

**Simulation Assisted Analysis of the Ablation of Thin,  
Transparent and Semiconducting Films with Ultrashort  
Pulsed Laser Radiation**

**Simulationsgestützte Analyse der Ablation dünner,  
transparenter und halbleitender Schichten mit ultrakurz  
gepulster Laserstrahlung**

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# Kurzfassung

Das Abtragen dünner, transparenter halbleitender Schichten mittels ultrakurzer Laserstrahlung gewinnt durch immer kleiner werdende Strukturen in integrierten Schaltkreisen oder funktionalen Oberflächen zusehend an Bedeutung. Zur Kontrollierbarkeit des Ablationsprozesses ist ein genaues Verständnis der grundlegenden physikalischen Mechanismen unabdingbar. Vor diesem Hintergrund wird der Ablationsmechanismus dünner, transparenter halbleitender Schichten mittels ultrakurzer Laserstrahlung untersucht.

Um den Einfluss der wichtigsten Laserparameter auf die Ablationsdynamik zu charakterisieren, wird ein numerisches Prozessmodell entwickelt, welches die zugrundeliegenden, physikalischen Mechanismen beschreibt. Das Modell beinhaltet die Beschreibung der sich während des Laserpulses ändernden optischen Eigenschaften über die freie Elektronendichte, die aus der absorbierten Energie resultierende Temperaturverteilung und die daraus folgende mechanische Ausdehnung. Die Lösungen werden auf Grundlage experimenteller Beobachtungen validiert.

Zusätzlich wird zur Modellierung der geometrischen Form von Ablationskratern ein reduziertes Modell für Metalle dahingehend erweitert, dass ein Abtragen transparenter Halbleiter und Isolatoren ebenfalls mit experimenteller Übereinstimmung beschrieben werden können.



# Abstract

Precise ablation of thin, transparent semiconducting layers using ultrashort laser radiation is becoming increasingly important due to the decreasing structure-size in integrated circuits or functional surfaces. An accurate understanding of the fundamental physical mechanisms is essential for the controllability of the ablation process. For this reason, the ablation mechanism of thin, transparent semiconducting layers is being investigated using ultrashort laser radiation.

In order to characterize the influence of the most important laser parameters on the ablation dynamics, a numerical process model is developed which describes the underlying physical mechanisms. The model includes the description of the changing optical properties during the laser pulse via the free electron density, the temperature distribution resulting from the absorbed energy and the subsequent mechanical expansion. The solutions are validated based on experimental observations.

In addition, to model the crater shape, a reduced model for metals is extended to also describe the ablation crater geometry accurately in transparent semiconductors and insulators with experimental agreement.



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# 1 Introduction

With the steadily decreasing size of microchips and optoelectronic devices, precise processing techniques become increasingly important. Microchips and optoelectronic devices are built out of complex layered structures which themselves consist of thin films of metals, insulators, and semiconductors. Typical film thicknesses range from some tens of micrometers down to only a few nanometers. The demand for faster computers with higher computational capacity led to the growth of the semiconductor industry. In 1965 Gordon Moore empirically predicted the number of transistors would double every two years. This is known as Moore's law, and he believed himself that it would only hold for ten years only [1]. Strikingly, Moore's law remained valid to date with now several billion transistors on a microchip, leading to computers and devices with increasing computational capacity [2] and boosting the impact of semiconductor industry on today's society. In 2022 the market size of the semiconductor industry was 573.44 billion USD and is predicted to grow with a compound annual growth rate (CAGR) of 12.2 % to 1380.79 billion USD by 2029 [3]. In many technical applications, such as thin film solar cells, display applications and wafer dicing, it is necessary to locally remove certain films without damaging the adjacent material around the processing region and beneath the films. Depending on the application, processing techniques range from lithography, chemical micro etching, mechanical micro grinding to cutting or laser ablation [4, 5].

The use of laser ablation significantly reduces the number of process steps compared to the other processing techniques. Additionally, no aggressive chemicals are necessary, and the variety of possible ablation geometries is increased. For this reason, laser processing is already used in industrial process chains for the aforementioned

technical applications. However, for complex multilayer structures with sometimes unknown composition, it is often difficult to set up a robust ablation process. The interplay of the material properties and the different physical phenomena ranging from interferences of the laser radiation within the thin films, ionization of semiconducting materials and thereby temporally changing its optical and electric properties, heating, thermal expansion, phase transitions and phase explosion governs the ablation process. The identification of the relevant physical mechanisms leads to controllability of the ablation process and may lead to a reduction of damage such as heat affected zones, cracks, or delamination.

### 1.1 Technical Motivation

Indium tin oxide (ITO) is a material particularly important for many technical applications, such as thin film solar cells or displays, where electrical conductivity and optical transparency are necessary. In the case of passive matrix organic light-emitting diode (PMOLED) displays, the pixels consist of individual organic light-emitting diodes (OLEDs). The size of the individual OLED is reduced to achieve a high display resolution, leaving no room for metallic contacts between the OLEDs. The high optical transparency and electrical conductivity of thin ITO films make ITO a promising candidate for display electrodes. To maintain both optical transparency and a high display resolution, a thin ITO film is applied to the display glass. Individual control of the OLEDs is achieved by scribing conductive paths into the ITO film. A simplified schematic sketch of a PMOLED can be found in fig. 1.1 The scribing process for the conductive paths in the ITO layer has to selectively remove the layer without damaging the substrate. Therefore, ultrashort pulsed laser ablation can be used to selectively ablate the ITO layer with minimal damage. Thus, the full functionality and optical transparency of the display is ensured.

Another technical application where thin film ablation with ultrashort laser pulses is important is wafer dicing. Typically, wafers consist

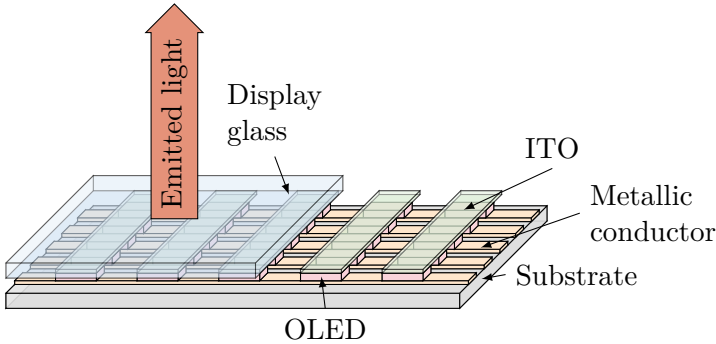


**Figure 1.1:** Simplified schematic structure of a passive matrix OLED (PMOLED) display. Transparent front-side electrodes are required for the OLEDs to emit light through the display glass. Due to the great electrical conductivity and optical transparency, ITO is currently the most widely used material for frontside electrodes.

of multiple thin layers and structures on a silicon (Si) substrate which form individual integrated circuits (ICs). The film thicknesses range from some nanometers to several hundreds of micrometers. The individual ICs are spatially separated by low- $\kappa$  dielectrics. Low- $\kappa$  materials belong to a group of materials which is specifically designed to exhibit a smaller dielectric function than silicon dioxide ( $\text{SiO}_2$ ). The small dielectric function results in a smaller parasitic capacitance which enables higher switching frequencies in silicon components. To secure the complex structures on the wafer from the influence of external influences such as moisture or oxidation, the layered structures are encapsulated with a  $\text{SiN}_x$ -layer. After production, the ICs on the wafer must be separated. This process is often called “dicing”. There are multiple established dicing methods including dicing by grinding, precise mechanical sawing, laser dicing, stealth dicing, plasma dicing, and water jet assisted laser dicing [6]. Damage to the valuable ICs must be avoided to ensure full functionality. Typical damage mechanisms that occur include cracks or delamination of the layered structures

or residual mechanical stress. A reduction of the mechanical load on the multilayer structures during the dicing process can be achieved by "grooving". During the grooving process, trenches are introduced next to the actual cut to prevent cracks from propagating into the ICs. Typically, ultrashort pulsed lasers in the ultraviolet (UV) are used to generate the grooves by specifically removing the individual layers between the ICs.

## 1.2 Goal Formulation and Approach

Both examples in section 1.1 (ablation of thin ITO films and laser grooving of low- $\kappa$  materials for wafer dicing) illustrate the importance of precise micromachining and selective ablation of thin semiconducting or dielectric films. The goal of this work is the development of a numerical process model for the ablation of transparent semiconducting thin films, which is able to predict the ablation crater shape and identifies the relevant physical mechanisms during the ablation process. Fundamental understanding of the relevant physical mechanisms during the ablation of thin films is necessary to avoid substrate damage, heat affected zones, cracks, or delamination of the film. Within the scope of this work, a numerical model is developed, which describes the relevant physical processes during the interaction of intense laser radiation with thin transparent films. The general outline of this work is therefore divided into the following structure:

- Identification of dominant time and length scales and physical mechanisms based on the current state of knowledge
- Formulation and reduction of the mathematical model based on physical and phenomenological assumptions to allow for reasonable computation times
- Model validation and comparison with experimental results

The scientific research questions that are to be answered in this work will be addressed in the next section (c.f. section 1.2.1).

### 1.2.1 Research Questions

Depending on the laser parameters and the composition of a layered stack of thin films, the laser ablation process includes a variety of different mechanisms, that are either photo-thermally or photo-mechanically driven (see also fig. 2.3) [6]. Thus, the first research question is:

#### Research Question 1

- For which parameter values is the laser ablation of a thin transparent layer photo-thermally and for which is it photo-mechanically dominated?
- Is the ablation mechanism controllable, e.g., via the effective energy penetration depth  $\delta_{\text{eff}}$  and the film thickness  $\delta_{\text{film}}$ ?

$$\delta_{\text{eff}} > \delta_{\text{film}} \quad \text{photo-mechanical?}$$

$$\delta_{\text{eff}} \leq \delta_{\text{film}} \quad \text{photo-thermal?}$$

#### Research Hypothesis 1

- If the effective energy penetration depth is larger than the film thickness  $\delta_{\text{eff}} > \delta_{\text{film}}$ , the whole film and the substrate are heated by the laser radiation. The heating causes the materials to expand thermally and cause pressure waves which lead to photo-mechanical ablation mechanisms.
- If the effective energy penetration depth is equal to or smaller than the film thickness  $\delta_{\text{eff}} \leq \delta_{\text{film}}$ , only the film gets heated leading to melting and evaporation of the material. Consequently, the ablation mechanism is thermal in nature.

Additionally, the geometric shape of the ablation crater has a significant influence on the functionality of the layer stack. In the case of

PMOLEDs it is important to fully ablate the ITO-layer to ensure electrical insulation (c.f. section 1.1 and fig. 1.1). To model the ablation crater shape in a reasonable computation time for metals it has been proven useful to use a threshold intensity or alternatively a threshold fluence as a phenomenological ablation criterion [7]. In glasses the phenomenological ablation criterion is given by the critical electron density [6, 8, 9]. Consequently, the second research question is:

### Research Question 2

- Is it possible to model the ablation crater of thin semiconducting films with a phenomenological ablation criterion?
- Can exceeding of a critical electron density be defined as a phenomenological ablation criterion for the ablation of thin semiconducting films?

### Research Hypothesis 2

In glasses the critical electron density can be used as an ablation and damage criterion. The ionization process in semiconductors and insulators (such as glasses) is very similar. For this reason, it is anticipated, that exceeding the critical electron density can be used as an ablation criterion.

