectance spectra will be presented and different imaging methods for the laser marks will be introduced. The work on laser-induced shifting of antenna array resonance frequency positions by applying femtosecond laser pulses was published in [83]. Moreover, two Master’s theses regarding the local switching of antennas [240, 251] were supervised by the author of this thesis.

7.1 Switching of phase-change materials with laser pulses

The necessary temperature treatment for optically (and electrically) triggered switching of PCMs can be summarized as follows: a laser pulse heats the amorphous PCM to a temperature above $T_C$ and thus, allows for structural re-arrangement to the crystalline phase. A much shorter pulse of higher energy increases the PCM temperature in the illuminated area above the liquidus temperature $T_L$ and melts the crystalline phase. A subsequent very fast cooling leads to so-called melt-quenching and as a consequence, to a re-amorphized PCM. This has been described in chapter 3 before. The described switching events can be repeated in cycles up to $5 \times 10^5$ by applying optical pulses [150]. Laser-induced reversible switching of PCMs can be achieved with pulses on a femtosecond [252, 253], picosecond [254] and nanosecond [153, 154] timescale. The relevant the electron and lattice processes in the laser-excited material differ.

In general, if semiconductors, such as PCMs, are excited by laser pulses, the following processes can be described according to Sundaram et al. [255]: After the solid has been excited by a laser pulse with an energy larger than the bandgap $E_G$, photons are absorbed. Due to scattering, electrons and
phonons are re-distributed and the coherent effects of electron-hole pairs oscillating between valence and conduction band are lost. By subsequent carrier-carrier scattering, the energy of the carriers remains unchanged, while carrier-phonon scattering leads to a change in the free carrier energy by phonon absorption and emission. By the latter energy is transferred into the solid lattice and after many scattering processes thermal equilibrium between carriers and lattice can be reached. As soon as electron and phonon system are thermally equal, a single semiconductor temperature is reached. Carrier-carrier scattering occurs between 10 and 100 fs, while thermalization due to carrier-phonon scattering takes several ps\(^1\). Even though thermal equilibrium is reached after several ps, the excess carriers need several \(\mu\)s to decay fully. Their energy can relax to lattice vibrational modes by means of emitted LO phonons. As a consequence the solid is heated above \(T_\text{m}\) in case of sufficient laser pulse energy. Due to a necessary timespan of several ps [256], this simple thermal model can only be valid for ps and ns pulses.

Regarding ultrafast fs laser pulses, the process of melting needs to be discussed further. For fs laser pulses, \(T > T_\text{m}\) can be reached in the solid, however, the material can neither melt, nor vaporize on a sub-ps timescale and thus, is superheated first. As soon as the liquid phase heterogeneously nucleates, which starts from the surface, this melting front expands into the semiconductor. By assuming the maximum melt front velocity given by the speed of sound [257] and a layer thickness \(t = 46\) nm (assumed for C-GST-326 layers used in this work), this so-called heterogeneous melting takes about 135 ps. This approximation follows the principle introduced in [256]. Strong superheating to about 1.5 \(\cdot T_\text{m}\) can lead to so-called homogeneous melting in the sub-ps regime which has been shown for tellurium [258]. If the fs laser excitation is in the intensity range of TW/cm\(^2\), a high-density electron-hole plasma can be generated. As a consequence lattice disordering on a timescale of about 100 fs occurs, which has been observed for GaAs and Si [259], as well as for InSb [257], and can be assumed for many more covalently bonded\(^2\) semiconductors. Due to the much shorter timespan necessary compared to thermal melting processes, this excitation of lattice instabilities is called non-thermal melting. Thermal diffusion leads to a temperature decrease in the illuminated sample area, which is accompanied by re-solidification of the molten phase. On a \(\mu\)s timescale room temperature can be established. Additionally, ablation of individual atoms or ions from the optically excited solid can be caused by the electron-hole plasma generated of high intensity fs pulses as described above. The ultrafast laser excitation transfers the semiconductor in a non-equilibrium state of high \(T\) and high pressure [256]. As already introduced for heterogeneous melting, a wave front (rarefaction wave) proceeds into the material starting at the surface with the speed of sound. Thus, melting can occur on shorter timescales than ablation (or expansion). In case of pulse intensities close to the ablation threshold, liquid and gas phase can coexist in bubble-like structures, which are evident as so-called Newton fringes [256].

Depending on the desired switching mechanism - re-crystallization or re-amorphization - different laser intensities, as well as different pulse durations need to be considered. In the following, both mechanisms of the laser-induced PCM phase transition are discussed briefly.

\[^1\]Carrier concentrations \(n = 10^{17} \ldots 10^{22} \text{ cm}^{-3}\) are assumed [255], matching \(n\) measured for GST compounds [115].

\[^2\]In contrast to Si, which is covalently bonded, GaAs and InSb show a mixed ionic-covalent bonding.
7.1 Switching of phase-change materials with laser pulses

Crystallization

As described in the fundamental chapter on PCMs, crystallization is based on an ordering process of the atoms in a solid state at \( T_m > T > T_C \). Hence, an excitation pulse with a pulse duration \( \tau_C \) needs to allow for this structural re-arrangement, which would be interrupted by an early temperature decrease below \( T_C \). According to the general description of laser-induced processes in semiconductors given on the previous page, laser pulses with \( \tau \) of several ns can be considered as direct heating of the sample, since thermal equilibrium is reached in the illuminated sample and excess carriers are decayed. As a consequence, PCM thin films can be crystallized by single laser pulses with pulse durations \( \tau_C \) in the range of several ns or even longer. Single pulse crystallization with a pulse duration of \( \tau = 30 \text{ ps} \) has been shown for an optimized sample design regarding the diffusivity of all layers [254]. Nevertheless, crystallization is more problematic to achieve with ultrashort pulses in the fs range due to the existence of a minimum time required for stable crystalline nuclei to form and grow. Hence, a sequence of several fs pulses needs to be applied for crystallization of fully amorphous PCM films\(^3\). This can be realized with consecutive pulses and an adjusted inter-pulse delay. The first pulse leads to an increased electron density, which can be kept during the pulse sequence in case of a delay time between subsequent pulses below the decay time of the increased electron density. This switching process is called stimulated crystallization. For re-amorphized melt-quenched MQ-GST-225, a maximum delay time of 100 ps, which is interpreted as effective carrier lifetime, has been found [252].

Amorphization

To melt-quench a re-crystallized PCM, the thin film needs to be transferred into its liquid state. The pronounced difference in melting on the fs and ns timescale has been discussed in detail on the previous page. Compared to the laser-induced crystallization, much higher laser pulse intensities are necessary to amorphize PCM thin films. The temperature in the GST needs to exceed \( T_m \). Even a relatively high laser intensity is required, the maximum values are limited by the onset of ablation. A second necessary condition for amorphization of PCMs is melt-quenching. This process is associated with a very fast cooling rate and crucial to freeze the disordered phase. This undercooling necessary for amorphization to take place, can be achieved by using a substrate with a relatively high thermal conductivity \( k_T \) as heat sink. As can be seen from table 7.1, silicon can act as efficiently heat sink for GST compounds.

<table>
<thead>
<tr>
<th>material</th>
<th>( k_T / \text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1} )</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>142</td>
<td>[220]</td>
</tr>
<tr>
<td>SiC</td>
<td>3.6...4.9</td>
<td>[260]</td>
</tr>
<tr>
<td>Si₃N₄</td>
<td>3</td>
<td>[261]</td>
</tr>
<tr>
<td>GST-326</td>
<td>0.6...0.7</td>
<td>[262]</td>
</tr>
<tr>
<td>GST-8211</td>
<td>0.5...0.5</td>
<td>[262]</td>
</tr>
</tbody>
</table>

\(^3\)In case of existing "crystalline embryos", single fs pulses have been reported to induce crystallization [252].
In the literature on laser-induced switching of PCMs, laser pulses on different timescales ranging from fs to ns were applied. Thereby, the laser energy is given either as laser pulse peak power $P_0$ in mW or as peak fluence $F_0$ in mJ/cm$^2$. The fluence $F$ describes the energy incorporated into the sample and is defined as the ratio of the incident beam energy to the irradiated sample area. The peak fluence $F_0$ can be calculated as follows:

$$F_0 = \frac{2P_0\tau}{\pi r_0^2} \quad (7.1)$$

where $\tau$ describes the pulse duration and $r_0$ is defined as the beam radius, which includes about 86% of the beam intensity (intensity decreased to $1/e^2$) [263]. It has to be noted that a circular laser beam profile is assumed in equation 7.1. For an elliptical cross section of the laser beam, $r_0$ can be replaced by the two axes of the ellipse $L_x$ and $L_y$, since the area of an ellipse is defined by $\pi \cdot L_x \cdot L_y$. The axis in $x$-direction of the elliptical laser beam cross section is given by $L_x$, while the axis in $y$-direction is $L_y$.

It depends on the thermal transport processes relevant for the specific pulse timescale, if power $P$ or fluence $F$ are chosen to describe the energy applied to the PCM film. As long as equilibrium thermodynamics do not apply - as for fs pulses - $F$ is chosen over $P$, while $P$ is used in the framework of ns experiments. In appendix B.5, detailed parameters for laser pulse switching are listed for exemplary studies. It can be seen that the studies on fs laser switching led to much larger PCM areas with a successfully conducted phase change, than the experiments with ns laser pulses. The power of the laser diodes applied for ns laser-induced switching of the PCMs is too small to illuminate areas of $10^4 \mu$m$^2$, which in contrast was realized by fs laser sources. As a consequence, the laser setup can be chosen according to the supposed application. For the switching of large GST-326 thin films covering (multiple) nanoantenna arrays, fs laser pulses were applied in this work. In contrast, to locally switch the GST-326 thin film on (single) metal nanostructures, a setup suited for laser pulses on a ns timescale was built during the Master’s thesis of T. Kalix. In the following, both setups and the related experimental results will be discussed.

### 7.2 Laser-induced switching of large areas of phase-change material

Major parts of the following work have been published in [83]. Due to a collaboration with Zalden and Lindenberg at the Stanford University, the use of a setup for fs laser pulses at the Stanford Linear Accelerator Center (SLAC) was possible. The areas of the PCM, which were addressed by laser pulses to induce a phase change and where an effect on the PCM is visible, will be called spots in the following. The fs laser excitation allowed for the switching of large areas with a long axis of the switched spots $LA$ of more than 200 $\mu$m on the samples. Since the spots showed an elliptical shape, the term "axis" instead of diameter has been used.

In the following, the laser setup will be described first. Afterwards, the fluence and temperature profile characteristic for fs laser-induced switching will be discussed. Finally, antenna arrays with GST-326 superstrates have been addressed by fs laser pulses and the corresponding antenna array reflectance spectra will be presented.
7.2 Laser-induced switching of large areas of phase-change material

7.2.1 Setup and sample specifications for femtosecond laser switching

With the fs laser source, single pulses were emitted by a sequential arrangement of a Ti:sapphire oscillator and a Ti:sapphire regenerative amplifier. The energy of each pulse was 1.65 mJ, while a rotatable polarizing beam splitter was used for attenuation of the optical pulses. The laser provided a beam with 800 nm (12500 cm\(^{-1}\)) central wavelength. The setup was also operated in a repetitive mode with a repetition rate of 960 Hz. The laser beam was focused by a spherical lens with 400 mm focal length. The total power of the laser at a given repetition rate was measured with a calibrated power meter behind the focal spot. The sample was positioned with an \(xyz\)-translation stage at the focal spot. Furthermore, this stage was used to scan a knife edge through the focal spot in order to determine the laser fluence at the position of the sample as a function of the transmission through the polarizing beam splitter. At the position of this stage, a Gaussian beam profile with FWHM of 230 - 270 µm on the surface of the PCM thin film was recorded.

Preliminary experiments on bare GST-326 layers have been conducted to determine the necessary fluence for re-amorphization \(F_{MQ}\) and crystallization \(F_{RC}\), the pulse duration \(\tau\) as well as the duration of the pulse sequence \(\tau_{seq}\) required to crystallize the amorphous thin film. The starting values for \(F\) and \(\tau\) have been chosen according to publications on fs laser-induced switching of GST compounds, such as the work of Cotton et al. [252]. There, GST-225 thin films with thickness \(t_C = 40\) nm, deposited on a SiO\(_2\)/Si substrate were re-crystallized with at least three consecutive pulses of \(F_{RC} = 17\) mJ/cm\(^2\), while re-amorphization was realized with \(\tau_{MQ} = 100\) fs and \(F_{MQ} = 53\) mJ/cm\(^2\). Based on these parameters, the laser fluence \(F\) was varied between about 12 mJ/cm\(^2\) < \(F_C < 32\) mJ/cm\(^2\) regarding crystallization and about 22 mJ/cm\(^2\) < \(F_{MQ} < 108\) mJ/cm\(^2\) regarding re-amorphization, while the pulse duration was set to \(\tau = 50\) fs for the investigations shown here. The corresponding camera images and spectra of bare GST-326 addressed by fs laser pulses are discussed in appendix B.6.

![Graphs showing experimental and calculated thin film spectra](image)

Figure 7.1: On the left, experimental spectra for a thin film of GST-326 in all investigated phases A (dashed black), C (solid black), MQ (solid red) and RC (solid gray) normalized to a Au mirror are shown. These thin films have been used for normalization of the antenna array reflectance spectra. The reflectance of the differently treated thin film displayed here, has been used to prove the structural phase of the GST-326 superstrate. This has been further confirmed by comparing the experimental data with the calculated TFIs for A- and C-GST-326 displayed on the right already known from figure 5.9. Thus, the chosen laser parameters allow for reversible switching of the investigated GST-326 film, which has been sputter-deposited on a silicon substrate.
A single laser pulse with the fluence $F_{MQ} = 52.7 \text{ mJ/cm}^2$ was sufficient to induce re-amorphization from C- to MQ-GST-326 and a fs excitation sequence of about 960 pulses (1 s repetitive pulsing) with $F_C = 29.5 \text{ mJ/cm}^2$ drove the re-crystallization process. FTIR spectra of the MQ-GST-326 and the RC-GST-326 thin films show that the parameters chosen for fs laser-induced switching of the GST-326 allowed for successful re-amorphization and re-crystallization as can be seen in figure 7.1. There, the measured amorphous as-deposited and melt-quenched GST-326 thin films show a nearly identical normalized reflectance. The same accounts for the annealed and re-crystallized GST-326 thin films. Furthermore, the normalized reflectance spectra match the calculated thin film interferences (cf. chapter 5) very well. According to the experimental spectra the femtosecond laser induced switching of GST-326 thin films was successful.

In figure 7.2, the fluence and temperature profiles $F(t)$ and $T(t)$ for re-amorphization and re-crystallization are sketched including the determined parameters fluence $F_C$, $F_{MQ}$ and pulse duration $\tau_{seq}$. For the re-amorphization of the C-GST-326 layer, the crystal lattice was molten with a pulse of a high fluence $F_{MQ}$ and subsequently quenched to $T_R$ to avoid any re-crystallization of the atomic structure. In contrast, crystallization was induced by the repetitive laser excitation and in turn the reflectance of the PCM thin film - and thus, the temperature $T$ - has been assumed to continuously increase. This assumption was suggested by the fs pump-probe experiments on the PCM AIST published by Zalden et al. [84]. There, it was supposed that heat accumulates in the silicon substrate and as a consequence, a temperature offset added up to the crystallization process, which is shown as $\Delta T$ in figure 7.2. Indications for increased reflectance implying partial crystallization just by repetitive fs laser pulses have also been given for GST-225 by the investigations of Cotton et al. [252] and Wang et al. [264]. Due to the relatively long inter-pulse delay ($>100$ ps), the switching mechanism applied in this work is different from stimulated crystallization described on page 123.

The same sample design as already introduced in chapter 6 - antenna arrays with a 50 nm A-GST-326 superstrate, embedded in the GST-326 and on a GST-326 substrate - were investigated regarding fs laser induced switching of large GST-326 areas. More specifically, the exact same sample was used for the antenna array resonance tuning described in chapter 6, as well as for the switching experiments with femtosecond laser pulses. Thus, the samples were annealed on a hot plate before the laser switching experiments and hence, the initial phase of the GST-326 for the switching experiments was crystalline. In turn, the laser-induced phase changes studied were re-amorphization and re-crystallization. In figure 7.3, the sample treatment is schematically displayed. The A-GST-326 thin film with a thickness of $t_A = 50 \text{ nm}$ was crystallized (➀) on a hot plate by annealing for 30 min at $T = 180^\circ\text{C}$. Single fs laser pulses were used to switch the phase of large GST-326 areas covering specific writefields (denoted as a and b in figure 7.3) including several antenna arrays of different antenna length $L$ (500 and 400 nm). The GST-326 areas, which were directly addressed by a single fs laser pulse, changed in its re-amorphized phase MQ-GST-326 (➁). Finally, one of the two investigated writefields was re-crystallized (➂) with a fs laser pulse sequence $\tau_{seq} = 1 \text{s}$. The antenna arrays covered with MQ- and RC-GST-326 were separated on one sample which allowed for a comparison of the antenna array spectra after the laser excitation experiments were concluded. This was necessary, since the fs laser excitation was conducted at the Stanford University, while the reflectance spectra were collected at the RWTH Aachen University afterwards.
7.2 Laser-induced switching of large areas of phase-change material

Figure 7.2: The temperature profile $T(t)$ in the GST-326 layer, which is triggered by fs laser pulses, and the corresponding fluence profile $F(t)$ (red) are schematically shown for re-amorphization $C \rightarrow MQ$ and re-crystallization $MQ \rightarrow RC$. The top panel visualizes $F$ and the single laser pulse for $C \rightarrow MQ$, as well as the applied pulse sequence for $MQ \rightarrow RC$. The pulse duration $\tau$ is kept constant, while $F$ is decreased for re-crystallization compared to re-amorphization. As a consequence of the fs laser pulses, $T$ in the PCM changes strongly. The timescales relevant for $C \rightarrow MQ$ are compared in the inset next to the $T(t)$ profile for re-amorphization. The pulse sequence used to re-crystallize the GST-326 layer leads to a temperature increase $\Delta T$ over the entire sequence time of $1$ s ($\approx 960$ pulses). It can be assumed that $\Delta T < 50^\circ$C [265]. The $T(t)$ and $F(t)$ diagrams are not to scale, while axis breaks indicate the differences in timescale regarding laser excitation and evolution of $T$. The room temperature is marked by $T_R$. Neither the crystallization $T_C$, nor the liquidus temperature $T_L$ are marked since these parameters are only valid for specific heating and cooling rates, which are not given in the context of ultrashort laser pulses.

Figure 7.3: The treatment for samples including nanoantenna arrays and a GST-326 thin film is described schematically. A 50 nm A-GST-326 superstrate with writefields $a$ and $b$ has been heated on a hot plate for 30 min with $T = 180^\circ$C, which has led to crystallization (studied in chapter 6). A dark field light microscopy image (only the light scattered by the sample has been collected by the objective lens) of a writefield is shown (white scale bar: 50 nm). Hereafter, the sample has been excited with single fs laser pulses. Thus, only the C-GST-326 on $a$ and $b$ has been re-amorphized to its melt-quenched phase $\oplus$ (red) and the untreated GST-326 thin film has remained crystalline. The size of the MQ-GST-326 spot has been defined by its long axis $LA$. Finally, a pulse sequence has been used to re-crystallize the MQ-PCM cover layer on $b \ominus$ (RC, gray). While single spots have been sketched multiple overlapping spots can be found in a sample image detail taken with the FTIR microspectrometer camera (black scale bar: 100 mm). The original image is discussed in detail in appendix B.6. The symbols $\ominus$, $\otimes$ and $\ominus$ are used according to the terminology given in table B.5.
7.2 Laser-induced switching of large areas of phase-change material

Figure 7.4: The reflectance spectra of the antenna arrays covered with as-deposited A-GST-326 (dashed black) and annealed C-GST-326 (solid black) are displayed in the upper panels. The fs laser excitation has led to the spectra for MQ-GST-326 (solid red and dashed black) and RC-GST-326 (solid gray and solid black) shown in the middle panel (raw data compared to moving average of a subset of 35 data points). The dips at about 2350 cm\(^{-1}\) have been ascribed to atmospheric CO\(_2\) absorption. The arrows in the spectra indicate the direction of the antenna array resonance frequency shift \(\Delta\tilde{\nu}_{\text{res}}\) upon the induced phase change. The bottom panel represents all peak positions listed according to the sample history. The line and color scheme has been chosen according to figure 7.3.

7.2.2 Far-field reflection spectra of antenna arrays

Following the sample history presented in figure 7.3, reflectance spectra were collected with a 36-fold objective, while the light incided under an angle of about 27° and was polarized along the antennas. Each spectrum was taken under ambient conditions with a resolution of 4 cm\(^{-1}\) and averaged by 200 scans. An aperture of about (20 × 20) \(\mu\text{m}\)\(^2\) defined the area the light reflected by the sample was collected from. The spectra of the antenna arrays were normalized to background spectra of bare GST-326 films, which were collected on equal terms. As it was mentioned in chapter 6, the background spectra - GST-326 thin films on Si substrates - were taken on the sample the antenna arrays are fabricated on, but on a position next to the writefields. These writefields were encircled by thick metallic frames. Exemplary sample images are shown in appendix, figure B.3. The reflectance spectra for arrays with antenna lengths \(L = 500\) nm and \(L = 400\) nm are displayed in figure 7.4, while the corresponding background spectra were already introduced in figure 7.1. In the upper panel of figure 7.4, the reflectance spectra of the antenna arrays covered with as-deposited A-GST-326 and annealed C-GST-326 can be seen. These spectra for A- and C-GST-326 were already depicted in figure 6.2. The middle panel relates to the spectra for reversible switching using fs laser pulses, upon which C-GST-326 was re-amorphized to MQ-GST-326 and in turn was re-crystallized to RC-GST-326. Both reflectance spectra were collected on the same sample, but on different writefields as it is described by
The resonance frequency positions $\tilde{\nu}_{\text{res}}$ corresponding to all shown spectra are visualized by empty (amorphous phases) and filled circles (crystalline phases) in the bottom panel.

After the sample was addressed by single fs laser pulses, pronounced antenna array resonance peaks with their resonance frequency position $\tilde{\nu}_{\text{res}}$ were detected by FTIR microspectroscopy. The single fs laser pulse which was applied for re-amorphization has led to a shift of the resonance frequency position $\Delta \tilde{\nu}_{\text{res}}$ from 2164 to 2600 cm$^{-1}$ for antennas with length $L = 500$ nm and from 2605 to 3136 cm$^{-1}$ for antennas with length $L = 400$ nm. Upon re-crystallization a resonance frequency shift $\Delta \tilde{\nu}_{\text{res}}$ of 175 cm$^{-1}$ ($L = 500$ nm) and of 246 cm$^{-1}$ ($L = 400$ nm) back to lower wavenumbers was observed.

While the resonance position of the antenna arrays covered with GST-326 was shifted to higher, as well as to lower wavenumbers by the means of fs laser excitation, a decreased peak reflectance was determined. It has been assumed that oxidation of the GST-326 thin film has led to this lowering. Oxidation has been reported to be enhanced at high temperatures during the switching experiments [87]. Therefore, the sample storage between the annealing and the laser experiments (about 6 months) as well as the excitation by the laser pulses has been assumed to contribute to a progressed GST-326 oxidation. This situation will be further described in section 7.3.5 which discusses the application of an oxidation protection layer of $(\text{ZnS})_{80}(\text{SiO}_2)_{20}$.

The raw data of the measured antenna array reflectance spectra covered with GST-326 thin films, which were excited by fs laser pulses, have been found to be much more noisy than the spectra associated with A- and C-GST-326. All spectra have been detected with the same resolution (4 cm$^{-1}$) while the number of averaged scans has been higher for the spectra associated with MQ- and RC-GST-326 than for the spectra with A- and C-GST-326. Later it has been found that the FTIR microspectrometer was slightly misaligned and identified as the reason for the noise of the spectra for MQ- and RC-GST-326.

Besides, the resonance frequency positions of the amorphous phases $\tilde{\nu}_{\text{A}}$ and $\tilde{\nu}_{\text{MQ}}$ and especially of the crystalline phase $\tilde{\nu}_{\text{C}}$ and $\tilde{\nu}_{\text{RC}}$ differ: $\tilde{\nu}_{\text{MQ}} - \tilde{\nu}_{\text{A}} \approx 120$ nm and $\tilde{\nu}_{\text{RC}} - \tilde{\nu}_{\text{C}} \approx 273$ nm (averaged for both antenna lengths $L$). The resonance shift due to re-crystallization $\tilde{\nu}_{\text{MQ}} - \tilde{\nu}_{\text{RC}}$ is much smaller than the resonance shift associated with the sample annealing $\tilde{\nu}_{\text{A}} - \tilde{\nu}_{\text{C}}$. Furthermore, the resonance frequency position related to the MQ-GST-326 $\tilde{\nu}_{\text{MQ}}$ is at higher wavenumbers than the resonance frequency position associated with A-GST-326 $\tilde{\nu}_{\text{A}}$.

The successful switching of the GST-326 thin films (figure 7.1) and the differences between the antenna array reflectance spectra of the two amorphous and the two crystalline phases (figure 7.4) indicate that the presence of the nanoantenna arrays has influenced the laser-induced switching of the GST-326 phase. In the following a possible damage of the nanorod antennas, a difference in the local absorption of the GST-326 in close vicinity of the antennas and the bare GST-326 thin film, as well as a damage in the PCM thin film close to the antennas will be discussed.
7.2 Laser-induced switching of large areas of phase-change material

antenna arrays with GST-326 thin films as superstrate, \( t_A = 50 \text{ nm} \)

<table>
<thead>
<tr>
<th>antenna length ( L = 500 \text{ nm} )</th>
<th>antenna length ( L = 400 \text{ nm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>phase ( ar{\nu}_{\text{res}} ) / \text{ cm}^-1</td>
<td>phase ( ar{\nu}_{\text{res}} ) / \text{ cm}^-1</td>
</tr>
<tr>
<td>shift ( \Delta \bar{\nu}_{\text{res}} ) / %</td>
<td>shift ( \Delta \bar{\nu}_{\text{res}} ) / %</td>
</tr>
<tr>
<td>FWHM ( \Delta \bar{\nu}_{\text{res}} ) / \text{ cm}^-1</td>
<td>FWHM ( \Delta \bar{\nu}_{\text{res}} ) / \text{ cm}^-1</td>
</tr>
<tr>
<td>TFOM ( i )</td>
<td>TFOM ( i )</td>
</tr>
<tr>
<td>-----------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>A 2490</td>
<td>A 3006</td>
</tr>
<tr>
<td>598</td>
<td>775</td>
</tr>
<tr>
<td>C 2164</td>
<td>C 2605</td>
</tr>
<tr>
<td>326 13.1</td>
<td>401 13.3</td>
</tr>
<tr>
<td>757 0.55</td>
<td>1028 0.52</td>
</tr>
<tr>
<td>MQ 2600</td>
<td>MQ 3136</td>
</tr>
<tr>
<td>436 20.1</td>
<td>531 20.4</td>
</tr>
<tr>
<td>463 0.58</td>
<td>617 0.52</td>
</tr>
<tr>
<td>RC 2425</td>
<td>RC 2890</td>
</tr>
<tr>
<td>175 6.7</td>
<td>246 7.8</td>
</tr>
<tr>
<td>425 0.38</td>
<td>513 0.40</td>
</tr>
</tbody>
</table>

Table 7.2: This table summarizes antenna array resonance frequency positions \( \bar{\nu}_{\text{res}} \), the shifts of these positions \( \Delta \bar{\nu}_{\text{res}} \) and the peak widths FWHM for a GST-326 antenna superstrate extracted from the normalized reflectance spectra shown in figure 7.4. The phase changes have been realized by thermal annealing (crystallization to C-GST-326), as well as by fs laser pulses (re-amorphization to MQ-GST-326 and re-crystallization to RC-GST-326). Two different antenna lengths \( L = 500 \) and 400 nm have been investigated. The tuning figure of merit TFOM has been related to the initial phase \( i \). The spectral data for A- and C-GST-326 has been taken from tables 6.3 and 6.4.

Consideration of a possible antenna damage

The reflectance spectra of the A- and MQ-GST-326 thin films are similar, as well as of the C- and RC-GST-326 thin films (figure 7.1), which indicates a successful reversible switching of the GST-326 phases with the chosen laser pulse fluence \( F \) and pulse duration \( \tau \). However, the resonance positions \( \bar{\nu}_{\text{MQ}} \) and \( \bar{\nu}_{\text{A}} \) differ by more than 100 cm\(^{-1}\) while \( \bar{\nu}_{\text{RC}} \) and \( \bar{\nu}_{\text{C}} \) differ even by more than 250 cm\(^{-1}\). One possible reason might be damaged antennas due to the fs laser excitation, since the central wavelength of the excitation laser is equal to the energy of the aluminum interband transition\(^4\) at about 1.55 eV (800 nm).

Since the SEM images show rectangularly shaped nanoantennas (cf. figure 7.7) no general damage, but only a decrease of the antenna length \( L \) due to fs laser-induced damage is assumed. This decrease of the antenna length \( L \) would be accompanied by a shift of the antenna array resonance frequency position \( \Delta \bar{\nu}_{\text{res}} \) to higher wavenumbers compared to the resonance frequency position of the antennas with the initial length \( L \). Indeed, the resonance frequency position associated with the MQ-GST-326 thin film \( \bar{\nu}_{\text{MQ}} \) is shifted to higher wavenumbers compared to the resonance frequency position associated with A-GST-326 \( \bar{\nu}_{\text{A}} \). This could match with a possible decrease of the antenna length \( L \). The same behavior can be seen for the comparison between \( \bar{\nu}_{\text{RC}} \) and \( \bar{\nu}_{\text{C}} \). However, the shortening of the antennas of more than 20 nm (observational error of the used SEM [199]) upon annealing was excluded by using SEM images of the antenna arrays (cf. figure 7.7). Furthermore, a decrease in the antenna length \( L \) of less than 20 nm would not be sufficient to explain the shifts \( \bar{\nu}_{\text{MQ}} - \bar{\nu}_{\text{A}} \) and \( \bar{\nu}_{\text{RC}} - \bar{\nu}_{\text{C}} \). As an example, a decrease of the antenna length \( L \) from 500 nm to 446 nm would have led to the measured resonance frequency position \( \bar{\nu}_{\text{RC}} = 2425 \text{ cm}^-1 \) using the approximation of the antenna array resonance frequency position given by equation 2.13 and assuming a constant real part

\(^4\)The optical interband absorption of fcc Al originates mainly from transitions between parallel bands near the \( K \) point, which are separated by \( \approx 1.55 \text{ eV} \) [15].
of the refractive index of the antenna surrounding \( n_{\text{eff}} \) for the spectral range between \( \tilde{\nu}_{C} \) and \( \tilde{\nu}_{RC} \):

\[
\lambda_{\text{res}} = 2 \cdot n_{\text{eff}} \cdot L
\]  

(7.2a)

\[
\tilde{\nu}_{C,L=500\text{ nm}} = 4621 \text{ nm}
\]

(7.2b)

\[
n_{\text{eff, C-GST}} = \frac{\tilde{\nu}_{C,L=500\text{ nm}}}{2 \cdot L} = \frac{4621 \text{ nm}}{2 \cdot 500 \text{ nm}} \approx 4.62
\]

(7.2c)

\[
\tilde{\nu}_{RC,L=500\text{ nm}} = 4124 \text{ nm}
\]

(7.2d)

\[
L_{RC} = \frac{\tilde{\nu}_{RC,L=500\text{ nm}}}{2 \cdot n_{\text{eff, C-GST}}} = \frac{4124 \text{ nm}}{2 \cdot 4.62} = 446 \text{ nm}
\]

(7.2e)

This decrease of the antenna length by about 54 nm was excluded by SEM imaging. Thus, the difference between the antenna array resonance positions of amorphous GST-326 phases \( \tilde{\nu}_{MQ} - \tilde{\nu}_{A} \) and crystalline GST-326 phases \( \tilde{\nu}_{RC} - \tilde{\nu}_{C} \) was not based on the fs laser-induced shortening of the antennas.

A further discussion of the fs laser-induced sample damage can be found in appendix B.6 on page 197, where SEM images of damaged samples (GST-326 as substrate and as embedding medium) are shown.

### Absorption at the femtosecond laser wavelength

The influence of the aluminum antennas on the absorption of the fs excitation laser beam has been studied by calculating the absorption spectra of as-deposited A-GST-326 and annealed C-GST-326 thin films without antenna arrays and with antennas covered by the GST-326. These calculations performed with the software CST Microwave Studio are displayed in figure 7.5. The fs laser beam wavelength is visualized in the inset of figure 7.5a. It has to be emphasized, that the dielectric data for optically re-amorphized MQ-GST-326 has not been available and therefore, the dielectric data for as-deposited A-GST-326 has been used for the shown calculations. However, the permittivity of MQ-GST-326 might not deviate from A-GST-326, since its electronic properties seem to be similar \[266\] \[^5\]. Furthermore, the reflectivity of as-deposited and melt-quenched GST-225 was reported to be identical \[267, 268\].