## 2 State of the Art

Transparent conducting oxides (TCOs) represent a class of materials with pivotal roles in optoelectronic applications. Particularly ITO is widely used in many technical applications. This chapter delves into the essential physical properties of TCOs, including electrical conductivity, optical transparency, and mechanical characteristics, elucidating their significance in thin film and optoelectronic applications. Moreover, the contemporary relevance of laser ablation techniques for TCO and especially ITO thin films is summarized. Laser ablation, a precise material removal process, plays a vital role in structuring TCO thin films, a critical step in electronic and optoelectronic device fabrication. Furthermore, a comprehensive overview of the state-of-the-art simulation models for laser ablation of transparent thin films is provided.

### 2.1 Transparent Conducting Oxides

TCOs belong to a group of materials that are both electrically conducting and transparent in the visible range of the electromagnetic spectrum. Due to these two attributes, they are widely used in optoelectronic devices where transparency and electric conductivity are both necessary (e.g., touch screens, solar cells, or smart windows).

A material is optically transparent if the bandgap  $\Delta$  is larger than the incoming photon's energy  $E_{\text{ph}} = hc_0/\lambda$  (with Planck's constant  $h$  and the vacuum speed of light  $c_0$ ). The visible range of the electromagnetic spectrum extends from wavelengths about  $\lambda = 380 \text{ nm}$  to  $780 \text{ nm}$ , i.e., from blue to red (or  $E_{\text{ph}} = 3.2 \text{ eV}$  to  $1.6 \text{ eV}$ ). For this reason, optically transparent materials have  $\Delta \geq 3.2 \text{ eV}$ . If the photon energy  $E_{\text{ph}}$  exceeds the bandgap  $\Delta$ , i.e.,  $E_{\text{ph}} \geq \Delta$  electrons are excited from

the valence to the conduction band. Within the conduction band the electrons can move (almost) freely through the atomic lattice. Hence, they are often called “quasi free electrons” or “free electrons”, where the latter is used throughout this manuscript. To achieve metallic conductivity, a sufficient density of free electrons must be available, and the mobility of these electrons must be large enough to support an electrical current. The free electron density is temporarily enhanced if electrons are excited from the valence band to the conduction band. The excitation of electrons from the valence band to the conduction band can be realized either thermally or optically. Thermal excitation at room temperature 300 K (which corresponds to 0.026 eV) is not sufficient for overcoming bandgaps of several electronvolts. Optically, the free electron density in the valence band can be temporarily enhanced by linear absorption (if  $E_{\text{ph}} \geq \Delta$ ) or nonlinear absorption (e.g., via multiphoton ionization (MPI) or tunnel ionization).

Due to the strong interaction between free electrons and electromagnetic radiation, electrically conductive materials (e.g., metals) show high reflectivity and small optical penetration depths of a few nanometers in the visible spectral range (also see section 3.1.4). For this reason, transparent materials often have large bandgaps and low free electron densities. In contrast to this, a group of intrinsic semi-conducting oxides combines the contradictory properties of optical transparency (i.e.,  $\Delta \geq 3.2$  eV) and high free electron densities in the order of  $1 \times 10^{20} \text{ cm}^{-3}$  to  $1 \times 10^{21} \text{ cm}^{-3}$  if they are strongly doped. Depending on the amount and choice of doping atoms, the electrical conductivity can be increased if the doping atoms increase the number of free electrons or holes in the crystalline lattice. In the case of TCOs, most of these oxides consist of zinc (Zn), cadmium (Cd), indium (In) and tin (Sn) [10]. Particularly outstanding properties with respect to chemical and mechanical stability, high optical transparency and a simultaneously high electrical conductivity can be found in  $\text{SiO}_2\text{:F}$  [11],  $\text{ZnO:Al}$  [12] and ITO ( $\text{In}_2\text{O}_3\text{:Sn}$ ) [13]. Introducing doping atoms into the crystalline lattice can lead to an increase of the free electron density, but also newly formed energy states within the bandgap which reduce the optical transparency. The electrical conductivity of a material  $\sigma_{\text{el}}$

depends on the charge carrier density  $n_{\text{ch}}$ , which is a combination of the electron density  $n_e$  and the hole density  $n_h$  and their respective carrier mobilities  $\mu_{\text{ch}}$ :

$$\sigma_{\text{el}} = e\mu_{\text{ch}}n_{\text{ch}} \quad (2.1)$$

where  $e$  corresponds to the electron charge. Therefore, to increase the electrical conductivity, while maintaining optical transparency, the charge carrier mobility  $\mu_{\text{ch}}$  has to be increased since increasing the carrier density results in higher reflectivity and absorption. In order to ensure optical transparency, a reasonable amount of doping has to be chosen. An increase of the charge carrier mobility can be achieved by improving the manufacturing process, resulting in a reduction of crystal defects [14]. The defects act as scattering centers and reduce the charge carrier mobility.

A variety of different techniques can be used for preparation of TCO films ranging from evaporation in vacuum [13, 15] or reactive atmospheres [13, 16], sputtering in reactive and nonreactive atmospheres [17], reactive ion plating [18] to chemical vapor deposition (CVD) [19–21]. The physical properties of the TCO layers are strongly influenced by the process parameters in the process chamber. Relevant process parameters are for example, the air or oxygen pressure in the process chamber and the electric and magnetic field strengths used for acceleration of the ions to bombard the target material for ejecting atoms or molecules from the target surface. Ceramic targets find use in direct magnetron sputtering [14]. To reduce the number of defects, thermal post treatment in the form of annealing is often applied [13].

### 2.1.1 Indium Tin Oxide

Due to its large optical transparency in the visible spectral regime of more than 80 % and electrical conductivities ranging from  $\sigma_{\text{el}} \approx 3 \times 10^4 \text{ S m}^{-1}$  to  $2.6 \times 10^5 \text{ S m}^{-1}$ , ITO is one of the most used TCOs in optoelectronics [22]. Its applications are e.g., display technologies, touch screen devices, thin-film-solar cells, and thermally reflective window coatings [13, 23, 24]. As already described, the large electrical

conductivity in semiconductors is achieved by introducing free electrons via doping. To obtain ITO, indium oxide ( $\text{In}_2\text{O}_3$ ) is doped with a volume content of 9-20 % of tin dioxide ( $\text{SnO}_2$ ). Thereby, electron densities in the range of  $1 \times 10^{20} \text{ cm}^{-3}$  to  $1 \times 10^{21} \text{ cm}^{-3}$  can be achieved [25]. Starting with  $\text{In}_2\text{O}_3$ , in the following the electronic structure of ITO is described.

### Electronic structure

The crystal structure of  $\text{In}_2\text{O}_3$  is quite complex with around 80 atoms per unit cell. The filled valence band of  $\text{In}_2\text{O}_3$  consists mainly of the oxygen 2p-orbitals while the conduction band is formed by the 5s-orbitals. The fermi level of the undoped material lies within the bandgap. Substitution of an  $\text{In}^{3+}$  by a  $\text{Sn}^{4+}$  leads to donor states below the 5s conduction band of the host material. The donor states are formed because one of the electrons of the  $\text{Sn}^{4+}$  atoms does not form a bond. Additionally, oxygen vacancies act as double electron donor states with an energy 0.03 eV below the conduction band [26] while excess oxygen atoms in the ITO layer trap free electrons [27]. A schematic illustration of the crystal structure with Sn doping and an oxygen vacancy is given in figs. 2.1a and 2.1b, respectively.

Stabilization of the surrounding  $\text{In}^{3+}$  ions is achieved by releasing two electrons to the conduction band [28]. Large  $\text{SnO}_2$  doping contents lead to a transformation of the donor energy states to a donor energy band, which partially overlaps with the conduction band [31]. A schematic sketch of the band structure of ITO is shown in fig. 2.2. The Mott criterion can be used to estimate the material dependent critical electron density which is necessary to induce an insulator-metal-transition [13]:

$$n_{\text{e,crit}}^{\frac{1}{3}} a_{\text{B}} \approx 0.25 \quad (2.2)$$

where  $a_{\text{B}} = 1.3 \text{ nm}$  is the effective Bohr radius of ITO [13]. For doping levels resulting in charge carrier densities exceeding the Mott criterion ( $n_{\text{e}} \geq 1 \times 10^{18} \text{ cm}^{-3}$  to  $1 \times 10^{19} \text{ cm}^{-3}$ ), ITO can be considered as

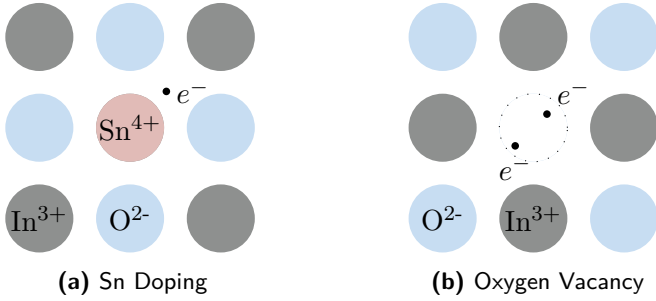


**Figure 2.1:** Oversimplified sketch of the crystal structure of  $\text{In}_2\text{O}_3$  with (a) Sn-doping and (b) an oxygen vacancy . After [29, 30].

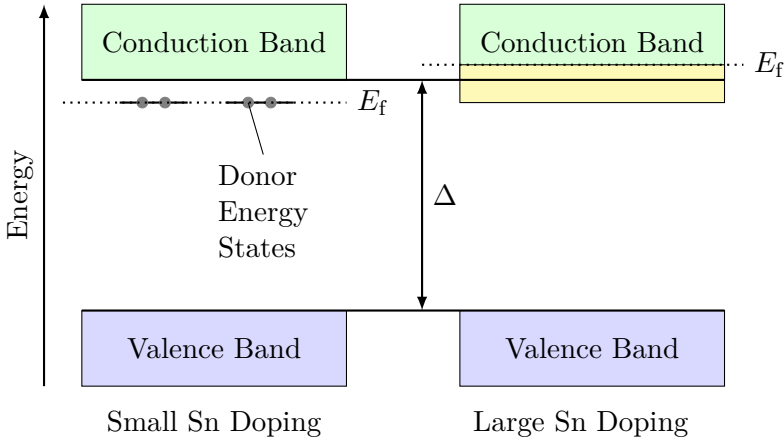


**Figure 2.2:** Schematic energy bands for ITO with different doping levels. Small doping generates energy states just below the conduction band. For large doping the energy states form a band that partially overlaps the conduction band [26, 28].

a semiconductor having a full valence band and a parabolic conduction band partially filled by a degenerate free electron gas [13, 32].

## 2.2 Laser Ablation of Thin Indium Tin Oxide Films

After the deposition of ITO films, material processing techniques like photolithography and wet etching still find use in industrial environments. Lately, these techniques have mostly been replaced by laser structuring [33]. In comparison to wet etching, the use of laser structuring is advantageous because the number of process steps is drastically reduced, no aggressive chemicals are necessary and there is a flexibility in the choice of ablation geometries [34, 35].

Nanosecond-laser pulses were mostly used for ablation of ITO films on transparent substrates due to high ablation rates. The absorption properties of the substrate strongly influence the ablation behavior of the ITO films [36, 37]. Using nanosecond laser pulses, full delamination of the ITO film was demonstrated. However, large heat affected zones and ridge formation with a height of a few hundred nanometers are the consequence of the thermal ablation process [36–38]. Especially the ridge formation has to be avoided for the use in OLED and thin-film solar cells, where the typical film thickness is in the order of the ridge height. In these applications the ridges can penetrate additional layers and are able to promote the formation of electrical bypasses [39].