The presence of the antenna arrays led to an increase of the calculated normalized absorption of A-GST-326 by about 11.5% compared to the calculated absorption of the bare PCM thin film. In contrast, the antennas led to an increase of the absorption of the annealed C-GST-326 only by about 3.9%. Since this increase can be ascribed exclusively to the antennas, these values are related to the antenna area. The per cental area of the substrate, which is covered by aluminum antennas was discussed in section 6.3.2 already. The sample coverage with antennas is 5% for antennas with length \( L = 500 \text{ nm} \) and 6.25% for antennas with length \( L = 400 \text{ nm} \) (calculations in appendix B.1). Thus, 5% of the sample area have led to a 11.5% increase of the absorption of the entire sample including the antennas and the A-GST-326 layer. This pronounced absorption increase could have led to an increased temperature of the MQ-GST-326 on top of the antennas during the re-crystallization process. In turn, this could have led to a re-amorphization of the GST-326 on top of the antennas.

\[^5\] Nevertheless, structural differences were reported for GST-326 \[266, 267\].
7.2 Laser-Induced Switching of Large Areas of Phase-Change Material

Figure 7.5: The calculated normalized absorption spectra of a GST-326 thin film (left spectra: A-GST-326, right spectra: C-GST-326) with (gray) and without an antenna array (black) are displayed for the spectral range of the fs laser beam. The antenna arrays were calculated with antenna length \( L = 500 \) nm, width \( w = 110 \) nm, height \( h = 35 \) nm and separation distance \( (d_x, d_y) = (2L, 2L) \). The inset shows the fs laser beam spectrum, while the dashed lines mark the spectral range with a laser beam intensity larger than \( 1/e \) of the peak value. Fundamentals regarding the simulation parameters are given in appendix C.

Figure 7.6: The calculated total electromagnetic loss per volume (color coded, calculated at \( 800 \) nm) for A-GST-326 on a silicon substrate (top) and as antenna superstrate (bottom) is depicted in 7.6a. Due to the presence of the antennas (black) with length \( L = 500 \) nm, the electromagnetic loss is strongly increased. The increased loss suggests two sample schemes prior and after the fs laser-induced crystallization are given in figure 7.6b. While the bare MQ-GST-326 thin film have been fully re-crystallized (top scheme), the presence of the antennas has led to re-amorphization in vicinity of the antennas. In the area, where no antenna is present, the re-crystallization of the MQ-GST-326 can be achieved. Thus, the antenna array resonance frequency position is influenced by an effective medium based on RC-GST-326, as well as MQ-GST-326.
Based on these findings, the total electromagnetic loss per volume was calculated for as-deposited A-GST-326 at the wavelength of the fs laser beam (800 nm) as shown in figure 7.6a. The calculation for A-GST-326 is assumed to be valid for MQ-GST-326 as well. The numerical results were realized using the finite integration method with the software CST Microwave Studio (cf. appendix C).

The calculated electromagnetic loss at the wavelength of the excitation is strongly increased due to the presence of the antennas. This matches the calculated absorption shown in figure 7.5a. This can be explained by taking into account that the aluminum interband transition is at the center wavelength of the laser (800 nm or 1.55 eV). As a consequence the re-amorphization has occurred in the GST-326 covering the antennas which is illustrated in figure 7.6b. Thus, the antenna array resonance frequency position has been influenced by a mixture of amorphous and crystalline phases of the GST-326. Since the real part of the dielectric function of A-GST-326 $\varepsilon_{1,A}$ is much smaller than the real part of the dielectric function of C-GST-326 $\varepsilon_{1,C}$, the re-amorphized "antenna covers" shift the antenna array resonance frequency position $\nu_{\text{res}}$ to higher wavenumbers relative to a fully crystalline GST-326 superstrate. Furthermore, the amorphous volume fraction in the vicinity of the antennas influences the antenna array resonance position $\nu_{\text{res}}$ stronger as it would in a uniform and random distribution of the re-crystallized and re-amorphized GST-326, since the field enhancement is locally concentrated in the near field of the antennas.

**Indication for visible density contrast of GST-326**

In SEM images of antenna arrays with an optically switched GST-326 antennas cover layer vermicular features around the antennas can be identified. These might represent small topographical features due to volume changes in the PCM. Amorphous and crystalline phases exhibit a pronounced density contrast. Upon crystallization of the GST-326, the density increases from 5.80 to 6.25 g/cm$^3$ (cf. table 3.1). Repeated volume changes can lead to a local buildup of stress in the thin film and finally to physical voids and phase separations in GST compounds [269]. According to the corresponding SEM image of antennas covered by a GST-326 thin film shown in figure 7.7, stress and small cracks in the GST-326 thin film on top of the antennas might have occurred, especially in close vicinity of the antennas. As a consequence, a local decrease of the real part of the refractive index of the antenna surrounding $n_{\text{eff}}$ (stronger influence of $n_{\text{air}} = 1$ close to the antennas) and could serve as (additional) explanation for the shift of the antenna array resonance frequency positions associated with RC-GST-326 $\nu_{RC}$ to higher wavenumbers compared to the antenna array resonance frequency positions associated with C-GST-326 $\nu_{C}$ (cf. figure 7.4).

![Figure 7.7: Shown is a SEM image of aluminum antennas ($l = 600$ nm) covered with GST-326, which was annealed on a hot plate, re-amorphized by a single femtosecond laser pulse and re-crystallized by a femtosecond laser pulse sequence. The image was extensively post-processed to highlight features in the GST-326 thin film. The contrast, the exposure and the sharpness of the image were maximized upon condition that the main information on the image is maintained.](image-url)
7.3 Laser-induced switching of small areas of phase-change materials

7.2.3 Summary

It has been shown that single femtosecond laser pulses allowed for a re-amorphization of large areas of GST-326 thin films while a pulse sequence led to re-crystallization of these areas. The determined switching parameters laser fluence $F$ and pulse duration $\tau$ were applied to switch the GST-326 thin film which covered several antenna arrays as well. Detected reflectance spectra showed pronounced antenna array resonance peaks and a shift of the antenna array resonance frequency position $\Delta \tilde{\nu}_{\text{res}}$ upon the laser-induced phase transitions. A mismatch between the antenna array resonance frequency positions for the amorphous phases (A- and MQ-GST-326) $\tilde{\nu}_{\text{MQ}} \neq \tilde{\nu}_A$ and the crystalline phases (C- and RC-GST-326) $\tilde{\nu}_{\text{RC}} \neq \tilde{\nu}_C$ respectively was detected. Thus, a strong influence of the antennas on the switching process has been assumed. An enhanced sample absorption due to the presence of the nanoantennas has been found. Based on the calculated total electromagnetic loss a possible explanation for the mismatch between the resonance frequency positions ($\tilde{\nu}_{\text{MQ}} \neq \tilde{\nu}_A$, $\tilde{\nu}_{\text{RC}} \neq \tilde{\nu}_C$) would be the re-amorphization on top of the antennas during the re-crystallization process.

7.3 Laser-induced switching of small areas of phase-change materials

In section 7.2, the excitation of the sample by femtosecond laser pulses allowed for the switching of elliptical GST-326 areas with axes of $L_A > 200 \mu m$. Due to these large axes an entire antenna array was addressed at once. Considering applications in the field of metamaterials or metasurfaces, the local change of their optical properties could lead to a (gradual fine-)tuning of their resonance properties and thus, even to new functionalities. For the realization of local addressing, the optical properties of single nanostructures need to be controlled. To introduce a suited concept, the same sample architecture as described earlier was investigated: arrays of nanorods covered with GST-326 thin films. If only single nanoantennas are supposed to be addressed, the phase of the GST-326 needs to be changed for small areas with axes between about $0.5 \mu m \leq L_A \leq 2 \mu m$ depending on the antenna size and separation. Here, single nanosecond laser pulses have been chosen to investigate the individual addressing of nanoantennas, as well as the shift the nanoantenna resonance frequency position $\tilde{\nu}$.

As already has been described in the introduction of section 7.1, the excitation of PCMs with nanosecond laser pulses can be described as a kind of laser-induced annealing [255]. In the literature, Yamada et al. studied the nanosecond laser-induced switching of GST-124 [270], while Salinga et al. [153] investigated the use of nanosecond laser pulses for the reversible switching of the PCM Ag$_4$In$_3$Sb$_{26}$Te$_{26}$ (cf. table B.5). In the following, a similar concept regarding the nanosecond laser-induced switching of GST-326 thin films will be described. After the setup is described and different sample imaging methods are introduced, the generated power-time-effect diagrams (PTEs) of GST-326 thin films will be evaluated in detail, especially regarding the controllable spot sizes. Additionally, the addressing of the GST-326 adjacent to single nanoantennas and the related reflectance spectra will be presented. These experimental results have been collected in the framework of the Master’s thesis of De Rose [240]. The combination of the controllable spot sizes in GST-326 and the precise addressing of the GST-326 can lead to gradual antenna array resonance switching, which will be described afterwards. Finally, calculations regarding the influence of a $(\text{ZnS})_{80}-(\text{SiO}_2)_{20}$ capping layer on the antenna array resonance spectra will be presented. This capping layer will be investigated regarding its application as
oxidation protection layer to prevent the PCM thin film from aging as well as to hinder gold diffusion into the PCM.

7.3.1 Setup and sample specifications for nanosecond laser switching

A scheme and a picture of the setup are shown in figure 7.8. The beam of a AlGaInP semiconductor laser diode (*Mitsubishi ML101U29*) with a central wavelength of $\lambda = 660\,\text{nm}$ (red line in figure 7.8a) and maximum laser pulse peak power of $P_0 = 400\,\text{mW}$ is collimated by an aspheric lens with a numerical aperture of $NA = 0.5$. Subsequently, the laser beam is guided through an 10-fold objective with a numerical aperture of $NA = 0.25$, which focusses the light on the sample surface. The sample is moved three-dimensionally on a $xyz$-stage including micrometer screws for a coarse and a fine adjustment, allowing for a maximum travel range of $4\,\text{mm}$. By using a dichroic beam splitter, the laser beam is guided to the sample surface. Additionally, the light of a cold white light emitting diode (LED) is guided to the sample surface by using a 50:50 beam splitter. Thereafter, the light is backreflected to the beam splitter, where it is transmitted to a plano-convex lens. Thus, the backreflected light is focussed on the chip of a CMOS camera which allows for a sample monitoring. Due to safety reasons, the setup is shielded. The available pulse duration $\tau$ range is $1\,\text{ns} \leq \tau \leq 10\,\mu\text{s}$ with a maximum pulse rate of $2\,\text{MHz}$ and a decay time of $300\,\text{ps}$. The pulse power is adjusted by controlling the laser voltage $V$, which depends linearly on the laser pulse peak power $P_0$. The setup for nanosecond laser switching of PCM thin films was built in the framework of the Master’s thesis of KALIX and a detailed characterization of the setup is given in [240, 251]. Recently, automated (programmable) switching has been realized by HANS [271] and allows for a faster and more precise addressing of nanostructure arrays with this setup.

![Diagram](image)

*Figure 7.8:* The setup used for local addressing of the nanoantenna arrays covered with PCM thin films is sketched in figure 7.8a, while the encircled numbers can be identified with the numbers in the picture of the setup in 7.8b. To allow for an identification of the optical elements applied in the setup, it was un-shielded before the picture was taken. Both figures were adapted from [251].
According to the general description of laser-induced processes in semiconductors given in section 7.1, laser pulses with a duration \( \tau \) of several ns can be considered as direct heating of the sample, since thermal equilibrium is reached in the illuminated sample. For the sample crystallization, a single pulse with a power \( P_C \) that allows for a sample heating above the crystallization temperature \( T_C \), but below the liquidus temperature \( T_L \), has been applied. Thereby, the pulse duration \( \tau_C \) has been chosen to allow for a ordering of the atoms into the crystalline lattice. The corresponding sample temperature and laser pulse profile are schematically displayed in figure 7.9. There, exemplary pulse parameters are given for crystallization, such as \( \tau_C = 35 \text{ ns} \) and \( P_C = 48 \text{ mW} \). According to equation 7.1 and with the elliptical cross section of the laser beam with \( L_x = (3.26\pm0.4) \mu\text{m} \) and \( L_y = (2.08\pm0.22) \mu\text{m} \) [251], the given pulse power \( P_C \) and duration \( \tau_C \) are equal to a peak fluence \( F_{0,C} \approx 15.8 \text{ mJ/cm}^2 \).

Re-amorphization of a crystallized sample has been realized by choosing a much higher pulse power \( P_A \) of e.g. 360 mW and a much shorter pulse of duration \( \tau_A \) compared to the laser pulse parameters applied for crystallization. Due to the short pulse duration \( \tau_A \) of e.g. 10 ns no ordering of the atoms was possible and thus, the molten state was quenched. Similar to crystallization the peak fluence for re-amorphization can be calculated as \( F_{0,A} \approx 33.8 \text{ mJ/cm}^2 \).

![Figure 7.9](image.png)

**Figure 7.9:** For the crystallization of the as-deposited amorphous (A) phase the sample has been heated above the crystallization temperature \( T_C \), while for amorphization of the crystalline (C) to the melt-quenched (MQ) phase the PCM thin film has been molten (liquidus temperature \( T_L \)). The temperature profile is shown in black. The corresponding pulse parameters are schematically shown in gray. A single pulse with a relatively low pulse power \( P_C \) and long pulse duration \( \tau_C \) has been applied for crystallization, while for amorphization a much higher pulse power \( P_A \) and shorter pulse duration \( \tau_A \) has been used.

### 7.3.2 Power-time-effect diagrams for crystallization and amorphization

To indentify suited switching parameters, a study of a broad pulse power \( P \) and pulse duration \( \tau \) range was conducted on the investigated sample system. Here, GST-326 thin films with an as-deposited thickness of \( t_A = 50 \text{ nm} \) on a silicon substrate were addressed with single laser pulses. As a result a matrix was generated, which showed the effect on the GST-326 thin film for each combination of pulse power and duration \( (P, \tau) \). This matrix or so-called power-time-effect diagram (PTE) was generated for the crystallization, as well as for the re-amorphization process, which are both shown in figure 7.11. Referring to the latter, the GST-326 thin film was annealed on a hot plate (30 min at 180°C) in advance of the laser-induced switching. The spots were imaged by different characterization techniques, such as confocal laser scanning microscopy (CLSM), atomic force microscopy (AFM) and scanning near-field
optical microscopy (SNOM), to rate the corresponding laser pulse parameters power $P$ and duration $\tau$ regarding a successful phase change. These imaging methods will be described in the following.

### Imaging of locally switched GST-326 by confocal laser scanning microscopy

In the literature, the PCM thin films, which were addressed by laser pulses, are imaged either in a bichromatic laser setup ($\lambda_{\text{probe}}$) subsequently to the switching process ($\lambda_{\text{switch}}$), or by an external characterization method, which required the removal of the sample from the laser setup. Furthermore, the images of both methods are combined to get a deeper insight into the laser-induced switching process. The bichromatic laser setup, which was used by Weidenhof et al. [272, 273], Siegel et al. [254] and Salinga et al. [153] for example, allowed for a probing of the reflectance of the sample position directly after the pump laser pulse was applied to the PCM thin film (or more complex investigated layer stack). The continuous-wave probe laser was of much lower intensity to exclude a laser-induced effect on the sample. A relative change of the reflectance $\Delta R$ detected by the probe laser, was defined as follows:

$$\Delta R = \frac{R_C - R_A}{R_C}$$

with $R_A$ and $R_C$ being the reflectance of the amorphous and the crystalline phase respectively [154, 272]. Hence, the increase of the reflectance change is a measure for how much of the previously amorphous PCM was crystallized by the laser pulse. In contrast, a relative decrease of the reflectance was detected in case of re-amorphization of a previously crystalline PCM [153].

In this thesis, characterization techniques, which are not implemented in the laser setup, such as atomic force microscopy (AFM) [274], confocal laser scanning microscopy (CLSM) [275] and scattering-type scanning near-field optical microscopy (s-SNOM) [276], were applied to the GST-326 thin films.

AFM, which allows for the collection of sample topography images, is an established method for the investigation of laser-induced phase changes, as can be seen in [162, 272, 273] and [269]. Due to the density contrast between the amorphous and the crystalline phase of a PCM, topography images of the spots allowed for an identification of the present phase, as well as of additional (undesired) effects, such as ablation.

In the framework of the Master’s theses of Kalix and De Rose, CLSM was introduced as a characterization method for the relative change in reflectance $\Delta R$. In this thesis, the focus lies on the evaluation of the spot sizes in the PTE diagrams for crystallization and re-amorphization displayed in figure 7.11. These diagrams have been composed of CLSM images and, thus, only this characterization method will be described in the following. However, with SNOM imaging, single spots can be characterized with a much higher resolution than it would be possible for CLSM. For example, Lewin et al. imaged amorphous and crystalline regions of the PCM $\text{Ag}_4\text{In}_5\text{Sb}_{0.7}\text{Te}_{26}$ with s-SNOM [277].

CLSM is typically applied for biomedical research applications, such as single molecule fluorescence spectroscopy and live cell imaging for example [275]. In contrast to conventional light microscopy where the sample is flooded by light, CLSM uses a laser source and point illumination for the investigation of the object. Therefore, a pinhole is used to block the laser light that is out of focus. Then, the investigated object of interest is scanned point-by-point, which allows for a relatively fast scanning of sample regions and the collection of sample overview images, which is not possible by s-SNOM for example. The CLSM system MicroTime 200 from the company Picoquant with an Olympus microscope
body was operated with a central wavelength of \( \lambda = 633 \text{ nm} \), while the resolution was achieved by using a water immersion objective with a numerical aperture \( NA = 1.2 \). The maximum imaging range is limited to \((80 \times 80) \mu\text{m}^2\) \[278\]. Further information on the CLSM setup can be found in \[279\]. For the images presented in this thesis, the GST-326 samples were characterized by the CLSM in reflection mode with the laser beam focussed on the sample surface. The laser beam, which is backreflected from the sample, is collected with a photon avalanche detector. The higher the reflectance of the investigated GST-326 film the more photons are collected.

The resolution of the CLSM is determined by the diffraction limit of the illuminating laser beam \((\sim 300 \text{ nm})\). Additionally, the intensity distribution of the light can be described by a Bessel point spread function. This intensity distribution is scanned in steps of about 0.17 \( \mu\text{m} \) while each step leads to a pixel. It has to be kept in mind that the resolution of the CLSM is not equal to this "resolution" associated with the pixel.

To estimate the reflectance contrast \( \Delta R_{\text{calc}} \) of the GST-326 thin film upon crystallization the reflectance \( R \) was calculated based on the Fresnel equations (cf. appendix B.2). Therefore, the spectral position of the CLSM laser \((\lambda = 633 \text{ nm})\) and the GST-326 film thicknesses \( t_A \) and \( t_C \) were taken into account. The following was found:

\[
\Delta R_{\text{calc}} \approx \frac{R_C - R_A}{R_C} \approx \frac{0.5483 - 0.3855}{0.5483} \approx 29.67\% \quad (7.4a)
\]

with \( R_A \) and \( R_C \) being the calculated reflectance of the amorphous and the crystalline GST-326 respectively. In other words, the reflectance of the crystalline spot was expected to increase by about 30% compared to the amorphous spot.

In figure 7.10a, a CLSM image of C-GST-326 spots, as well as of re-amorphized MQ-GST-326 spots can be seen in an A-GST-326 "matrix". The counted photons reflected from the sample surface (measured intensity) \( N \) have been normalized to the reference value of the A-GST-326 thin film \( N_{A,\text{GST}} \). Thus, the normalized count rate \( N/N_{A,\text{GST}} > 1.0 \) is equal to an increase of the sample reflectance compared to the amorphous "background". The evaluation of the CLSM images will be discussed in more detail in the context of the PTE diagrams. The spots show an elliptical shape with a long \( LA \) and a short axis \( SA \). This shape is based on the divergence of the emitted laser beam in \( x \)- and \( y \)-direction. The two axes were determined by moving a knife edge across the beam. Thereby, the beam width is determined, while the beam intensity is detected with a power meter. This procedure was conducted for both axes \( L_x \) and \( L_y \) of the laser beam and led to \( L_x = (3.26 \pm 0.4) \mu\text{m} \) and \( L_y = (2.08 \pm 0.22) \mu\text{m} \) (as mentioned on page 136) \[251\]. This elliptical cross section of the Gaussian laser beam led to an elliptically shaped spot with a long \( LA \) and a short axis \( SA \) visible in the GST-326 thin film, which was addressed by a single ns laser pulse. Thereby, the long axis \( LA \) and the short axis \( SA \) can be smaller than the axes of the laser beam \( L_x \) and \( L_y \), which is due to the fluence distribution \( F(z) \) of the Gaussian laser beam as it is visualized in the figures 7.10b to 7.10d.

The necessary fluence to achieve a phase transition, the so-called threshold fluence \( F_{\text{th}} \), is only given for a distinct diameter of the Gaussian laser beam. For sample areas, which were addressed with smaller
fluences $F < F_{\text{th}}$, the supposed phase change did not occur. This is visualized for the short axis of a crystallized spot $S_{\text{AC}}$ and the threshold fluence for crystallization $F_{\text{th},\text{C}}$ in figure 7.10b. To re-amorphize the GST-326 thin film, the fluence was increased to reach the threshold fluence for re-amorphization $F_{\text{th},\text{A}} > F_{\text{th},\text{C}}$ displayed in figure 7.10c. Since the Gaussian laser beam profile was not modified by a top-hat beam shaper for example, which would convert the Gaussian laser beam into a collimated flat top beam, each re-amorphization was necessarily associated with a re-crystallization of the outer region of the MQ-GST-326 spot. These MQ-GST-326 spots with a RC-GST-326 outline can be seen in the spots in figure 7.10a, which were two times, four times and six times addressed by single laser pulses. The AFM line plots shown in figures 7.10e and 7.10f confirm this interpretation of the CLSM images. It should be noted that the laser pulse parameters $(P, \tau)$ for the spots shown in the CLSM images differ from those shown in the AFM line plots, since no AFM characterization was conducted on the spots\(^6\) displayed in figure 7.10a. However, the comparison of these images is justified, since regarding crystallization, both laser pulse parameters $(P_{\text{C}}, \tau_{\text{C}})$ refer to a range of parameters leading to successful crystallization with the only difference being the size of the crystallized spots. Regarding re-amorphization, the same accounts for the laser pulse power $P_{\text{A}}$ and duration $\tau_{\text{A}}$, which led to successful re-amorphization of differently sized spots.

The AFM line plots reveal the thickness decrease due to a density increase of the GST-326 film upon crystallization. In contrast, the sample height of the center of the re-amorphized spot is relatively similar to the A-GST-326 film. The outline of the MQ-GST-326 spot was characterized by an increase in reflectance and by a decrease in sample height associated with the crystalline phase of the GST-326. In case of a fluence larger than the ablation threshold $F < F_{\text{abl}}$, as schematically displayed in figure 7.10d, the center of the Gaussian laser beam was irreversibly damaged. The small dark spot in the center of the MQ-GST-326 spot, which was addressed by six laser pulses (right spot in figure 7.10a) reveals a normalized count rate $N/N_{A,\text{GST}} < 1.0$. This could be an indication for local ablation.

\(^6\)During the Master’s thesis of De Rose only few AFM images were collected.
7.3 Laser-Induced Switching of Small Areas of Phase-Change Materials

(a) CLSM images of local (re-)crystallization (R)C and re-amorphization (MQ) of GST-326 with one to six laser pulses

(b) beam profile for crystallization  (c) beam profile for amorphization  (d) beam profile for ablation

(e) AFM line plot of C-GST-326 spot  (f) AFM line plot of MQ-GST-326 spot

Figure 7.10: (Re-)crystallization laser pulses with the pulse power \( P_C = 48 \text{ mW} \) and duration \( \tau_C = 35 \text{ ns} \) and re-amorphization laser pulses with the pulse power \( P_R = 360 \text{ mW} \) and duration \( \tau_R = 10 \text{ ns} \) were applied to locally switch the phase of a GST-326 thin film (thickness \( t_A = 50 \text{ nm} \)). The corresponding CLSM images of spots caused by multiple switching events are displayed in figure 7.10a (number of applied pulses in the bottom). The C-GST-326 outline of the MQ-GST-326 spots was based on the Gaussian laser beam profile which is depicted for three different peak fluences \( F_0 \) in figures 7.10b to 7.10d. The AFM line plots along the short spot axis \( S_A \) confirm the crystalline phase of the outline and the amorphous phase of the MQ-GST-326 spot center. The C-GST-326 spot in figure 7.10e was generated by a laser pulse with \( P_C = 158 \text{ mW}, \tau_C = 30 \text{ ns} \) and the re-amorphized spot depicted in figure 7.10f was switched with a laser pulse of \( P_R = 307 \text{ mW}, \tau_R = 18 \text{ ns} \). The black arrows mark the short axis \( S_A \) of the crystalline spot (or visible crystalline spot outline in 7.10f), while the red arrow marks the short axis \( S_A \) of the re-amorphized spot area. Figure 7.10a was adapted from [240] and the raw data of figures 7.10e and 7.10f was collected by Phämassing.

140
Evaluated power-time-effect diagrams

In figure 7.11, the PTE diagrams for crystallization (top) and re-amorphization (bottom) are depicted. Both diagrams were assembled from smaller images by De Rose [240], since the CLSM only allows for imaging areas with a size of maximal $(80 \times 80) \mu m^2$, which can be seen by the differently colored squares in each PTE diagram. The visualized contrast was evaluated by dividing the measured intensity $N$ by a reference value, which was the intensity of a A-GST-326 thin film $N_{A\text{-GST}}$ in case of crystallization (figure 7.11a) and the intensity of a C-GST-326 thin film $N_{C\text{-GST}}$ regarding the re-amorphization (figure 7.11b). These relative intensities $N/N_{A\text{-GST}}$ and $N/N_{C\text{-GST}}$ are related to the relative reflectance contrast $\Delta R$ as follows:

$$\Delta R_i = \frac{N}{N_{C\text{-GST}}} j - \frac{N}{N_{A\text{-GST}}} k$$

with the normalized count rates $(N/N_{CGST})_{\text{spot}}$ and $(N/N_{GST})_{\text{BG}}$ of the spot and the background respectively. Crystallization is marked by $\circledast$ and re-amorphization is marked by $\circledcirc$.

According to the calculated relative reflectance change $\Delta R_{\text{calc}} \approx 30\%$ (cf. equation 7.4) and taking into account that the normalized count rate of the background $(N/N_{GST})_{\text{BG}} = 1.0$, the expected count rates of the spots are estimated:

$$\text{if } \Delta R_i = \Delta R_{\text{calc}} \Rightarrow (N/N_{C\text{-GST}})_{\text{spot}} = 0.7 \text{ and } (N/N_{A\text{-GST}})_{\text{spot}} = 1.43$$

(7.6)

which means that a spot showing $(N/N_{C\text{-GST}})_{\text{spot}} = 0.7$ can be rated as fully crystallized and a spot with $(N/N_{A\text{-GST}})_{\text{spot}} = 1.43$ is rated as fully re-amorphized. This is based on the relative reflectance of the as-deposited and the melt-quenched A-GST-326, as well as of the annealed and the laser-induced C-GST-326 being equal. Based on the normalized count rates given by equation 7.6, the detected spots were rated. However, in figure 7.11 it can be seen that the normalized count rate of the background varies for some of the small "subimages", the PTE diagrams were assembled from. In both PTE diagrams in figure 7.11, regions of similar effects on the GST-326 thin film are indentified:

(A) The laser pulse power and duration $(P, \tau)$ in the range applied in A did not lead to any change in the GST-326 thin film. Neither for crystallization, nor for re-amorphization spots were detected.

(B) The laser pulse parameters $(P, \tau)$ associated with area B led to statistically occurring spots. The normalized count rates $(N/N_{CGST})_{\text{spot}}$ are lower than the calculated values given in equation 7.6 which indicates crystallization and amorphization respectively.

(C) The pulse power $P$ and pulse duration $\tau$ applied in C led to spots with a normalized count rate $(N/N_{CGST})_{\text{spot}}$ that matches the preliminary calculated reflectance contrast $\Delta R$ (cf. equation 7.6). For increasing laser pulse power $P$ as well as for increasing pulse duration $\tau$, the spot size (short and long axes $SA$ and $LA$) increases. Consequently, the parameters $(P, \tau)$ in this area can be used for nanosecond laser pulse induced crystallization and amorphization respectively.

(D) Considering crystallization, a fourth area is identified. Re-amorphization is observed in the centers of the crystallized spots (cf. inset of figure 7.11a). Thus, the pulse power and duration $(P_C, \tau_C)$ corresponding to area D cannot be used for crystallization.
Neither for crystallization, nor for re-amorphization ablation occurred for the laser pulse parameter range \((P, \tau)\) in figure 7.11.

The maximum and minimum pulse power \(P\) and duration \(\tau\), which have led to a successful crystallization and amorphization over a broad parameter range have been identified in figure 7.11 and marked by dashed outlines. The corresponding spot sizes with their short and long axes \(SA\) and \(LA\) have been evaluated by considering constant pulse power \(P\) and duration \(\tau\), while the respective second parameter was varied. Regarding crystallization, the constant pulse powers \(99\ mW \leq P_C \leq 151\ mW\) have been investigated, while the pulse duration \(\tau_C\) has been varied between \(15\ ns \leq \tau_C \leq 43\ ns\). Furthermore, the pulse durations \(\tau_C = 27\ ns\) and \(\tau_C = 43\ ns\) have been kept constant, while the pulse power \(P_C\) has been varied between \(P_C = 48\ mW\) and \(P_C = 182\ mW\). The short and the long axes \(SA\) and \(LA\) of the crystallized spots have been determined by using the software ImageJ. The spot axes have been measured according to the pixels, which have shown a relative reflectance \(\Delta R_\text{rel}\) defined by equation 7.5 that matches the calculated reflectance contrast \(\Delta R_{\text{calc}}\) of about 30\% given by equation 7.4. A similar procedure has been conducted for re-amorphization, where the constant pulse powers \(P_A = 279\ mW\) and \(P_A = 349\ mW\) have been studied for a varied pulse duration \(10\ ns \leq \tau_A \leq 30\ ns\). Additionally, the pulse durations \(\tau_A = 16\ ns\) and \(\tau_A = 30\ ns\) have been kept constant while the power has been varied between \(249\ mW \leq P_A \leq 360\ mW\) (for \(\tau_A = 16\ ns\)) and \(P_A = 349\ mW\) respectively. The corresponding amorphous spot sizes with the short and long axes \(SA\) and \(LA\) have been determined with ImageJ as well. Since the contrast between the amorphous and the crystalline phase \(\Delta R\) is pronounced, a clear identification has been possible. By evaluation of every spot for the data set \((P_{\text{vary}}, \tau_{\text{const}})\) and for every second data point of the data set \((P_{\text{const}}, \tau_{\text{vary}})\), the diagrams shown in figure 7.12 have been generated.

In the diagrams shown in figure 7.12, a large variation of the switchable spot sizes can be found. By adjusting the laser pulse parameters \(P_C\) and \(\tau_C\) between \((48\ mW,27\ ns) < (P_C, \tau_C) < (151\ mW,43\ ns)\) crystalline spots with a size of about \((0.44\ \mu m,0.66\ \mu m) < (SA_C, LA_C) < (1.87\ \mu m,2.65\ \mu m)\) were generated. This means that an increase of the laser pulse power \(P_C\) by about 315\% and an increase of the laser pulse duration \(\tau_C\) by about 159\% led to an increase of the short axis \(SA_C\) by about 367\% while the long axis \(LA_C\) increased even by about 400\%. Furthermore, these changes were shown to be tunable in relatively narrow steps along a linear slope. Regarding crystallization, a variation of the pulse power \(P_C\) has a stronger influence on the spot size \((SA_C, LA_C)\) than the variation of the pulse duration \(\tau_C\). Regarding re-amorphization, amorphous spots with a size in the range of about \((0.68\ \mu m,1.02\ \mu m) < (SA_A, LA_A) < (2.04\ \mu m,3.40\ \mu m)\) were generated with a laser pulse parameter variation \((249\ mW,10\ ns) < (P_A, \tau_A) < (349\ mW,30\ ns)\). Thus, an increase of the laser pulse power \(P_A\) by about 140\% and of the pulse duration \(\tau_A\) by about 188\% allowed for an increase of the short amorphous spot axis \(SA_A\) by about 300\% and an increase of the long axis \(LA_A\) by about 333\%. 

142
7.3 Laser-induced Switching of Small Areas of Phase-change Materials

(a) power-time-effect diagram for crystallization of a 50 nm A-GST-326 thin film on Si

(b) power-time-effect diagram for re-amorphization of a C-GST-326 film

Figure 7.11: The PTE diagram for crystallization was generated by single ns laser pulses applied to a 50 nm A-GST-326 thin film sputter deposited on a silicon wafer. The pulse power $P$, as well as the pulse duration $\tau$ were varied. The spots were investigated by CLSM and, thereby, the contrast was evaluated by dividing the measured intensity $N$ by a reference value, which is the intensity of a thin film of A-GST-326 $N_{A-GST}$. The differently denoted areas A, B, C and D are chosen to separate between different effects visible on the sample: in A no crystallization can be observed, while in B crystallization occurs statistically. Crystallization can be ascribed to all spots assigned to area C. In D, re-amorphization is assumed, since the center of the spots is darker than the outline (cf. inset). In the PTE diagram shown in figure 7.11b three areas can be identified: no re-amorphization (A), statistical re-amorphization (B) and successful re-amorphization (C). The investigated pulse power $P$ is higher than in figure 7.11a, since amorphization of a C-GST-326 thin film involves melting and melt-quenching. The amorphized spots are darker than the untreated PCM layer. The measured intensity is normalized to $N_{C-GST}$. The crystalline and amorphous spots for the parameters marked by dashed outlines in both diagrams are evaluated in figures 7.12. Both PTE diagrams were assembled of smaller images and adapted from [240].
Figure 7.12: The PTE diagrams displayed in figure 7.11 were evaluated regarding the spot size accessible by the setup for ns laser switching. Since the spots are elliptical, they are characterized by a short SA and a long axis of the spot LA. Combinations of P and τ, which led to successful crystallization - figures 7.12a to 7.12d - and to re-amorphization - figures 7.12e to 7.12g, were considered. Thereby, either τ is fixed and P is varied or the other way around. The fixed values for pulse duration τ and power P were chosen to cover the lower (gray marks and lines) and upper limit of the switching parameters (black marks and lines) studied in the PTE diagrams (cf. dashed outlines in figure 7.11). The marks represent the experimental data, while the lines were generated by linear fits of the data sets and serve as guide to the eye. In general, the increase of the varied parameter leads to an increase of the spot axes. However, the increase of the crystallization pulse duration τc from 27 to 43 ns did not lead to a pronounced increase of SA and LA in case of crystallization.
The clear trends which have been identified for an influence of the laser pulse parameters \((P, \tau)\) on the spot size allow for predictions, which pulse power \(P\) and duration \(\tau\) need to be chosen to achieve a distinct spot size. Unfortunately, this evaluation has to be repeated for different PCMs, a different GST-326 layer thickness or layer stacks which might even include a capping layer of \((\text{ZnS})_{80}-(\text{SiO}_2)_{20}\) (cf. section 7.3.5).

An additional evaluation of the spot size \((SA, LA)\) can be seen in figure 7.13. The depicted line plots along the short axis \(SA\) of the investigated spots show the exact values of the normalized count rates \(N/N_{\text{GST}}\) as a function of the position. The background normalized count rate is on average \((N/N_{A-\text{GST}})_{\text{BG}} \approx 1.0\pm0.08\) for the amorphous background in figure 7.13a and \((N/N_{C-\text{GST}})_{\text{BG}} \approx 1.0\pm0.12\) for the crystalline background in figure 7.13b. In the histograms, this variation around \(N/N_{\text{GST}} = 1.0\) is elucidated. Regarding crystallization, the normalized count rate \(N/N_{A-\text{GST}}\) increased from \(N/N_{A-\text{GST}} = 1.0\) to the averaged normalized count rate of the spot \((N/N_{A-\text{GST}})_{\text{spot}} = 1.6\), which is about 10% larger than the calculated value of about 1.43 (cf. equation 7.6). Besides, the length of the short axis was determined for the CLSM image line plot in figure 7.13a as \(S_{A_C} \approx 1.9\, \mu\text{m}\) by using the software ImageJ. Thereby, the length of the short axis \(S_{A_C}\) was determined for a contrast of the normalized count rate of \((N/N_{A-\text{GST}})_{\text{spot}} = 1.382\), which is 80% of maximum experimental \(N/N_{A-\text{GST}}\), cf. appendix B.7. Regarding the amorphous spot, the normalized count rate \(N/N_{C-\text{GST}}\) decreased to the averaged normalized count rate of the spot \((N/N_{C-\text{GST}})_{\text{spot}} = 0.62\). This is about 11% smaller than the calculated value of about 0.7. For the evaluation of the spot size, the 80% criterion was applied similar to the evaluation of the crystallized spot. This means that as soon as 80% of the minimum count rate contrast \(N/N_{C-\text{GST}}\) (reflectance contrast) are reached, the effect in the GST thin film is rated as re-amorphization. A detailed evaluation of both line plots \((N/N_{A-\text{GST}}\) and \(N/N_{C-\text{GST}}\) as a function of the position) is shown in appendix B.7.

The deviation is assumed to be based on the difference of the dielectric data used for the calculations [136] and the investigated sample (cf. appendix A.2). Furthermore, it is assumed that the reflectance of the as-deposited and the melt-quenched amorphous GST-326 are similar. The same is assumed for the annealed and the laser-induced crystalline phase. These assumptions might be too simplistic and contributed to the mismatch between \(\Delta R_{\text{calc}}\) and \(\Delta R_{\text{_refl}}\) and \(\Delta R_{\text{_refl}}\) respectively. Effects of the CLSM itself, such as offset counts might have contributed as well.

In summary, the evaluation of the short and long axes \(SA\) and \(LA\) of the switched spots showed that the spot size can be adjusted over a broad size range by adjusting the laser pulse power \(P\) and duration \(\tau\), while no modification of the focussing optics is needed. In the following section it will be shown how this behaviour can be used for the stepwise shifting of the antenna resonance frequency \(\tilde{\nu}_{\text{res}}\).
7.3 Laser-Induced Switching of Small Areas of Phase-Change Materials

(a) crystallized spot generated by laser pulse parameters \((P_d, T_d) = (141 \text{ mW, } 34 \text{ ns})\)

(b) re-amorphized spot generated by laser pulse parameters \((P_d, T_d) = (360 \text{ mW, } 30 \text{ ns})\)

Figure 7.13: A crystallized and an amorphous spot have been evaluated by line plots along the short axis SA spot. These reveal the exact values for the normalized count rates \(N_{C,GST}\) and \(N_{C,GST}\). The background (1.0) and the priorly calculated normalized count rates of the spots (1.43 and 0.7, cf. equation 7.6) are marked by gray horizontal lines in both line plots. The red lines and arrows mark the short axes \(SA_C\) and \(SA_A\) determined based on 80% of the maximum (crystallization) or minimum (amorphization) count rate \(N_{C,GST}\). Furthermore, two histograms are shown which represent the number of counts for each normalized count rate \(N_{C,GST}\) with a step width of 0.025. The shown line plots contain 120 counts in total. The CLSM line plots are evaluated in detail in appendix B.7 the images were adapted from [240].
7.3 Laser-induced switching of small areas of phase-change materials

7.3.3 Switching of individual nanostructures with nanosecond laser pulses

After suited laser pulse parameters for crystallization and re-amorphization were determined by the evaluation of the PTE diagrams shown in figure 7.11, single antennas covered with a GST-326 thin film were addressed by single laser pulses. Therefore, the sample design displayed in figure 7.14a was used. A GST-326 thin film with the thickness \( t_A = 50 \text{ nm} \) was deposited on antennas arranged as an array. This array geometry was chosen by De Rose on the one hand to minimize antenna coupling and on the other hand to allow for local addressing without an overlap of adjacent spots. The first consideration was based on the fact that the optical properties of arrays do not significantly differ from those of single nanoantennas for an antenna separation in \( x \)- as well as in \( y \)-direction of \((d_x, d_y) = (5 \mu \text{m}, 5 \mu \text{m})\) [22, 31]. However, based on the antenna coupling in an array discussed in chapter 5, this layout is not well-suited considering narrow resonance peaks. For the separation \( d_x = 5 \mu \text{m} \) the averaged lattice resonance (Rayleigh anomaly) lies at about \( \tilde{\nu}_{RA,(1,0), 5 \mu \text{m}} = 581 \text{ cm}^{-1} \), which is far from the antenna resonance.

In figure 7.14a the sample treatment is sketched. The GST-326 superstrate was locally crystallized by single ns laser pulses while the position of each spot was controlled manually. Laser-induced re-amorphization was conducted on the same sample, but on different antennas by crystallization and subsequent re-amorphization on each antenna position of the GST-326. In the optical microscope image in figure 7.14b, a corresponding sample design is shown. There, the GST-326 on top of antenna dimers (length \( L = 600 \text{ nm} \) and gap size of 80 nm) was addressed. These samples were studied in [240] and will not be discussed in this thesis. Instead, only single antennas will be discussed in the following. However, the microscope image was chosen to be displayed since not only the spots, but also the antenna dimers, which are twice as long as the single antennas, are visible. The crystallization of the re-amorphized spots was already discussed earlier (cf. figure 7.10) and can be associated with the bright outlines of the MQ-GST-326 spots in the microscope image in figure 7.14b.

Due to the manual control of the laser beam and the restricted resolution of the camera monitoring unit of the laser setup, an ideal center position of the antenna relative to the position of the switched spot is difficult. Thus, several spots were placed as depicted in the AFM images in figure 7.14c. As a consequence, the GST-326 was crystallized in the vicinity of the upper tip of the nanorods shown in figure 7.14c, while only a small fraction of the GST-326 is crystallized in the vicinity of the lower tip. In contrast, a centered placing of the spot relative to the antenna would lead to a stronger resonance shift \( \Delta \tilde{\nu}_{res} \) than the expected shift for the partly "mis-placed" spots shown in figure 7.14c.

Besides, in these topography plots it can be seen that there was no difference visible between the spot of C-GST-326 with or without the influence of an aluminum antenna underneath the GST-326 thin film. The decrease of the height due to the density increase upon crystallization was similar on all three investigated sample areas.

The successful addressing of single antennas was further evaluated by FTIR reflectance spectra displayed in figure 7.14d. The three FTIR reflectance spectra of about \( 7 \times 7 \) antennas (aperture of about \( (30 \times 30) \mu \text{m}^2 \)) were collected on one sample, but from different antennas. These antennas were either addressed by single laser pulses for local crystallization or by subsequent single laser for local crystallization and re-amorphization. All three reflectance spectra were normalized to a spectrum of an A-GST-326 thin film without antennas present.
7.3 Laser-induced switching of small areas of phase-change materials

(a) laser-induced crystallization ① and re-amorphization ② of A-GST-326 on Al antennas, spots size (LA, SA)

(b) spots of C- and MQ-GST-326 in A-GST-326 covering antennas

(c) AFM image C-GST-326 spots with/without antenna

(d) FTIR reflectance spectra

Figure 7.14: Local crystallization and re-amorphization by single laser pulses of power $P$ and duration $\tau$ is schematically shown in figure 7.14a. The GST-326 thin film (thickness $t_A = 50$ nm) directly on top of the antennas was addressed by single ns laser pulses with $(P_C, \tau_C)$, which generated elliptic spots of C-GST-326. After a subsequent treatment by single laser pulses of $(P_A, \tau_A)$ the GST-326 cover was locally re-amorphized. The density increase upon crystallization leads to a height contrast of the C- and MQ-GST-326 spot and the A-GST-326 thin film (sample sketches in the right of figure 7.14a). Due to the Gaussian beam profile, re-amorphization was accompanied by crystallization of the spot outline. This can be seen in the optical microscope image in figure 7.14b as well (maximized image contrast). The A-GST-326 on top of the antennas (here: antenna dimers with length $L = 600$ nm and gap size of about 60 nm, which were discussed in [240], exemplary SEM image in figure B.27) was locally crystallized with $(P_C = 48$ mW, $\tau_C = 35$ ns) (seven columns of five antenna dimers on the right) and crystallized and re-amorphized $(P_A = 360$ mW, $\tau_A = 10$ ns) (seven columns of five antenna dimers on the left). In figure 7.14c AFM topography images for three C-GST-326 spots are depicted. The middle and the right spot cover an aluminum antenna, while the left spot is depicted for comparison. The lower height of the crystalline spot in figure 7.14c is based on the density increase upon crystallization. Normalized reflectance spectra for about 7 x 7 antennas with length $L = 600$ nm were collected and are shown in figure 7.14d. The resonance frequency position $\tilde{\nu}_{res}$ is shifted by local crystallization and re-amorphization of the GST-326. The spectral feature at about 2350 cm$^{-1}$ relates to the atmospheric CO$_2$ absorption. The raw data of figures 7.14b and 7.14d were collected by De Rose while the images in figure 7.14c were taken by Prämassing. Figure 7.14d was adapted from [240].
Due to the small sample coverage with antennas (0.24%) and the lack of coupling compared to closely arranged antennas as discussed in the chapters before, the measured peak reflectances are much lower than the peak reflectances determined in chapter 6 and fs laser-induced switching of large areas of the GST-326.

Even the spots were not always placed centered relative to the antennas (cf. figure 7.14c) the effective refractive index of the antenna surrounding \( n_{\text{eff}} \) was changed by the local laser-induced switching of the GST-326. Thus, the marked resonance positions were shifted from 1980 cm\(^{-1} \) by about \( \Delta \tilde{\nu}_{\text{res}} = 183 \text{ cm}^{-1} \) to 1797 cm\(^{-1} \) upon crystallization (blue spectrum in figure 7.14d) and back by about \( \Delta \tilde{\nu}_{\text{res}} = 183 \text{ cm}^{-1} \) to 1980 cm\(^{-1} \) upon re-amorphization. It has to be noted that the antenna resonance peak associated with antennas covered by spots of MQ-GST-326 is relatively broad compared to the antenna reflectance spectra for A-GST-326 and C-GST-326. Since the averaged lattice resonance \( \tilde{\nu}_{\text{RA}(1,0),5 \mu m} \) is much smaller than the antenna resonance positions \( \tilde{\nu}_{\text{res}} \), the peak width FWHM is larger than what can be expected from a closer antenna separation and thus, from a RA position closer to the antenna resonance (cf. figure 6.8). The broad peaks hamper the determination of the resonance frequency position \( \tilde{\nu}_{\text{res}} \) and therefore, a deviation of about \( \tilde{\nu}_{\text{res}} \pm 20 \text{ cm}^{-1} \) has to be considered. Since all spectra were normalized to a thin film of A-GST-326 (thickness \( t_A = 50 \text{ nm} \), measured next to the antenna arrays) the thin film interference for C-GST-326 is visible in the spectrum for the antennas covered with C-GST-326 spots\(^7\). Hence, the increase of the reflectance for wavenumbers \( \tilde{\nu} > \tilde{\nu}_{\text{res}} \) visible for the spectrum associated with MQ-GST-326 can be related to the crystalline outlines of the re-amorphized spots as well.

The total shift \( \Delta \tilde{\nu}_{\text{res}} = 183 \text{ cm}^{-1} \) upon crystallization is smaller than the shift realized by annealing (223 cm\(^{-1} \) for \( L = 600 \text{ nm} \)) but larger than the shift realized by fs laser induced switching (175 cm\(^{-1} \) for \( L = 500 \text{ nm} \))\(^8\). The smaller shift for fs laser excitation is based on the (undesired) re-amorphization on top of the antennas described earlier in this chapter. The smaller shifts compared to annealing can be related to the amorphous surrounding of the spots as sketched in figure 7.15. For the spots, the effective refractive index \( n_{\text{eff}} \) influencing the antenna array resonance position is composed of \( n_A \approx 3.5, n_C \approx 6.3, n_{\text{Si}} \approx 3.4 \) and \( n_{\text{air}} \approx 1.0 \) (at \( \tilde{\nu} = 3000 \text{ cm}^{-1} \)), while no influence of \( n_A \) occurs in case of crystallization on a hot plate. Since \( n_A < n_C \), the effective index \( n_{\text{eff}} \) for switched spots is smaller than for an annealed sample (or for what could be expected from successful laser-induced switching of large sample areas).

The crystallized spots cover about 4.8% of the investigated sample area of \((30 \times 30) \mu \text{m}^2 \) (aperture). It is striking that this small crystallized fraction in the A-GST-326 thin film allows for the resonance frequency shift \( \Delta \tilde{\nu}_{\text{res}} \) of 183 cm\(^{-1} \), which is only 18% smaller than the shift realized with annealing. This is based on the sensitivity of the antennas for their close vicinity\(^9\). It should be noted that the sample coverage of 4.8% were calculated by the short and long spot axis \( S_{A_C} \) and \( L_{A_C} \) extracted from the PTE diagram in figure 7.11a, as well as from the AFM images in figure 7.14c. These slightly different spot areas were averaged and divided by the aperture size to obtain the sample coverage.

---

\(^7\)The normalization of a reflectance spectrum of an antenna array covered with or placed on a C-GST-326 thin film to a C-GST-326 thin film reflectance spectrum without antennas present cancels the TFI out and only the antenna array signal remains.

\(^8\)No results were obtained for \( L = 600 \text{ nm} \).

\(^9\)The closer the change of the refractive index or the dielectric function, the stronger is the influence on the antenna resonance (position).
7.3 Laser-induced switching of small areas of phase-change materials

Figure 7.15: The spots with long axes $L_A$ generated by single ns laser pulses influence the refractive index in the antenna surrounding locally. This refractive index distribution is sketched here. After re-amorphization, the refractive index distribution around the antenna includes the crystalline rim caused by the Gaussian intensity distribution of the laser beam. The values for the real part of the refractive indices refer to $\bar{\nu} = 3000 \text{ cm}^{-1}$.

The initial antenna resonance position $\bar{\nu}_A$ of the arrays studied in chapter 6 and section 7.2 (antenna separation $d = 2L = 1.2 \mu m$ for $L = 600 \text{ nm}$) differs only slightly from the resonance position of the antennas studied here ($d = 5 \mu m$): $\bar{\nu}_{A,1.2 \mu m} = 2096 \text{ cm}^{-1}$ and $\bar{\nu}_{A,5 \mu m} = 1980 \text{ cm}^{-1}$. Therefore, the increase of the refractive index $n_C$ for increasing wavenumbers, which has an influence on the realized shift $\Delta \bar{\nu}_{\text{res}}$ as well, is not considered here.

Besides, it is striking that the resonance positions $\bar{\nu}_{\text{res}}$ for the antennas covered with A-GST-326 and MQ-GST-326 are equal, since each re-amorphized spot shows a crystalline outline (bright rims visible in the microscope image in figure 7.14b). Thus, the effective refractive index $n_{\text{eff}}$ in the vicinity of the antennas is distributed as shown in figure 7.15. However, the shift of the resonance position $\bar{\nu}_C$ back to the initial position $\bar{\nu}_{MQ} = \bar{\nu}_A$ indicates that the crystalline rim ($n_C$) has no (or only a very weak) contribution to the antenna surrounding. This could be based on the distance of the crystalline rim to the antenna tips, where the field enhancement is the largest. In turn, this implies that only the refractive indices of the media very close to the antennas (or antenna tips) have a strong influence on the effective refractive index $n_{\text{eff}}$.

Generally, it was shown that a laser-induced switched spot can be placed on individual nanoantennas and thus allows for controlled local switching. Furthermore, this switching is a reversible process and thus, allows for applications beyond proof of concept studies.

7.3.4 Gradual shifting of antenna resonances by variation of the spot size

In the introduction of this chapter, it was mentioned that a local change of the optical properties of nanoantennas can be applied in the field of metamaterials or metasurfaces. There the local addressing of resonant nanostructures could lead to a (gradual fine-)tuning of their resonance properties and thus, even to new functionalities.

Gradual resonance tuning by using a PCM was published by Chen et al. [32]. A GST-225 thin film, which was applied as substrate for gold nanodisks, crystallized delayed in time due to annealing at temperatures slightly below the crystallization temperature $T_C$. The heating was conducted for 60 min, while an increase of the crystalline fraction up to 86% during this annealing process was postulated. As a result, the resonance frequency position of the gold nanodisks was shifted from $5291 \text{ cm}^{-1}$ to $4405 \text{ cm}^{-1}$ with $152 \text{ cm}^{-1}$ being the smallest step size of the resonance shift. This gradual tuning lacks the reversibility of the shifts, as well as a directed addressing of the phase transition, since the crystalline fraction increases for the entire GST-225 thin film upon increased annealing time.

A concept for the reversible and directed gradual tuning of the resonance frequency position of nanostructures will be explained in the following. Therefore, the broad range of the laser pulse power and duration ($P, \tau$), which was found to successfully lead to crystallization and re-amorphization, will
be applied. The laser pulse parameter variation is accompanied by a broad range of realizable spot sizes quantified by the short and long spot axis \((SA, LA)\). The combination of varied spot sizes and the addressing of single antennas led to the calculations displayed in figure 7.16. The reflectance spectra of an array of antennas with length \(L = 600\) nm, height \(h = 40\) nm and width \(w = 110\) nm covered by a thin film of A-GST-326 with a thickness of \(t_A = 50\) nm were calculated with the software CST Microwave Studio. The crystalline phase of the GST-326 on top of the antennas was restricted to a volume with an elliptical cross section while the GST-326 "matrix" of these spots has remained in its amorphous state. The ellipse represented the crystallized spot and its size was defined by the short and the long axis \((SA_C, LA_C)\). Due to the AFM images of the crystallines spots on single antennas depicted in figure 7.14c, the long axis was assumed to be twice as long as the short axis \(LA_C = 2SA_C\). For each spectrum this size was increased. As high and low wavenumber limit of the resonance frequency position \(\tilde{\nu}_{\text{res}}\) the reflectance spectrum for a fully amorphous GST-326 and a fully crystalline GST-326 superstrate were calculated. Further details regarding the simulation can be found in appendix C.

The spectra displayed in figure 7.16 show that the calculated resonance frequency position \(\tilde{\nu}_{\text{res}}\) shifts to lower wavenumbers upon a spot size increase. For spots smaller than the covered antenna with \(L > LA_C = 0.3 - 0.5\) \(\mu\)m only a small incremental shift between the resonance frequency positions \(\Delta\tilde{\nu}_{\text{step}} = 35 - 65\) cm\(^{-1}\) associated with adjacent spot sizes occurs. The largest incremental shift with \(\Delta\tilde{\nu}_{\text{step}} = 90\) cm\(^{-1}\) was found for the spot size increase from \(L = LA_C = 0.6\) \(\mu\)m to \(L < LA_C = 0.7\) \(\mu\)m. This is based on the fact that a spot with \(LA_C = 0.7\) \(\mu\)m exceeds the nanoantenna tips and thus, the area in which the fields are enhanced experiences the increase of the effective index of the surrounding \(n_{\text{eff}}\) due to crystallization of the GST-326. In contrast, a crystalline spot with the long axis \(LA_C = 0.6\) \(\mu\)m is as long as the antenna and therefore the enhanced fields do not experience this increase of the surrounding’s permittivity \(n_{\text{eff}}\) as strong as for the larger spot with \(LA_C = 0.7\) \(\mu\)m. For a further increase of the spot size with \(LA_C = 0.8 - 1.2\) \(\mu\)m the incremental resonance frequency shifts \(\Delta\tilde{\nu}_{\text{step}}\) are not as large as the shift between \(LA_C = 0.6\) \(\mu\)m and \(LA_C = 0.7\) \(\mu\)m, but as small as the incremental resonance frequency shifts \(\Delta\tilde{\nu}_{\text{step}}\) which are observed for the small spots with \(LA_C = 0.3 - 0.5\) \(\mu\)m. Besides, the calculated incremental resonance frequency shift \(\Delta\tilde{\nu}_{\text{step}}\) between the spectrum for spots with a long axis \(LA_C = 1.2\) \(\mu\)m and the spectrum for a fully crystalline film is the largest calculated shift.

The calculated reflectance spectra shown in figure 7.16 are not related to the experimental reflectance spectra displayed in figure 7.14d quantitatively since the sample designs differ regarding the antenna separation \(d\). While in [240] the antennas were arranged with a large separation \((d = 5\) \(\mu\)m\) to exclude overlapping spots, the calculations were conducted with the same sample design as studied for resonance frequency shifting by sample annealing and large area laser-induced switching \((d = 2L = 1.2\) \(\mu\)m for \(L = 600\) nm). Since the spot sizes applied for the calculated spectra in figure 7.16 were realized experimentally and due to an optimization of the driving unit of the ns laser setup (programmable stage), no overlap of the spots is expected. Thus, the optimized antenna separation of \(d = 2L\) applied in the calculations and for experimental results shown earlier, which allows for much narrower resonance peaks, should be chosen for the experimental realization of this concept.

To complete the study of the relation between the resonance peak width and the position of the lattice resonance, the calculated reflectance spectra shown in figure 7.16 were evaluated regarding the relation between the FWHM and the distance of the resonance frequency position \(\tilde{\nu}_{\text{res}}\) to the spectral
position of the averaged Rayleigh anomaly $\tilde{\nu}_{RA, (1, 0), 2L}$ according to the results shown in section 6.3.3. These results are shown in appendix B.7 and match well with the findings presented earlier.

In summary it has been shown theoretically that the resonance frequency position of antennas $\tilde{\nu}_{res}$ can be varied over a spectral range of about 400 cm$^{-1}$ with the smallest resonance shift of about 15 cm$^{-1}$ by adjusting the parameters of ns laser pulses. Thus, the presented calculations are very promising regarding an application for tunable metamaterials. It is important to emphasize that the spectra in figure 7.16 are not supported by any experiment so far and require experimental verification.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image1.png}
\caption{Scheme of the local laser induced switching with an increasing spot size.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image2.png}
\caption{Calculated reflectance spectra for an increasing spot size leading to stepwise shifting.}
\end{figure}

Figure 7.16: The shown reflectance spectra were calculated for an antenna array with antenna length $l = 600$ nm, a separation of $(d_t, d_x) = (1.2 \mu m, 1.2 \mu m)$, width $w = 110$ nm and height $h = 40$ nm and a GST-326 superstrate of thickness $t_A = 50$ nm. For fully amorphous and crystalline thin films the gray spectra have been calculated. Furthermore, elliptical spots of size $(SA_c, LA_c)$ with the long axis $LA_c$ being twice as large as the short axis $SA_c$ (according to the findings from the AFM of the C-GST-326 spots in figure 7.14c) were placed on top of the antennas and their size was increased stepwise. The corresponding sample scheme is shown in figure 7.16a (only $LA_c = 0.5 \mu m$ is not shown). An increase of the spot size led to an incremental shift of the antenna array resonance frequency position $\Delta \tilde{\nu}_{res}$. By extracting these shifts the gradual switching of the antenna array resonance position upon spot size increase is displayed in the inset. The black arrows indicate the increasing spot size. The sharp feature at 2423 cm$^{-1}$ originates from the Rayleigh anomaly for an antenna separation of $(d_t, d_x) = (1.2 \mu m, 1.2 \mu m)$ while the increase of the reflectance of the spectrum for C-GST-326 at higher wavenumbers is based on the thin film interferences.
7.3 Laser-induced switching of small areas of phase-change materials

7.3.5 Influence of a \((\text{ZnS})_{80}-(\text{SiO}_2)_{20}\) capping layer

\((\text{ZnS})_{80}-(\text{SiO}_2)_{20}\) as oxidation protection layer

Aging of PCM samples, which describes the oxidation of the PCM surface with increasing depth for increasing storage times\(^\text{10}\), was reported [240]. This oxidation is enhanced at high temperatures during the switching experiments [87]. Oxidized GST compounds showed different properties, such as resistivity [280], reflectivity and crystallization temperature [281, 282] compared to the non-oxidized GST. Thus, the optical properties of the GST thin films with an advanced oxidized surface are changed relative to the GST with less progressed oxidation.

To prevent PCM thin films from oxidation, as well as from evaporation at elevated temperatures, the application of capping layers of \((\text{ZnS})_{80}-(\text{SiO}_2)_{20}\) was reported [153, 264, 281, 283, 284]. Thus, the investigated samples were capped with thin films of the dielectric. Thereby a thickness \(t_{\text{cap}}\) between several nm to about 100 nm was deposited. The deposition of the capping layer as well as of the PCM thin film was conducted during a single sputter deposition procedure, since a transfer of the samples through air could have already led to oxidation of the PCM [285].

However, in this thesis the capping layer was avoided to allow for a sample characterization by scattering-type scanning near-field microscopy (s-SNOM) [277, 286] and AFM [154, 287]. Nevertheless, for samples which are not supposed to be used for s-SNOM or AFM, a capping layer of \((\text{ZnS})_{80}-(\text{SiO}_2)_{20}\) would prevent the sample from oxidation.

To investigate the influence of the capping layer on the antenna array resonance spectra, calculations were performed with the software CST Microwave Studio. Antenna arrays with length \(L = 600\) nm, width \(w = 115\) nm, height \(h = 30\) nm and a separation of \((d_x, d_y) = (2L, 2L)\) have been covered with a GST-326 thin film and a \((\text{ZnS})_{80}-(\text{SiO}_2)_{20}\) capping layer of thickness \(t_{\text{cap}} = 10\) nm and \(t_{\text{cap}} = 100\) nm. The dielectric function of the capping layer \((\text{ZnS})_{80}-(\text{SiO}_2)_{20}\) has been taken from measurements conducted by the company Sentech Instruments GmbH in 2014 [288]. The calculations have been performed for an amorphous GST-326 superstrate of thickness \(t_A = 50\) nm, as well as for a crystalline GST-326 superstrate of thickness \(t_C = 46\) nm. The spectra are shown in figure 7.17.

![Figure 7.17](image-url)

(a) antennas below A-GST-326 and \((\text{ZnS})_{80}-(\text{SiO}_2)_{20}\)
(b) antennas below C-GST-326 and \((\text{ZnS})_{80}-(\text{SiO}_2)_{20}\)

Figure 7.17: Reflectance spectra of antenna arrays covered by a GST-326 thin film with thickness \(t_A = 50\) nm (black spectra) and an oxidation protection layer of \((\text{ZnS})_{80}-(\text{SiO}_2)_{20}\) with thickness \(t_{\text{cap}} = 10\) nm (gray) and \(t_{\text{cap}} = 100\) nm (red) are shown. In figure 7.17a the GST-326 film is in its amorphous phase (dashed lines) and in figure 7.17b in its crystalline phase (solid lines). The sample scheme is displayed as inset of figure 7.17b.

\(^{10}\)In chapter 3, aging was described as structural relaxation.
The simulations show that the (ZnS)\textsubscript{80}-(SiO\textsubscript{2})\textsubscript{20} capping with a thickness of \( t_{\text{cap}} = 10\text{ nm} \) influences the antenna array reflectance spectra only weakly with a resonance frequency position shift of \( \Delta \nu_{\text{res}} = 16\text{ cm}^{-1} \) (A-GST-326) and \( 12\text{ cm}^{-1} \) (C-GST-326) respectively and no change of the peak reflectance. The tenfold increase of the capping layer thickness revealed a much stronger influence on the antenna array resonance peak \( \tilde{\nu}_{\text{res}} \) compared to the thinner film. The 100 nm thick capping layer shifts the resonance frequency position by about \( \Delta \tilde{\nu}_{\text{res}} = 62\text{ cm}^{-1} \) (A-GST-326) and \( 48\text{ cm}^{-1} \) (C-GST-326) respectively. In consequence, the total reflectance shift of the resonance frequency position \( \Delta \tilde{\nu}_{\text{res}} = |\tilde{\nu}_A - \tilde{\nu}_A| \) upon crystallization decreased due to the thick capping layer with \( t_{\text{cap}} = 100\text{ nm} \) by about 9.4\% compared to the shift \( |\tilde{\nu}_A - \tilde{\nu}_A| \) referring to the samples without capping. For A-GST-326 with 100 nm (ZnS)\textsubscript{80}-(SiO\textsubscript{2})\textsubscript{20} a 2\% decrease of the peak reflectance was detected while for C-GST-326 with 100 nm (ZnS)\textsubscript{80}-(SiO\textsubscript{2})\textsubscript{20} no change of the peak reflectance was detected.

Thus, a thin capping layer of (ZnS)\textsubscript{80}-(SiO\textsubscript{2})\textsubscript{20} will be suited for protection against oxidation for samples including a PCM thin film and nanoantenna arrays without a negative influence on the spectral properties. However, it was shown that the activation energy for crystal growth was strongly influenced by (ZnS)\textsubscript{80}-(SiO\textsubscript{2})\textsubscript{20} layers, e.g. for a 20 nm Sb\textsubscript{2}Te layer it increases from 2.4 to 3.4 eV by introducing a 3 nm capping layer [285]. Regarding the laser parameters for laser-induced switching of the PCM thin film, changes of the laser pulse powers \( P \) and durations \( \tau \) compared to the parameters \( P \) and \( \tau \) for samples without capping were reported [281]. These findings were assumed to be based on the interfacial energy between the capping and the PCM. As a consequence, it was expected that the PTE diagrams collected for GST-326 thin films on silicon shown in figure 7.11 would need to be repeated for samples which include a capping layer.

**(ZnS)\textsubscript{80}-(SiO\textsubscript{2})\textsubscript{20} as thermal barrier**

In the literature (ZnS)\textsubscript{80}-(SiO\textsubscript{2})\textsubscript{20} was applied as thermal barrier between the silicon substrate and the PCM layer which in turn is sandwiched between two (ZnS)\textsubscript{80}-(SiO\textsubscript{2})\textsubscript{20} layers then [153, 277, 281]. It was mentioned earlier that the silicon substrate acts as a heat sink for the PCM film due to its high thermal conductivity \( \kappa_T = 142\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1} \) [220] compared to the thermal conductivity of GST-326 \( \kappa_T = 0.6\ldots0.7\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1} \) [262] for example (cf. table 7.1). In contrast (ZnS)\textsubscript{80}-(SiO\textsubscript{2})\textsubscript{20} offers a thermal conductivity of \( \kappa_T \approx 0.657\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1} \) [283] which is very similar to the thermal conductivity of the PCM thin film. As a consequence the heat introduced into the sample by a single laser pulse remains longer in the PCM film than without this thermal barrier. It was reported that (ZnS)\textsubscript{80}-(SiO\textsubscript{2})\textsubscript{20} sandwich layers accelerated the crystallization of GST-225 at very high heating rates (above 5000 K s\textsuperscript{-1}), while it was impeded for lower heating rates [289]. However, successful crystallization is possible without a thermal barrier of (ZnS)\textsubscript{80}-(SiO\textsubscript{2})\textsubscript{20} as it is shown in this thesis for example.