Replacing the nanosecond laser sources with ultrashort pulsed lasers leads to a reduction of the size of the heat affected zone and ridge height to several 10 nm [38, 39]. During ultrashort pulsed laser ablation of thin films on transparent substrates, different dominant ablation mechanisms can be observed. These ablation mechanisms are summarized in fig. 2.3. For film side irradiation, if the film is not transparent for the incident light, direct ablation is observed (c.f. fig. 2.3a). For substrate side irradiation and non-transparent films, the laser radiation is transmitted through the substrate and absorbed in the film. Thereby, a confined energy situation is created which leads to a laser lift-off (c.f. fig. 2.3b). Analogous to fig. 2.3b, if the film is transparent and the sub-

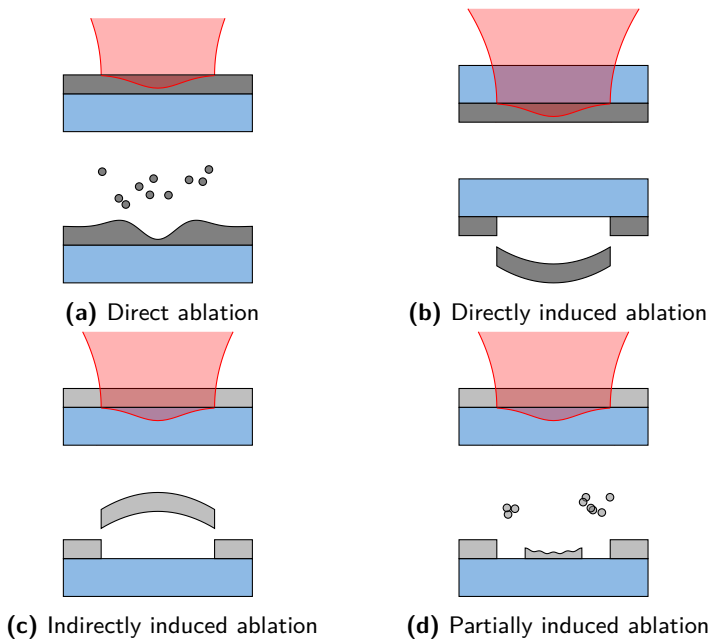


**Figure 2.3:** Schematic illustration of ablation mechanisms for processing of thin films. (a) Direct ablation for film side irradiation and non-transparent films. (b) Directly induced ablation for substrate side irradiation and non-transparent films. The laser radiation is transmitted through the substrate and absorbed in the film. This generates a confined energy situation at the film-substrate interface and results in a laser lift-off. (c) Indirectly induced ablation for film side irradiation and transparent films. The laser radiation is transmitted through the film and absorbed in the substrate. Analogous to (b) this generates a confined energy situation at the film-substrate interface and may result in a laser lift-off. (d) Partially induced ablation for film side irradiation and transparent films. For high laser intensities the film changes its optical properties during the pulse and is only transmissive in the outer spatial regions where the laser intensity is low. This may result in both a laser lift-off in the outer spatial, where the laser intensity is small regions and direct ablation in the center where the intensity is large.

strate absorbs the laser radiation a laser lift-off can be induced by film side irradiation (c.f. fig. 2.3c). For high laser intensities, the optical properties change due to excitation of free electrons from the valence to the conduction band (c.f. sections 3.1.4 and 3.1.6). This leads to a reduction of the optical penetration depth in and stronger reflectivity of the film in the center of the gaussian intensity distribution of the laser pulse. In the outer regions, where the generated electron density is not large enough, the radiation is transmitted into the substrate, where it can lead to a confined energy situation. Therefore, the ablation mechanisms result in a combination of a laser lift-off in the outer regions and direct ablation in the center (c.f. fig. 2.3d). If the laser radiation is absorbed in the substrate, substrate damage has to be avoided to maintain high optical transparency of the sample. Experimentally, film side irradiation with wavelength of 800 nm and a pulse duration of 150 fs was performed without substrate damage, which is caused due to the differences in ablation thresholds. The ablation thresholds for ITO were ( $0.07 \text{ J cm}^{-2}$ ) and the glass substrate ( $1.2 \text{ J cm}^{-2}$  to  $1.6 \text{ J cm}^{-2}$ ), respectively [40]. The measured ridge height was 10 nm to 20 nm and was caused by melt expulsion due to the hydrodynamic pressure in the ablation volume [40, 41]. Studies with picosecond laser pulses with pulse durations of 10 ps to 15 ps and wavelengths of 343 nm, 515 nm and 1064 nm showed ridge heights below 20 nm to 70 nm and no heat affected zones [39, 42].

### 2.3 Simulation of Laser Processing of Semiconductors

So far, only experimental studies have been mentioned. In the following, a summary of the state-of-the-art simulation approaches for laser processing of glasses, semiconductors and semiconducting thin films is given.

In [42–44] McDonnell et al. investigate the interaction of nanosecond and femtosecond laser pulses with very thin 20 nm to 100 nm ITO films on polyethylene terephthalate (PET) and glass substrates. The

material removal was caused by thermal expansion of the PET substrate due to laser heating. This was found to be independent of the incident wavelength (266 nm, 355 nm, 532 nm and 1056 nm) and pulse duration (500 fs to 20 ns). In order to model the temperature distribution during and after laser excitation, a parabolic two temperature model (TTM) is used and compared to the experimental ablation craters. However, to model the laser-matter interaction only equilibrium optical properties were used.

Similar to [42–44] in [45], Chen et al. also utilize a TTM. However, on a femtosecond timescale, nonequilibrium thermodynamics predict that Fourier’s law should be corrected to take the relaxation of the heat flow into account [46, 47]. This leads to a hyperbolic formulation of the TTM (instead of the parabolic equations) and was applied in one dimension to 1  $\mu\text{m}$  gold films irradiated with femtosecond laser pulses in [45]. Additionally, the mechanical stresses were modeled by a combination of thermal stresses and the electron blast force. The electron blast force describes the lattice deformation which is caused by hot electrons moving through the lattice.

Later the hyperbolic two temperature model was applied to predict the ablation threshold in bulk Si [48] by extension to free charge carrier dynamics and transport. The presented fully self-consistent model describes the transport dynamics in bulk Si due to ultrashort pulsed laser heating.

A similar model was presented by R  mer et al. in [49] to theoretically predict the ablation thresholds in bulk Si. In contrast to [48], where the optical properties were electron temperature dependent, a Drude model was implemented to account for the highly transient optical properties of Si during the irradiation with 100 fs 800 nm laser pulses. The TTM and Drude-model both incorporated different electron-hole and carrier-phonon collision times strongly influences the lattice temperatures and therefore the ablation thresholds. Additionally, it is found that a TTM is sufficient to predict the ablation threshold while neglecting degeneracy and transport effects.

In [50] Gamaly and Rode model transient optical properties for laser wavelengths 800 nm and 1300 nm in bulk Si and SiO<sub>2</sub>. The transient

optical properties are described using the dielectric function which describes the contribution of bound and free electrons. For large laser intensities, it was found that the latter dominate the optical response of the material and swift ionization leads to metallization of Si.

A model predicting the ablation craters in bulk SiO<sub>2</sub> using 800 nm femtosecond laser pulses is given by Aldana et al. [8]. Beginning with a wave equation for the electric field, the pulse propagation within the material is described in time domain, including a temporally changing dipole moment density is solved. The spatial distribution of the electron densities is computed by the electric field distribution using rate equations. Due to the short pulse duration the recombination terms in the rate equation are neglected. The crater shape is accurately predicted by using the ablation criterion that the free electron density exceeds the critical electron density.

Using the critical electron density as ablation criterion was also used by Sun et al. [9]. In contrast to solving a full time-dependent wave equation as in [8], a beam propagation method (BPM) was used to describe multi-pulse ablation craters in bulk soda lime glass. The BPM consists of the paraxial Helmholtz equation which computes the spatial distribution of the electric field. Depending on the electric field strength the free electron density is locally estimated using a metamodel.

A full three-dimensional atomistic approach to model the laser excitation of bulk Si by molecular dynamics (MD) simulations was done by Watanabe et al. [51]. It was found that the velocity of the laser generated shock wave agreed well with elastic theory. Furthermore, laser excitation causes the Si surface to rise due to thermal expansion. Afterwards particles form small clusters and are expelled from the ablation crater. The maximum force acting on the atoms was found to be at a depth of 25 nm.

For thin metal films consisting out of aluminum, nickel or gold, there are various models describing the ablation process with hydrodynamic considerations. The equations that are typically solved are Euler equations in combination with a two-temperature model [52–54]. In [52] Olbrich et al. describe the interaction of ultrashort laser pulses with

a 150 nm gold film in one dimension. A comparison between experimental ablation craters and pump probe reflectometry measurements is also provided. The interplay of heating, phase transitions and the propagation of shock and rarefaction waves was able to explain the flat ablation structures in the experimental results.



# 3 Phenomenology of Laser Ablation of Thin Films

Laser ablation of thin semiconducting films is a consequence of the complex interaction between intense laser pulses and solid materials. The ablation process with ultrashort laser pulses is based on the interplay of different physical effects including the propagation and absorption of laser light within the material, ionization of free electrons, which alter the optical properties, heating of the atomic lattice or phase transitions and phase explosions. This chapter focusses on these phenomena and describes the relevant physical models that are obligatory to model the ablation process. This incorporates the laser radiation propagation in thin films, the description of optical properties, electron dynamics, heating and mechanical pressure waves.

## 3.1 Physical Processes

### 3.1.1 Optical Phenomena in Semiconductors

The optical properties of semiconductors play a crucial role in various optoelectronic devices and applications ranging from solid state lighting to solar energy harvesting and telecommunications. The precise optical properties of a semiconductor depend on its material composition, doping level and crystal structure. If light travels through a semiconductor different phenomena can occur [55]:

- Absorption becomes relevant if the light's frequency is resonant with the transition frequencies of the atoms in the medium.
- Refraction causes the light wave's propagation velocity to be

smaller than in free space. As described by Snell's law this leads to bending of light waves at material interfaces.

- Reflection arises at the material interface between two adjacent media due to a change of the refractive index.
- Transmission at a material interface is related to the reflection of light at the interface. It is the fraction of the light which is not reflected at the interface.
- Transmission of a sample (i.e., the transmission of a volume) is related to absorption  $A$  and reflection since only the fraction of unabsorbed light that is not reflected at any material interface of the sample  $R$  can be transmitted:  $T = 1 - A - R$
- Photoluminescence occurs if photons excite electrons from the valence to the conduction band. After a characteristic material dependent delay time, the excited electrons recombine and re-emit photons by spontaneous emission. This process is called fluorescence. If excited electrons cannot easily recombine from the excited state because the transition is forbidden due to momentum conservation the recombination occurs slowly. Then the characteristic timescale is much larger in comparison to fluorescence. This process is called phosphorescence.
- While photons propagate through matter they interact with the atoms and quasiparticles, which scatter them away. Scattering causes light to change its direction and potentially its frequency during travelling through a medium. Typical scattering mechanisms are e.g.,
  - Mie scattering: elastic process where the size of the (spherical) particles is in the order of the wavelength.
  - Rayleigh scattering: this is an elastic process where the size of the atoms, molecules or impurities is small compared to the incident wavelength.

- Phonon scattering: interaction between acoustic and optical phonons with the photons
- Inelastic scattering: Raman scattering or Compton scattering
- Nonlinear optics become relevant if the light intensity becomes very high due to the (weak) nonlinear dependence of the optical parameters on the intensity. Some examples for nonlinear effects are self-focusing (Kerr effect), second harmonic generation (SHG) or MPI.