**(ZnS)\textsubscript{80}-(SiO\textsubscript{2})\textsubscript{20} as diffusion barrier**

Aluminum has been given preference over gold as antenna material due to the diffusion of gold into the PCM [110, 147, 225] (cf. chapter 5). According to [38, 223] the introduction of a (ZnS)\textsubscript{80}-(SiO\textsubscript{2})\textsubscript{20} layer hindered the diffusion of gold into the PCM. To estimate the influence of a (ZnS)\textsubscript{80}-(SiO\textsubscript{2})\textsubscript{20} diffusion barrier on the antenna array reflectance spectra corresponding calculations were conducted. The antennas of an array were designed with length \( L = 600\text{ nm} \), width \( w = 110\text{ nm} \), height \( h = 30\text{ nm} \) and separation \( (d_x, d_y) = (2L, 2L) \). The A-GST-326 superstrate thickness was chosen as \( t_A = 50\text{ nm} \).
and the (ZnS)$_{80}$-(SiO$_2$)$_{20}$ layer thickness was chosen as $t_{\text{cap}} = 40 \text{ nm}$ referring to the (ZnS)$_{80}$-(SiO$_2$)$_{20}$ thickness applied in [38] ($t_{\text{cap}} \leq 30 \text{ nm}$). The antenna height $h$ was adapted to allow for a coverage of the antennas with (ZnS)$_{80}$-(SiO$_2$)$_{20}$ at the antenna ends. Thus, the antennas had to be lower than the capping thickness.

The calculated reflectance spectra are displayed in figure 7.18c. Upon crystallization of the GST-326 superstrate the antenna array resonance frequency position $\tilde{\nu}_A$ is shifted to lower wavenumbers ($\tilde{\nu}_C$). Thereby, the introduction of the diffusion barrier of 40 nm (ZnS)$_{80}$-(SiO$_2$)$_{20}$ led to a pronounced decrease of the antenna array resonance frequency shift $\Delta \tilde{\nu}_{\text{res}}$ from 440 cm$^{-1}$ (black arrow in figure 7.18c) to 237 cm$^{-1}$ (gray arrow). Furthermore the peak reflectance decreased from about 0.68 to 0.58 upon a change of the sample layout from the aluminum antenna array with a GST-326 superstrate to the gold antenna array with a (ZnS)$_{80}$-(SiO$_2$)$_{20}$ capping layer and a GST-326 superstrate.

The decrease of the resonance frequency shift $\Delta \tilde{\nu}_{\text{res}}$ can be explained by the distance between the nanoantenna arrays and the GST-326 superstrate due to the (ZnS)$_{80}$-(SiO$_2$)$_{20}$ barrier. Thus, the enhanced antenna field at the nanorod tips is not influenced by the refractive index of the GST-326 superstrate as much as in the case of the aluminum array in direct contact with the GST-326. However due to the refractive index of the (ZnS)$_{80}$-(SiO$_2$)$_{20}$ $n_{\text{eff}} \approx 2.1 + 0i$ (at $\tilde{\nu} = 2000 \text{ cm}^{-1}$) [288] the effective refractive index of the antenna surrounding $n_{\text{eff}}$ was decreased compared to the situation shown in figure 7.18a, where $n_{\text{eff}}$ is only influenced by $n_{\text{Si}}$ and $n_A$. As a consequence of the decreased $n_{\text{eff}}$, the antenna array resonance frequency position $\tilde{\nu}_A$ was expected to be shifted to higher wavenumbers upon the introduction of the capping layer. This behavior was only observed for the antenna array resonance frequency position $\tilde{\nu}_C$, while $\tilde{\nu}_A$ was shifted to lower wavenumbers instead of higher wavenumbers.

It should be noted that the chosen sample design with a GST-326 superstrate was chosen according to a future application for laser-induced reversible shifting of the resonance frequency position. The GST-326 substrate, which led to the highest TFOM (cf. chapter 6), was not investigated, since it is expected to be less suited for optical switching than the GST-326 antenna superstrate.

Figure 7.18: Comparison of calculated reflectance spectra of an aluminum antenna array with a GST-326 superstrate (black spectra) and a gold antenna array with a (ZnS)$_{80}$-(SiO$_2$)$_{20}$ diffusion barrier (thickness $t_{\text{cap}} = 40 \text{ nm}$) and a GST-326 superstrate (gray spectra). Both A-GST-326 superstrates have a thickness $t_A = 50 \text{ nm}$. The antennas have been designed as follows: length $L = 600 \text{ nm}$, width $w = 110 \text{ nm}$, height $h = 30 \text{ nm}$ and separation $(d_x,d_y) = (2L,2L)$. The reflectance spectra for A-GST-326 superstrates are displayed as dashed lines, while spectra related to C-GST-326 are visualized by solid lines. The resonance shifts upon crystallization of the GST-326 superstrate $\Delta \tilde{\nu}_{\text{res}}$ are marked by a black arrow (referred to sample 7.18a) and a gray arrow (referred to sample 7.18b). The sharp feature at 2422 cm$^{-1}$ refers to the Rayleigh anomaly position related to the investigated antenna arrays.
7.4 Summary

In this chapter, nanosecond and femtosecond laser pulse induced switching of GST-326 thin films adjacent to antenna arrays was discussed. Switching of large areas was realized by femtosecond laser pulses, while nanosecond laser pulses were applied to locally switch the GST-326 thin films.

It was shown that single femtosecond laser pulses allowed for a re-amorphization of large areas of GST-326 thin films, while a pulse sequence led to re-crystallization of these areas. The determined switching parameters laser fluence $F$ and pulse duration $\tau$ were applied to switch the GST-326 thin film which covered several antenna arrays as well. Detected reflectance spectra showed pronounced antenna array resonance peaks and a shift of the antenna array resonance frequency position $\Delta \tilde{\nu}_{\text{res}}$ upon the laser-induced phase transitions. A mismatch between the antenna array resonance frequency positions for the amorphous phases (A- and MQ-GST-326) $\tilde{\nu}_{\text{MQ}} \neq \tilde{\nu}_{\text{A}}$ and the crystalline phases (C- and RC-GST-326) $\tilde{\nu}_{\text{RC}} \neq \tilde{\nu}_{\text{C}}$ respectively was detected. Thus, a strong influence of the antennas on the switching process has been assumed. An enhanced sample absorption due to the presence of the nanoantennas was calculated. Based on the calculated total electromagnetic loss it was concluded that a re-amorphization on top of the antennas occurred during the re-crystallization. This can explain the mismatch between the resonance frequency positions ($\tilde{\nu}_{\text{MQ}} \neq \tilde{\nu}_{\text{A}}, \tilde{\nu}_{\text{RC}} \neq \tilde{\nu}_{\text{C}}$).

For local addressing of single resonant nanostructures a setup for ns laser induced switching was built. By a variation of the laser pulse parameters pulse power $P$ and pulse duration $\tau$, the realized spot size was varied over a size range of a few $\mu$m. Calculated reflectance spectra showed that the application of the spot size variation can allow for a gradual resonance frequency shift $\Delta \tilde{\nu}_{\text{res}}$. A gradual reversible and local resonance frequency tuning has not been shown in the literature yet and a realization of the theoretically investigated concept would be very promising regarding future programmable metamaterials.

Besides, the application of $(\text{ZnS})_{80}-(\text{SiO}_2)_{20}$ as protection layer against sample oxidation (especially PCM oxidation), thermal barrier for accelerated crystallization, as well as barrier against metal diffusion into the PCM was discussed. Calculated antenna array reflectance spectra showed the influence on the resonance switching: a thin oxidation protection layer had no negative effect on the resonance shifting, while a diffusion barrier led to a strongly decreased antenna array resonance shift $\Delta \tilde{\nu}_{\text{res}}$. 


CHAPTER 8

Summary and outlook

8.1 Summary of the presented results

In this thesis, phase-change materials (PCMs) have been used to influence the spectral position of nanoantenna resonance frequencies. Therefore, the sample design including geometry and applied materials has been optimized (chapter 5). Experimental results proving the general concept have been discussed in detail (chapter 6). Since the reversible switching between the amorphous and the crystalline phase of PCMs can allow for applications of the presented tuning of antenna resonance frequency beyond scientific concepts, laser-induced switching has been investigated (chapter 7). The following discussion will recapitulate the most central conclusions.

To avoid diffusion of the metal into the PCM, aluminum has been chosen as antenna material with a chromium adhesive layer necessary for the nanostructure fabrication process. The antenna geometry has been selected to realize a resonance position in the mid-infrared (MIR) spectral range. To detect pronounced antenna reflectance peaks the rod-shaped nanoantennas have been arranged in an array with an optimized spacing relative to the lattice resonance (Rayleigh anomaly). Furthermore, the dielectric functions of different PCMs have been evaluated showing the largest contrast of the refractive index in combination with a small imaginary part of the permittivity for wavenumbers between 2000 and 6000 cm\(^{-1}\) for Ge\(_2\)Sb\(_2\)Te\(_6\) (GST-326), Ge\(_8\)Sb\(_2\)Te\(_{11}\) (GST-8211) and Ge\(_2\)Sb\(_2\)Te\(_5\) (GST-225). Additionally, InSb has been identified as "non-standard PCM" offering a pronounced contrast of the refractive index with an opposite sign compared to the GST compounds. As a consequence, a shift of the antenna array resonance frequency position to higher wavenumbers was shown for InSb, while a shift to lower wavenumbers was shown for the investigated GST compounds. The thickness of the PCM layers has been chosen to exclude strong thin film interferences, which would have interfered with the antenna resonance and the Rayleigh anomaly.

For experimental investigations nanoantenna arrays and PCM thin films have been combined and the reflectance spectra of the samples have been collected with Fourier transform infrared (FTIR) microspectroscopy. The phase transition of the PCMs has been conducted on a hot plate. In turn, the antenna array resonance position has been shifted up to 16.6% relative to the initial resonance position. Thereby, the placement of the antennas on top of a PCM thin film led to the largest shifts. Regarding the comparison of GST-326, GST-225 and GST-8211, the latter allowed for the largest percental shifts.
of the antenna array resonance frequency position. Concerning the resonance peak width, a correlation
between the position of the Rayleigh anomaly relative to the antenna array resonance peak has been
found. The narrowest resonance peaks have been determined for antenna arrays with a resonance
position at lower wavenumbers than the Rayleigh anomaly, but with a minimum difference between
both positions. The experimental reflectance spectra have been evaluated based on the tuning figure
of merit (TFOM), which is the ratio between the resonance shift and the resonance peak width. The
comparison of the results presented in this thesis and the results published in the literature revealed
that the concepts for the tuning of the antenna resonance position based on PCMs, especially the ones
presented here, led to very large TFOMs between 0.94 and 1.20.

Reversible phase transitions of GST-326 thin films have been realized by applying laser pulses on
the femtosecond and nanosecond timescale. The laser source available for femtosecond laser pulses
allowed for the simultaneous switching of entire antenna arrays. With a single femtosecond laser pulse
re-amorphization was realized, while a pulse sequence led to re-crystallization. Hence, the resonance
position of the addressed antenna arrays was (reversibly) shifted to higher, as well as to lower wavenum-
bers. However, a distinct difference between the resonance positions of the antenna arrays covered
with annealed crystalline and re-crystallized GST-326 has been detected, which has been explained by
the strongly increased absorption in the GST-326 thin film directly above the antennas. In turn, this
has led to the assumption that the PCM covering the antennas has been re-amorphized, while the
majority of the PCM - the PCM thin film between each antenna - has been re-crystallized. The second
approach for reversible switching of the GST-326 covering the nanoantennas has concerned nanosecond
laser pulses. Therefore, a setup has been built and power-time-effect diagrams have been evaluated to
determine the range of the spot sizes addressable with the laser setup. Based on the determined spot
sizes, calculations have been performed to predict stepwise shifting of the nanoantenna array resonance
frequency position by increasing and decreasing respectively the spot size on top of the nanoantennas.
Additionally, the use of \((\text{ZnS})_{80}-(\text{SiO}_2)_{20}\) as a protection layer against oxidization of the PCM thin film
has been investigated numerically. It has been shown that the shift of the antenna array resonance
position due to the phase change of a GST-326 thin film is maintained for a thin protection layer of
\((\text{ZnS})_{80}-(\text{SiO}_2)_{20}\) and thus, its application has been recommended. Furthermore, the use of \((\text{ZnS})_{80}-(\text{SiO}_2)_{20}\)
as a diffusion barrier between a gold antenna and a GST-326 thin film has been found to
strongly decrease the antenna array resonance shift. Therefore, aluminum as nanoantenna material
has been recommended for future sample designs as well.

8.2 Perspectives for future developments

The insights gained by the presented experimental and numerical results have shown that PCMs allow
for a non-volatile influencing of the resonance position of nanoantennas accompanied with relatively
low losses. While relatively simple nanorod antennas have been discussed in this thesis, the concept
has been applied for more complex nanostructures, such as a mid-infrared absorber [50], as well as
stacked nanorods which show a chiroptical response [223]. The latter will be described briefly in the
following.

The gold nanorod pairs stacked at their tips as illustrated in figure 8.1a are enantiomers, which
means that they are mirror image pairs. Therefore, the stacked nanorods are chiral\(^1\) metamolecules,

\(^1\)Chiral objects consist of two mirror images, which can not be superimposed on each other similar to the right and
which can act as the subunits or building blocks of a metamaterial (MM). Upon illumination with left-handed circularly polarized (LCP) and right-handed circularly polarized (RCP) light the difference in absorption and transmission $T_{RCP} - T_{LCP}$ respectively, shows different signs for the enantiomers. This is the chiroptical response (the response of the chiral nanostructure determined by FTIR spectroscopy) of the chiral nanostructures [223] and defined as circular dichroism (CD) [290].

A thin film layer stack of (ZnS)$_{80}$-(SiO$_2$)$_{20}$. A-GST-326 and (ZnS)$_{80}$-(SiO$_2$)$_{20}$ was deposited between the nanorods as shown in figure 8.1a and thus, their chiroptical response allowed for a shift of about 18% upon crystallization. Furthermore, another sample design with the combination of a left-handed and a right-handed enantiomer with a GST-326 layer between the nanorods of the right-handed enantiomer (cf. figure 8.1b) led to a sign flip in the CD signal upon crystallization of the GST-326. This behavior is based on the fact that the overall chiroptical response of the combined enantiomers is the sum of the individual signals. Here, the enantiomer stack was designed with a CD signal generated by enantiomers of both handedness, while the amplitude of the tunable enantiomere (with GST-326) is twice the amplitude compared to the enantiomer with the opposite handedness. Since the CD signals of both enantiomers possess opposite signs, the overall CD signal of the sample stack is equal to the chiroptical response of the tunable enantiomere with the amplitude lowered by 50%. Upon crystallization the tunable CD signal was shifted out of the initial spectral range and as a consequence, the non-tunable CD signal was revealed as depicted in figure 8.1c. There, both enantiomers were studied as tunable, as well as as non-tunable chiral nanostructure and confirmed the reproducibility of the concept. These results show that the CD signal can be shifted and flipped in sign while the enantiomer geometry is static by implementing a thin film of PCMs.

![Diagram](image)

(a) sample with chiral structure  (b) combined stack  (c) sign flip in circular dichroism (CD) for combined stack

Figure 8.1: Tip-stacked orthogonal gold nanorods build a right-handed (RH) enantiomer as shown in 8.1a. Its chiroptical signal can be shifted due to the sandwiched GST-326 thin film (red). On a second sample, the layer stack consists of a spin-on polymer (pale red), (ZnS)$_{80}$-(SiO$_2$)$_{20}$ barriers and a CaF$_2$ substrate (blue). The combination of a RH and a left-handed (LH) enantiomer is depicted in 8.1b, while the spectral position of the RH circular dichroism (CD) signal can be shifted with GST-326 depicted in 8.1c. The experimental reproducibility is shown by a LH enantiomer with a GST-326 layer (blue spectra), as well as by a RH enantiomer (red, as given in 8.1b). The crystallization of the PCM led to the sign flip of the CD signal (marked by an arrow). The figures have been adapted from [223].

Thus, the concept of PCMs used for the shifting of the nanoantenna resonance frequency position can be transferred to complex nanostructures, which enable additional optical functionalities, such as spectrally selective absorption [50] or the change of the polarization of light as for the chiral structures left hand. The Greek word “kheir” means “hand”.

$^2$This work was based on a collaboration between the I. Institute A at the RWTH Aachen University and the University of Stuttgart.
described above. Applications beyond these proof of concept studies rely on the reversible switching of the PCMs.

**Active plasmonics**

PCMs can introduce a post-fabrication tunability of the optical response of metamaterial (MM) or metasurface (MS) structures, which broadens their spectral applicability, as well as allows for further functionalities. This is the aim of the research field active plasmonics. The term active plasmonics was introduced in a publication by Krassavin et al. in 2004 [291] and has been addressed by numerous studies since then, e.g. in [292, 293, 294, 295, 296, 297]. Concerning actively tuneable metamaterials Zheludev et al. named PCMs as one of the most promising future platforms to alter the functionalities of resonant nanostructures due to their high property contrast between the amorphous and crystalline phase, as well as their reversible cyclability [48]. Compared to the phase change achieved by using vanadium dioxide (VO$_2$), PCMs allow for a non-volatile change of its dielectric function, which is much more energy efficient than volatile phase transitions.

Regarding an optically induced phase change the nanosecond switching is easier to implement compared to optical switching based on femtosecond laser pulses due to the lower energy necessary and the smaller required space for the laser source. A first attempt was published by Gholipour et al. [38], where ns laser pulses were used to change the phase of a GST-225 thin film in vicinity of gold ASRSs. However, ASRS spectra demonstrating successful reversibly switching were not shown. As has been calculated in this thesis, local addressing of (partial areas of) nanoantennas can allow for a precise tuning of the nanostructure resonance frequency position leading to a definite control of the optical properties of MMs and MSs.

In terms of a chip-scale data transport, ultrafast switching is demanded and therefore, electrically induced switching of PCMs seems to be necessary. A first approach was presented by Samson et al. [71], where gallium lanthanum sulfide was applied to shift the resonance position of an array of split-ring slit resonators coupled to bar nanoantennas. However, reversible switching was not shown and comparable concepts have not been published yet.

Recently, Zalden et al. presented electrical crystallization on a picosecond timescale [298]. Crystallization is the time-restricting switching step, since it is more time consuming than re-amorphization due to the ordering of the atoms. Therefore, the ultrafast realization of the crystallization is crucial for the application in future photonic data storage and transfer technologies.

The implementation of electrically induced switching of the PCM in optical devices depends on well-engineered designs. The electrical contacts can either be thought of as resonant nanostructures by themselves or have to be designed to exclude resonant optical responses in the spectral range of the real nanostructure, which could disturb the initially engineered optical signal.

**Beyond metallic nanorods**

New optical device architectures could also include structures supporting surface phonon polariton (SPhP) resonances. It was already shown that by using a quartz substrate, SPhPs were confined due to directly written patterns of C-GST-326 in a thin film of A-GST-326 [231]. Subsequently, the SPhPs were launched by using a scattering-type scanning near-field microscopy (s-SNOM) tip or by far-field radiation impinging on nanostructures.

Apart from quartz, localized surface phonon polariton (LSPHP) resonances with extremely narrow linewidth (7 - 24 cm$^{-1}$) can be supported by silicon carbide (SiC) nanopillars. These narrow resonances lead to high quality ($Q$) factors, defined as the ratio between the resonance frequency position and the
The use of PCM nanoparticles is promising regarding their increased stability (higher crystallization temperature $T_C$) and decreased necessary switching energy (lower liquidus temperature $T_L$) compared to PCM thin films [299]. Furthermore, PCM nanoparticles can be placed locally in very small gaps of resonant nanostructures, e.g. nanorod dimers, coupled split-ring resonators (SRR) or coupled bowties. Thereby, the resonance of such a nanostructure itself could be used to switch the phase of the PCM nanoparticles placed at the region of the highest field enhancement of the nanostructure, such as the split in a SRR or the gap between a bowtie or a nanorod dimer.

Future progress will also depend on the development of patterning techniques on a sub-micrometer scale. Complex fabrication processes relying on focused ion beam milling (FIB) or multi-step electron beam lithography (EBL) are relatively expensive and time-consuming. Alternatively, extreme ultraviolet (EUV) proximity lithography could allow for a less expensive and less time consuming fabrication of nanostructures for larger wafer sizes [300].

**Multistep shifting** As it was shown by Chen et al. PCMs can allow for a multistep resonance tuning due to the possibility of achieving stable effective media composed of a mixture of amorphous and crystalline states of the PCM [32]. By increasing the annealing temperature and duration the percentage of the crystallized PCM increased. While Chen et al. applied annealing on a hot plate for slow and stepwise crystallization, the gradual increase of the laser-induced spot size theoretically shown in chapter 7 is an alternative approach for the stepwise shifting of the resonance position of resonant nanostructures. A similar result is expected to be realizable by rotating a laser spot of constant size about the center of a nanorod for example.

In summary, the use of PCMs regarding plasmonic and photonic nanostructures led to a variety of published concepts introducing the active tunability of the optical properties of the resonant nanoantennas. A relatively constant refractive index, as well as small imaginary parts of the permittivity were applied, similar to the studies presented in this thesis. The pronounced change of the permittivity of PCMs in the visible spectral range has not been applied yet and promises exciting new possibilities, such as the variation between a positive and a negative real part of the permittivity for example. Additionally, the variety of PCM compounds has not been exploited in the field of active plasmonics yet. However, PCMs best-suited for the individual photonic or plasmonic application can be identified by studying their dielectric function (as in this thesis), their thermal properties, their electrical properties and so on. A precise selection of PCMs based on a deep understanding of this material class can allow for much better device performances in future applications.

The published concepts showed that PCMs can build a platform for a fast development in the field of active plasmonics and photonics. The next steps, which could allow for a breakthrough beyond the proof of concept, are expected to be the demonstration of electrical switching, as well as the realization of optical switching with smaller device sizes, possibly based on existing read-write technologies as known from rewritable optical discs including PCMs. Furthermore, the electrical and the optical concepts need to show a large number of reproducible switching cycles without a (gradual) attenuation of the resonant optical responses.
APPENDIX
A.1 Comments on the optical properties of metals

Skin depth in aluminum In chapter 2, the Drude model was introduced to describe the dielectric function of noble metals such as aluminum. Furthermore, the extinction coefficient $\kappa$ was introduced. The extinction coefficient is the imaginary part of the complex refractive index $\tilde{n}$, which is defined as follows [11]:

\[ n(\tilde{\nu}) = n + ik \]  
\[ n(\tilde{\nu}) = \frac{1}{\sqrt{2}} \sqrt{\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2}} \]  
\[ \kappa(\tilde{\nu}) = \frac{1}{\sqrt{2}} \sqrt{-\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2}} \]

According to Beer’s law the incident field decays exponentially in the metal. The evaluation of equation 2.5 (definition of $\delta_{sk}$) by using $\kappa$ given in equation A.1c leads to a skin depth $\delta_{sk}$ in aluminum of about 17 nm in the MIR spectral range. This is depicted in figure A.1a. For increasing wavenumbers $\tilde{\nu}$, the skin depth $\delta_{sk}$ increases, which is based on the strong decrease of the imaginary part of the complex refractive index $\kappa(\tilde{\nu})$ for increasing wavenumbers displayed in figure A.1b.

Reflectivity of aluminum The reflectivity $R$ (In this thesis, $R$ is used to denote the reflectance.) of noble metals is defined by the real and the imaginary part of the complex refractive index $\tilde{n}$ as follows [11]:

\[ R(\tilde{\nu}) = \frac{(n - 1)^2 + \kappa^2}{(n + 1)^2 + \kappa^2} \]

In figure A.2 it can be seen that the reflectivity is nearly 100% for wavenumbers below the plasma wavenumber $\tilde{\nu}_p \approx 94500 \text{ cm}^{-1}$ and drops to zero for the plasma wavenumber. At very high wavenumbers metals can become transparent, which is known as UV transparency of metals [11]. Since the reflectivity $R$ is based on the real and the imaginary part of the complex refractive index $\tilde{n}$, the real part is depicted in figure A.2b, while the imaginary part was already introduced in figure A.1b.
A.1 Comments on the optical properties of metals

Figure A.1: The skin depth $\delta_{sk}(\tilde{\nu})$ and the extinction coefficient $\kappa(\tilde{\nu})$ were evaluated for aluminum described by the Drude model $\varepsilon_D(\tilde{\nu})$. In the MIR spectral range, the field penetrates only about 17 nm of the aluminum while the skin depth $\delta_{sk}$ increases again for wavenumbers $\tilde{\nu}$ above 20000 cm$^{-1}$. At the same time the extinction coefficient $\kappa$ decreases and approaches zero.

Figure A.2: The reflectivity $R(\tilde{\nu})$ of aluminum, shown in figure A.2a, was calculated for the Drude model $\varepsilon_D(\tilde{\nu})$. For the wavenumbers below the plasma frequency $\tilde{\nu}_p$ aluminum shows a nearly 100% reflectivity. Close to $\tilde{\nu}_p$ the reflectivity drops to zero and aluminum becomes transparent. The real part of the refractive index $n(\tilde{\nu})$, which is used to calculate the reflectivity, is depicted in figure A.2b.

Dispersion relation of surface plasmon polaritons The dispersion relation of surface plasmon polaritons (SPPs) was introduced in chapter 2. There, the dielectric function of the metal (here aluminum) is calculated by the Drude model $\varepsilon_D(\tilde{\nu})$, while the damping rate $\gamma_D$ is assumed to be much smaller than the wavenumber ($\gamma_D \ll \tilde{\nu}$) and thus, is neglected. Air, as well as a dielectric ($\varepsilon_d = 3.4$, silicon) are considered as second infinite medium at the interface to the infinite aluminum. The aluminum/air interface is shown by black lines in figure A.3 and the aluminum/dielectric interface is depicted by gray lines in figure A.3. In this figure the wave vector and the wavenumber are normalized to the plasma wave vector $k_p$ and the plasma wavenumber $\tilde{\nu}_p$. The SPP dispersion splits in two branches, which correspond to a low-frequency and a high-frequency mode. In the regime of large wave vectors the dispersion relation approaches the surface plasmon wavenumber $\tilde{\nu}_{sp}$ as asymptotic limit and the wave vector $k_x$ is real. The surface plasmon wavenumber is defined by $\tilde{\nu}_{sp} = \tilde{\nu}_p / \sqrt{1 + \varepsilon_d}$ [11]. Between the regime of radiative SPP modes, $\tilde{\nu} > \tilde{\nu}_p$, and bound modes, $\tilde{\nu} < \tilde{\nu}_{sp}$, the wave vector in $x$-direction $k_x$ is imaginary and no propagation of the SPPs is allowed. For small wave vectors $k_x$, the SPP dispersion approaches the light line of the corresponding dielectric medium (air with $\varepsilon_d = 1.0$ and the dielectric medium $\varepsilon_d = 3.4$). Thus, the SPPs extend far into the dielectric (multiples of the
A.1 Comments on the optical properties of metals

incident wavelengths $\lambda$). Since the SPP dispersion relation lies right to the light line, the wave vector $k_{x,1}$ of the SPP is larger than the wave vector of the propagating light $\omega/c = 2\pi\tilde{\nu}$. Therefore, the SPPs are bound and can neither decay by photon emission, nor be excited by an incident plane wave. Coupling of light to the SPP depends on matching $k_{x,1}$ and $\tilde{\nu}$. Different configurations including a prism and attenuated total reflection named after Otto and Kretschmann allow for a coupling between light and SPPs [301]. Besides, nanostructures can be used to excite SPPs as well [302]. A detailed discussion of SPPs and the dispersion relation can be found in [11] and [13].

Figure A.3: The dispersion relation for SPPs $\tilde{\nu}(k_{x,1})$ (equation 2.10) is given at the interface between aluminum and air (black solid lines) and at the interface between aluminum and a dielectric with $\varepsilon_d = 3.4$ (gray solid lines). The wave vector $k$ has been normalized by $k_p = 2\pi\tilde{\nu}_p$. The light line for photons in air (black dashed line) and for photons in the dielectric with $\varepsilon_d = 3.4$ (gray dashed) are shown. The surface plasmon and the plasmon wavenumbers $\tilde{\nu}_sp$ and $\tilde{\nu}_p$ are asymptotes for the two branches the SPP dispersion relation splits into.

Hybridized resonant modes of asymmetric split-ring resonators In section 2.3 the shift of the resonance position of asymmetrical split-ring resonators (ACSRRs) was discussed. Besides the two individual resonance frequency positions, the coupling of the two SRRs leads to two hybridized resonant modes. Their energy (or resonance frequency) is higher and lower compared to the two individual SRR resonances as depicted in figure A.4.

It should be noted that due to the symmetry breaking by using different SRR arm lengths $l_y$ (ACSRRs) so-called dark modes are excited [52]. Since these modes allow for more narrow resonances compared to symmetrically coupled SRRs, Pryce et al. chose ACSRRs for their study on the resonance shifts based on the varied coupling by using an elastomeric substrate [36]. The increase of the coupling distance (moving the SRRs apart) leads to a shift of the dark-mode resonance wavelength to shorter wavelengths and to a shift of the LC resonance position to longer wavelengths [52].
A.2 Fit parameters for dielectric functions

Figure A.4: The tip coupling of two asymmetric SRRs leads to a hybridization of the resonant modes. The charge distribution is marked by “+” and “-”. The hybridized modes are denoted by “|ω₊⟩” and “|ω₋⟩” [303]. The dark coupled mode (|ω₋⟩) is marked in gray, while the bright mode (|ω₊⟩) shows a much higher frequency and energy respectively [304]. Liang et al. described the full hybridization scheme of symmetrically coupled SRRs, which includes the magnetic fields, as well as the energies of each resonance [305].

A.2 Fit parameters for dielectric functions

Initial dielectric functions for used PCMs As discussed in subsection 3.3.2 on page 46, the dielectric functions have been determined by Kremers [110]. There, the initial data was measured with FTIR spectroscopy and ellipsometry. The first was used to collect data in the spectral range between 0.03 and 1.00 eV, while the latter was used for the energy range up to 2.50 eV. The resulting reflection and transmission spectra taken by FTIR spectroscopy and ellipsometry were analyzed with the software SCOUT from the company W. Theiss Hard- und Software. This allows for fitting optical models as Drude or Tauc-Lorentz (cf. 3.3) to measured spectra. The final data set (steps of 20 meV), which is the dielectric function of e.g. GST-225, GST-326 and GST-8211 in its amorphous and crystalline state, is a result of this fitting routine.

Re-fit with Drude and Tauc-Lorentz In this work, the given data sets of discrete values for ε₁ and ε₁ [136] were re-fitted with the same oscillator models as in [110] to find a continuous function ε in the MIR spectral range. The fit parameters listed in table A.1 originate from the Drude and Tauc-Lorentz oscillators, which were used to model the measured reflectance and ellipsometry spectra of the given PCMs. This routine was described by Shportko et al. [103] and was discussed in detail by Kremers [110] and for amorphous PCMs by Rüttchen [306]. In the amorphous phase the oscillator strength A, the broadening term C, the energy $E_g$ (or $ω_g$ in rad·s$^{-1}$)$^1$, the peak transition energy $E_0$ (or $ω_0$ in rad·s$^{-1}$), as well as $ε_{\text{const}}$ needed to be evaluated, while an additional Drude contribution with the plasma frequency $ω_p$ and the damping constant $γ_D$ needed to be considered in the crystalline phase. The fit generated a continuous function $ε(E)$, $ε(ω)$ or $ε(\tilde{ν})$ in a given frequency range, which needed to be adapted according to the accuracy of the fit, as can be seen in figure A.5. The model was solved within the software Wolfram Mathematica 9.

It has to be noted that in case of C-InSb, the description with a Drude and a Tauc-Lorentz oscillator, which was applied in this thesis, is insufficient for energies above 1 eV [147]. Therefore, Kremers applied an additional Kim oscillator for interband transitions, which allows for the description of the absorption at about 1 eV. In the work presented here, InSb was mainly used for experiments and the corresponding simulations of the reflectance spectra were conducted by applying the dielectric data set given by [136]. In contrast, the calculation of thin film interferences of InSb, which is based on the re-fit of the dielectric data sets (for InSb shown in figures A.5c and A.5d) was avoided, since the fit

$^1$The notations $E_g$ and $ω_g$ was preferred to $E_G$ and $ω_G$, since the fit parameter of the Tauc-Lorentz oscillator is not necessarily equivalent to the actual band gap of the material [307].
for C-InSb is considered to be insufficient (the fit and the given dielectric data set for C-InSb deviate for the small frequency range as shown in figure A.5d).

**Tauc-Lorentz oscillator for amorphous PCMs** The Tauc-Lorentz oscillator applied for amorphous PCMs was discussed in detail in chapter 3. Here, the explicit expressions for the parameterized dielectric function $\varepsilon_{TL}$ will be given. The following equations were taken from the work of Jellison and Modine in [144] and [140].

To calculate the imaginary part of the Tauc-Lorentz oscillator $\varepsilon_{2,TL}$, the imaginary part $\varepsilon_2$ of a Lorentz oscillator (equation 3.11) is combined with the Tauc joint density of states (equation 3.12), which leads to the following expression [140]:

$$
\varepsilon_{2,TL}(E) = \frac{A \cdot E_0 \cdot C \cdot (E - E_g)^2}{(E^2 - E_0^2)^2 + C^2 \cdot E^2} \cdot \frac{1}{E} \quad \text{for } E > E_g
$$

(A.3a)

$$
\varepsilon_{2,TL}(E) = 0 \quad \text{for } E \leq E_g
$$

(A.3b)

With the Kramers-Kronig integration, the real part of the permittivity $\varepsilon_{1,TL}$ is derived from $\varepsilon_{2,TL}$. It has to be noted that the integral is taken over positive $E$. As a result, the real part is given as a function of the energy as follows:

$$
\varepsilon_{1,TL}(E) = \varepsilon_{\text{const}} + \frac{A \cdot C}{\pi \cdot \xi^4} \cdot \frac{a_{\text{ln}}}{2 \alpha \cdot E_0} \cdot \ln \left( \frac{E^2 + E_g^2 + \alpha \cdot E_g}{E^2 + E_g^2 - \alpha \cdot E_g} \right) - \frac{A}{\pi \cdot \xi^4} \cdot \frac{a_{\text{atan}}}{E_0} \cdot \left[ \pi - \text{atan} \left( \frac{2E_g + \alpha}{C} \right) + \text{atan} \left( \frac{-2E_g + \alpha}{C} \right) \right] + 2 \cdot \frac{A \cdot E_0 \cdot C}{\pi \cdot \xi^4} \cdot E_g \cdot (E^2 - \gamma^2) \cdot \left[ \pi + 2 \cdot \text{atan} \left( \frac{\gamma^2 - E_g^2}{\alpha \cdot C} \right) \right] - \frac{A \cdot E_0 \cdot C}{\pi \cdot \xi^4} \cdot \frac{E^2 + E_g^2}{E} \cdot \ln \left( \frac{|E - E_g|}{E + E_g} \right) + 2 \cdot \frac{A \cdot E_0 \cdot C}{\pi \cdot \xi^4} \cdot E_g \cdot \ln \left[ \frac{|E - E_g| \cdot (E + E_g)}{\sqrt{(E_0^2 - E_g^2)^2 + E_g^2 \cdot C^2}} \right]
$$

(A.4)

The factors $\xi^4$, $a_{\text{ln}}$, $\alpha$, $a_{\text{atan}}$ and $\gamma$ are described as listed:

$$
\xi^4 = (E^2 - \gamma^2)^2 + \frac{\alpha^2 \cdot C^2}{4}
$$

(A.5a)

$$
a_{\text{ln}} = (E_g^2 - E_0^2) \cdot E^2 + E_g^2 \cdot C^2 - E_0^2 \cdot (E_0^2 - 3E_g^2)
$$

(A.5b)

$$
\alpha = \sqrt{4E_0^2 - C^2}
$$

(A.5c)

$$
a_{\text{atan}} = (E^2 - E_0^2) \cdot (E_0^2 + E_g^2) + E_g^2 \cdot C^2
$$

(A.5d)

$$
\gamma = \sqrt{E_0^2 - \frac{C^2}{2}}
$$

(A.5e)
A.2 Fit parameters for dielectric functions

Finally, the dielectric function of amorphous PCMs can be expressed as follows (cf. equation 3.13a):

$$\varepsilon_A(\omega) = \varepsilon_{\text{const}} + \varepsilon_{\text{TL}}(\omega) \quad \text{with} \quad \varepsilon_{\text{TL}}(\omega) = \varepsilon_{1,\text{TL}} + i \varepsilon_{2,\text{TL}}$$ (A.6)

The complex dielectric function of crystalline PCMs was described in chapter 3 as follows:

$$\varepsilon_C(\omega) = \varepsilon_{\text{const}} + \varepsilon_{\text{TL}}(\omega) + \varepsilon_D(\omega) \quad \text{with} \quad \varepsilon_D(\omega) = -\frac{\omega_p^2}{\omega^2 + i \gamma_D \omega}$$ (A.7)

The seven fit parameters found in this thesis are listed in table A.1:

- oscillator strength $f_{ij}$, denoted as $A$ by Tauc et al.
- broadening term $C$
- $E_g$ or $\omega_g$ is associated with the band gap (cf. footnote 1 on page 168)
- peak transition energy or frequency $E_0$ or $\omega_0$
- $\varepsilon_{\text{const}}$
- plasma frequency $\omega_p$
- damping rate $\gamma_D$

In figure A.6 the dielectric function of GST-8211 is compared for the complex permittivity $\varepsilon_C$ with the Drude contribution $\varepsilon_D$ and without it $\varepsilon_{\text{noD}}$. The latter was used to calculate the optical dielectric constant $\varepsilon_{\infty,C}$ [103]. At $E = 0.05 \text{eV}$, which was set as low-energy limit of the real part of the permittivity here, the subtraction of the Drude contribution led to an increase of $\varepsilon_{\infty,C}$ from 37 to 39 for GST-8211 here.

<table>
<thead>
<tr>
<th></th>
<th>Ge$_3$Sb$_2$Te$_6$</th>
<th>Ge$_3$Sb$<em>2$Te$</em>{11}$</th>
<th>Ge$_2$Sb$_2$Te$_5$</th>
<th>InSb</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A / 10^{17} \text{rad s}^{-1}$</td>
<td>1.324</td>
<td>3.166</td>
<td>0.966</td>
<td>2.965</td>
</tr>
<tr>
<td>$C / 10^{15} \text{rad s}^{-1}$</td>
<td>5.167</td>
<td>2.431</td>
<td>2.104</td>
<td>2.105</td>
</tr>
<tr>
<td>$\omega_g / 10^{14} \text{rad s}^{-1}$</td>
<td>9.262</td>
<td>7.137</td>
<td>8.602</td>
<td>6.976</td>
</tr>
<tr>
<td>$\omega_0 / 10^{15} \text{rad s}^{-1}$</td>
<td>4.068</td>
<td>1.852</td>
<td>3.418</td>
<td>2.150</td>
</tr>
<tr>
<td>$\varepsilon_{\text{const}}$</td>
<td>0.425</td>
<td>2.253</td>
<td>2.533</td>
<td>0.031</td>
</tr>
<tr>
<td>$\omega_p / 10^{15} \text{rad s}^{-1}$</td>
<td>-</td>
<td>3.007</td>
<td>-</td>
<td>1.435</td>
</tr>
<tr>
<td>$\gamma_D / 10^{15} \text{rad s}^{-1}$</td>
<td>-</td>
<td>19.92</td>
<td>-</td>
<td>1.033</td>
</tr>
</tbody>
</table>

Table A.1: This table summarizes fit parameters for the Tauc-Lorentz (amorphous A and crystalline phase C) and an additional Drude term (C) for the PCMs GST-326 and GST-8211, GST-225, as well as for InSb. The parameters were calculated for $\varepsilon(\omega)$, which leads to the fact that the parameters are given in rad s$^{-1}$ instead of eV, as e.g. in [140]. If the calculated parameters are normalized to eV by multiplying with $\hbar$, the values are in the same order of magnitude as the fit results given in [140]. For clarity, the fit parameters with more than 3 digits are round half away from zero here. The parameters given for InSb have to be considered with reservation, since the description with the given oscillator models is insufficient, especially above 1 eV ($\approx 1.51 \times 10^{15} \text{rad s}^{-1}$) [147].
A.2 Fit parameters for dielectric functions

Figure A.5: The comparison between the dielectric data (symbols) set of A-GST-326, C-GST-8211, A-InSb and C-InSb given by KREMERS [136] and the additional fits (lines) is shown here. The real parts $\varepsilon_1$ are shown in black and the imaginary parts $\varepsilon_2$ are shown in gray. The data sets (only every 10th data point is shown) and the fits match very well for A-GST-326, C-GST-8211 and A-InSb, while C-InSb can not be described by the oscillator models introduced in chapter 3. It has to be noted, that the initial equations are solved in angular frequencies $\omega$.

Figure A.6: The real (black) and the imaginary part (gray) of the permittivity $\varepsilon$ of GST-8211 is shown as a function of the energy $E$ and the wavenumber $\nu$. Data for amorphous (dashed) and crystalline (solid) GST-8211 was collected by KREMERS [110] and taken from [136]. The strong dependency on $E$ (or $\nu$), as well as on the structural phase is clearly visible. The change of the real part $\Delta \varepsilon_1$ and the imaginary part $\Delta \varepsilon_2$ upon crystallization is marked by a black and a gray arrow. The dielectric constant $\varepsilon_\infty$ was determined from the dielectric function as $\varepsilon_1(E = 0.05 \text{ eV})$, while the optical dielectric constant $\varepsilon_{\text{opt}}$ was determined after the Drude contribution was subtracted following SHPORTEKO et al. [103]. The difference $\Delta \varepsilon_\infty$ is marked in red.
A.3 Sample fabrication and characterization

In chapter 4, the fabrication method electron beam lithography and the characterization methods scanning electron microscopy and Fourier transform infrared microspectroscopy have been introduced. To complete different aspects discussed there, additional tables on electron beam lithography regarding conducted sample fabrication steps, as well as on used chemicals and source materials are shown. Furthermore, physical vapor deposition (thermal evaporation and sputtering) has been applied. A brief overview on the used methods will be given here as well.

A.3.1 Electron beam lithography

**Materials relevant for the sample fabrication**

During the fabrication of the samples, different substrates, chemicals and source materials were used. These are listed in table A.2, including the product specifications and information on the suppliers.

A.3.2 Physical vapor deposition

**Thermal evaporation**

Thermal evaporation and sputtering are physical vapor deposition (PVD) methods. In PVD methods, a target is used to deposit a material thin film on a substrate. The method of thermal evaporation uses resistive heating to remove the material from the target. Thicknesses of several nm up to several µm can be achieved. Vacuum chambers allow for very smooth films.

Thermal evaporation is well-established as deposition method for films of a single material. The equilibrium vapor pressure\(^2\) defines at which temperature (with a given pressure in the evaporation chamber) and with it at which electric current a source material evaporates or sublimes. Sublimation can be observed for the metal chromium (Cr) for example [308]. A co-evaporation of different sources to fabricate a compound thin film is difficult, since the vapor pressures are different. The evaporation of a compound source is difficult as well, since the source material may undergo chemical reactions (e.g. decomposition) during evaporation. Furthermore, the elements of the compound source are likely to be evaporated with different velocities (depending on the vapor pressure of each element).

In figure A.7, a thermal evaporation chamber is schematically shown. The chamber is pumped down to high vacuum (A). For thermal evaporation with the available setup a pressure down to about 5 \(\times 10^{-6}\) mbar is used. The source material (B) is resistively heated via electrodes (C). This heating results in vaporization of the source material (D). The sample (E) is placed on top of the source material. A quartz oscillator crystal (F) enables the detection of the material deposition rate, given as Å/s. For aluminum a rate of about 0.8 Å/s in average was applied.

Due to the high vacuum (base pressure: 5...6 \(\times 10^{-6}\) mbar) the mean free path is larger than the distance between source and substrate (distance between B and E in figure A.7). Collisions between source and residual gas particles are minimized. Nevertheless, the quality of the evaporated thin film on the substrate can be improved by rotation of the sample. This technique allows for a more homogeneous film thickness. A very detailed description of thermal evaporation can be found in [308].

---

\(^2\)The pressure at which the liquid and the vapor phase are in thermodynamic equilibrium in a closed system. The equilibrium vapor pressure depends on the temperature.
The target materials used in this thesis are listed in table A.2. Details on the thermal evaporation of aluminum are discussed in appendix on page 180.

Figure A.7: Displayed is a scheme of a thermal evaporation setup. The chamber is set under high vacuum (A, empty arrow head). The target - here as a boat (B) - is clamped to electrodes (C), which resistively heat the boat to vaporize the source material (D, filled arrow heads). The substrate (E) is placed towards the source boat. Clamps hold the substrate on a substrate holder. A quartz oscillator crystal (F, black) allows for the measurement of the evaporation rate. The scheme is based on figure 5.6 in [309].

Sputter deposition

In contrast to thermal evaporation, in sputtering the material is dislodged from the target by means of a plasma. Element and rather complex alloy films can be deposited, whereas the latter can be realized by sputtering from a compound or from an elemental target.

In plasma-based sputtering positive ions are accelerated towards the target. Relative to the plasma the target is at negative potential. The sputtering system can be based either on a direct current (DC) or on a radiofrequency (RF) principle. The ionization or plasma source can also be placed separately, which is called vacuum-based sputtering. After the acceleration, the plasma is then extracted into a processing chamber under vacuum. For this process, the mean bombarding energy is generally higher relative to the standard process [310]. The details of the sputtering process in general are discussed in [311].

For the PCM thin film deposition dynamic magnetron sputtering is used, which allows for higher sputter rates due to an additional magnetic field. The magnetic field is generated by magnetrons behind the target (cathode).

The thin films of different PCMs used for the experiments in the framework of this thesis are deposited at the institute. In detail, magnetron sputtering with a Ardenne LS 320S system is used. Between the PCM target\(^3\) (e.g. GST-326) and the substrate (e.g. Si) a direct current voltage is applied. Thus, the substrate acts as a positively charged electrode and the target as a negatively charged electrode. A simultaneous deposition of the PCM on multiple substrates is enabled by a rotating substrate holder. During sputtering, argon is used as inert gas with a flow of about 20 sccm. By impact ionization of argon atoms a plasma is built. As a result, the target material is removed and accelerated towards the substrate. Hence thin films of the particular PCM are deposited. Additionally, for magnetron sputtering a magnetic field is applied behind the target, which allows for a higher sputter rate, a lower ultimate pressure and finally, for a better PCM film quality. The base pressure in the sputter system is about \(5 \cdot 10^{-6}\) mbar, while the ultimate pressure during the sputter process is about \(3 \cdot 10^{-3}\) mbar.

\(^3\)The specific targets used in this thesis are listed in appendix A.3.
<table>
<thead>
<tr>
<th>Type</th>
<th>Supplier</th>
<th>Additional Information</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Electrodeposition</strong></td>
<td>Kurt J. Lesker Company</td>
<td>3 mm diameter</td>
</tr>
<tr>
<td><strong>Electrodeposition</strong></td>
<td>Kurt J. Lesker Company</td>
<td>0.2 mm diameter</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Type</th>
<th>Supplier</th>
<th>Additional Information</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Metal Evaporation</strong></td>
<td>Kurt J. Lesker Company</td>
<td>0.3 mm diameter</td>
</tr>
<tr>
<td><strong>Metal Evaporation</strong></td>
<td>Kurt J. Lesker Company</td>
<td>0.2 mm diameter</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Type</th>
<th>Supplier</th>
<th>Additional Information</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sputtering</strong></td>
<td>Umicore Thin Film Products AG</td>
<td>Thin film products AC</td>
</tr>
<tr>
<td><strong>Sputtering</strong></td>
<td>Umicore Thin Film Products AG</td>
<td>Thin film products AC</td>
</tr>
<tr>
<td><strong>Sputtering</strong></td>
<td>Umicore Thin Film Products AG</td>
<td>Thin film products AC</td>
</tr>
<tr>
<td><strong>Sputtering</strong></td>
<td>Umicore Thin Film Products AG</td>
<td>Thin film products AC</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Type</th>
<th>Supplier</th>
<th>Additional Information</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chemical Vapor Deposition</strong></td>
<td>Metallochrome 99.99% purity, 0.5-2 mm diameter</td>
<td>0.1 mm diameter</td>
</tr>
<tr>
<td><strong>Chemical Vapor Deposition</strong></td>
<td>Metallochrome 99.99% purity, 0.5-2 mm diameter</td>
<td>0.1 mm diameter</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Type</th>
<th>Supplier</th>
<th>Additional Information</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Photolithography</strong></td>
<td>AR-P679.04 Allresist GmbH</td>
<td>Poly(methylmethacrylate), solids content 4%, viscosity 43.4 mPa·s, baking recommended at 150-190°C for 2-5 min, 220 nm thickness for spin coating with 6000 rpm used for single resist layer process, cf. [312]</td>
</tr>
<tr>
<td><strong>Photolithography</strong></td>
<td>AR-P617.03 Allresist GmbH</td>
<td>Poly(methylmethacrylate), solids content 3%, viscosity 7 mPa·s, baking recommended at 200°C for 10 min, 80 nm thickness for spin coating with 6000 rpm used for double resist layer process, can also be used for planarization, 220 nm thickness for spin coating with 6000 rpm used for single resist layer process, cf. [312]</td>
</tr>
<tr>
<td><strong>Photolithography</strong></td>
<td>AR-P679.02 Allresist GmbH</td>
<td>Poly(methylmethacrylate), solids content 2%, viscosity 7.8 mPa·s, baking recommended at 150-190°C for 2-5 min, 60 nm thickness for spin coating with 6000 rpm used for double resist layer process, cf. [312]</td>
</tr>
<tr>
<td><strong>Photolithography</strong></td>
<td>AR-P617.02 Allresist GmbH</td>
<td>Poly(methylmethacrylate), solids content 2%, viscosity 7.8 mPa·s, baking recommended at 150-190°C for 2-5 min, 60 nm thickness for spin coating with 6000 rpm used for double resist layer process, can also be used for planarization, 220 nm thickness for spin coating with 6000 rpm used for single resist layer process, cf. [312]</td>
</tr>
<tr>
<td><strong>Photolithography</strong></td>
<td>AR-P679.03 Allresist GmbH</td>
<td>Poly(methylmethacrylate), solids content 3%, viscosity 7 mPa·s, baking recommended at 200°C for 10 min, 80 nm thickness for spin coating with 6000 rpm used for double resist layer process, can also be used for planarization, 220 nm thickness for spin coating with 6000 rpm used for single resist layer process, cf. [312]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Type</th>
<th>Supplier</th>
<th>Additional Information</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chemical Vapor Deposition</strong></td>
<td>Metallochrome 99.99% purity, 0.5-2 mm diameter</td>
<td>0.1 mm diameter</td>
</tr>
<tr>
<td><strong>Chemical Vapor Deposition</strong></td>
<td>Metallochrome 99.99% purity, 0.5-2 mm diameter</td>
<td>0.1 mm diameter</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Type</th>
<th>Supplier</th>
<th>Additional Information</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Photolithography</strong></td>
<td>AR-P679.04 Allresist GmbH</td>
<td>Poly(methylmethacrylate), solids content 4%, viscosity 43.4 mPa·s, baking recommended at 150-190°C for 2-5 min, 220 nm thickness for spin coating with 6000 rpm used for single resist layer process, cf. [312]</td>
</tr>
<tr>
<td><strong>Photolithography</strong></td>
<td>AR-P617.03 Allresist GmbH</td>
<td>Poly(methylmethacrylate), solids content 3%, viscosity 7 mPa·s, baking recommended at 200°C for 10 min, 80 nm thickness for spin coating with 6000 rpm used for double resist layer process, can also be used for planarization, 220 nm thickness for spin coating with 6000 rpm used for single resist layer process, cf. [312]</td>
</tr>
<tr>
<td><strong>Photolithography</strong></td>
<td>AR-P679.02 Allresist GmbH</td>
<td>Poly(methylmethacrylate), solids content 2%, viscosity 7.8 mPa·s, baking recommended at 150-190°C for 2-5 min, 60 nm thickness for spin coating with 6000 rpm used for double resist layer process, can also be used for planarization, 220 nm thickness for spin coating with 6000 rpm used for single resist layer process, cf. [312]</td>
</tr>
<tr>
<td><strong>Photolithography</strong></td>
<td>AR-P617.02 Allresist GmbH</td>
<td>Poly(methylmethacrylate), solids content 2%, viscosity 7.8 mPa·s, baking recommended at 150-190°C for 2-5 min, 60 nm thickness for spin coating with 6000 rpm used for double resist layer process, can also be used for planarization, 220 nm thickness for spin coating with 6000 rpm used for single resist layer process, cf. [312]</td>
</tr>
<tr>
<td><strong>Photolithography</strong></td>
<td>AR-P679.03 Allresist GmbH</td>
<td>Poly(methylmethacrylate), solids content 3%, viscosity 7 mPa·s, baking recommended at 200°C for 10 min, 80 nm thickness for spin coating with 6000 rpm used for double resist layer process, can also be used for planarization, 220 nm thickness for spin coating with 6000 rpm used for single resist layer process, cf. [312]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Type</th>
<th>Supplier</th>
<th>Additional Information</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Photolithography</strong></td>
<td>AR-P679.04 Allresist GmbH</td>
<td>Poly(methylmethacrylate), solids content 4%, viscosity 43.4 mPa·s, baking recommended at 150-190°C for 2-5 min, 220 nm thickness for spin coating with 6000 rpm used for single resist layer process, cf. [312]</td>
</tr>
<tr>
<td><strong>Photolithography</strong></td>
<td>AR-P617.03 Allresist GmbH</td>
<td>Poly(methylmethacrylate), solids content 3%, viscosity 7 mPa·s, baking recommended at 200°C for 10 min, 80 nm thickness for spin coating with 6000 rpm used for double resist layer process, can also be used for planarization, 220 nm thickness for spin coating with 6000 rpm used for single resist layer process, cf. [312]</td>
</tr>
<tr>
<td><strong>Photolithography</strong></td>
<td>AR-P679.02 Allresist GmbH</td>
<td>Poly(methylmethacrylate), solids content 2%, viscosity 7.8 mPa·s, baking recommended at 150-190°C for 2-5 min, 60 nm thickness for spin coating with 6000 rpm used for double resist layer process, can also be used for planarization, 220 nm thickness for spin coating with 6000 rpm used for single resist layer process, cf. [312]</td>
</tr>
<tr>
<td><strong>Photolithography</strong></td>
<td>AR-P617.02 Allresist GmbH</td>
<td>Poly(methylmethacrylate), solids content 2%, viscosity 7.8 mPa·s, baking recommended at 150-190°C for 2-5 min, 60 nm thickness for spin coating with 6000 rpm used for double resist layer process, can also be used for planarization, 220 nm thickness for spin coating with 6000 rpm used for single resist layer process, cf. [312]</td>
</tr>
<tr>
<td><strong>Photolithography</strong></td>
<td>AR-P679.03 Allresist GmbH</td>
<td>Poly(methylmethacrylate), solids content 3%, viscosity 7 mPa·s, baking recommended at 200°C for 10 min, 80 nm thickness for spin coating with 6000 rpm used for double resist layer process, can also be used for planarization, 220 nm thickness for spin coating with 6000 rpm used for single resist layer process, cf. [312]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Type</th>
<th>Supplier</th>
<th>Additional Information</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Photolithography</strong></td>
<td>AR-P679.04 Allresist GmbH</td>
<td>Poly(methylmethacrylate), solids content 4%, viscosity 43.4 mPa·s, baking recommended at 150-190°C for 2-5 min, 220 nm thickness for spin coating with 6000 rpm used for single resist layer process, cf. [312]</td>
</tr>
<tr>
<td><strong>Photolithography</strong></td>
<td>AR-P617.03 Allresist GmbH</td>
<td>Poly(methylmethacrylate), solids content 3%, viscosity 7 mPa·s, baking recommended at 200°C for 10 min, 80 nm thickness for spin coating with 6000 rpm used for double resist layer process, can also be used for planarization, 220 nm thickness for spin coating with 6000 rpm used for single resist layer process, cf. [312]</td>
</tr>
</tbody>
</table>
A.3.3 Comments on FTIR microspectroscopy

Parameters during FTIR sample characterization

The experimental reflectance spectra displayed in this thesis were collected by FTIR microspectroscopy with the following parameters:

<table>
<thead>
<tr>
<th>Spectra</th>
<th>Aperture / µm²</th>
<th>Objective</th>
<th>Resol. / cm⁻¹</th>
<th>Polarization</th>
<th>Scans</th>
<th>Background</th>
</tr>
</thead>
<tbody>
<tr>
<td>figure 6.1</td>
<td>40 × 27</td>
<td>36-fold</td>
<td>4</td>
<td>along antennas</td>
<td>250</td>
<td>Si wafer</td>
</tr>
<tr>
<td>figure 6.2b</td>
<td>40 × 27</td>
<td>36-fold</td>
<td>4</td>
<td>along antennas</td>
<td>250</td>
<td>PCM on Si *</td>
</tr>
<tr>
<td>figure 6.2c</td>
<td>40 × 27</td>
<td>36-fold</td>
<td>4</td>
<td>along antennas</td>
<td>250</td>
<td>PCM on Si *</td>
</tr>
<tr>
<td>figure 6.3</td>
<td>40 × 27</td>
<td>36-fold</td>
<td>4</td>
<td>along antennas</td>
<td>250</td>
<td>Si wafer</td>
</tr>
<tr>
<td>figure 6.5</td>
<td>40 × 27</td>
<td>36-fold</td>
<td>4</td>
<td>along antennas</td>
<td>250</td>
<td>PCM on Si *</td>
</tr>
<tr>
<td>figure 6.11</td>
<td>40 × 30</td>
<td>36-fold</td>
<td>4</td>
<td>along antennas</td>
<td>200</td>
<td>PCM on Si *</td>
</tr>
<tr>
<td>figure 7.1a</td>
<td>20 × 20</td>
<td>36-fold</td>
<td>4</td>
<td>none</td>
<td>200</td>
<td>Au mirror</td>
</tr>
<tr>
<td>figure 7.4</td>
<td>20 × 20</td>
<td>36-fold</td>
<td>4</td>
<td>along antennas</td>
<td>250</td>
<td>PCM on Si *</td>
</tr>
<tr>
<td>figure 7.14d</td>
<td>30 × 30</td>
<td>36-fold</td>
<td>4</td>
<td>along antennas</td>
<td>500</td>
<td>A-PCM on Si</td>
</tr>
<tr>
<td>figure B.5</td>
<td>110 × 110</td>
<td>15-fold</td>
<td>4</td>
<td>along antennas</td>
<td>150</td>
<td>PCM on Si *</td>
</tr>
<tr>
<td>figure B.13</td>
<td>110 × 110</td>
<td>15-fold</td>
<td>4</td>
<td>along antennas</td>
<td>150</td>
<td>PCM on Si *</td>
</tr>
<tr>
<td>figure B.17</td>
<td>67 × 70</td>
<td>15-fold</td>
<td>4</td>
<td>none</td>
<td>200</td>
<td>Au mirror</td>
</tr>
</tbody>
</table>

Table A.3: The displayed experimental reflectance spectra were collected with the FTIR microspectrometer by applying the listed parameters. The aperture size was defined with two transparent knife-edge apertures. Two Schwartzschild-type Cassegrain objectives were used with a 15-fold and a 36-fold magnification. The spectral resolution ("resol.") defines the distance between two distinguishable spectral features. The final spectrum is an average of the total number of automatically collected scans. Each spectrum is normalized to the background spectrum detected before. The symbol * marks the background spectra with the PCM phase, which matches the PCM phase of the (main) reflectance spectrum.
FTIR microspectrometer setup

Figure A.8: A scheme of the optical beam path of the Hyperion 2000 microscope from the company Bruker Optik GmbH is displayed. The visible illumination (VIS Lamp) allows for the localization of the sample region of interest. With the apertures, local spectroscopy is possible. Furthermore, polarization-dependent experimental data is accessible by using linear polarizers. Depending on the requested spectrum - reflectance or transmittance spectroscopy - either a single or two Schwarzschild-type Cassegrain objectives are used. Thus, in case of transmittance experiments, the Cassegrain condenser below the sample stage is used. The direction of the illumination with the external infrared light source also depends on the measurement techniques. Two detectors are available, which differ regarding their detector area ($A_1 = 2.5 \times 2.5 \text{ mm}^2$, $A_2 = 0.5 \times 0.5 \text{ mm}^2$), their spectral range (detector 1: $1.2 \times 10^5 - 6 \times 10^5 \text{ cm}^{-1}$, detector 2: $1.0 \times 10^6 - 6 \times 10^6 \text{ cm}^{-1}$) and their signal-to-noise ratio* (for apertures below $A = 400 \mu\text{m}^2$, detector 2 shows a higher SNR relative to detector 1) [206]. The image is displayed by courtesy of Bruker Optik GmbH.

*The signal-to-noise ratio SNR describes the ratio of the signal intensity to the background intensity. The higher the SNR, the stronger is the signal relative to the background.
APPENDIX B

Appendix on experimental results

B.1 Geometric and spectral aspects of the metal antenna arrays

Imaging of antenna arrays

The fabricated antenna arrays were imaged with a scanning electron microscope (SEM) as shown in figure B.1. These antennas were separated by a distance $d = 2L$ in $x$-, as well as in $y$-direction. Furthermore, the surface of the aluminum antennas seems rough and grainy. This could cause a broadening and shifting of the antenna array resonance frequency $\tilde{\nu}_{\text{res}}$, as well as a damping of the peak reflectance.

Each antenna array is part of an electron beam lithography writefield as shown in figure B.2. A writefield is a structural unit, which was written into the photoresist during one exposure process without movement of the sample stage. In case of a structure larger than the available writefield, the instrument’s stage needs to be moved. Figure B.2a shows a writefield in a positive tone photoresist after exposure to the electron beam and after development of the resist. The antenna arrays appear as bright squares and even single antennas can be distinguished. The frame, which is necessary to identify the antenna array in the FTIR microspectrometer setup or in the laser setup for reversible switching, as well as the note for sample identification (sample number, date, etc.) are visible. Three different antenna lengths are studied. For each length, an array of $40 \times 40$ antennas were fabricated. In the scheme in figure B.2b the position of the antenna arrays in the displayed writefield were marked. The numbers inside each square corresponds to the length $L$ of the antennas in nm.

The samples shown in figure B.3 were covered with GST-326, which enhances the contrast of the antennas and the writefield marks in the camera image. The rectangles mark the writefield and allow for a one-to-one relation between the arrays, which means that a specific antenna array can be identified easily. In this work, the background spectra were taken on the substrate (including the PCM thin film) next to the arrays, for example as shown in figure B.3b. There, the knife edge apertures used in the FTIR microspectrometer appear as black stripes.
B.1 Geometric and Spectral Aspects of the Metal Antenna Arrays

Figure B.1: The displayed SEM images show Al nanoantennas (very thin Cr adhesive layer underneath) on Si substrates. The surface is very roughly structured and the shape of the nanorods varies. This can be caused by the evaporation during the antenna fabrication. The designed antenna geometry was chosen as follows: width $w = 100$ nm, length $L = 400$, 500 and 600 nm and total height $h = 35$ nm. The white scale bar equals 500 nm.

(a) top view: 400 nm antennas  
(b) top view: 500 nm antennas  
(c) side view: 600 nm antennas

Figure B.2: In this microscope image of an Al antenna array design written in a single layer positive tone photoresist, the antennas are placed on top of an amorphous 50 nm thin film of GST-8211, which was sputter deposited on a silicon substrate. No metal was deposited. In the scheme the positions of the antenna arrays with antenna length $L$ of 600, 500 and 400 nm are marked. Each fabricated antenna array consists of about 1600 antennas. The writefield is about $(150 \times 150) \mu m^2$ ($X\times Y$) in size.

(a) microscope image of writefield  
(b) scheme of antenna writefield

Figure B.3: The sample images were taken with the FTIR microspectrometer camera by using a 5-fold objective in the visible mode in B.3a and a 15-fold objective in the visible mode in B.3b respectively. Figure B.3a appears yellowish due to the applied polarization filter. The depicted writefield (80 $\times$ 40 antennas) in the left figure includes three different arrays ($L = 400$, 500 and 600 nm). In the camera image on the right, the position, where the background spectrum was taken, is shown (marking Al rim of the writefield visible). The size of the area, the signal is collected from, is confined by knife edge apertures (black stripes in the image).
Figure B.4: The antennas of an array are characterized by scanning electron microscopy prior and after annealing. "RT" denotes the room temperature. Both panels belong to the same antenna row of the same antenna array. However, the antennas are not identical. No change of the antenna geometry was found. Influences on the antenna roughness can not be identified by these two images. The contrast and brightness were maximized, while a tonal filter was applied to enhance the image features.

Spectral influence of chromium adhesion layers

Normalized reflectance spectra of aluminum antenna arrays with an adhesive chromium layer are compared to arrays without chromium, which is shown in figure B.5.

The chromium adhesive layer led to a shift of the antenna array resonance frequency position $\Delta \tilde{v}_{\text{Cr}}$ to higher wavenumbers by about 150 to 220 cm$^{-1}$. Thereby, no dependency on the antenna length $L$ was found. The resonance frequency positions are summarized in table B.5, while it has to be noted that the determination of the resonance frequency positions was difficult due to the relatively broad peaks. The total shifts of the resonance frequency positions $\Delta \tilde{v}_{\text{Cr}}$, /cm$^{-1} = |\tilde{v}_{\text{Cr,Al}} - \tilde{v}_{\text{Al}}|$, as well as the percental shifts $\Delta \tilde{v}_{\text{Cr}} / % = |\tilde{v}_{\text{Cr,Al}} - \tilde{v}_{\text{Al}}| / \tilde{v}_{\text{Cr,Al}}$ are listed. The same definitions hold for the peak reflectances with $\Delta R = |R_{\text{Cr,Al}} - R_{\text{Al}}|$ and $\Delta R / % = |R_{\text{Cr,Al}} - R_{\text{Al}}| / R_{\text{Cr,Al}}$. The effect of chromium on the peak reflectances is between about 0.09% and 0.74%. This low impact on the peak reflectance is similar to what has been already found for the annealing of aluminum arrays.

Figure B.5: Reflectance spectra taken with a FTIR microspectrometer are shown for aluminum antenna arrays with (solid) and without a chromium adhesive layer (dashed). The spectra were normalized to the reflectance spectrum of the substrate (silicon). The small absorption peak at around 2350 cm$^{-1}$ is due to atmospheric CO$_2$ absorption. The data was smoothened by a moving average of 20 data points, whereas the spectra were collected with a resolution of 4 cm$^{-1}$ (FTIR parameter in table A.3).