### 3.1.2 Time Scales During Ultrashort Pulsed Laser Ablation of Thin Transparent Films

The interaction of intense ultrashort laser pulses with thin, transparent dielectric films gives rise to multiple physical effects ranging from optics to thermodynamics and mechanics which all happen on different time scales. Figure 3.1 depicts the most important effects and their physical causality. Depending on the film thickness  $\delta_{\text{film}}$  and the wavelength  $\lambda$  of the incident laser pulse the laser pulse needs a time  $t = n(\lambda)\delta_{\text{film}}/c_0$  to travel through the film. Here  $n$  corresponds to the refractive index of the material and  $c_0$  to the speed of light in vacuum. For an ITO-film with a thickness of  $\delta_{\text{film}} = 100$  nm and a laser wavelength of 1056 nm ( $n(\lambda = 1056 \text{ nm}) \approx 1.09$  [56]) the time equals  $t \approx 0.36$  fs.

A detailed mathematical description of an electro-magnetic wave travelling through a (dielectric) medium is given by the Maxwell equations (see section 3.1.3). During the propagation, laser radiation gets absorbed due to ionization of the material either by inverse bremsstrahlung absorption of free electrons or multiphoton absorption (c.f. section 3.1.6). The generated free electrons change the dielectric function locally and temporally leading to refraction of the laser radiation. The absorbed energy is deposited in the electronic system leading to a strong disequilibrium between the temperatures of the electronic and lattice subsystems [57, 58]. The disequilibrium of temperatures relaxes via the electron-phonon-coupling. Mathematically, this can be

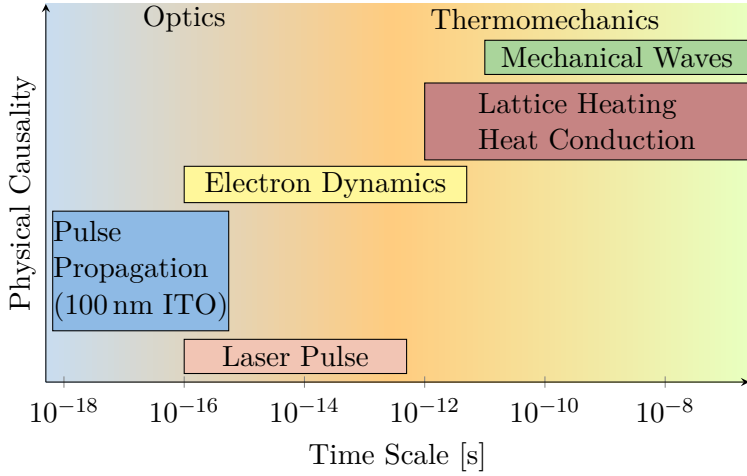


**Figure 3.1:** Schematic overview of time scales and causalities of physical effects during the interaction of a femtosecond laser pulse and a transparent semiconductor. The length of the boxes indicates the typical timescale of the physical effect.

described by the TTM (see section 3.1.8) [45, 47, 49, 57]. The material dependent strength of the electron phonon coupling dictates the timescale on which the two systems relax. Typical values for the electron phonon coupling constant in metals are e.g.,  $3.5 \times 10^{16} \text{ W cm}^{-3} \text{ K}^{-1}$  for gold or  $56.9 \times 10^{16} \text{ W cm}^{-3} \text{ K}^{-1}$  for aluminum [47]. In semiconductors the electron phonon coupling is non-constant as it depends on the electron density and electron temperature [59]. The relaxation results in lattice heating and heat conduction of the phononic system [48, 60]. For ultrashort laser pulses, the time  $t$  in which the energy is deposited ( $t < 1 \text{ ps}$ ) within the material is much shorter than the time required to transfer the energy to the lattice ( $\approx 10 \text{ ps}$  to  $20 \text{ ps}$ ). An estimate for the thermal penetration depth for laser pulses with pulse durations of several picoseconds or longer can be made with the thermal conductivity, where the temperature dropped to the  $1/e$ -th fraction of its maximum value:  $\delta_{\text{eff}} = 2\sqrt{D_{\text{th}} \cdot \tau_p}$ . The thermal penetration depth for pulses with a pulse duration smaller than  $10 \text{ ps}$  is in the order of some

10 nm while for nanosecond laser pulses it extends over some  $\mu\text{m}$  [61]. The lattice heating causes thermal expansion and leads to pressure waves within the material. If the energy deposition is faster than the time necessary to distribute the energy into the surrounding material a confined energy situation is achieved [62, 63]. This leads to overheating of the interaction volume, that results in ultrafast phase transitions and phase explosion after 10 ps which can cause shock waves in the material [64–66]. In the following subsections, the relevant physical processes and their corresponding models are described in more detail.

### 3.1.3 Maxwell's Equations

The mathematical description of the interaction of electromagnetic radiation with matter is governed by Maxwell's equations. Maxwell's equations in matter units are given by (in SI units):

$$\nabla \cdot \mathbf{D} = \frac{n_e}{\varepsilon_0} \quad (3.1)$$

$$\nabla \cdot \mathbf{B} = 0 \quad (3.2)$$

$$\nabla \times \mathbf{E} = -\partial_t \mathbf{B} \quad (3.3)$$

$$\nabla \times \mathbf{H} = \mathbf{J}_f + \varepsilon_0 \partial_t \mathbf{D} \quad (3.4)$$

with  $\mathbf{E}$  being the electric field strength,  $n_e$  the free electron density  $\mathbf{D}$  the displacement field,  $\mathbf{B}$  the magnetic flux density,  $\mathbf{H}$  the magnetic field strength and  $\mathbf{J}_f$  the current density of the free charge carriers respectively.  $\mathbf{D}$  and  $\mathbf{H}$  are connected to  $\mathbf{E}$  and  $\mathbf{B}$  via the electric dipole moment density  $\mathbf{P}$  and the magnetization  $\mathbf{M}$ :

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} \quad (3.5)$$

$$\mathbf{H} = \frac{1}{\mu_0} \mathbf{B} - \mathbf{M} \quad (3.6)$$

From Maxwell's equations (eqs. (3.1) and (3.4)) a wave equation for the electric field can be derived:

$$\begin{aligned} \frac{1}{c_0^2} \partial_t^2 \mathbf{E} - \nabla^2 \mathbf{E} = & -\mu_0 \partial_t \mathbf{J}_f - \mu_0 \partial_t^2 \mathbf{P} \\ & - \frac{1}{\varepsilon_0} \nabla n_{e,\text{tot}} - \mu_0 \partial_t (\nabla \times \mathbf{M}) \end{aligned} \quad (3.7)$$

with the total electron density  $n_{e,\text{tot}}$ , consisting of the bound electron density  $n_b$  and free electron density  $n_e$ :  $n_{e,\text{tot}} = n_b + n_e$  and  $\mu_0 \varepsilon_0 = 1/c_0^2$ . Apart from the assumption that the material laws may be averaged over the volumes, in eq. (3.7) no further assumptions have been applied so far. Thus, there is no loss of generality. For non-magnetic materials, the magnetization  $\mathbf{M}$  can be neglected  $\mathbf{M} = 0$ . Then eq. (3.7) reads:

$$\frac{1}{c_0^2} \partial_t^2 \mathbf{E} - \nabla^2 \mathbf{E} = -\mu_0 \partial_t \mathbf{J}_f - \mu_0 \partial_t^2 \mathbf{P} - \frac{1}{\varepsilon_0} \nabla n_{e,\text{tot}} \quad (3.8)$$

#### Gaussian Beam & Laser Pulses

In free space with absence of charge carriers eq. (3.7) can be reduced to:

$$\frac{1}{c_0^2} \partial_t^2 \mathbf{E} - \nabla^2 \mathbf{E} = 0 \quad (3.9)$$

Separation of variables ( $\mathbf{E}(r, t) = \mathbf{E}(\mathbf{r}) \exp(i\omega t)$ ) leads to the Helmholtz equation where  $k = \omega/c_0$  is the magnitude of the wave vector  $\mathbf{k}$ :

$$\nabla^2 \mathbf{E} + k^2 \mathbf{E} = 0 \quad (3.10)$$

Laser radiation is distributed in a small spatial area and propagates into one primary direction. Assuming the primary propagation direction is aligned along the  $z$ -axis, the following ansatz is expedient:

$$\mathbf{E} = \mathbf{E}_0 \exp(ikz) \quad (3.11)$$

where  $\mathbf{E}_0$  is the (complex) amplitude of the electric field. Using the slowly varying envelope approximation (assuming that the angle  $\theta_{\text{opt}}$

between  $\mathbf{k}$  and the optical axis is small  $\theta_{\text{opt}} \ll 1$ ) gives:  $|k\partial_z| \gg \partial_z^2$ . Thus, eq. (3.10) becomes:

$$(\partial_x^2 + \partial_y^2) \mathbf{E} + 2i\mathbf{k}\partial_z \mathbf{E} = 0 \quad (3.12)$$

One solution to eq. (3.12) is given by the transverse electro-magnetic (TEM)-modes, where the  $(m, n)$  mode TEM<sub>m,n</sub> equals [67]:

$$\begin{aligned} E_{m,n}(x, y, z) = E_0 \frac{w_0}{w(z)} \mathcal{H}_m \left( \frac{\sqrt{2}x}{w(z)} \right) \mathcal{H}_n \left( \frac{\sqrt{2}y}{w(z)} \right) \\ \cdot \exp \left( -(x^2 + y^2) \left( \frac{1}{w(z)} + \frac{ik}{2R_c(z)} \right) \right) \\ \cdot \exp(-ikz - i(m+n+1)\zeta) \end{aligned} \quad (3.13)$$

where  $\mathcal{H}_m$  is the Hermite polynomial of order m:

$$\mathcal{H}_m(x) = (-1)^m \exp(x^2) \frac{d^m}{dx^m} \exp(-x^2) \quad (3.14)$$

further are  $w(z)$  the beam radius,  $R_c(z)$  the curvature of the wavefront and  $\zeta$  the Gouy-phase which are given by:

$$w(z) = w_0 \sqrt{1 + \left( \frac{z}{z_R} \right)^2} \quad (3.15)$$

$$R_c(z) = z \left( 1 + \left( \frac{z_R}{z} \right)^2 \right) \quad (3.16)$$

$$\zeta = \arctan \left( \frac{z}{z_R} \right) \quad (3.17)$$

$$z_R = \frac{\pi w_0^2}{\lambda M^2} \quad (3.18)$$

Here  $z_R$  corresponds to the Rayleigh length, which is the distance along the optical axis where the cross-sectional area of the laser beam is doubled with respect to the area to the focal position. As a Gaussian beam propagates, it undergoes a phase shift along its direction of

propagation, distinct from the phase shift experienced by a plane wave with the equivalent optical frequency. This distinction is referred to as the Gouy-phase shift  $\zeta$ . For a Gaussian beam propagating through a focus the phase shift (for the far fields on either sides of the focus) equals  $-\pi$  [68]. For  $n = m = 0$  the TEM<sub>mn</sub> mode (eq. (3.13)) reduces to the fundamental TEM<sub>00</sub> Gaussian mode:

$$E(r, z) = E_0 \frac{w_0}{w(z)} \cdot \exp\left(-\frac{r^2}{w^2(z)}\right) \cdot \exp\left(-i\left(kz + \frac{kr^2}{2R_c(z)} - \zeta\right)\right) \quad (3.19)$$

where  $r = \sqrt{x^2 + y^2}$  corresponds to the radial coordinate in cylindrical coordinates. In many cases the fundamental TEM<sub>00</sub> Gaussian mode, also known as Gaussian beam, is sufficient to describe the propagation of laser radiation along the optical axis. Given the electric field (eq. (3.19)) the corresponding intensity distribution  $I(r, z)$  can be calculated using  $I = |E|^2/(2/\eta_0)$  with the characteristic impedance of free space  $\eta_0 \approx 377 \Omega$ :

$$I(r, z) = I_0 \left(\frac{w_0}{w(z)}\right)^2 \exp\left(-\frac{2r^2}{w^2(z)}\right) \quad (3.20)$$

The time dependence of the wave equation has been omitted for the equations above and continuous radiation is considered. For laser ablation however, it is often advantageous to use pulsed lasers because higher peak intensities can be achieved. The mathematical description for the temporal distribution of ultrashort gaussian laser pulses with a pulse duration  $\tau_p$  (measured at the full width at half maximum (FWHM)) is given by:

$$I(t) = I_0 \exp\left(-4 \ln(2) \frac{(t - t_0)^2}{\tau_p^2}\right) \quad (3.21)$$

Hence, the spatial and temporal intensity distribution for a gaussian pulse is at  $z = 0$  given by:

$$I(r, t) = I(r, z) \cdot I(t) \quad (3.22)$$

$$= I_0 \exp\left(-\frac{2r^2}{w_0^2}\right) \exp\left(-4 \ln(2) \frac{(t - t_0)^2}{\tau_p^2}\right) \quad (3.23)$$

The fluence  $F$  is obtained by integration over time:

$$F(r) = \int_{-\infty}^{\infty} I(r, t) dt \quad (3.24)$$

Integration of the fluence over the area gives the pulse energy:

$$E_p = \int_0^{2\pi} \int_0^{\infty} F(r) \cdot r dr d\phi \quad (3.25)$$

### 3.1.4 Optical Properties & Dielectric Function

The abrupt change of the refractive index at a material causes light waves to be reflected and refracted. The reflectivity  $R$  of the material interface depends on the complex refractive indices  $n_1, n_2$  of the materials 1 and 2 and the polarization of the incident light. Using Fresnel's formulae for s and p polarized light the respective reflectivities  $R_s, R_p$  for nonmagnetic media given by:

$$R_s = \left| \frac{n_1 \cos(\alpha_{\text{inc}}) - n_2 \sqrt{1 - \left(\frac{n_1}{n_2} \sin(\alpha_{\text{inc}})\right)^2}}{n_1 \cos(\alpha_{\text{inc}}) + n_2 \sqrt{1 - \left(\frac{n_1}{n_2} \sin(\alpha_{\text{inc}})\right)^2}} \right|^2 \quad (3.26)$$

$$R_p = \left| \frac{n_2 \cos(\alpha_{\text{inc}}) - n_1 \sqrt{1 - \left(\frac{n_1}{n_2} \sin(\alpha_{\text{inc}})\right)^2}}{n_2 \cos(\alpha_{\text{inc}}) + n_1 \sqrt{1 - \left(\frac{n_1}{n_2} \sin(\alpha_{\text{inc}})\right)^2}} \right|^2 \quad (3.27)$$

For unpolarized light the Fresnel reflectivity  $R_F$  is given by:

$$R_F = 0.5R_p + 0.5R_s \quad (3.28)$$

The complex refractive index is connected to the dielectric function by  $n = \sqrt{\varepsilon}$ . The dielectric function  $\varepsilon$  is a complex function depending on the angular frequency of the light  $\omega$  and other parameters such as the temperature, mass density or the free charge carrier density  $n_e$ . In some publications, the temperature dependence of the dielectric function is modeled via a temperature-dependent free electron density (see e.g. [49]). In laser material processing, the temperature of the material is related to the incident laser intensity. Therefore, within the scope of this manuscript, the free electron densities are computed as a function of the laser intensities instead of temperatures (c.f. section 3.1.6). Thus, the temperature-dependence of other parameters (e.g. mass density) are neglected and just the free charge carrier contribution to the dielectric function is considered:

$$\varepsilon = \varepsilon(\omega, n_e) \quad (3.29)$$

The dielectric function describes the response of a material to an external electric field. On a microscopic scale, the dielectric function can be derived from the equation of motion for the displacement  $x$  of the individual electrons driven by an electric field  $E$  [55]:

$$m_e \frac{d^2 x}{dt^2} + m_e \gamma_{\text{el}} \frac{dx}{dt} + m_e \omega_{\text{res}}^2 x = -eE \quad (3.30)$$

where  $m_e$  and  $e$  are the mass and charge of the electron,  $\gamma_{\text{el}}$  corresponds to the collision frequency of the electrons and  $\omega_{\text{res}}$  to the resonance frequency of a harmonic oscillator, respectively. The displacement  $x$  for the electrons from their initial position induces a dipole moment. The dipole moment density  $P$  is given by:

$$P = -n_e e x \quad (3.31)$$

where  $n_e$  corresponds to the free electron density. Assuming a harmonic oscillating electric field  $E$  with amplitude  $E_0$  and angular frequency  $\omega$

$$E = E_0 \cdot \exp(-i\omega t - \Phi) \quad (3.32)$$

the dielectric function  $\varepsilon(\omega, n_e)$  can be derived. In the following, the solutions for the relevant dielectric functions are described briefly.

## Drude Model

To model the free charge carrier contribution to the dielectric function  $\varepsilon$  of metals and doped semiconductors the most commonly used model is the Drude model [55]. Since the electrons can freely follow the electric field, no resonances are available. Therefore, the last term on the left-hand side of eq. (3.30) vanishes  $\omega_{\text{res}} = 0$ , which leads to:

$$\varepsilon_{\text{Drude}}(\omega, n_e) = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + i\gamma_{\text{el}}\omega} \quad (3.33)$$

$$\omega_p = \sqrt{\frac{n_e e^2}{\varepsilon_0 m_e^*}} \quad (3.34)$$

Here  $\omega_p$  corresponds to the plasma frequency,  $\gamma_{\text{el}}$  to the electron collision frequency,  $e$  to the electron charge,  $\varepsilon_0$  to the vacuum permittivity and  $m_e^*$  to the electron effective mass, respectively.  $\varepsilon_{\infty}$  describes the dielectric background. When the angular frequency of the laser radiation reaches the plasma frequency  $\omega_p$  the transmission at the material interface increases drastically leading to a strong decrease of reflectivity. The plasma frequency  $\omega_p$  depends on the electron density  $n_e$  and corresponds to the critical electron density  $n_{e,\text{crit}}$  where the material surface becomes transparent (c.f. eqs. (3.33) and (3.34)). In doped semiconductors the polarizability of the bound electrons  $\varepsilon_{\text{pol}}$  and the dielectric background  $\varepsilon_{\infty}$  contributes to the dielectric function. Therefore, the effective plasma frequency  $\tilde{\omega}_p$  becomes [55]:

$$\tilde{\omega}_p = \sqrt{\frac{n_e e^2}{\varepsilon_{\infty}^* \varepsilon_0 m_e^*}} \quad (3.35)$$

with  $\varepsilon_{\infty}^* = \varepsilon_{\text{pol}} + \varepsilon_{\infty}$ . Most of the radiation becomes absorbed within the optical penetration depth. If the free electron density  $n_e$  exceeds the critical electron density  $n_{e,\text{crit}}$ , the material becomes metallic leading to a strong increase of the reflectivity. Simultaneously, the optical penetration depth  $\delta_{\text{opt}}$  is drastically reduced. The optical penetration depth  $\delta_{\text{opt}}$  is inversely proportional to the absorption coefficient  $\alpha_{\text{abs}}$ .

The absorption coefficient itself is proportional to the imaginary part of the complex refractive index  $\Im(n) = \Im(\sqrt{\varepsilon})$  and  $c_0$  corresponds to the speed of light:

$$\delta_{\text{opt}}(\omega, n_e) = \frac{1}{\alpha_{\text{abs}}(\omega, n_e)} \quad (3.36)$$

$$\alpha_{\text{abs}}(\omega, n_e) = \frac{2\omega}{c_0} \Im(\sqrt{\varepsilon(\omega, n_e)}) \quad (3.37)$$

If the bound electrons are exposed to electromagnetic radiation, this leads to polarization of the material. For the bound electron contribution different models have been proposed: e.g., the Drude-Lorentz model or a Tauc-Lorentz model. [50, 55, 69].

#### Drude-Lorentz Model

The dynamics of bound electrons, ions or permanent dipoles can be modeled using the Drude-Lorentz model resulting from a damped harmonic oscillator with a resonance frequency  $\omega_{\text{res}}$  (c.f. eq. (3.30)) [55]:

$$\varepsilon_{\text{DL}}(\omega, n_b) = \varepsilon_{\infty} + \frac{n_b e^2}{\varepsilon_0 m_e^*} \cdot \frac{1}{\omega_{\text{res}}^2 - \omega^2 - i\gamma_{\text{el}}\omega} \quad (3.38)$$

Here  $n_b$  is the bound electron density,  $e$  the electron charge,  $\varepsilon_0$  the vacuum permeability,  $m_e^*$  the effective mass,  $\gamma_{\text{el}}$  the electron collision frequency and  $\varepsilon_{\infty}$  is the dielectric background once again.

In general, the electron collision frequency  $\gamma_{\text{el}}$  is not constant but depends on the electron density  $n_e$ . As described in [8], the frequency of electron-electron collisions increases with the electron density and saturates to a maximum value  $\gamma_{\text{max}}$ :

$$\gamma_{\text{el}} = \frac{1}{\tau_e} = \gamma_{\text{max}} \cdot \frac{n_e}{n_e + \beta n_{e,\text{crit}}} \quad (3.39)$$

The Drude dielectric function  $\varepsilon_{\text{Drude}}$  and the Drude-Lorentz dielectric function  $\varepsilon_{\text{DL}}$  differ in the fact that the Drude-Lorentz model

incorporates a resonance frequency  $\omega_{\text{res}}$ . The resonance frequency in the Drude-Lorentz model accounts for interband transitions which are not considered in the Drude model. Moreover, the first factor in the second term includes the bound electron density  $n_b$  instead of the free electron density  $n_e$ . Thus, compared to the Drude model, the cut-off frequency where the reflectivity vanishes is at higher frequencies.

### Tauc-Lorentz Model

In 1968, J. Tauc developed a model to determine the optical bandgap of amorphous semiconductors from its absorption spectrum [70]. Tauc's expression for the imaginary part of the dielectric function above the band edge refers to the density of electronic states participating in the absorption process that leads to the creation of electron-hole pairs. The imaginary part of the dielectric function is given by [69, 70]:

$$\varepsilon_{T,2}(E_{\text{ph}}) = A_T \frac{(E_{\text{ph}} - \Delta)^2}{E_{\text{ph}}^2} \quad (3.40)$$

where  $E_{\text{ph}}$  is the energy of the photons and  $A_T$  is a proportionality factor and  $\Delta$  corresponds to the bandgap of the material, respectively. Using this expression, the optical bandgap of a material can be obtained by using the Tauc-plot (sometimes also called Tauc analysis), which is schematically shown in fig. 3.2 [71]. The Tauc plot is typically expressed in the form of  $(\alpha_{\text{abs}} \cdot \hbar\omega)^n$  versus the photon energy  $E_{\text{ph}} = \hbar\omega$ , and the linear region of the plot is extrapolated to find the intercept on the energy axis. The intersection point gives an estimate of the optical bandgap energy of the material. The exponent  $n$  represents the nature of the transition, where  $n = 1/2$  corresponds to directly allowed interband transitions,  $n = 3/2$  to forbidden direct interband transitions,  $n = 2$  to indirect allowed, and  $n = 3$  indirect forbidden interband transitions, respectively [71]. Amorphous semiconductors often have an exponential decay of the absorption coefficient  $\alpha_{\text{abs}}$  into the bandgap. This decay is called Urbach tail and results from localized states or defects in the material's bandgap.