It has to be noted that the separation of the antennas was different to the samples discussed earlier in this thesis, since it was selected prior to the optimization of the antenna separation (cf. chapter 5). Concerning the non-optimized arrangement of the arrays in figure B.5, the antennas were separated by 2L in x-direction, while the distance in y-direction was 2 $\mu$m. Thus, it has not been surprising, that the corresponding resonance peaks are much broader than the resonance peaks, which were found for antenna arrays with optimized separation (e.g. figure 6.1). However, the investigation of the chromium adhesive layer has not been repeated with optimized arrays due to the difficulties regarding the fabrication of antenna arrays without chromium adhesive layer. The sample investigated here was the only sample out of six, which was successfully fabricated without the adhesive layer.
B.1 Geometric and spectral aspects of the metal antenna arrays

<table>
<thead>
<tr>
<th>length L/nm</th>
<th>with Cr $\nu_{Cr,Al}$/cm$^{-1}$</th>
<th>no Cr $\nu_{Al}$/cm$^{-1}$</th>
<th>change $\Delta\nu_{res}$/cm$^{-1}$</th>
<th>with Cr $\Delta\nu_{res}$/%</th>
<th>no Cr $\Delta\nu_{res}$/%</th>
<th>change $\Delta R$/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>4460</td>
<td>4237</td>
<td>223</td>
<td>5.0</td>
<td>1.131</td>
<td>1.128</td>
</tr>
<tr>
<td>500</td>
<td>3938</td>
<td>3814</td>
<td>124</td>
<td>3.1</td>
<td>1.112</td>
<td>1.111</td>
</tr>
<tr>
<td>400</td>
<td>3021</td>
<td>2874</td>
<td>147</td>
<td>4.9</td>
<td>1.076</td>
<td>1.084</td>
</tr>
</tbody>
</table>

Table B.1: This table summarizes the resonance frequency positions and the normalized reflectance of each resonance peak for aluminum antenna arrays (antenna length $L$) with and without chromium as adhesive layer.

Aluminum antennas on GST-326 thin films

Antenna arrays have not only been covered with GST-326 thin films in the framework of this thesis, but have also been fabricated on GST-326. No adaption regarding the sample cleaning procedure was necessary. In contrast the resist baking procedure prior to the electron beam writing was changed substantially. While the supplier of the EBL resist suggested 60s baking at about 180°C [312], the temperature was reduced to about 140°C to decrease the risk of unintentional crystallization. As a consequence, the baking time was increased to about 180s. This adaption has led to successful antenna fabrication, while no direct crystallization of the GST-326 thin films was determined. In figure B.6, antennas on C-GST-326 are shown. Small circles arranged in little clusters form a "cauliflower-like" structure on the PCM surface. This might be ascribed either to oxidation during the lithography procedure on GST thin films, or to aging effects of the PCM, which are not related to the lithography. To prevent PCMs from oxidation or evaporation, capping layers, such as (ZnS)$_{80}$-(SiO$_2$)$_{20}$ can be applied [153]. However, a thin film of capping material would interrupt the direct contact between the antennas and the PCM, which was chosen to strongly influence the antenna array resonance position. Simulations involving (ZnS)$_{80}$-(SiO$_2$)$_{20}$ layers are discussed in chapter 7.

Evaporation of aluminum

Chromium and aluminum were thermally evaporated during the antenna fabrication process. A tungsten boat was used to evaporate chromium and aluminum powder. For the evaporation of aluminum, which has shown a high wettability, specific tungsten boat type - a flat tub or a dimple boat (cf. figure B.7) - was used to prevent the coating metal from creeping up the clamps. It was experienced, that the aluminum takes longer to wet the dimple boat compared to a common flat boat and hence, the dimple boats delay the breakage of the boat. Due to this behavior, about 80 to 100 nm was found to be the maximum aluminum layer thickness, which was successfully evaporated during a single evaporation process step. For thicker films, the boat needed to be exchanged based on the fact that as soon as the aluminum has crepted up the clamps. Moreover, the deposition rate has changed continuously during the aluminum evaporation process while the current was set constant. In turn, the current was adapted manually to achieve a constant deposition rate. The continuous change of the rate was not observed for chromium or gold evaporation and hence, was associated with the aluminum wetting the boat surface (cf. figure B.7). The breakage of the boats was experienced after a sudden and very strong increase of the deposition rate (from about 0.8 Å/s in average to about 1.8 Å/s in average). To
avoid cracks in the boat, they were exchanged early, for example after about 35 nm aluminum were evaporated twice. Usually, no damage of the boats during the evaporation process was found then.

Thermally evaporated Al tends to show a grainy structure as can be seen in figure B.8a and a very rough surface as already shown in figures B.1. The grain size is much smaller than the wavelength in the MIR, which allows the use of these metal structures for MIR nanooptics.

Figure B.6: The displayed SEM image shows Al nanorod antennas ($L = 400 \text{ nm}$, $w = 120 \text{ nm}$) fabricated on GST-326 thin film, which was sputtered on a Si substrate. By annealing at 180°C, the GST-326 was crystallized, while the nanorods remained unchanged. "Cauliflower-like" structures can be found on the surface of the GST-326 thin film. The contrast and brightness were maximized, while a tonal filter was applied to enhance the image features.

Figure B.7: The shown tungsten dimple boat was used for the evaporation of thick aluminum layers of about 100 nm. The aluminum, which has crept up the clamps can be seen. A black arrow marks the crack in the boat.

Figure B.8: Here, a part of an aluminum outline and the sample label used for the identification of the writefields as shown in figure B.2 are displayed. The rough surface which has been related to the process of thermal evaporation of aluminum, is clearly visible.
Study of varied antenna separation in an array

In chapter 5, the influence of the Rayleigh anomaly on the resonance peak width of antenna arrays was discussed. There, only selected calculated reflectance spectra were shown. In figure B.9 the entire calculated data set is shown.

Figure B.9: The shown reflectance spectra were calculated for an Al antenna array (length \( L = 600 \) nm, width \( w = 100 \) nm and height \( h = 35 \) nm, distance \((d_x, d_y)\) was varied between 0.8 and 1.8 \( \mu \)m) on an A-GST-326 substrate layer \((t_A = 50 \) nm) deposited on a Si substrate. In the inset, every tenth data point of the calculated results for \( d = 0.8 \) \( \mu \)m is given as empty mark to proof the quality of the calculated spectra. Consequently, spectral features, which could have arisen from interpolation, were excluded.

Calculation of sample coverage with metallic nanoantennas

To approximate the coverage of the sample area with metallic nanoantennas \( SC \), the antenna area \( A_{ant} \) was related to the area of the unit cells \( A_{uc} \). These parameters have been defined as follows:

\[
A_{ant} = w \cdot L \quad \text{(B.1a)}
\]

\[
A_{uc,\text{sym}} = (2L)^2 \quad \text{and} \quad A_{uc,\text{asym}} = 2L \cdot (2\mu m + L) \quad \text{(B.1b)}
\]

\[
SC = \frac{A_{ant}}{A_{uc}} \quad \text{(B.1c)}
\]

with the antenna width \( w \) being 100 nm and the antenna length \( L \), which was varied. The antenna separation is abbreviated by "sym." for the nanorods equally spaced in \( x \)- and \( y \)-direction and "asym." for the non-equally spaced nanoantennas. The results are listed in table B.2.

<table>
<thead>
<tr>
<th>( L/10^{-6} )m</th>
<th>( A_{ant}/10^{-14} )m(^2 )</th>
<th>( A_{uc,\text{sym}}/10^{-12} )m(^2 )</th>
<th>( A_{uc,\text{asym}}/10^{-12} )m(^2 )</th>
<th>( SC_{\text{sym}}/% )</th>
<th>( SC_{\text{asym}}/% )</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>6.0</td>
<td>1.44</td>
<td>3.12</td>
<td>4.17</td>
<td>1.92</td>
</tr>
<tr>
<td>500</td>
<td>5.0</td>
<td>1.00</td>
<td>2.50</td>
<td>5.00</td>
<td>2.00</td>
</tr>
<tr>
<td>400</td>
<td>4.0</td>
<td>6.40</td>
<td>1.92</td>
<td>6.25</td>
<td>2.08</td>
</tr>
</tbody>
</table>

Table B.2: This table summarizes the coverage of the sample area \( SC \) with metallic nanoantennas of area \( A_{ant} \).
B.2 Comments on the thin film interferences of phase-change material layers

Fresnel equations

In chapter 5, the calculated and experimentally determined reflectance of GST-326 thin films on Si substrates are discussed as a function of the wavenumber $\tilde{\nu}$ in the MIR/NIR spectral range. The calculations are based on Fresnel equations, which are given in the following.

The amplitude reflection coefficient for the boundary between medium 1 (air) and 2 (PCM thin film) and perpendicular polarization in reflection mode is calculated as follows [314]:

$$\xi_{12} = \frac{n_1 \cdot \cos \theta_i - n_2 \cdot \cos \theta_t}{n_1 \cdot \cos \theta_i + n_2 \cdot \cos \theta_t}$$  \hspace{1cm} (B.2)

with the refractive indices $n_1 = 1$ (air) and $n_2(\tilde{\nu})$ (PCM), the angle of incidence $\theta_i$ and the angle of the transmitted light $\theta_t$ as marked in figure B.10. The angles can be calculated with the following equations:

$$\theta_i = \arcsin \left( \frac{n_1}{n_2} \cdot \sin \theta_t \right)$$  \hspace{1cm} (B.3)

$$\theta_t = \vartheta$$ \hspace{2cm} (B.4)

$$\theta_{tt} = \arcsin \left( \frac{n_2}{n_3} \cdot \sin \theta_t \right)$$  \hspace{1cm} (B.5)

For parallel polarization in reflection mode, the amplitude reflection coefficient is calculated as follows:

$$\xi_{12} = \frac{n_2 \cdot \cos \theta_i - n_1 \cdot \cos \theta_t}{n_2 \cdot \cos \theta_i + n_1 \cdot \cos \theta_t}$$  \hspace{1cm} (B.6)

For the boundary between medium 2 and medium 3 (silicon substrate), the amplitude reflection coefficients can be calculated as follows:

$$\xi_{23} = \frac{n_2 \cdot \cos \vartheta_i - n_3 \cdot \cos \theta_t}{n_2 \cdot \cos \vartheta_i + n_3 \cdot \cos \theta_t}$$  \hspace{1cm} (B.7a)

$$\xi_{23} = \frac{n_3 \cdot \cos \theta_i - n_2 \cdot \cos \vartheta_t}{n_3 \cdot \cos \theta_i + n_2 \cdot \cos \vartheta_t}$$  \hspace{1cm} (B.7b)
Thus, for thin films the so-called *Fresnel coefficients* can be written as:

\[
I_{f,r} = \frac{t_{12,r} + t_{23,r} \cdot e^{2ih}}{1 + t_{12,r} \cdot t_{23,r} \cdot e^{2ih}} \tag{B.8a}
\]

\[
I_{f,p} = \frac{t_{12,p} + t_{23,p} \cdot e^{2ih}}{1 + t_{12,p} \cdot t_{23,p} \cdot e^{2ih}} \tag{B.8b}
\]

with the coefficient \(2b\) as:

\[
2b = \frac{4\pi}{\lambda} \cdot t \cdot n_2 \cdot \cos\theta_t \tag{B.9}
\]

Finally, the reflectance for unpolarized light can be determined as follows [315]:

\[
R = \frac{1}{2} \left( |I_{f,r}|^2 + |I_{f,p}|^2 \right) \tag{B.10}
\]

In figures 5.8 and 5.10, the calculated reflectance \(R\) is shown as a function of the wavenumber \(\tilde{\nu}\).

**Comments on the differences between experiment and calculation**

**Sample design**  In the work of Kremers [110] thin films of PCMs were analyzed and the dielectric data sets for various PCMs were determined. For the PCM GST-326, the sample layer stack Kremers used consisted of a silicon substrate with a native oxide layer, 0.15 \(\mu\)m aluminum luminuma sr and a GST-326 layer with a thickness \(t_A = 0.59 \mu\)m and \(t_C = 0.51 \mu\)m (cf. table B.3). The PCM thin film samples used in this thesis consisted of a silicon substrate with a native oxide layer and a PCM layer with a thickness of about 0.05 \(\mu\)m (amorphous), which reduces to about 0.46 \(\mu\)m after annealing at 180\(^\circ\)C [111]. The aluminum reflector used in [110] and [306] is a non-perfect mirror in the MIR spectral range with about 98% reflectivity. For a perfect mirror and in the energy range below the band gap, a reflectance of 1.0 can be assumed for PCM films, which are transparent for low energies [306]. Only a small decrease in the mirror reflectivity leads to a reflectance of the PCM film below 1.0 even for energies below the band gap (the contribution of wave \(E_5\) in figure B.10 is not negligible anymore). In this thesis, the PCM thin films were deposited on silicon, which shows a much lower reflectance as aluminum for the same wavenumber range. Due to this, the maximum reflectance of the measured spectra is assumed to be slightly shifted to lower \(R\) compared to the spectra collected by Kremers.

**Deposited layer thickness**  Additionally, the deposited film thickness might deviate from the adjusted value. Both parameters were studied for a 50 nm amorphous GST-326 film, which is summarized in figure B.11. More importantly, a PCM film thickness deviating from the adjusted 50 nm can not explain the observed deviations of the reflectance \(R\). In figure B.11a the as-deposited film would need to be nearly twice as thick as it was supposed to be (nearly 95 nm) to match \(R_{exp}\) for the lower depicted wavenumber range. However, between 6000 and 7000 cm\(^{-1}\) the qualitative behavior of 95 nm A-GST-326 differs strongly from the experimental. Additionally, upon crystallization, the calculated data set of 40 nm matches very well with the experimental data between 1000 and 6000 cm\(^{-1}\). In contrast, for 6000 < \(\tilde{\nu}\) < 7000 cm\(^{-1}\), the qualitative behavior of 46.1 nm is much more similar to the experimental data set than the curve shape of 40 nm. Hence, neither can the thickness variation including a density increase of about 58% (\(t_A = 95 \text{ nm to } t_C = 40 \text{ nm}\)) explain the deviations in \(R\), nor does this density increase agree with the fundamental physics of PCMs.
B.2 Comments on the thin film interferences of phase-change material layers

<table>
<thead>
<tr>
<th>parameter</th>
<th>Kremers [110], Herpers [147]</th>
<th>this work</th>
</tr>
</thead>
<tbody>
<tr>
<td>thickness $t_A$</td>
<td>A-GST-326 590 nm</td>
<td>50 nm</td>
</tr>
<tr>
<td></td>
<td>A-GST-8211 750 nm</td>
<td>50 nm</td>
</tr>
<tr>
<td></td>
<td>A-GST-225 1 µm</td>
<td>50 nm</td>
</tr>
<tr>
<td></td>
<td>A-InSb 800 nm</td>
<td>50 nm</td>
</tr>
<tr>
<td>substrate</td>
<td>GST-326 Si with Al mirror</td>
<td>Si</td>
</tr>
<tr>
<td></td>
<td>GST-8211 Si with Al mirror</td>
<td>Si</td>
</tr>
<tr>
<td></td>
<td>GST-225 Si with Au mirror</td>
<td>Si</td>
</tr>
<tr>
<td></td>
<td>InSb Si with Al mirror</td>
<td>Si</td>
</tr>
</tbody>
</table>

Table B.3: The spectral measurements on the PCM thin films by Kremers (GST compounds) and Herpers (InSb) and related to this work were conducted with different parameters, such as as-deposited PCM film thickness $t_A$ and substrate material. The small deviations of the calculated and the measured reflectance spectra as in figure 5.9 are assumed to be based on these differences between the samples the TFIs were calculated (and the initial dielectric data set was determined) with and the TFIs were measured with.

Figure B.11: To investigate the quantitative mismatch of the reflectance $\Delta R = R_{\text{calc}} - R_{\text{exp}}$ as it was shown in figure 5.9, the film thickness $t$ was varied in the calculations of $R$. The thickness was adapted to match the experimental data set. The best approximations regarding $R_{\text{calc}} \approx R_{\text{exp}}$ is found for a set of $t$ values ($t_A = 95 \text{ nm}$ and $t_C = 40 \text{ nm}$, both red), which implies a huge density change $\Delta \rho$ contradictory to the knowledge on $\rho_{\text{PCM}}$. Regarding the FTIR measurements ("experiment" in figures B.11a and B.11b), only every 60th data point is shown.
B.3 Determination of the Peak Width

The reflectance spectra of the antenna arrays were evaluated regarding their resonance frequency position $\tilde{\nu}_{\text{res}}$, as well as their resonance peak width FWHM. Due to the asymmetric shape of the resonance peaks, the baselines of each peak had to be determined to calculate the peak width. In figure B.12 the baselines and the minimum and maximum wavenumber, which define the peak width FWHM, are marked. It can be seen that the baseline was not defined by the "real" minimum of each peak, but by the minimum reflectance in the measured wavenumber range (1000 - 6000 cm$^{-1}$). As a consequence, the FWHM depends on the measured spectral range. To be precise, a fit function for each peak would need to be applied leading to a minimum even beyond the experimentally covered spectral range. In the extreme case depicted in figure B.12b the FWHM is underestimated by the sketched routine for its determination. By considering the shorter antennas (as in figure B.12a, the systematic underestimation of the peak width is less pronounced.

These difficulties regarding the evaluated peak widths FWHM of the reflectance spectra given in chapters 6 and 7 are especially relevant for antennas with $L = 600$ nm and a C-PCM thin film, which led to a resonance position shift to lower wavenumbers. The sample layout including the GST-326 superstrate (all antenna lengths $L$), as well as the embedding medium ($L = 600$ nm) led to reflectance peaks with a pronounced asymmetric shape, for which the evaluated FWHM are likely to be overestimated. In contrast, the reflectance spectra with the GST substrates (GST-326, GST-8211 and GST-225) show relatively symmetric baselines right and left to the resonance peaks and thus, the determined FWHM seems unlikely to be overestimated. In turn, the largest values for the TFOM were achieved by GST substrate samples and thus, the corresponding TFOM is unlikely to be underestimated.

![Figure B.12](image-url)

Figure B.12: The width of the antenna array resonance peaks FWHM was determined by adjusting a baseline to the peak (solid gray). For resonance peaks with a superstrate of A-GST-326, the determination was straightforward as can be seen in the exemplary figure B.12a. The peak width FWHM (red) is defined by the wavenumbers in the middle of the vertical line, which connects the resonance peak maximum with the baseline (dotdashed gray). In contrast, for a C-GST-326 superstrate, the minimum of the spectrum at high wavenumbers was determined by fitting an averaged line (dashed gray) as shown in figure B.12b. Thus, the baseline was defined by connecting the measured reflectance at low wavenumbers with the averaged reflectance at high wavenumbers. All reflectance spectra were displayed in figure 6.2.
B.4 Spectral influence of the GST-326 superstrate thickness

To study the influence of the GST-326 superstrate thickness, two different samples were investigated experimentally. A-GST-326 thin films with a thickness of $t_A/2 = 25$ and $t_A = 50$ nm were deposited on antenna arrays with different antenna lengths $L$. It was expected that a thicker GST-326 film would have led to a larger shift of the antenna array resonance frequency position $\Delta \tilde{\nu}_{\text{res}}$ due to the field decay in the PCM, which was shown in chapter 5 (figure 5.3.2). Moreover, the calculation of the scattered field confirmed, that the 50 nm A-GST-326 layer was fully penetrated by the scattered electromagnetic field (cf. figure 6.7). However, it has to be noted that a 25 nm thin film is likely to not fully cover the antennas, which were fabricated with a height $h$ of about 35 nm.

The spectra shown in figure B.13 were collected by FTIR microspectroscopy, while for normalization spectra of PCM thin films on silicon substrates were measured on the same sample at a position next to the arrays. Thus, only the spectral contribution of the antenna arrays was measured in the final normalized spectra. The incident light was polarized along the long antenna axis ($y-$direction). The samples were annealed for 30 min at 180°C on a hot plate in a cleanroom environment. It has to be noted that the antenna separation of the investigated arrays was different to all arrays shown in this thesis. There, the antennas were separated by $2L$ in $x-$, as well as in $y-$direction. In contrast, the antennas presented here were separated by $(d_x, d_y) = (2L, 2\mu m + L)$ in the array.

The resonance peak positions associated with amorphous GST-326 were shifted to lower wavenumbers upon crystallization (dashed to solid lines, indicated by black arrows). The antenna array resonance frequency position shift $\Delta \tilde{\nu}_{\text{res}}$ increases for decreasing antenna length $L$, which is related to the general inverse proportionality between the resonance position $\tilde{\nu}_{\text{res}}$ and the antenna length $L$, as well as to the increase of the dielectric difference between the amorphous and crystalline phase of the GST-326 film $\Delta \epsilon_{\text{PCM}}^{-1/2}$ for increasing wavenumbers (or decreasing antenna length $L$ respectively).

For a thicker GST-326 film a larger effective refractive index $n_{\text{eff}}$ and in turn, a larger shift $\Delta \tilde{\nu}_{\text{res}}$ was expected. This assumption was confirmed by the experimental spectra, where the resonance shifts $\Delta \tilde{\nu}_{\text{res}}$ increased by a factor between about 1.3 and 1.5 due to the doubling of the layer thickness $t_A$.

Referring to the peak width FWHM it was found earlier that the resonance peaks broadened upon crystallization of the GST-326 and the InSb superstrates (cf. tables 6.3 and 6.4). This finding was in contrast to the results found for the sample layout with antenna arrays embedded with GST-326, as well as for the GST-326 substrate. There, the resonance peaks narrowed upon crystallization. Here, it was found that the resonance peaks narrowed upon crystallization as well, except of the sample with the antenna length $L = 400$ nm and the thickness $t_A = 50$ nm. There, the antenna array resonance peak associated with the thicker C-GST-326 layer shows a shoulder at about $\tilde{\nu} \approx 2100$ cm$^{-1}$, which aggravated the determination of the peak width FWHM$_C$. For the five other investigated samples, no clear trend regarding the peak width FWHM was found.

Since the tuning figure of merit TFOM is defined by the resonance frequency shift $\Delta \tilde{\nu}_{\text{res}}$ and the peak width FWHM, no clear trends were identified either.

It has to be kept in mind, that the arrangement of the antennas in the array here differed from the samples discussed in the framework of the GST-326 and InSb superstrate films as well as from

---

1The antenna separation $(d_x, d_y) = (2L, 2\mu m + L)$ was adapted from [31] and used before the calculations on the optimized antenna separation (cf. section 5.4) were conducted.
B.4 Spectral influence of the GST-326 superstrate thickness

the samples investigated regarding the sample layout. However, since only the antenna separation in $y$-direction differed, the RA position $\lambda'_{RA,(1,0),d}$ does not change.

![Diagram](image)

(a) $t_A = 25$ nm GST-326 superstrate  
(b) $t_A = 50$ nm GST-326 superstrate

![Graph](image)

(c) $t_A = 25$ nm GST-326 superstrate  
(d) $t_A = 50$ nm GST-326 superstrate

Figure B.13: Normalized reflectance spectra of antennas with length $L = 500$ nm and $t_A/2 = 25$ (left) or $t_A = 50$ nm (right) GST-326 superstrates are depicted. The GST-326 is in its amorphous as-deposited (dashed black) and in its crystalline annealed (solid black) state. The incident light was polarized along the long antenna axis. The shift of the antenna array resonance position upon crystallization $\Delta \tilde{\nu}_{\text{res}}$ was marked by black arrows.
B.4 Spectral influence of the GST-326 superstrate thickness

Figure B.14: The plot shows the peak widths FWHM_A and FWHM_C of the antenna array resonance peaks as a function of the resonance frequencies \( \nu_A \) and \( \nu_C \). The data is based on the evaluation of the reflectance spectra of antenna arrays given in figure B.13. Different amorphous superstrate thicknesses \( t_A \) are color coded, while different antenna length \( L \) are marked by different lines, which match the representation given in figure 6.6.

antenna arrays with GST-326 thin films, \( t_A = 25 \) and 50 nm

<table>
<thead>
<tr>
<th>length ( L/\text{nm} )</th>
<th>( \overline{\nu}_A/\text{cm}^{-1} )</th>
<th>( \overline{\nu}_C/\text{cm}^{-1} )</th>
<th>( \Delta \nu_{\text{res}}/\text{cm}^{-1} )</th>
<th>( \Delta \nu_{\text{res}}/% )</th>
<th>FWHM_A/\text{cm}^{-1}</th>
<th>TFOM_A</th>
<th>FWHM_C/\text{cm}^{-1}</th>
<th>TFOM_C</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 nm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>2391</td>
<td>2263</td>
<td>128</td>
<td>5.4</td>
<td>1277</td>
<td>0.10</td>
<td>1261</td>
<td>0.10</td>
</tr>
<tr>
<td>500</td>
<td>2792</td>
<td>2626</td>
<td>166</td>
<td>5.9</td>
<td>1080</td>
<td>0.15</td>
<td>864</td>
<td>0.19</td>
</tr>
<tr>
<td>400</td>
<td>3486</td>
<td>3209</td>
<td>277</td>
<td>7.9</td>
<td>795</td>
<td>0.35</td>
<td>636</td>
<td>0.44</td>
</tr>
<tr>
<td>50 nm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>2264</td>
<td>2071</td>
<td>193</td>
<td>8.5</td>
<td>567</td>
<td>0.34</td>
<td>439</td>
<td>0.44</td>
</tr>
<tr>
<td>500</td>
<td>2630</td>
<td>2383</td>
<td>247</td>
<td>9.4</td>
<td>748</td>
<td>0.33</td>
<td>547</td>
<td>0.45</td>
</tr>
<tr>
<td>400</td>
<td>3243</td>
<td>2893</td>
<td>350</td>
<td>10.8</td>
<td>930</td>
<td>0.38</td>
<td>1157</td>
<td>0.30</td>
</tr>
</tbody>
</table>

Table B.4: This table summarizes the resonance frequency positions of each resonance peak for aluminum antenna arrays (antenna length \( L \), antenna separation in the array is \( (d_x, d_y) = (2L, 2\mu m + L) \)) with 25 and 50 nm GST-326 antenna array superstrates. The layer thickness \( t \) refers to the as-deposited amorphous GST-326 thin film. In figure B.13d it can be seen that the resonance peak for \( L = 400 \) nm shows a shoulder around \( \nu \approx 2100 \text{cm}^{-1} \), which aggravated the determination of the peak width TFOM_C. Thus, the determined value is written in italic letters.

Figure B.15: The difference between the calculated averaged resonance frequency position of the Rayleigh anomaly \( \nu_{RA,(1,0),2L} \) and the experimentally determined antenna array resonance frequency position \( \nu_{res} \) is displayed for GST compounds of different stoichiometry. The data set, which corresponds to one sample (PCM thickness and phase are constant, \( L \) varies), is color coded. The arrow heads indicate the decreasing antenna length \( L \).
B.5 Literature comparison for laser-induced switching

This table summarizes laser-induced switching of PCM thin films on different timescales. It can be seen that the different laser sources and laser pulse parameters, which were applied, led to switched areas of much different size.

<table>
<thead>
<tr>
<th>author</th>
<th>Cotton et al.</th>
<th>Sokol.-T. et al.</th>
<th>Siegel et al.</th>
<th>Salinga et al.</th>
<th>Kaldenbach</th>
</tr>
</thead>
<tbody>
<tr>
<td>publication</td>
<td>[252]</td>
<td>[253]</td>
<td>[254]</td>
<td>[153]</td>
<td>[154]</td>
</tr>
<tr>
<td>category</td>
<td>femtosecond</td>
<td>femtosecond</td>
<td>picosecond</td>
<td>nanosecond</td>
<td>nanosecond</td>
</tr>
<tr>
<td>PCM switch</td>
<td>GST-225</td>
<td>GeSb$<em>{23}$Sb$</em>{77}$</td>
<td>GST-225</td>
<td>Ag$<em>4$In$<em>3$Sb$</em>{26}$Te$</em>{25}$</td>
<td>Ag$<em>4$In$<em>3$Sb$</em>{26}$Te$</em>{25}$</td>
</tr>
<tr>
<td>wavelength $\lambda$</td>
<td>800 nm</td>
<td>620 nm</td>
<td>514.5 nm</td>
<td>658 nm</td>
<td>658 nm</td>
</tr>
<tr>
<td>pulse duration $\tau$</td>
<td>100 fs</td>
<td>100 fs</td>
<td>30 ps</td>
<td>30 ns</td>
<td>$\tau$: 1.18 ms</td>
</tr>
<tr>
<td>given fluence $F_0$</td>
<td>$\tau$: 53 mJ/cm$^2$</td>
<td>$\tau$: 45 mJ/cm$^2$</td>
<td>$\tau$: 52 mJ/cm$^2$</td>
<td>$\tau$: 83 mW</td>
<td>$\tau$: 25.1 mW</td>
</tr>
<tr>
<td>given power $P_0$</td>
<td>$\tau$: 17 mJ/cm$^2$</td>
<td>$\tau$: 24 mJ/cm$^2$</td>
<td>$\tau$: 2.12 mW</td>
<td>$\tau$: 80.5 mW</td>
<td></td>
</tr>
<tr>
<td>given radius $R_0$</td>
<td>$\tau$: 180 $\mu$m, 112 $\mu$m$^b$</td>
<td>$\tau$: 1.22 $\mu$m</td>
<td>$\tau$: 1.22 $\mu$m</td>
<td>$\tau$: 24 $\mu$m$^c$</td>
<td></td>
</tr>
<tr>
<td>switched area</td>
<td>$\tau$: (65 x 40) $\mu$m$^2$</td>
<td>$\tau$: not given</td>
<td>$\tau$: not given</td>
<td>$\tau$: (0.57 x 0.57) $\mu$m$^2$</td>
<td>$\tau$: (0.5 x 0.5) $\mu$m$^2$</td>
</tr>
</tbody>
</table>

Table B.5: This table summarizes experimental parameters of exemplary literature, which describe the laser-induced switching between the structural phases of different PCMs. The PCM thin film layers are as-deposited in their amorphous state $A$, and can be annealed to their crystalline structure $C$, either by laser pulses or by means of an oven or a hot plate. Laser-induced switching can lead to a re-amorphized melt-quenched phase $MQ$, as well as to a re-crystallized phase $RC$. Crystallization $\tau$, re-amorphization $\tau$ and re-crystallization $\tau$ are investigated by using single laser pulses of different pulse duration $\tau$, except for the re-crystallization $\tau$ in Cotton et al., which was realized by ten fs laser pulses. The laser beam is characterized by the wavelength $\lambda$ and the pulse energy which is given as peak fluence $F_0$ or as peak power $P_0$. The beam radius $R_0$ is similar for both works on nanosecond switching ([153], [154]), since the same setup with the same fibre was used. Each switching mechanism and laser setup referenced here led to a different size of the switched PCM. Even sample volumes were switched only the size of the areas ws given.

$^a$It has to be noted, that this phase - marked by $C^*$ - is not a thermodynamically stable crystalline phase, but rather a nonequilibrium disordered phase, which shows similar reflectance as a stable crystalline phase [316].

$^b$The pump beam was focused to an elliptical spot with two axes instead of a radius.

$^c$This pump beam was guided along a different path and therefore, the spot was circular.
B.6 Comments on the femtosecond laser experiments

Study of pulse power and sequence on bare GST-326 films

Bare GST-326 thin films with spots of a different size and reflectance are shown in figure B.16. These spots are associated with laser-induced crystallization and re-amorphization in the PCM. One benefits from the strong reflectance contrast between A-GST-326 (or MQ-GST-326) and (R)C-GST-326 in the VIS spectral range $\Delta R$, which allows for a preliminary selection of the laser parameters at first glance. To induce phase-changes, fs laser pulses with a pulse duration $\tau = 50$ fs were chosen. Thereby crystallization was realized by pulse sequences of different duration $\tau_{\text{seq}}$ with a constant repetition rate $f_{\text{rep}} = 960$ Hz, while amorphization was induced by single pulses. For both switching processes, the laser power $P$ and thus, the fluence $F$ was varied as listed in table B.6. The FWHM of the beam measured by a knife edge scan is in the range between about 244 and 270 $\mu$m. The beam profile is Gaussian, but with one axis widened relative to the other. In respect of the transversal beam profile, the FWHM refers to the long axis of the spot. In all spots a rippled outline can be identified, which can be assigned to self-interference of the laser beam. Additionally, narrow rims with a lowered reflectance contrast $\Delta R$ can be observed. This is assumed to be based on the Gaussian intensity profile of the laser beam. However, the influence of the ripples and the rims on the antenna arrays can be minimized by placing the laser beam in a way, that antenna arrays are close to the center of the spot, where a relatively homogeneous $\Delta R$ can be realized.