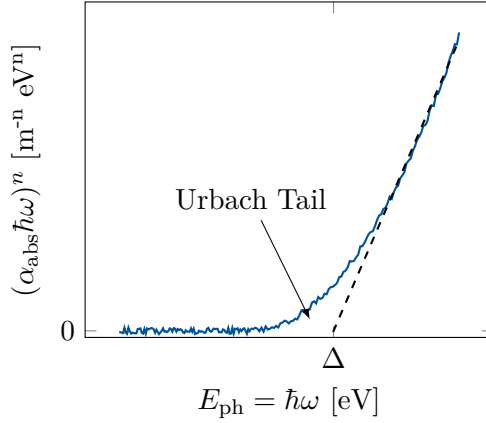


**Figure 3.2:** Schematic Tauc plot illustrating the relationship between the absorption coefficient multiplied by photon energy  $(\alpha_{\text{abs}} \cdot \hbar\omega)^n$  and the photon energy  $E_{\text{ph}} = \hbar\omega$ . The linear region near the absorption edge is extrapolated to estimate the optical bandgap  $\Delta$  of the material. The illustration is inspired by [71].

The material properties of thin films can drastically differ from bulk material. Therefore, Forouhi and Bloomer formulated a mathematical description of the extinction coefficient for amorphous semiconductors and insulators [72]. This formalism was later extended to crystalline semiconductors and metals but yielded some fundamental problems [69, 73]. The absorption coefficient  $\alpha_{\text{abs}}$  did not vanish for photon energies  $E_{\text{ph}}$  smaller than the bandgap  $\Delta$ . This behavior is unphysical as interband transitions cannot occur for  $E_{\text{ph}} < \Delta$  and insulators are optically transparent. Moreover, the experimentally observed decay of the absorption coefficient should be decaying to 0 with  $1/E_{\text{ph}}^3$  or faster for  $E_{\text{ph}} \rightarrow \infty$  but is predicted to be constant for  $E_{\text{ph}} \rightarrow \infty$ . This is particularly important for Kramer-Kronig integration. To overcome these problems, Jellison et al. introduced a new parametrization by multiplying the Tauc density of states with the imaginary term of the dielectric function for a collection of single atoms. The proposed model

is called Tauc-Lorentz model and is given by [69, 74]:

$$\varepsilon_{\text{TL}} = \varepsilon_{\text{TL},1} + i\varepsilon_{\text{TL},2} \quad (3.41)$$

$$\varepsilon_{\text{TL},2} = \begin{cases} \frac{AE_{0,\text{TL}}(E_{\text{ph}} - \Delta)^2}{(E_{\text{ph}}^2 - E_{0,\text{TL}}^2)^2 + CE_{\text{ph}}^2} \frac{1}{E_{\text{ph}}} & E_{\text{ph}} \geq \Delta \\ 0 & E_{\text{ph}} < \Delta \end{cases} \quad (3.42)$$

where  $A$  is the strength,  $E_{0,\text{TL}}$  the resonance energy,  $C$  the broadening of the Lorentzian oscillator and  $\Delta$  the bandgap, respectively. To obtain the real part of the Tauc-Lorentz dielectric function  $\varepsilon_{\text{TL},1}$ , Kramer-Kronig relations can be used. The solution can be formulated in closed form, giving [75]:

$$\begin{aligned} \varepsilon_{\text{TL},1}(E_{\text{ph}}) = & \varepsilon_{\infty} + \frac{1}{2} \frac{A}{\pi} \frac{C}{\xi_{\text{TL}}^4} \frac{a_{\text{ln}}}{\alpha_{\text{TL}} E_{0,\text{TL}}} \\ & \ln \left( \frac{E_{0,\text{TL}}^2 + \Delta^2 + \alpha_{\text{TL}} \Delta}{E_{0,\text{TL}}^2 + \Delta^2 - \alpha_{\text{TL}} \Delta} \right) \\ & - \frac{A}{\pi \xi_{\text{TL}}^4} \cdot \frac{a_{\text{atan}}}{E_{0,\text{TL}}} \\ & \cdot \left[ \pi - \arctan \left( \frac{2\Delta + \alpha_{\text{TL}}}{C} \right) \right. \\ & \left. + \arctan \left( \frac{-2\Delta + \alpha_{\text{TL}}}{C} \right) \right] \\ & + 2 \cdot \frac{AE_{0,\text{TL}}\Delta}{\pi \xi_{\text{TL}}^4 \alpha_{\text{TL}}} \cdot (E_{\text{ph}}^2 - \gamma_{\text{TL}}^2) \\ & \cdot \left[ \pi + 2 \arctan \left( 2 \cdot \frac{\gamma_{\text{TL}}^2 - \Delta^2}{\alpha_{\text{TL}} C} \right) \right] \\ & - \frac{AE_{0,\text{TL}}C}{\pi \xi_{\text{TL}}^4} \cdot \left[ \frac{E_{\text{ph}}^2 + \Delta^2}{E_{\text{ph}}} \ln \left( \frac{|E_{\text{ph}} - \Delta|}{E_{\text{ph}} + \Delta} \right) \right. \\ & \left. + 2 \cdot \Delta \ln \left( \frac{|E_{\text{ph}} - \Delta| \cdot (E_{\text{ph}} + \Delta)}{\sqrt{(E_{0,\text{TL}}^2 - \Delta^2)^2 + \Delta^2 C^2}} \right) \right] \end{aligned} \quad (3.43)$$

where the following terms are used:

$$a_{\text{ln}} = (\Delta^2 - E_{0,\text{TL}}^2)E_{\text{ph}}^2 + \Delta^2 C^2 - E_{0,\text{TL}}^2(E_{0,\text{TL}}^2 + 3\Delta^2) \quad (3.44)$$

$$a_{\text{atan}} = (E_{\text{ph}}^2 - E_{0,\text{TL}}^2)(E_{0,\text{TL}}^2 + \Delta^2) + \Delta^2 C^2 \quad (3.45)$$

$$\xi_{\text{TL}}^4 = (E_{\text{ph}}^2 - \gamma_{\text{TL}}^2)^2 + \frac{\alpha_{\text{TL}}^2 C^2}{4} \quad (3.46)$$

$$\alpha_{\text{TL}} = \sqrt{4E_{0,\text{TL}}^2 - C^2} \quad (3.47)$$

$$\gamma_{\text{TL}} = \sqrt{E_{0,\text{TL}}^2 - C^2/2} \quad (3.48)$$

The Tauc-Lorentz model finds extensive use in calibration of the dielectric function and ellipsometric parameters of thin film semiconductors.

#### 3.1.5 Thin Film Interference

A material interface causes light to be reflected due to an abrupt change of refractive index (c.f. section 3.1.4). At the surface, the non-reflected fraction of light is transmitted into the material, where it is primarily absorbed within the optical penetration depth. For transparent thin films however, where the optical penetration depth might exceed the film thickness, the travelling light waves hit multiple material interfaces while propagating through the film stack. At each interface light is transmitted and reflected, leading to interference of the incoming and outgoing electro-magnetic waves. As the amplitudes of the electro-magnetic fields add up on interference, this can cause significantly higher field amplitudes within the film stack compared to the incident field amplitude outside the films. The characteristics of the electromagnetic fields are schematically depicted in fig. 3.3. The interferences not only cause potentially larger field amplitudes within the films, but also can drastically change the reflectivity spectrum of the whole sample in comparison to bulk material [76, 77].

Mathematically, the thin film interferences can be modeled by solving Maxwell's equations or wave equations for the electro-magnetic fields within the film stack. In the case for plane electro-magnetic waves:

$$\mathbf{E}(\mathbf{r}, t) = \mathbf{E}_0 \exp(i(\mathbf{k} \cdot \mathbf{r} - \omega t)) \quad (3.49)$$

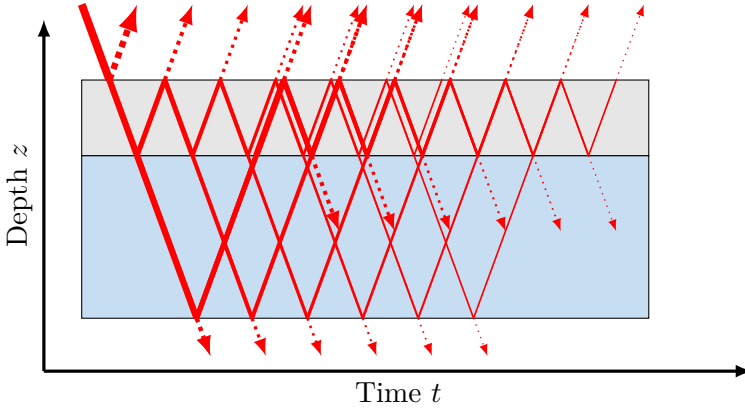


**Figure 3.3:** Schematic space-time diagram for the propagation of the laser radiation (red line) within a thin film stack. A fraction of the laser radiation gets reflected at every material interface. Each reflected portion of the laser radiation interferes with the incoming radiation and therefore leads to thin film interferences

incident on a stack of parallel films into  $z$ -direction, the computation of Maxwell's equations can be simplified using the transfer matrix method (TMM) [76, 78]. In the following, it is assumed that the sample surface is aligned along the  $x$ - $y$ -plane and the light is  $s$ -polarized and therefore parallel to the sample surface:  $\mathbf{E} = (0, E, 0)$ . For isotropic and homogeneous optical properties, described by the dielectric function  $\varepsilon$  and the magnetic permeability  $\mu$  within each film the plane wave can be decomposed into a superposition of a transmitted wave  $E_l^+$  moving forward and a reflected wave moving backwards  $E_l^-$ . Then the total electric field for a layer  $E_l$  within the film stack is expressed as a superposition of  $E_l^+$  and  $E_l^-$  [76]:

$$\begin{aligned} E_l(x, z, t) &= (E_l^+(z) + E_l^-(z)) \cdot \exp\left(i\left(\frac{\omega}{c}x \sin(\alpha_{\text{inc}}) - \omega t\right)\right) \\ &= \left(E_l^+ \exp\left(i\frac{\omega}{c}\tilde{n}_l z\right) + E_l^- \exp\left(-i\frac{\omega}{c}\tilde{n}_l z\right)\right) \\ &\quad \cdot \exp\left(i\left(\frac{\omega}{c}x \sin(\alpha_{\text{inc}}) - \omega t\right)\right) \end{aligned} \quad (3.50)$$

where  $\alpha_{\text{inc}}$  corresponds to the angle of incidence and

$$\tilde{n}_l = \sqrt{\varepsilon\mu - \sin^2(\alpha_{\text{inc}})} \quad (3.51)$$

to the generalized index of refraction. With the generalized index of refraction, the corresponding complex reflection and transmission coefficients for the electric field a material interface between two adjacent layers  $(l - 1)$  and  $l$  are given by:

$$\tilde{r}_{l,l-1} = \frac{\tilde{n}_l/\mu_l - \tilde{n}_{l-1}/\mu_{l-1}}{\tilde{n}_l/\mu_l + \tilde{n}_{l-1}/\mu_{l-1}} \quad (3.52)$$

$$\tilde{t}_{l,l-1} = \frac{2\tilde{n}_l/\mu_l}{\tilde{n}_l/\mu_l + \tilde{n}_{l-1}/\mu_{l-1}} \quad (3.53)$$

Then the reflected and transmitted waves  $E_{l+1}^+$  and  $E_{l+1}^-$  at the interface  $(l + 1)$  are given by:

$$\begin{pmatrix} E_l^+ \\ E_l^- \end{pmatrix} = \underbrace{\begin{pmatrix} \Phi_l^{-1} & 0 \\ 0 & \Phi_l \end{pmatrix} \cdot \begin{pmatrix} 1/\tilde{t}_{l,l-1} & \tilde{r}_{l,l-1}/\tilde{t}_{l,l-1} \\ \tilde{r}_{l,l-1}/\tilde{t}_{l,l-1} & 1/\tilde{t}_{l,l-1} \end{pmatrix}}_{=\underline{C}_l} \cdot \begin{pmatrix} E_{l-1}^+ \\ E_{l-1}^- \end{pmatrix} \quad (3.54)$$

$$\Phi_l = \exp\left(i\frac{\omega}{c}\tilde{n}_l\delta_{\text{film},l}\right) \quad (3.55)$$

Here  $\delta_{\text{film},l}$  is the film thickness of layer  $l$ . Hence, the reflected  $\tilde{r}$  and transmitted  $\tilde{t}$  fraction of the electric wave can be computed for an arbitrary stack of  $N$  thin films using:

$$\begin{pmatrix} 1 \\ \tilde{r} \end{pmatrix} = \prod_{l=1}^N \underline{C}_l \cdot \begin{pmatrix} \tilde{t} \\ 0 \end{pmatrix} \quad (3.56)$$

The reflected power is related to the reflectivity of the electric field  $\tilde{r}$  and can be computed by  $R = |\tilde{r}|^2$

#### 3.1.6 Electron Dynamics

As already mentioned in section 3.1.4, the optical properties of semiconductors strongly depend on the material composition, doping, bandgap,

and free electron density. To accurately describe the optical properties during the laser-matter interaction, the free electron density needs to be known. The free electron density  $n_e = n_e(t)$  depends on the incident laser intensity  $I$  and can be modeled using different approaches. One approach is considering first principle calculations including the density of states (DOS). Excitation of an electron from the valence to the conduction band results in the generation of an electron hole in the valence band. In the case for semiconductors with a direct bandgap and parabolic valence and conduction bands, such as silicon the DOS for the electrons  $D_e$  and holes  $D_h$  are calculated via [49]:

$$D_e(\hat{E}) = \frac{m_e^{*3/2}}{\hbar^3 \pi^2} \sqrt{2(\hat{E} - \hat{E}_C)} \quad (3.57)$$

$$D_h(\hat{E}) = \frac{m_h^{*3/2}}{\hbar^3 \pi^2} \sqrt{2(\hat{E}_V - \hat{E})} \quad (3.58)$$

with respective energies  $\hat{E}_V$ ,  $\hat{E}_C$  for the valence and conduction band. Since the shape of the valence and conduction band are often different, the electrons and holes often have different effective masses which are denoted as  $m_e^*$  and  $m_h^*$  in eqs. (3.57) and (3.58), respectively.

The free charge carrier density can then be obtained by integration of the charge carrier distribution multiplied by the DOS. In order to compute the DOS, precise knowledge of the band structure is mandatory, which is well understood for bulk materials, e.g., silicon or nickel [79, 80]. However, material properties of thin films are different from bulk material [81]. Therefore, the exact band structure is often difficult to obtain for many thin film materials. For this reason, following Kennedy, Noack and Vogel, in this work, the temporal evolution of the free electron density is described by rate equations instead of the DOS [82–84]:

$$\partial_t n_e = w_{\text{SFI}}(I) + w_{\text{casc}}(I, n_e) - w_{\text{diff}}(n_e) - w_{\text{rec}}(n_e) \quad (3.59)$$

The first two terms of eq. (3.59) correspond to the electron generation through the electric field.  $w_{\text{SFI}}$  is the probability of strong field ionization, e.g., due to multiphoton absorption or tunneling.  $w_{\text{casc}}$

corresponds to the ionization rate due to impact ionization caused by collisions between free and bound electrons. The third and fourth terms  $w_{\text{diff}}$  &  $w_{\text{rec}}$  describe the diffusion of hot electrons and the recombination rate, respectively. The recombination rate itself consists of radiative two-particle recombination and the non-radiative Auger recombination.

In dielectrics, there are typically very few initial free electrons in the non-excited state. Thus, the first electrons are mainly generated due to strong field ionization. The limiting regimes are tunnel ionization and multiphoton ionization. To identify the relevant strong field ionization process the Keldysh parameter can be defined, which is the ratio of the optical frequency  $\omega$  with the tunneling frequency  $\omega_{\text{T}}$  [82]:

$$\gamma_{\text{K}} = \frac{\omega}{\omega_{\text{T}}} = \frac{\omega \sqrt{m_{\text{e}}^* \Delta}}{eE} \quad (3.60)$$

$$\omega_{\text{T}} = \frac{eE}{\sqrt{m_{\text{e}}^* \Delta}} \quad (3.61)$$

The tunnel frequency  $\omega_{\text{T}}$  is proportional to the electric field  $E$  as stronger electric fields distort the lattice potential and therefore increase the tunneling probability. For a Keldysh parameter  $\gamma_{\text{K}} < 1$  the dominant ionization process is tunnel ionization. If the Keldysh parameter exceeds 1  $\gamma_{\text{K}} > 1$  multiphoton ionization has to be considered [85]. For ITO and the intensities used in this work the resulting Keldysh parameter is  $\gamma_{\text{K}} = 1.46 \geq 1$  [77]. Consequently, Kennedy's approximation applies describing multiphoton ionization  $w_{\text{SFI}} = w_{\text{MPI}}$ . To ionize an atom within a material with the bandgap  $\Delta$  the required number of photons  $K = \lfloor \Delta/(\hbar\omega) + 1 \rfloor$  with  $\lfloor x \rfloor$  being the floor function. Following Keldysh's theory, the multiphoton ionization rate  $w_{\text{MPI}}$  depends on the angular frequency  $\omega$  and the intensity  $I$  of the incoming

laser light [82–84]:

$$w_{\text{MPI}} = \frac{2\omega}{9\pi} \left( \frac{m_e^* \omega}{\hbar} \right)^{3/2} \left( \frac{e}{16\omega c_0 \varepsilon_0 n m_e^* \Delta} \cdot I \right)^K \cdot \exp(2K) \cdot \Phi_D \left( \sqrt{2K - \frac{2\Delta}{\hbar\omega}} \right) \quad (3.62)$$

with  $m_e^*$  being the electron effective mass,  $c_0$  the vacuum speed of light,  $\varepsilon_0$  the vacuum permeability and  $n$  the refractive index of the material, respectively. The Dawson integral  $\Phi_D$  is given by [86]:

$$\Phi_D(x) = \exp(-2x) \int_0^x \exp(y^2) dy \quad (3.63)$$

The second term in eq. (3.59) describes the impact ionization. As the acceleration of free electrons via inverse bremsstrahlung is not instantaneous but takes time, the free electrons contributing to the cascade ionization rate are retarded by the time:  $t_{\text{ret}} = K \cdot \tau_e$ . In a first order approximation, the retarded cascade is given by [84]:

$$w_{\text{casc}} = \alpha_{\text{casc}} \cdot n_e \quad (3.64)$$

$$\alpha_{\text{casc}} = \begin{cases} \frac{\eta_{\text{casc}}}{1 + \eta_{\text{casc}} t_{\text{ret}}} \cdot n_e & V \cdot n_e \geq 0.5 \\ 0 & V \cdot n_e < 0.5 \end{cases} \quad (3.65)$$

$$\eta_{\text{casc}} = \frac{1}{\omega^2 \tau_e^2 + 1} \cdot \frac{e^2 \tau_e}{c_0 n m_e^* \Delta} \cdot I \quad (3.66)$$

The electron collision time is the inverse of the electron collision frequency  $\tau_e = 1/\gamma_{\text{el}}$  (see also eqs. (3.30) and (3.39)) and is typically in the order of several femtoseconds [84, 87]. The cascade ionization is only considered when the chance of finding an electron in the focal volume  $V = \pi w_0^2 \delta_{\text{opt}}$  exceeds 50%, with  $w_0$  being the beam radius and the optical penetration depth  $\delta_{\text{opt}}$  [84].

Figure 3.4 sketches the ionization processes, relevant in semiconductors and wide bandgap materials. As soon as the first electrons are excited by strong field ionization from the valence to the conduction

band, the electrons absorb energy from the laser radiation via inverse bremsstrahlung absorption. If the kinetic energy of an electron exceeds a critical value  $E_{\text{crit}} \geq 1.5\Delta$  it can ionize the next electron due to collisions. The factor of 1.5 originates from the assumption that the effective masses of the valence and the conduction band are equal [84]. Within the scope of this manuscript it is assumed that the effective masses for electrons and holes are equal for ITO. Hence the critical value  $E_{\text{crit}} \geq 1.5\Delta$  can be used. If the free electron density

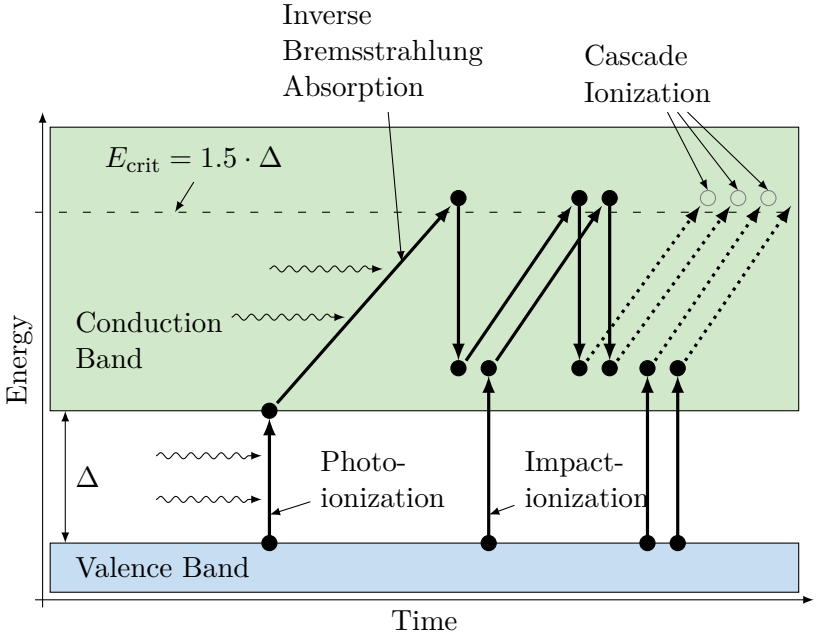


**Figure 3.4:** Schematic illustration of the ionization processes involved exciting electrons from the valence band into the conduction band. Photoionization generates “seed” electrons which absorb energy via inverse bremsstrahlung absorption. If the electrons’ energy exceeds  $E_{\text{crit}}$  new atoms are ionized via impact ionization. This process then repeats itself and leads to an electron cascade. The illustration is inspired by [84].

$n_e$  becomes large:  $n_e \geq 1 \times 10^{10} \text{ cm}^{-3}$  cascade ionization becomes the controlling process for ionization during an intense laser pulse.