<table>
<thead>
<tr>
<th>Spot</th>
<th>Spot Power $P$/mW</th>
<th>Fluence $F$/mJcm$^{-2}$</th>
<th>Sequence $\tau_{\text{seq}}$/s</th>
<th>Spot Power $P$/mW</th>
<th>Fluence $F$/mJcm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14.6</td>
<td>32.4</td>
<td>1</td>
<td>12.0</td>
<td>26.6</td>
</tr>
<tr>
<td>2</td>
<td>14.6</td>
<td>32.4</td>
<td>2</td>
<td>17.3</td>
<td>38.3</td>
</tr>
<tr>
<td>3</td>
<td>12.0</td>
<td>26.6</td>
<td>3</td>
<td>23.8</td>
<td>52.7</td>
</tr>
<tr>
<td>4</td>
<td><strong>12.0</strong></td>
<td><strong>26.6</strong></td>
<td>4</td>
<td><strong>32.0</strong></td>
<td><strong>70.8</strong></td>
</tr>
<tr>
<td>5</td>
<td>9.5</td>
<td>21.0</td>
<td>5</td>
<td>41.7</td>
<td>92.3</td>
</tr>
<tr>
<td>6</td>
<td>9.5</td>
<td>21.0</td>
<td>1</td>
<td>49.2</td>
<td>108.9</td>
</tr>
<tr>
<td>7</td>
<td>7.0</td>
<td>15.5</td>
<td>5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table B.6: The laser parameters $P$, $F$ and $\tau_{\text{seq}}$ used for preliminary crystallization and re-amorphization studies are listed here. The spots are marked in figures B.16a and B.16b. $F$ was calculated as follows: $F = E/(\pi \cdot R^2)$ with $E = P/f_{\text{rep}}$, while the constant repetition rate is given by $f_{\text{rep}} = 960$ Hz. The radius $R$ is determined as FWHM /2 of the beam, which leads to $R \approx 122 \mu$m. The switching applied on the antenna-PCM samples was conducted with the parameters marked by $\ast$, while the parameters in boldface were chosen due to the visible appearance of the spots (homogeneous reflectance in the VIS spectral range). The difference is due to the presumably increased initial laser beam energy between the days of experimental work. It has to be noted, that it is assumed that parameters leading to crystallization should also be suited for re-crystallization. Further comments on $F_{\text{C}}$ can be found on page 195.
B.6 Comments on the femtosecond laser experiments

(a) crystallization of A-GST-326 by repetitive fs laser excitation with varied fluences and pulse sequences

(b) re-amorphization of C-GST-326 by single fs laser pulses with varied fluences

Figure B.16: Camera images of crystallized spots in A-GST-326, as well as re-amorphized spots in annealed C-GST-326 were taken with a 10-fold objective of a FTIR microscope (Stanford University, laboratory of M. Brongersma). For crystallization, as well as for re-amorphization fs laser pulses with $\tau = 50$ fs were used. Further parameters, such as fluence $F$ and laser pulse sequences $\tau_{\text{seq}}$ were applied to each numbered area (1 to 7 in figure B.16a and 1 to 5 in B.16b) as listed in table B.6, while $F$ has been varied with an intensity filter. In figure B.16a, crystallized spots (bright) in an as-deposited A-GST-326, thickness $t = 50$ nm, are generated by various sequences $\tau_{\text{seq}}$. $F$ and $\tau_{\text{seq}}$ used for spot 1 lead to an inhomogeneous spot, whereas the darker color of area a compared to b might indicate a re-amorphization process in the center of the spot. The same might have occurred in spot 3, where a small area a shows less reflectance than the spot itself. In spots 6 and 7, $F$ has been too low to successfully crystallize the PCM. The best results regarding a homogeneously bright area were generated by $F$ and $\tau_{\text{seq}}$ chosen for spot 4. The two spots in the upper right were generated by the use of intensity filter positions applied to spots 4 and 7 before. The visible appearance of the spots has changed, which has been assumed to be related to an increase of $F$ and thus of the initial laser beam energy. In figure B.16b, the MQ-GST-326 spots in C-GST-326, $t \approx 46$ nm, are generated by single fs laser pulses. In spot 1, the used $F$ is too low to re-amorphize the crystalline thin film. By increasing $F$, the area of the MQ spots increases, whereas in spot 5 a strong change in the spot’s center marked by a can be determined, while the outer region b remains as dark as seen in the previous spots. This change in a might be caused by ablation. The best results regarding a homogeneously bright area were generated by $F$ chosen for spot 4. The ripples visible in the outline of each spot in figures B.16a and B.16b are assumed to be based on the self-interference of the fs laser pulse. In both figures black spots are visible, as well as peculiar dark dots in spots 1 and 3 of figure B.16a, marked by c, which can all be referred to as dirt. It has to be noted, that the shadows in the edges of the camera images originate from the illumination of the sample in the FTIR microspectrometer. Trimming of the images led to partial appearance of these edges in both figures.
Figure B.17: Reflectance spectra in the IR spectral range were taken with a FTIR microspectrometer (4 cm⁻¹ resolution, 200 scans, 15-fold objective, aperture of about 67×70 μm², normalization to Au mirror) to study the laser parameters necessary for crystallization. Corresponding sample images are shown in figure B.16a. The assumed partly re-amorphization in the center of spot 1 can not be confirmed by the spectral study, which might be due to the crystalline surrounding, which might dominate the reflectance. The highest reflectance can be observed for spot 2. Spots 3 and 4 show a similar reflectance. Regarding spots 5 and 6, the reflectance decreases, while a mixed A- /C-GST-326 phase are examined (cf. figure B.19). Besides the obviously decreased contribution of lateral C-GST-326 area to the spectra, a decreased crystallization in GST-326 film depth can be assumed. Exemplary positions at which the spectra were collected, are marked in figure B.18.

Figure B.18: The shown exemplary images of different crystallized spots taken with the FTIR microspectrometer camera have been post processed regarding contrast and brightness. The black stripes represent the apertures, which are used to collect the reflectance of specific spot areas. These spectra are given in figure B.17. Dashed white outlines are used to illustrate less bright rims of the spots, which are especially clear for spot 1 and spot 5 (comparison to figure B.16a).

Besides the visible appearance of the spots compared in figure B.16, a spectral study of the crystallized spots has been conducted as it can be seen in figure B.17. The interpretation is based on the fact that a comparison between calculated thin film interferences (TFIs) and corresponding experimental spectra of GST thin films can be used to identify the structural phase of the investigated GST compounds as it has been shown in chapter 6 of this thesis. Spots 1 and 2 exhibit the largest normalized reflectance, while the spectra for spots 3 and 4, which are nearly congruent, show a slight constant decrease of the reflectance compared to 1 and 2. In contrast, the spots 5 and 6 with their much smaller major axis compared to the prior four, are less reflective in the MIR/NIR spectral range. It has been assumed that these spots refer to mixed-phase areas composed of A-GST-326 and C-GST-326. By applying so-called effective medium theories (EMTs), this assumption can be reviewed. Here, the two commonly used Maxwell-Garnett (MG), as well as the Bruggeman EMT are evaluated. EMTs assume a (at least) binary disordered material with a dielectric function ε_{MG} as heterogeneous dielectric mixture of represented by a single parameter, which is the concentration or volume fraction f. One material is considered as the so-called host and the second material as inclusion. Furthermore, two premises are given: the inclusions are spherical and only dipole interactions are considered [317]. More precisely, MG assumes
the inclusion being completely surrounded by the host. Thus, this approach is only valid for very small fractions $f_A$ or $f_C \leq 0.15$ of the respective inclusion [318]. The dielectric function for an amorphous and a crystalline GST-326 host are given in equations B.11a and B.11b repsectively. As inclusion the corresponding constituent - C- or A-GST-326 - is chosen.

$$\varepsilon_{\text{MG,}A}(\tilde{\nu}) = \varepsilon_A(\tilde{\nu}) \cdot \left( \frac{1+2f_C \left( \frac{\varepsilon_C(\tilde{\nu}) - \varepsilon_A(\tilde{\nu})}{\varepsilon_C(\tilde{\nu}) + 2\varepsilon_A(\tilde{\nu})} \right)}{1-f_C \left( \frac{\varepsilon_C(\tilde{\nu}) - \varepsilon_A(\tilde{\nu})}{\varepsilon_C(\tilde{\nu}) + 2\varepsilon_A(\tilde{\nu})} \right)} \right)$$  \hspace{1cm} (B.11a)

$$\varepsilon_{\text{MG,}C}(\tilde{\nu}) = \varepsilon_C(\tilde{\nu}) \cdot \left( \frac{1+2 \cdot f_C \left( \frac{\varepsilon_A(\tilde{\nu}) - \varepsilon_C(\tilde{\nu})}{\varepsilon_A(\tilde{\nu}) + 2\varepsilon_C(\tilde{\nu})} \right)}{1-(1-f_C) \left( \frac{\varepsilon_A(\tilde{\nu}) - \varepsilon_C(\tilde{\nu})}{\varepsilon_A(\tilde{\nu}) + 2\varepsilon_C(\tilde{\nu})} \right)} \right)$$  \hspace{1cm} (B.11b)

$$f_A = 1 - f_C$$  \hspace{1cm} (B.11c)

with $\varepsilon_{\text{MG,C}}(\tilde{\nu})$ being the complex dielectric function of the effective medium, $\varepsilon_C(\tilde{\nu})$ as permittivity of the host medium and $\varepsilon_A(\tilde{\nu})$ as permittivity of the inclusion. The volume fraction of the crystalline or amorphous reflectivity is given as $f_C$ or $f_A$ respectively. Since crystallization has been probed by the reflectance spectra in figure B.17, equation B.11b has been evaluated here. Bruggeman EMT, which is also known as so-called effective medium approximation (EMA), follows from an aggregate model with a random mixture of phase A- and C-GST-326 [319]. Hereby, EMA is symmetric regarding the constituent materials, which implies, that A- and C-GST-326 are embedded in the effective medium itself [318] with the constraints of small fluctuations in $\varepsilon_{\text{EMA}}(\tilde{\nu})$ and $0.05 < |\varepsilon_C(\tilde{\nu})/\varepsilon_A(\tilde{\nu})| < 20$. The EMA dielectric function is generally expressed as follows:

$$(1-f_C) \cdot \left( \frac{\varepsilon_A - \varepsilon_{\text{EMA}}}{\varepsilon_A + 2\varepsilon_{\text{EMA}}} \right) + f_C \cdot \left( \frac{\varepsilon_C - \varepsilon_{\text{EMA}}}{\varepsilon_C + 2\varepsilon_{\text{EMA}}} \right) = 0$$  \hspace{1cm} (B.12)

The positive square root solution $\pm \varepsilon_{\text{EMA}}(\tilde{\nu})$ leads to the following:

$$\varepsilon_{\text{EMA}}^+(\tilde{\nu}) = \frac{-K_{\text{EMA}}(\tilde{\nu}) + \sqrt{K_{\text{EMA}}^2(\tilde{\nu}) + 8(\varepsilon_A(\tilde{\nu}) \cdot \varepsilon_C(\tilde{\nu}))}}{4}$$  \hspace{1cm} (B.13a)

$$K_{\text{EMA}}(\tilde{\nu}) = (3f_C - 2) \cdot \varepsilon_A(\tilde{\nu}) + (1 - 3f_C) \cdot \varepsilon_C(\tilde{\nu})$$  \hspace{1cm} (B.13b)

while $K_{\text{EMA}}(\tilde{\nu})$ is only used for clarity, but without physical meaning. Equation B.11b is evaluated in figure B.19a, while the evaluation of equation B.13a is shown in figure B.19b. Regarding a large crystalline volume fraction $f_C$, both EMTs are nearly identical, while for $f_C \leq 0.7$ the models differ. It has been mentioned above, that $\varepsilon_{\text{MG,C}}(\tilde{\nu})$ is only valid for small $f_A$, which equals large $f_C$. Nevertheless, the EMT approximations have been calculated to estimate a presumable mixture of A- and C-GST present in the partly crystallized spots given in figures B.16a and B.17.

Due to the limited range of validity, spot 6 has to be examined by using EMA. Nevertheless, the measured normalized reflectance of spot 6 can not be approximated. For $2000 \text{ cm}^{-1} < \tilde{\nu} < 4000 \text{ cm}^{-1}$ the reflectance matches well with $f_C = 0.5$, although for higher wavenumbers the measured reflectance spectrum deviates strongly from any given calculated reflectance. Spot 5 resembles much better the
shown EMA with $f_C$ being in the range between 0.7 and 0.8. The nearly fully crystalline laser-induced spots can be assumed to be C-GST-326 (spot 2) and C-GST-326 with about 10% A-GST-326 or less (spot 4) by presuming a general offset between the calculated and measured reflectance spectra for $\tilde{\nu} > 5000 \text{ cm}^{-1}$. It has to be noted, that for smaller wavenumbers all measured spectra are shifted to a larger reflectance, which might be related to the atmospheric absorption of water vapor between 1000 and 2000 cm$^{-1}$ [31], as well as to the general difference between calculated TFIs and experimentally determined reflectance spectra.

It has to be noted that another assumption has been used regarding fs laser-induced crystallization: laser parameters leading to crystallization should also be suited for re-crystallization. Furthermore, even $F_C$, which has led to a degree of crystallization between 90 and 100%, as it has been approximated by calculated EMT results regarding spot no. 4, should be suited for re-crystallization. This assumption is based on the studies of Khulbe et al. [268] and confirmed by the successful final results regarding the antenna array resonance switching presented in this thesis. Khulbe et al. investigated crystallization of different amorphous phases of Ge$_2$Sb$_{2.3}$Te$_5$ and found the following relations: for MQ-Ge$_2$Sb$_{2.3}$Te$_5$ a significant decrease in minimum pulse power $P$ and crystallization onset time, as well as an increase in crystallization rate compared to A-Ge$_2$Sb$_{2.3}$Te$_5$ can be found. Thus, initial MQ-GST-326 has been assumed to lead to a decrease in the necessary crystallization time and power compared to A-GST-326. These findings allow for the conclusion, that the parameters related to spot no. 4 - 12 mW and 26.6 mJ/cm$^2$ with $\tau_{\text{seq}} = 1 \text{s}$ - are well-suited for re-crystallization of MQ-GST-326 thin films. However, the position of the intensity filter had to be changed, since the initial laser beam energy has seemed to have increased from one experimental day to the other (maintainance break: fuses of the

\footnote{Crystallization experiments had to be chosen, since a homogeneous thin film of A-GST-326 is available for laser excitation, while this is not the case for MQ-GST-326, which can only be prepared either by optical or by electrical pulses.}
laser setup have been exchanged). Thus, $F_C$ has been increased to about $29.5 \text{ mJ/cm}^2$ ($P = 13.3 \text{ mW}$) by $t_{\text{seq}} = 1 \text{ s}$. This parameter set has not been applied in the preliminary study on bare A-GST-326 as shown in figure B.16 and table B.6. However, it has been chosen as mean of the investigated values for $F_C = 32.4 \text{ mJ/cm}^2$ ($P = 14.6 \text{ mW}$, spots 3 and 4) and $F_C = 26.6 \text{ mJ/cm}^2$ ($P = 12.0 \text{ mW}$, spots 1 and 2).

Regarding the re-amorphization, the spectral studies are not as elaborate as it has been realized for (re-)crystallization, since the suited parameters have been relatively clear by first glance. Furthermore, the corresponding reflectance spectrum of the thin films in figure 7.1 confirms the parameters, which are chosen for further re-amorphization experiments.

Images of antenna arrays with femtosecond laser spots

Writefields with several antenna arrays are addressed by laser pulses. With a beam diameter between about 230 and 270 µm each array could be switched by a single pulse. During the time these experiments have been conducted, the laser setup had no monitored positioning unit. This led to a two-step sample positioning process: first, the writefield positions are measured using an optical microscope and second, the sample is placed in the beam path with micrometer screws according to the determined writefield positions. To ensure a switching of all arrays even though the addressed arrays can not be placed with a high accuracy, several laser spots are placed next to each other as visible in figure B.20.

![Image](image_url)

(a) C-GST-326 with spots of MQ- and RC-GST-326 on writefields  
(b) similar to B.20a, but further addressed by fs pulses

Figure B.20: The shown FTIR microspectrometer camera images show a sample with C-GST-326 covering antenna arrays placed on Si. In B.20a, the upper left writefield has been addressed by single fs pulses (dark elliptic areas) with an overlap in spot placement. In contrast, a similar writefield in the bottom left has been addressed by the re-crystallization pulse sequence. Thus, the reflectance in the VIS spectral range resembles the background of C-GST-326. However, the outline of these spots is slightly darkened. Both writefields and the nanostructure arrays within are darkened after fs laser excitation as well, which becomes especially clear by comparison with the writefields on the right. In B.20b, similar fs laser excitation has been applied to the writefields a and b including nanorod arrays with separation $d$ in $x$- and $y$-direction. The corresponding FTIR microspectrometer spectra are evaluated in chapter 7. B.20b is rotated counterclockwise compared to B.20a.

The writefields, which have been characterized with a FTIR microspectrometer, are marked with a
and b as in the sample scheme in figure 7.3. In B.20a, the two writefields on the left\textsuperscript{3} have been addressed, while in B.20b also both writefields on the right have been addressed by fs laser pulses. The GST-326 thin film covering writefield a (3 or 4 arrays framed with a rectangular frame) has been re-amorphized with single laser pulses, while the GST-326 on writefield b has been further re-crystallized with a pulse sequence. Amorphous GST-326 and crystalline GST-326 phases can be identified by the clear reflectance contrast in the camera images: the crystalline areas - annealed C-GST-326, as well as switched RC-GST-326 - are bright and the areas of re-amorphized MQ-GST-326 are dark. Interestingly, the nanostructure arrays of writefields a and b in figure B.20b appear distinctly less darkened by the fs pulses compared to the arrays in the writefields on the left of figure B.20a. Furthermore, the frames of the writefield covered with RC-GST-326 (especially of the arrays in writefield b depicted in B.20b), which are contaminated with dirt or residues from the lithography process look especially dark after switching, which could indicate some kind of combustion process.

**Inhomogeneities in re-amorphized MQ-GST-326 films** In B.20, MQ-GST-326 spots exhibit areas, which are less dark than the re-amorphized regions. To have a closer look, the changes in the MQ-GST-326 reflectance are separately marked in figure B.21. It was assumed that these changes refer to ablation, especially, if they occur in the center of the spots. Naturally, the peak fluence can be ascribed to the center of a focussed laser beam. This behavior has been observed in the framework of the fluence study in figure B.16b as well. Besides visible identification, these changes have not been characterized further, e.g. by atomic force microscopy (AFM). Since the presumable ablation of the MQ-GST-326 spots have occured only in areas, which are not part of the spectrally characterized antenna arrays, no further characterization effort has been expended. Although, for future fs laser-induced re-amorphization, a lower fluence should be applied to minimize the risk of inhomogeneities or even presumed ablation.

![Image](image.png)

Figure B.21: Re-amorphization might have been accompanied by partial ablation in the center of the fs laser excited spots. Suspicious areas, which exhibit a pale rim, are marked by dashed red lines. An area with a decreased reflectance compared to the surrounding re-amorphized GST-326 is marked by a dashed white line. There, no pale rim can be seen. Fortunately, these effects were not identified on the spectrally characterized writefields. However, a lower fluence $F_a$ should be applied in future experiments.

**Sample damage due to fs laser pulses** It has been mentioned earlier, that reflectance spectra have only been taken successfully on the sample with the GST-326 thin film as superstrate. In contrast, single fs pulses used for re-amorphization have led to a pronounced damage of the PCM film and the nanoantenna array geometry in case of the sample design including the GST-326 substrate layer. Exemplary SEM images are shown in figure B.22. The GST-326, which presumably has been brought in its

\textsuperscript{3}The arrays next to the characterized writefields a and b consist of so-called Dolmen-type antennas (shape is relatively similar to $\pi$-two vertical with one horizontal antenna on top and a small gap between the horizontal and vertical antennas), which have not been characterized spectrally. These arrays are on the left in figure B.20a.
re-amorphized state, has been damaged - holes, where antennas have been (figure B.22a) - or strongly changed - dark islands around well-ordered antennas (on the right of figure B.22b). Furthermore, some antennas have been moved from their initial position in the array, while most of the antennas have lost their original shape. In the inset of figure B.22b six antennas are shown, while one of them might has been melted. Only the bottom left antenna seems to be stable, while the other four antennas seem to be strongly re-shaped by the fs laser pulse. A corona-like rim seems to remain in the GST-326 layer in case of removed antennas, but it is also (weakly) visible for all other nanorods depicted in figure B.22b.

In figure B.22, different states of the sample damage can be seen, which might be related to a gradient of the laser fluence caused by overlapping pulses or by a placement of the Gaussian beam not well-aligned with the antenna array. Sample areas presumably excited with a higher $F$ (covered by the center of the fs laser beam or by two overlapping pulses), such as B.22a and on the left of figure B.22b, exhibit antennas with a damaged shape, removed nanorods or antennas strongly misaligned from the array.

Generally, the sample damage seems to have been restricted to GST-326 areas, which were covered by Al antennas. While for the covered antennas the fs laser beam interacts with the semiconductor first, it immediately hits the Al antennas in case of the sample with the GST-326 substrate. Ultrashort pulses on fs timescales can heat electrons in metals to very high temperatures, while the lattice remains relatively cool due to their difference in heat capacity. Depending of the fluence $F$, this transient nonequilibrium system will reach equilibrium by electron-phonon interaction or a solid-to-liquid phase transition occurs for sufficiently high $F$. Since the fs laser used in this study is in the region of the Al interband transition, the threshold for melting is strongly decreased due to the enhanced absorption. Guo et al. showed by pump-probe experiments, that fs electronic excitation at 1.55 eV modified the band structure of Al significantly and led to a lowered threshold for a solid-to-liquid phase transition ($F_{th} \approx 34 \text{ mJ/cm}^2$ for $\tau = 130 \text{ fs}$) due to the enhanced absorption at the interband transition [320]. It has to be noted that the native aluminum oxide does not interact with the NIR laser beam and thus, has no influence on the interband absorption [321]. It is surprising that the Al antennas have not been damaged more strongly by the fs laser excitation. Nevertheless, the increased absorption of Al in the center region of the used fs laser beam seems to explain the damage of the antennas, which might have involved a solid-to-liquid transition, well. The underlying GST-326 areas might have been locally heated by the excited Al.

However, features on the GST-326 surface do not have to be related to fs laser pulses, as it has been shown in figure B.6. Thus, the pulses might have influenced these structures, which has led to GST-326 deposits on the sample (visible in the inset of figure B.22b).

In summary, it can be stated, that a sample design including nanostructures covered by GST-326 should be chosen for further experiments, since the semiconductor acts as a protection layer then. The use of an additional very thin capping layer of e.g. ZnS:SiO$_2$ on top of the GST-326 might have been even more useful.

**Si$_3$N$_4$ membranes for fs laser excitation experiments**

During the preparation of the samples for fs laser-induced switching, nanostructures have been fabricated on SiN membranes as it can be seen in figure B.25. This was motivated by the use of such
Figure B.22: The antenna array (here with \( L = 400 \text{ nm} \)) is placed on a GST-326 thin film, which has been re-amorphized by single fs laser pulses. It can be seen, that the antennas are unstable regarding the fs laser-induced excitation. They have been either been moved, or the GST-326 film in close vicinity has been damaged. The latter is indicated by the dark spots on the left of the nanorods in figure B.22a, while the dislocated or even removed antennas can be seen in figure B.22b. The position of the laser spots is displayed in figure B.23, while the SEM images correspond to the smallest array on the top.

Figure B.23: Antenna arrays have been placed on a GST-326 thin film and excited by single fs laser pulses to re-amorphize the annealed C-GST-326 film. The image has been taken with a FTIR microspectrometer camera. In the upper whitefield, all antenna arrays (the largest includes nanorod antennas with \( L = 600 \text{ nm} \), while the smallest is composed of the same number of antennas, but of length \( L = 400 \text{ nm} \)) were reached by about two (array with \( L = 600 \text{ nm} \) has been partly influenced by a third pulse) pulses placed next to each other. Regarding the lower whitefield, only a part of the C-GST-326 below the 600 nm array was switched, while the entire 400 nm array was covered with the fs laser pulse. The latter one was investigated by SEM, given in figure B.22. Three spots on the right of the whitefields show similar effects as depicted in figure B.21.

membranes during experiments of P. ZALDEN and A. LINDENBERG at the used fs laser setup, since SiN and GST-326 are thermally more equivalent than Si and GST-326, as can be seen by comparing the thermal conductivity \( \kappa \) given in table 7.1. However, only antenna arrays on Si substrates have been finally investigated. Solely a 150 nm SiN membrane with a 100 nm bare GST-326 thin film has been tested for fs switching. In figure B.24, two fs laser-induced spots on this membrane are shown. It can be seen, that the fs laser pulse parameters applied for the GST-326/Si samples could have not been transformed easily to the GST-326/SiN/Si sample. Due to time constraints and the advantage of continued use of samples\(^5\) the investigations have been completed with nanoantennas on Si.

\(^5\)The experiments shown in the publications of the author [239] and [83] have been conducted with the same set of samples, while for [83] only the sample with GST-326 covering the antenna arrays led to successful switching of the PCM film with fs laser pulses.
Figure B.24: Fs laser-induced single pulse crystallization of a 100 nm A-GST-326 thin film on a 150 nm Si$_3$N$_4$ membrane was tested. The membrane is deposited on a circular Si substrate with a free-standing membrane area of (1 x 1) mm$^2$. While $\tau = 50$ fs was kept constant, $F_C = 108.9$ mJ/cm$^2$ and less did not lead to any change on the membrane (areas close to the black arrow). An increase to about $F_C = 116.1$ mJ/cm$^2$ allowed for the increased visible reflectance, while $F_C = 121.7$ mJ/cm$^2$ resulted in the strongly damaged area visible in the upper edge of the Si$_3$N$_4$. Even the laser beam hits the free-standing membrane, as well as the Si$_3$N$_4$ on Si, only a very small reflectance change can be seen on the Si$_3$N$_4$/Si area. Thus, single pulse crystallization on Al nanoantennas would have not been realizable, since these large values for $F$ would presumably destroy the Al nanostructures [320].

Aluminum nanoantenna arrays on Si$_3$N$_4$ membranes In preparation of the experiments at Stanford, successful fabrication of Al nanoantennas was achieved on 150 and 200 nm membranes. Thinner membranes broke during electron beam lithography. As critical steps have been identified the sample transfer, the resist development and the lift-off. During the Master’s thesis of L. JUNG [322], a sample holder has been designed, which has allowed for a much easier handling of the membranes. This holder has been used during the fabrication of the shown nanostructures. In comparison to the fabrication of nanoantennas on Si wafers, the lithography process had been adapted. The speed of the spin-coating, which is necessary to deposit the resist on the sample, has to be reduced (here: 2000 rpm). Furthermore, the movement of the sample in the developer solution and the acetone during lift-off had to be minimized. Thus, the lift-off could not be finished successfully at each time (cf. figures B.25a and B.25c). It turned out that the deposition of GST-326 thin films can stabilize the membranes. Thus, in the framework of this thesis it was found that it is easier to fabricate antenna arrays on membranes with a GST-326 layer (cf. figure B.25b) than without. As a consequence, Si$_3$N$_4$ membranes on Si are not well-suited for fs laser-induced switching of nanoantenna array resonance frequency positions, since it has been shown that only Al antennas covered with GST-326 remained stable after fs laser excitation.

![Figure B.25: The displayed microscope images show a 200 nm or 150 nm thick Si$_3$N$_4$ membrane, which is a rectangular window (yellowish in B.25a) in a circular Si substrate (green in B.25a). Al nanoantenna arrays were patterned on the membrane. In B.25a, the lift-off procedure was not successfully finished and the Al frames are visible. Additionally, the microscope stage can be seen on the right (grey). In B.25b, three frames with nanoantenna arrays were patterned with an electron beam on the membrane and the sample was developed. Thus, the resist still covers the sample. In B.25c, antenna arrays were fabricated on a 100 nm GST-326 layer, while the lift-off was not successfully finished. The images were detected with a 5-fold (B.25a) and a 20-fold (B.25b, B.25c) objective respectively.](image)
B.7 Comments on the nanosecond laser switching

Determination of the spot size based on CLSM line plots

In chapter 7 it was described that the reflectance contrast of the crystallized and amorphized spots, which was expected due to the calculated contrast, underestimated the experimentally determined contrast of the spots. To determine the spot sizes (long axis $L_A$ and short axis $S_A$), a criterion independent of the preliminary expectations of the normalized count rates $N/N_{GST}$ was defined. Thereby, 80% of the reflectance contrast maximum (in case of crystallization) or of the reflectance contrast minimum (in case of amorphization) defined the axis width. In figure B.26 the short axis $S_A$ is marked by red vertical lines. The corresponding CLSM images are shown in figure 7.13.

![CLSM line plots](image)

Figure B.26: The CLSM images shown in figure 7.13 were evaluated to determine the short axis of the switched spots. The calculated contrast ("calc."), which was calculated to approximate the expectable contrast, as well as the experimentally determined averaged contrast ("exp.") are marked by solid gray lines. The experimental data deviates by 12% (crystallization) and by 8% (amorphization) respectively (dashed gray lines). The 80% criterion, as well as the determined limits for the short axes $S_{A_A}$ and $S_{A_C}$ are marked by red thick lines.
B.7 Comments on the nanosecond laser switching

Nanoantenna dimer

In figure 7.14b a FTIR microscopy image of antenna dimers - partly addressed by single ns laser pulses - is shown. A single antenna dimer was characterized with a SEM and is given in figure B.27.

Figure B.27: The SEM image shows an aluminum antenna dimer with a Cr adhesion layer. The antenna geometry is as follows: length \( L = 610 \) nm, width \( w = 110 \) nm, height \( h = 40 \) nm and a gap size of about 60 nm. Arrays of antenna dimers were fabricated by EBL with a double layer resist process for the Master’s thesis of De Rose [240]. Comments to the visible roughness of the aluminum can be found in appendix B.1. The image contrast and brightness were strongly enhanced.

Influence of the Rayleigh anomaly on the resonance peak width

The calculated antenna array reflectance spectra for a locally crystallized GST-326 antenna superstrate are shown in chapter 7, figure 7.16. These resonance peaks were evaluated referring to the Rayleigh anomaly position \( \tilde{\nu}_{RA,(1,0),2L} \) and the peak width FWHM as discussed in chapter 6 on page 107 and displayed in figure B.28 (red dots). The trend described earlier was confirmed: an increase of the difference between the Rayleigh anomaly frequency position \( \tilde{\nu}_{RA,(1,0),2L} \) and the resonance position \( \tilde{\nu}_{res} \) can be related to a broadening of the antenna array resonance peaks.

Figure B.28: The difference between the calculated averaged resonance frequency position of the Rayleigh anomaly \( \tilde{\nu}_{RA,(1,0),2L} \) and the experimentally determined antenna array resonance frequency position \( \tilde{\nu}_{res} \) is displayed. The results calculated for a varied spot size (cf. spectra in figure 7.16) are included into the representation of figure 6.8 and marked by red dots, while the known parameter set is shown in black to emphasize the added data.
Appendix on simulations

C.1 Applied software

C.1.1 CST Microwave Studio

All calculated reflectance spectra shown in this work were performed in the frequency domain with the software Microwave Studio (MWS) by the company Computer Simulation Technology (CST)\(^1\). There, the finite integration technique was used.

The structure was meshed with tetrahedrals and an adaptive mesh refinement. At an incident angle of 27\(^\circ\) plane wave excitation was applied, as well as the Floquet port modes. An iterative matrix solver in the frequency domain was chosen to calculate scattering or so-called S parameters between 30 and 180 THz (1000 - 6000 cm\(^{-1}\)) with at least 75 frequency samples. Maximum 100 samples were adaptively added at positions, where features occured in the spectral behavior of the S parameters. By using template-based post processing, reflectance spectra were calculated out of dominant S parameters collected at the ports at position \(z_{\text{max}}\) (above the antenna).

Qualitative trends and distinct spectra were obtained by simplifying the sample structures (cf. table C.1). An infinite array of nanoantennas was simulated by periodic unit cell boundary conditions for both in-plane dimensions \(x\) and \(y\) (transverse direction) and perfectly matched layer (vertical direction).

The different materials were described by dispersion models fitted in the used frequency range. However, by calculations in the frequency range, only the input data is used. For GST-326, the dielectric data of Kremers [110] was used (cf. description in B.2). The complex dielectric function \(\varepsilon\) for aluminum was modeled with a Drude model (parameters taken from [323]) and silicon was modeled with a constant refractive index of 3.44, respectively.

C.1.2 Comsol Multiphysics software

The scattering cross-section \(\sigma_{\text{scat}}(\tilde{\nu})\), absorption cross section \(\sigma_{\text{abs}}(\tilde{\nu})\) and extinction cross section \(\sigma_{\text{ext}}(\tilde{\nu})\) of single nanorods of aluminum and gold were numerically analyzed using Comsol Multiphysics software in the frequency domain (similar to CST Microwavestudio). Thereby, a template created by D. Kumar [324], which followed the work of Yushanov [325], was applied. The single nanorod was

\(^1\)Only the calculated reflectance spectra of antennas arrays covered with an InSb thin film, conducted by T. Mass were performed with the software Lumerical.
placed in a spherical vacuum domain surrounded by a perfectly matched layer domain. The incident plane wave incident in z-direction (similar to CST Microwave Studio as well). Maxwell’s equations were solved to obtain the cross sections $\sigma(\vec{v})$, while for the absorption cross section $\sigma_{\text{abs}}(\vec{v})$ the energy absorption rate (energy loss integrated over the volume of the nanorod) was divided by the magnitude of the incident irradiance (intensity of the incident plane wave). The energy scattering rate (Poynting vector integrated of the surface of the spherical vacuum domain) was divided by the incident irradiance to obtain the scattering cross section $\sigma_{\text{scat}}(\vec{v})$. The extinction cross section $\sigma_{\text{ext}}(\vec{v})$ is defined as the sum of $\sigma_{\text{abs}}(\vec{v})$ and $\sigma_{\text{scat}}(\vec{v})$ as described in section 2.2.

C.2 Sample model for Microwave Studio calculations

C.2.1 Parameterized model

The sample model displayed in figure C.1 was created with Microwave Studio. The entire sample geometry was parameterized to allow for an easy adaption in case of the investigation of a different sample design. Furthermore, the nanorod antenna was modeled according to the SEM images, which led to the rounded tips (blending radius defined as half of the antenna width $w$, e.g. 55 nm for $w = 110$ nm) and smoothed edges (15°) as shown in figure C.1c. However, the (randomly distributed) rough surface of the aluminum was not included.

Figure C.1: For conducting the calculations in CST Microwave Studio, the sample scheme shown in C.1a was designed. The antenna (gray) was placed on a substrate (height 1.5 µm), while the antenna geometry was defined by length $L$, height $h$ and width $w$. The area of the unit cell was given by its periodicity $p$ with $p = 2l$ here. As superstrate, vacuum with a height of 2 µm was chosen. In case of added PCM or capping layer, the sample scheme in figure C.1a is extended according to C.1b. For a clear representation, a cross-sectional view is displayed (In figure C.1a, the position of the cross-sectional view is given by red dash-dote lines). The thickness of the PCM layer is denoted as $t$, while the thickness of the capping layer is marked as $c$. The aluminum nanorod antenna was modeled as a rectangle with rounded tips and smoothed edges according to the SEM images of the nanorods as it is shown in figure C.1c.

204
C.2.2 Comparison between experimental and simulated samples

As it was shown in section 5.2, aluminum antenna arrays were investigated in this thesis. The antenna geometry needed to be suited for the applied spectral range. Thus, reflectance spectra of antenna arrays of different lengths $L$ were calculated with *CST Microwave Studio* (MWS). Finally, antennas with $L = 600\, \text{nm}$, $L = 500\, \text{nm}$ and $L = 400\, \text{nm}$ were chosen. A comparison between calculated and experimental spectra of aluminum antennas (no PCM) is given in figure 6.1b. There, only an antenna length of $L = 600\, \text{nm}$ was considered. It can be seen, that the measured and the calculated spectral position of the arrays differ about $247\, \text{cm}^{-1}$. A comparison between calculated and experimental spectra of aluminum antennas (GST-326) is given in figure 6.10. A very good qualitative agreement was found, while quantitative differences occured. It has to be noted, that several differences between the considered samples exist, which are listed in table C.1.

<table>
<thead>
<tr>
<th>aspects</th>
<th>experiment - FTIR</th>
<th>calculation - CST MWS</th>
</tr>
</thead>
<tbody>
<tr>
<td>number of antennas</td>
<td>about 2000 antennas</td>
<td>infinite number</td>
</tr>
<tr>
<td>chromium adhesive layer</td>
<td>including chromium</td>
<td>no chromium considered</td>
</tr>
<tr>
<td>oxide layer</td>
<td>native silicon dioxide and aluminum oxide layer (1 - 10 nm [326])</td>
<td>no oxide layers considered</td>
</tr>
<tr>
<td>precise geometry</td>
<td>deviations from (CAD) design due to fabrication process as it can be seen</td>
<td>use of CAD design</td>
</tr>
<tr>
<td>antenna roughness</td>
<td>antenna surface is relatively rough as can be seen in figure B.1 for example</td>
<td>no roughness considered</td>
</tr>
<tr>
<td>polar angle $\theta_i$</td>
<td>$15^\circ \leq \theta_i \leq 29^\circ$</td>
<td>$\theta_i = 27^\circ$</td>
</tr>
<tr>
<td>azimuthal angle $\phi$</td>
<td>$-90^\circ \leq \phi \leq 90^\circ$</td>
<td>$\phi = 0^\circ$</td>
</tr>
</tbody>
</table>

Table C.1: By comparing calculated with experimentally determined reflectance spectra of antenna arrays, differences in the investigated sample properties and setup geometry need to be considered.
## List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>amorphous phase of a PCM</td>
</tr>
<tr>
<td>ACSRR</td>
<td>asymmetrically coupled SRR</td>
</tr>
<tr>
<td>ADC</td>
<td>analog-to-digital converter</td>
</tr>
<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
</tr>
<tr>
<td>AIST</td>
<td>silver indium antimony telluride</td>
</tr>
<tr>
<td>ASRS</td>
<td>asymmetric split-ring slit</td>
</tr>
<tr>
<td>ATR</td>
<td>attenuated total reflectance</td>
</tr>
<tr>
<td>BD-RE</td>
<td>Blu-ray disc recordable erasable</td>
</tr>
<tr>
<td>BEC</td>
<td>Born effective charge</td>
</tr>
<tr>
<td>BG</td>
<td>background</td>
</tr>
<tr>
<td>BH</td>
<td>Blackman-Harris</td>
</tr>
<tr>
<td>BVB</td>
<td>Ballspielverein Borussia 09 e.V. Dortmund</td>
</tr>
<tr>
<td>C</td>
<td>crystalline phase of a PCM</td>
</tr>
<tr>
<td>CAD</td>
<td>computer-aided design</td>
</tr>
<tr>
<td>CCD</td>
<td>charge-coupled device</td>
</tr>
<tr>
<td>CD-RW</td>
<td>compact disc rewritable</td>
</tr>
<tr>
<td>CLSM</td>
<td>confocal laser scanning microscope</td>
</tr>
<tr>
<td>CMOS</td>
<td>complementary metal-oxide-semiconduct.</td>
</tr>
<tr>
<td>CSRR</td>
<td>coupled split-ring resonator</td>
</tr>
<tr>
<td>CST</td>
<td>Computer Simulation Technology</td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>DRAM</td>
<td>dynamic random-access memory</td>
</tr>
<tr>
<td>DVD</td>
<td>digital versatile disc</td>
</tr>
<tr>
<td>EBL</td>
<td>electron beam lithography</td>
</tr>
<tr>
<td>EEMR</td>
<td>electric excitation coupling to magnetic resonance</td>
</tr>
<tr>
<td>fcc</td>
<td>face-centered cubic</td>
</tr>
<tr>
<td>FDTD</td>
<td>finite difference time domain</td>
</tr>
<tr>
<td>FiR</td>
<td>far infrared</td>
</tr>
<tr>
<td>FIT</td>
<td>finite integration</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>FWHM</td>
<td>full width at half maximum</td>
</tr>
<tr>
<td>GAO</td>
<td>grazing angle objective</td>
</tr>
<tr>
<td>GLS</td>
<td>gold lanthanum sulphide</td>
</tr>
<tr>
<td>GST</td>
<td>germanium antimony telluride</td>
</tr>
<tr>
<td>HV</td>
<td>high voltage</td>
</tr>
<tr>
<td>I</td>
<td>insulting phase of VO₂</td>
</tr>
<tr>
<td>IMT</td>
<td>insulator-to-metal transition</td>
</tr>
<tr>
<td>IST</td>
<td>indium antimony telluride compound</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>JDOs</td>
<td>joint density of states</td>
</tr>
<tr>
<td>LC(D)</td>
<td>liquid crystal (display)</td>
</tr>
<tr>
<td>LOR</td>
<td>lift-off resist</td>
</tr>
<tr>
<td>LSM</td>
<td>lattice surface modes</td>
</tr>
<tr>
<td>LSP(R)</td>
<td>localized surface plasmon (resonance)</td>
</tr>
<tr>
<td>M</td>
<td>metal phase of VO₂</td>
</tr>
<tr>
<td>MCT</td>
<td>mercury cadmium telluride</td>
</tr>
<tr>
<td>MIR</td>
<td>mid-infrared</td>
</tr>
<tr>
<td>MIT</td>
<td>metal-to-insulator transition</td>
</tr>
<tr>
<td>MG</td>
<td>Maxwell-Garnett</td>
</tr>
<tr>
<td>MM</td>
<td>metamaterial</td>
</tr>
<tr>
<td>MQ</td>
<td>melt-quenched phase of a PCM</td>
</tr>
<tr>
<td>MS</td>
<td>metasurface</td>
</tr>
<tr>
<td>NIR</td>
<td>near-infrared</td>
</tr>
<tr>
<td>OJL</td>
<td>O’Leary, Johnson and Lim</td>
</tr>
<tr>
<td>PCM</td>
<td>phase-change material</td>
</tr>
<tr>
<td>PCRAM</td>
<td>phase-change random access memory</td>
</tr>
<tr>
<td>PDMS</td>
<td>poly(dimethylsiloxane)</td>
</tr>
<tr>
<td>PEC</td>
<td>perfect electric conductor</td>
</tr>
<tr>
<td>PMGI</td>
<td>polymethylglutarimide</td>
</tr>
<tr>
<td>PMMA</td>
<td>polymethylmethacrylate</td>
</tr>
<tr>
<td>PTE</td>
<td>power-time-effect</td>
</tr>
<tr>
<td>PVD</td>
<td>physical vapor deposition</td>
</tr>
<tr>
<td>RA</td>
<td>Rayleigh anomaly</td>
</tr>
<tr>
<td>RC</td>
<td>re-crystallized phase of a PCM</td>
</tr>
<tr>
<td>RENS</td>
<td>resolution near-field structure</td>
</tr>
<tr>
<td>RT</td>
<td>room temperature</td>
</tr>
<tr>
<td>SC</td>
<td>semiconductor</td>
</tr>
<tr>
<td>SCM</td>
<td>storage-class memory</td>
</tr>
<tr>
<td>SCM</td>
<td>strongly correlated metal</td>
</tr>
</tbody>
</table>
**List of Abbreviations**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>SE</td>
<td>secondary electrons</td>
</tr>
<tr>
<td>SEIRA</td>
<td>surface enhanced infrared absorption</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>SL</td>
<td>sublattice</td>
</tr>
<tr>
<td>SNOM</td>
<td>scanning near-field optical microscopy</td>
</tr>
<tr>
<td>SNR</td>
<td>signal-to-noise ratio</td>
</tr>
<tr>
<td>SPhP</td>
<td>surface phonon polariton</td>
</tr>
<tr>
<td>SPP</td>
<td>surface plasmon polariton</td>
</tr>
<tr>
<td>SRAM</td>
<td>static random-access memory</td>
</tr>
<tr>
<td>SRR</td>
<td>split-ring resonator</td>
</tr>
<tr>
<td>SRS</td>
<td>split-ring slit</td>
</tr>
<tr>
<td>SSD</td>
<td>solid-state drive</td>
</tr>
<tr>
<td>TFI</td>
<td>thin film interference</td>
</tr>
<tr>
<td>TTT</td>
<td>time-temperature-transformation</td>
</tr>
<tr>
<td>UHV</td>
<td>ultra-high vacuum</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>VIS</td>
<td>visible</td>
</tr>
</tbody>
</table>
**INDICES**

- \( \alpha \) direction
- \( A \) index for amorphous phase of PCM
- \( C \) annealed (metastable) crystalline phase of PCM
- \( C^* \) stable crystalline phase of PCM
- \( d \) dielectric medium
- \( D \) Drude model
- \( f \) final state
- \( i \) initial (quantum) state; element
- \( j \) final quantum state
- \( k \) atom
- \( m \) metal
- \( MQ \) melt-quenched phase of PCM
- \( RC \) re-crystallized phase of PCM
- \( T \) Tauc model
- \( TL \) Tauc-Lorentz model
- \( PCM \) phase-change material

**GREEK SYMBOLS**

- \( \alpha \) absorption coefficient, in \( m^{-1} \)
- \( \alpha \) polarizability, in \( m^3 \)
- \( \alpha \) coefficient of thermal expansion, in \( K^{-1} \)
- \( \gamma \) ratio of band gap energies
- \( \gamma_D \) damping rate in Drude model
- \( \delta \) path difference
- \( \delta_{sk} \) skin depth, in \( nm \)
- \( \Delta G \) free energy difference
- \( \Delta L \) linear expansion
- \( \Delta \tilde{\nu}_{\text{ann}} \) total shift due to annealing, in \( cm^{-1} \)
- \( \Delta \tilde{\nu}_{\text{res}} \) total or percental shift of \( \tilde{\nu}_{\text{res}} \), in cm\(^{-1}\) or \% 
- \( \Delta \tilde{\nu}_{\text{step}} \) total incremental shift of \( \tilde{\nu}_{\text{res}} \), in cm\(^{-1}\)
- \( \epsilon \) complex permittivity, dielectric function
- \( \epsilon_0 \) vacuum permittivity
- \( \epsilon_1 \) real part of complex permittivity
- \( \epsilon_2 \) imaginary part of complex permittivity
- \( \epsilon_{00} \) optical dielectric constant
- \( \epsilon_{\text{const}} \) summarized polarizability of core electrons
- \( \mathcal{E} \) electromagnetic field
- \( \zeta \) ratio of optical dielectric constants
- \( \theta_i \) polar angle of incidence, in deg
- \( \theta_{\text{max}} \) maximum diffraction angle, in deg
- \( \theta_r \) angle of reflection, in deg
- \( \theta_t \) angle of transmission, in deg
- \( \kappa \) extinction coefficient
- \( \kappa_T \) thermal conductivity, in mW·cm\(^{-1}\)·K\(^{-1}\)
- \( \lambda \) wavelength, in \( \mu m^{-1} \)
- \( \lambda_0 \) wavelength of incident wave, in \( \mu m^{-1} \)
- \( \lambda_{\text{RA}} \) wavelength of Rayleigh anomaly, in \( m^{-1} \)
- \( \lambda'_{\text{RA}} \) averaged \( \lambda_{\text{RA}} \), in \( m^{-1} \)
- \( \lambda_{\text{res}} \) resonance wavelength, in \( m^{-1} \)
- \( \lambda_{\text{SPP}} \) surface plasmon polariton wavelength, in \( m^{-1} \)
- \( \mu \) mobility
- \( \mu_0 \) reduced mass
- \( \mu_0 \) magnetic permeability of free space
- \( \mu_{\text{eff}} \) effective permeability of MM
- \( \nu \) frequency, in \( s^{-1} \)
- \( \tilde{\nu} \) wavenumber, in \( cm^{-1} \)
- \( \tilde{\nu}_{\text{LC}} \) \( LC \) resonance wavenumber of SRR, in \( cm^{-1} \)
- \( \tilde{\nu}_{\text{p}} \) plasma wavenumber, in \( cm^{-1} \)
- \( \tilde{\nu}_{\text{res}} \) resonance frequency position, in \( cm^{-1} \)
- \( \tilde{\nu}_{\text{RT}} \) \( \tilde{\nu}_{\text{res}} \) referring to the room temperature, in \( cm^{-1} \)
- \( \rho \) density, in g·cm\(^{-3} \)
- \( \sigma \) interfacial energy per unit surface area
- \( \sigma_{\text{abs}} \) absorption cross section, in \( nm^2 \)
- \( \sigma_{\text{ext}} \) extinction cross section, in \( nm^2 \)
- \( \sigma_{\text{geo}} \) geometric cross section, in \( nm^2 \)
- \( \sigma_{\text{norm}} \) normalized cross section, in \( nm^2 \)
- \( \sigma_{\text{scat}} \) scattering cross section, in \( nm^2 \)
- \( \tau \) displacement of sublattice
- \( \tau \) laser pulse duration, in s
- \( \tau_{\text{seq}} \) duration of laser pulse sequence, in s
- \( \phi_i \) azimuthal angle of incidence, in deg
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi$</td>
<td>phase of electromagnetic field</td>
</tr>
<tr>
<td>$\chi$</td>
<td>electric susceptibility</td>
</tr>
<tr>
<td>$\Psi$</td>
<td>quantum state</td>
</tr>
<tr>
<td>$\omega$</td>
<td>angular frequency, in rad$\cdot$s$^{-1}$</td>
</tr>
<tr>
<td>$\omega_0$</td>
<td>short-wire-like SRR resonance frequency, in rad$\cdot$s$^{-1}$</td>
</tr>
<tr>
<td>$\omega_{LC}$</td>
<td>LC resonance frequency of SRR, in cm$^{-1}$</td>
</tr>
<tr>
<td>$\omega_p$</td>
<td>plasma frequency, in rad$\cdot$s$^{-1}$</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>optical phonon mode</td>
</tr>
</tbody>
</table>

**LATIN SYMBOLS**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>radius of metal sphere, in nm</td>
</tr>
<tr>
<td>$A(r)$</td>
<td>surface of crystalline nucleus</td>
</tr>
<tr>
<td>$A_{ij}$</td>
<td>fitted oscillator strength in TL model</td>
</tr>
<tr>
<td>$A_T(\delta)$</td>
<td>(triangular) weight function</td>
</tr>
<tr>
<td>$B(k_0)$</td>
<td>instrumentally modified intensity of FTIR source</td>
</tr>
<tr>
<td>$C$</td>
<td>capacitance, in F</td>
</tr>
<tr>
<td>$C_f$</td>
<td>fit parameter for $\lambda/2$-model</td>
</tr>
<tr>
<td>$C_L$</td>
<td>fitted broadening term in TL model</td>
</tr>
<tr>
<td>$d$</td>
<td>split-ring resonator gap size</td>
</tr>
<tr>
<td>$d_{x,y}$</td>
<td>antenna separation within arrays in $x$- and $y$-direction, in $\mu$m</td>
</tr>
<tr>
<td>$d_{\text{crit}}$</td>
<td>critical antenna separation within arrays, in $\mu$m</td>
</tr>
<tr>
<td>$D$</td>
<td>storage density</td>
</tr>
<tr>
<td>$\bar{D}$</td>
<td>electric displacement</td>
</tr>
<tr>
<td>$E$</td>
<td>energy, in eV</td>
</tr>
<tr>
<td>$E_0$</td>
<td>fitted peak transition energy in TL model</td>
</tr>
<tr>
<td>$E_F$</td>
<td>Fermi energy, in eV</td>
</tr>
<tr>
<td>$E_B$</td>
<td>band gap energy, in eV</td>
</tr>
<tr>
<td>$f_{ij}$</td>
<td>oscillator strength</td>
</tr>
<tr>
<td>$f_C$</td>
<td>crystalline fraction</td>
</tr>
<tr>
<td>$F$</td>
<td>fluence, in mJ$\cdot$cm$^{-2}$</td>
</tr>
<tr>
<td>$F_0$</td>
<td>peak fluence, in mJ$\cdot$cm$^{-2}$</td>
</tr>
<tr>
<td>$F_{\text{th}}$</td>
<td>threshold fluence, in mJ$\cdot$cm$^{-2}$</td>
</tr>
<tr>
<td>$F_{\text{abl}}$</td>
<td>ablation threshold fluence, in mJ$\cdot$cm$^{-2}$</td>
</tr>
<tr>
<td>FWHM</td>
<td>resonance peak width, in cm$^{-1}$</td>
</tr>
<tr>
<td>$g$</td>
<td>joint density of states</td>
</tr>
<tr>
<td>$G(k_0)$</td>
<td>responsivity</td>
</tr>
<tr>
<td>$\mathbf{G}_{ij}$</td>
<td>reciprocal lattice vector</td>
</tr>
<tr>
<td>$h$</td>
<td>antenna height, in nm</td>
</tr>
<tr>
<td>$\mathbf{H}$</td>
<td>magnetic field</td>
</tr>
<tr>
<td>$H(k_0)$</td>
<td>correction factor</td>
</tr>
<tr>
<td>$H'$</td>
<td>perturbation (by light wave)</td>
</tr>
<tr>
<td>$i$</td>
<td>quantum numbers of initial atomic level</td>
</tr>
<tr>
<td>$j$</td>
<td>quantum numbers of final atomic level</td>
</tr>
<tr>
<td>$j'$</td>
<td>circular current</td>
</tr>
<tr>
<td>$k$</td>
<td>wavevector</td>
</tr>
<tr>
<td>$k_0$</td>
<td>wavevector of incident wave</td>
</tr>
<tr>
<td>$K_p$</td>
<td>plasma wavevector</td>
</tr>
<tr>
<td>$K$</td>
<td>restoring constant regarding an atomic chain</td>
</tr>
<tr>
<td>$l_x, l_y$</td>
<td>split-ring resonator arm length, in nm</td>
</tr>
<tr>
<td>$L$</td>
<td>induction, in H</td>
</tr>
<tr>
<td>$L$</td>
<td>antenna length, in nm</td>
</tr>
<tr>
<td>$L_z$</td>
<td>propagation length in $z$-direction</td>
</tr>
<tr>
<td>$L_x, L_y$</td>
<td>axes length of laser beam in $z$-direction</td>
</tr>
<tr>
<td>$L_{\text{LA}}$</td>
<td>long axis of switched spot, in $\mu$m</td>
</tr>
<tr>
<td>$m$</td>
<td>oscillation mode</td>
</tr>
<tr>
<td>$m^*$</td>
<td>effective mass</td>
</tr>
<tr>
<td>$m_0$</td>
<td>electron mass</td>
</tr>
<tr>
<td>$M$</td>
<td>molar mass, in g$\cdot$mol$^{-1}$</td>
</tr>
<tr>
<td>$M$</td>
<td>transition matrix element</td>
</tr>
<tr>
<td>$n$</td>
<td>Hall carrier density, in cm$^{-3}$</td>
</tr>
<tr>
<td>$n$</td>
<td>real part of complex refractive index</td>
</tr>
<tr>
<td>$n_{\text{eff}}$</td>
<td>effective refractive index</td>
</tr>
<tr>
<td>$n'_{\text{eff}}$</td>
<td>averaged effective refractive index</td>
</tr>
<tr>
<td>$n_{\text{emb}}$</td>
<td>$n$ of embedding medium</td>
</tr>
<tr>
<td>$n_{\text{sub}}$</td>
<td>$n$ of substrate</td>
</tr>
<tr>
<td>$n_{\text{super}}$</td>
<td>$n$ of superstrate</td>
</tr>
<tr>
<td>$n_{\text{vac}}$</td>
<td>vacancy concentration</td>
</tr>
<tr>
<td>$N$</td>
<td>count rate</td>
</tr>
<tr>
<td>$N$</td>
<td>electron density, given in m$^{-3}$</td>
</tr>
<tr>
<td>$N$</td>
<td>number of the main group in the periodic system</td>
</tr>
<tr>
<td>$N_A$</td>
<td>numerical aperture</td>
</tr>
<tr>
<td>$\bar{\rho}$</td>
<td>dipole moment</td>
</tr>
<tr>
<td>$P$</td>
<td>laser pulse power, in W</td>
</tr>
<tr>
<td>$P$</td>
<td>periodicity in an antenna array, in $\mu$m or nm</td>
</tr>
<tr>
<td>$P$</td>
<td>macroscopic polarization per unit cell</td>
</tr>
<tr>
<td>$P_{\text{res}}$</td>
<td>resonant polarization</td>
</tr>
<tr>
<td>$Q$</td>
<td>quality factor</td>
</tr>
<tr>
<td>$R$</td>
<td>radius of nucleus</td>
</tr>
<tr>
<td>$r$</td>
<td>amplitude coefficient for reflection</td>
</tr>
<tr>
<td>$r_0$</td>
<td>laser beam radius, in $\mu$m</td>
</tr>
<tr>
<td>$r_C$</td>
<td>critical radius of nucleus</td>
</tr>
<tr>
<td>$r_f$</td>
<td>Fresnel coefficient for reflection</td>
</tr>
<tr>
<td>$R$</td>
<td>reflectivity</td>
</tr>
</tbody>
</table>
List of Symbols

\( R_{\text{max}} \) \hspace{1em} \text{peak reflectance}
\( S(\delta) \) \hspace{1em} \text{measured amplifier signal}
\( SA \) \hspace{1em} \text{short axis of switched spot, in } \mu \text{m}
\( t \) \hspace{1em} \text{amplitude coefficient for transmission}
\( t \) \hspace{1em} \text{layer thickness, in } \text{nm}
\( T \) \hspace{1em} \text{period}
\( T \) \hspace{1em} \text{temperature, in } ^\circ \text{C}
\( T_{AN} \) \hspace{1em} \text{annealing temperature, in } ^\circ \text{C}
\( T_C \) \hspace{1em} \text{crystallization temperature, in } ^\circ \text{C}
\( T_g \) \hspace{1em} \text{glass transition temperature, in } ^\circ \text{C}
\( T_{IMT} \) \hspace{1em} \text{IMT temperature, in } ^\circ \text{C}
\( T_L \) \hspace{1em} \text{liquidus temperature, in } ^\circ \text{C}
\( T_m \) \hspace{1em} \text{melting temperature, in } ^\circ \text{C}
\( T_{RT} \) \hspace{1em} \text{room temperature, in } ^\circ \text{C}
\( \text{TFOM} \) \hspace{1em} \text{tuning figure of merit}
\( U \) \hspace{1em} \text{acceleration voltage, in } \text{kV}
\( v \) \hspace{1em} \text{phase velocity}
\( V(r) \) \hspace{1em} \text{nucleus volume}
\( V_0 \) \hspace{1em} \text{unit cell volume}
\( w \) \hspace{1em} \text{antenna width, in } \text{nm}
\( W_{\text{opt}} \) \hspace{1em} \text{optical transition rate}
\( Z^{(T)} \) \hspace{1em} \text{transverse effective charge}

PHYSICAL CONSTANTS

\( c \) \hspace{1em} \text{speed of light, } 299792458 \text{ m s}^{-1}
\( e \) \hspace{1em} \text{elementary charge, } 1.6021766209 \times 10^{-19} \text{ C}
\( h \) \hspace{1em} \text{Planck constant, } 4.1356676623 \times 10^{-15} \text{ eV s}
\( \hbar \) \hspace{1em} \text{reduced Planck constant, } 6.582119544 \times 10^{-16} \text{ eV s}


Bibliography


Bibliography


Bibliography


Bibliography


[288] Sentech Instruments GmbH, 2014. The (ZnS)$_{80}$-(SiO$_2$)$_{20}$ thin films on silicon wafers have been fabricated by sputtering at the Institute in Aachen and have been sent to Sentech. The measured dielectric data of a (ZnS)$_{80}$-(SiO$_2$)$_{20}$ has been sent by S. Peters (Sentech) via e-mail on 04 Jun 2014.


Bibliography


List of publications

Articles in scientific journals related to this thesis:


Additional articles in scientific journals:


Talks and posters at international conferences:

1. Talk "Modelling of phase change material based tunable meta-materials" at the META conference 2016, Malaga (Spain), 2A18 SP7

2. Poster "Fine-tuning and individual addressing of mid-IR nanoantenna resonances by reversible optical switching of Ge3Sb2Te5 thin-films" at the MRS conference 2016, Phoenix, AZ (USA), EP8.6.05

3. Talk "Active mid-IR plasmonic metadevices" at the META conference 2015, New York, NY (USA), 3A20
4. Poster "Phase-change materials for reversible optical tuning of infrared antenna resonances" at the NFO conference 2014, Salt Lake City (USA)
5. Talk "Tuning high-Q surface phonon polariton resonances of SiC nanopillars" at the MRS conference 2014, San Francisco, CA (USA), KK8.09 *
6. Poster "Ink nanodroplet printing for fabrication of infrared nanoantennas" at the MRS conference 2014, San Francisco, CA (USA), KK3.12 *
7. Poster "Phase-change materials for reversible optical tuning of infrared antenna resonances" at the MRS conference 2014, San Francisco, CA (USA), KK3.11 *
8. Poster "Reversible optical tuning of infrared nanoantenna arrays using phase-change materials" at the Heraeus Seminar on Active Nanooptics and Metamaterial Dynamics 2014, Bad Honnef (Germany) *
9. Talk "Using low-loss phase-change materials for IR antenna resonance tuning" at the SPIE conference 2013, San Diego, CA (USA), 8806-99 *
10. Talk "Using low-loss phase-change materials for mid-infrared antenna resonance tuning" at the Nanometa conference 2013, Seefeld (Austria), SUN3s.2 *
11. Poster "Fabrication and characterization of solution-phase deposited GeTe nanocomposites" at the MRS conference 2012, San Francisco, CA (USA), F5.14 *

Talks and posters at national conferences:
1. Poster "Fine-tuning and individual addressing of mid-IR nanoantenna resonances by reversible optical switching of Ge$_3$Sb$_2$Te$_6$ thin-films" at the DPG conference 2016, Regensburg, O23.17
2. Talk "Neue Materialien für nanophotonische Strukturen im infraroten Spektralbereich" at the Cluster NMWP.NRW Symposium 2015, Essen *
3. Talk "Extreme ultraviolet proximity lithography for fast, flexible and large-scale fabrication of infrared antennas" at the DPG conference 2015, Berlin, O23.3
4. Talk "Material contrasts of layered phase change materials in s-SNOM" at the DPG conference 2015, Berlin, O23.8
5. Poster "Optical tuning of surface phonon polaritons with a phase-change material" at the DPG conference 2015, Berlin, O36.1
6. Talk "Active mid-IR plasmonic metasurfaces: Tunable and switchable chirality and flat-surface beam steering" at the DPG conference 2015, Berlin, O90.2
7. Talk "Large area optical tuning of mid-infrared resonant nanostructures by using low-loss phase-change materials" at the DPG conference 2014, Dresden, DS40.2
9. Poster "Analysis of the switching behavior of phase-change materials using s-SNOM" at the DPG conference 2014, Dresden, DS44.15
10. Talk "Tuning propagating surface phonon polaritons at mid-infrared frequencies using phase-change material" at the DPG conference 2014, Dresden, O71.2
11. Talk "Using low-loss phase-change materials for IR antenna resonance tuning" at the DPG conference 2013, Regensburg, O7.8 *
12. Poster "Indium microsoldering of graphene on silicon dioxide substrates" at the DPG conference 2010, Dresden, O27.7

The symbol * marks conference contributions, which have been presented by the author of this thesis.
Acknowledgements

I would like to thank Prof. Thomas Taubner for the possibility to work on this exciting topic. I am thankful for all his guidance and his interest he showed in my work and person. I appreciate that he gave me the opportunity to present my work at national and international conferences and I am very grateful for his support regarding different applications. He guided me throughout the last and most demanding phase of writing this thesis and for this, I am very grateful.

Furthermore, I thank Prof. Matthias Wuttig for co-supervising this thesis and providing the outstanding infrastructure of the I. Institute of Physics. I am grateful for his kind advice and support since I started working on my project thesis in his group in 2010.

I thank Prof. Gero von Plessen for the possibility to gain experience in the field of microgels, which allowed me to widen my horizon. Furthermore, I am very grateful for his encouragement and his guidance during the last year.

I would like to thank Prof. Aaron Lindenberg, Dr. Peter Zalden, Prof. Giessen, Xinghui Yin, Dr. Andreas Tittl, as well as Dr. habil. Dmitry Chigrin for their encouragement during shared publications. Especially Dr. Chigrin, who has been a mentor to me, is acknowledged for helping me with his honest advice. Discussing science with him has always been exciting and he motivated me to follow an academic career.

I would like to give thanks to Sarah Schlenter, Kathrin Gerth, Renate Betz and Oliver Lehmann regarding their help with administrative issues. I am grateful for the support by Stephan Hermes during the sputtering process and by Sebastian Mohrhenn during the work in the cleanroom, as well as with the FIB-SEM. Besides, Daryan Kempe helped a lot with the laser scanning microscope in the laboratory of Prof. Fitter.

Moreover, I would like to extend my gratitude to my colleagues in the group of Prof. Taubner and Prof. von Plessen for their help and encouragement. I appreciate that my former colleagues Dr. Benedikt Hauer, Dr. Mattis Hoffmann, Tobias Mass, Andreas Nedilko and Deepu Kumar made work much more fun. The Master’s students Thomas Kalix and Angela De Rose, who I supervised, did a great job I am grateful for. Especially Angela had to work independently since I was not present in the lab most of the time. Special thanks goes to the student assistants Hannes Böckmann and Peter Lingnau for their work. I would like to give thanks to my supervisors Prof. Taubner and Prof. Wuttig, as well as to Prof. von Plessen and Prof. Harald Giessen for their promotion regarding the RWTH Aachen Graduate Support Opportunities scholarship to which I would like to express my gratitude. The program financially supported me during the time of writing this thesis.
Surround yourself with good people,
friends who make you laugh,
those, who will support and help you to achieve
your dreams without expecting anything in return,
people with good stories, people that inspire you.

Billy Yang, filmmaker

I would like to thank Dr. Brian Hardin, Dr. Anne Ruminski and Dr. Daniel Anderson for being beloved friends and giving me a home far abroad. The time I spent with them broadened my horizon and they made some of the best moments I ever had possible. I look forward to another great trip to one of the National Parks together. Furthermore, I would like to thank Anne for introducing me to long-distance running. I enjoyed our runs in the bay area so much.
I thank Dr. Mattis Hoffmann for his honest and longtime friendship. I hope we will never lose sight of each other.

I thank my father Lothar Michel for his love and his unconditional support. It makes me incredibly sad he never saw me graduating. At the same time I am deeply grateful that he taught me everything I need to follow my dreams and to overcome difficulties along the way. I would like to thank my mother Jutta Michel for her love and encouragement. During my studies, she supported me with pragmatism and loving kindness. I would like to thank my grandmother Ursula Rank, as well as Ulrich Hackl for their support.

I am very grateful that Conny Kill-Frech and Heiner Kill inspired me with confidence and motivated me during the ups and downs of this thesis.
Finally, I would like to acknowledge Tim Frech who has shown incredible patience, humor and understanding throughout the writing of this thesis, and for this, I am truly grateful. During tough moments he guided me through and helped my keep in perspective what is important - something, which is all too easy to forget when submersed in the world of academia.