In degenerate semiconductors, the bandgap increases with excitation of electrons into the conduction band due to the Burstein-Moss-effect. The electrons in the valence band require more energy to populate states in the conduction band the more electrons are excited because the low energy states are already occupied. A schematic sketch of the Burstein-Moss-effect can be found in fig. 3.5. The energy shift  $\Delta_{\text{BM}}$  of

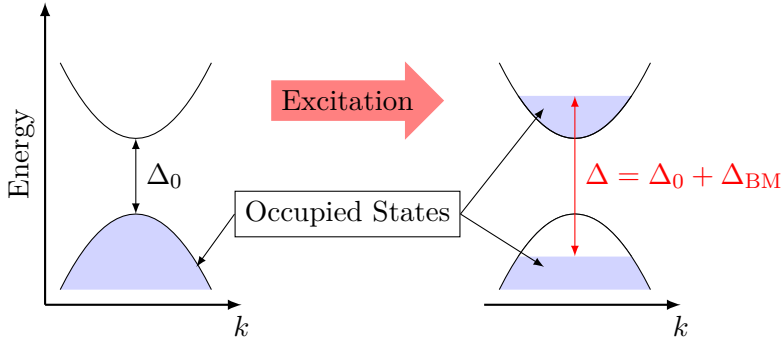


**Figure 3.5:** Schematic illustration of the Burstein-Moss-effect. The effective bandgap of degenerate semiconductors changes if electrons are excited from the valence to the conduction band. Due to Fermi's principle electrons are only allowed to occupy states with higher energy. The illustration is inspired by [88].

the bandgap  $\Delta$  towards higher energies for parabolic bands in ITO is given by [89]:

$$\Delta_{\text{BM}} = \frac{\hbar^2}{2m_e^*} (3\pi^2 n_e)^{2/3} \quad (3.67)$$

$$\Delta = \Delta_0 + \Delta_{\text{BM}} \quad (3.68)$$

The increase of the bandgap causes  $t_{\text{ret}}$  to increase because more photons are needed to overcome the bandgap, i.e., an increase of  $K$ . This influences both, the multiphoton ionization rate  $w_{\text{MPI}}$  and the cascade ionization rate  $w_{\text{casc}}$ . The dependence of the non-retarded cascade

ionization factor  $\eta_{\text{casc}}$  on the electron collision time  $\tau_e$  with a constant bandgap is shown in fig. 3.6. For a laser wavelength  $\lambda = 1056 \text{ nm}$

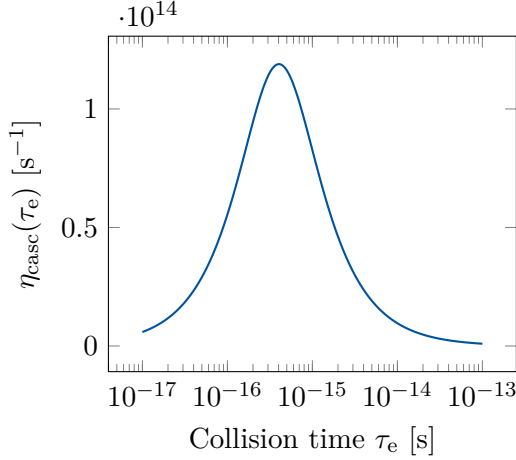


**Figure 3.6:** The non-retarded cascade ionization factor  $\eta_{\text{casc}}$  as a function of the electron collision time  $\tau_e$  with a constant bandgap for an infrared laser pulse with wavelength  $\lambda = 1056 \text{ nm}$ . The ionization factors  $\eta_{\text{casc}}$  maximum is located at  $\tau_e = 4.4 \times 10^{-16} \text{ s}$ .

the non-retarded cascade ionization factor  $\eta_{\text{casc}}$  exhibits a maximum for  $\tau_e = 0.44 \text{ fs}$ . As already described, both the electron collision time  $\tau_e(n_e)$  (c.f. eq. (3.39)) and the bandgap  $\Delta(n_e)$  (c.f. eq. (3.67)) depend on the free electron density  $n_e$  (c.f. fig. 3.7). On the one hand, an increase of the free electron density leads to a decrease of the electron collision time until it saturates at  $\tau_e = 1/\gamma_{\text{max}}$ . This alone would lead to an increase of the cascade ionization rate  $w_{\text{casc}}$ . On the other hand, an increase of the free electron density also increases the bandgap. This decreases the non-retarded cascade ionization factor  $\eta_{\text{casc}}$  and simultaneously increases the number of photons  $K$  necessary to overcome the bandgap. Therefore, the retarded  $\alpha_{\text{casc}}$  is reduced for electron densities larger than  $n_e = 3.2 \times 10^{27} \text{ m}^{-3}$ . The maximum free electron density during and after the laser pulse is not only limited by the Burstein-Moss-effect but also due to diffusion and recombination.

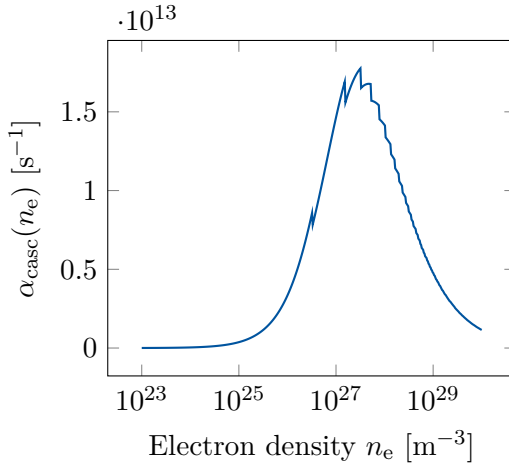


**Figure 3.7:** The retarded cascade ionization factor  $\alpha_{\text{casc}}$  as a function of the electron density  $n_e$ . The bandgap  $\Delta = \Delta_0 + \Delta_{\text{BM}}$  and the collision time  $\tau_e$  (eqs. (3.39) and (3.67)) are both functions of the electron density. The spikes of the retarded cascade ionization factor  $\alpha_{\text{casc}}$  are caused by the Burstein-Moss-effect which increases  $K$  and therefore  $t_{\text{ret}}$ . The used material parameters can be found in table 6.1.

The decrease of the electron density  $n_e$  in the focal volume due to diffusion is estimated by the electron diffusion rate [83]:

$$w_{\text{diff}} = g_{\text{diff}} \cdot n_e \quad (3.69)$$

$$g_{\text{diff}} = \frac{3\tau_e}{3m_e^*} \left[ \left( \frac{2.4}{w_0} \right)^2 + \left( \frac{1}{\delta_{\text{opt}}} \right)^2 \right] + \frac{1}{\omega^2 \tau_e^2 + 1} \cdot \frac{m_e^* \omega^2 \tau_e}{M_{\text{mole}}} \quad (3.70)$$

where  $M_{\text{mole}}$  is the molecular mass.

The recombination rate  $w_{\text{rec}}$  is assumed to consist out of two contributions, namely two particle recombination and Auger recombination. These contributions have been utilized to model recombination mechanisms in dielectrics and semiconductors [49, 84]. Two-particle recombination is dominant for direct bandgap materials and accompanied by photon emission. Contrarily, Auger recombination is non-radiative and the dominant for indirect bandgap materials like silica and for large electron densities [55]. However, excessive excitation of free electrons e.g. via intense laser radiation might lead to a change of the bandstructure due to changing of the lattice potentials [90]. Therefore, both recombination mechanisms are considered to model the recombination mechanisms adequately during laser excitation:

$$w_{\text{rec}} = \eta_{2p} n_e^2 + \eta_{\text{Auger}} n_e^3 \quad (3.71)$$

#### 3.1.7 Pulse Propagation in Transparent Media

Laser pulse propagation in transparent media can be described by a transport equation for the intensity  $I$  [91]:

$$\frac{1}{c_0/n} \partial_t I(z, t) + \partial_z I(z, t) = -\alpha_{\text{abs}} I(z, t) + S(z, t) \quad (3.72)$$

$$\alpha_{\text{abs}}(z, t) = \frac{(w_{\text{SFI}}(I, n_e) + w_{\text{casc}}(I, n_e)) \cdot E_{\text{av}}}{I(z, t)} \quad (3.73)$$

where  $c_0$  is the speed of light in vacuum,  $n$  the refractive index of the material,  $S$  a source term and  $\alpha_{\text{abs}}$  the absorption coefficient, respectively. As described in section 3.1.6, the absorption of electromagnetic

radiation and semiconductors is governed by the electron dynamics. Electrons absorb the energy of the laser pulse by either MPI or inverse bremsstrahlung absorption and thermalize after a few collisions. Therefore, each free electron is assumed to carry an average energy of  $E_{\text{av}} = 2.25\Delta$  [91]. Using eq. (3.73) nonlinear absorption mechanisms are evaluated. The formulation of the absorption coefficient in eq. (3.73) differs from the formulation given earlier in eq. (3.37):  $\alpha_{\text{abs}} = 2\omega/c_0\Im(\sqrt{\varepsilon(\omega, n_e)})$ . A comparison between the two absorption coefficients can be found in section 6.5.

### 3.1.8 Two Temperature Model

Since its formulation in the middle fifties, the TTM has found extensive use in modelling the heat induced into materials during pulsed laser-matter interaction. As the pulse duration for laser pulses became shorter into the sub-nanosecond range, the temporal relaxation of the heat flow in Fourier's law has to be taken into account [45, 47, 57]:

$$\tau\partial_t\mathbf{q} + \mathbf{q} = -K_{\text{th}}\nabla T \quad (3.74)$$

For thin films considered in this work, the film thickness  $\delta_{\text{film}}$  is much smaller than the lateral dimensions of the laser beam or the sample. For this reason, the governing equations are considered in one dimension. The timescale  $t_v$  in which the one-dimensional approach is valid for the thermal equations is estimated by use of the thermal penetration depth:  $\delta_{\text{therm}} = 2\sqrt{D_{\text{th}}t}$  where  $D_{\text{th}}$  corresponds to the thermal diffusivity and  $t$  to the time. The thermal diffusivity  $D_{\text{th}}$  is given by  $D_{\text{th}} = K_e/C_e$  which both depend on the free electron density (c.f. eqs. (3.79) and (3.81)). For ITO, the reached free electron densities during the laser pulse range from  $1.3 \times 10^{27} \text{ m}^{-3}$  to  $1 \times 10^{28} \text{ m}^{-3}$ . Larger electron densities lead to a larger thermal conductivity resulting in diffusion times between  $t_v \approx 3.9 \text{ ns}$  to  $1.6 \text{ ns}$  for a distance equal to 10% of the beam diameter of  $2 \cdot w_0$ . Within  $t_v$  the equations that need to be solved for the temperatures and heat fluxes of the electronic

$(T_e, q_e)$  and lattice  $(T_l, q_l)$  systems are given by [45, 47]:

$$C_e(T_e)\partial_t T_e = -\partial_z q_e - G(T_e - T_l) + S(z, t) - Q_{e,\text{ion}} \quad (3.75)$$

$$\tau_e \partial_t q_e + q_e = -K_e \partial_z T_e \quad (3.76)$$

$$C_l(T_l)\partial_t T_l = -\partial_z q_l - G(T_e - T_l) \quad (3.77)$$

$$\tau_l \partial_t q_l + q_l = -K_l \partial_z T_l \quad (3.78)$$

where  $C_e, C_l$  are the specific heat capacities and  $K_e, K_l$  the thermal conductivities for the electronic and the lattice system respectively. The term  $Q_{e,\text{ion}}$  corresponds to the energy required to excite electrons over the bandgap and is given by:  $Q_{e,\text{ion}} = \partial_t(\Delta \cdot n_e)$  [49].  $G$  describes the coupling between the two systems,  $S(z, t)$  is the volumetric heat source. The functions for the specific electronic heat capacity and thermal conductivity depend on the free electron density and temperature. They are given by [92]:

$$C_e(T_e, n_e) = \frac{\pi^2 k_B}{2T_f} T_e n_e \quad (3.79)$$

$$T_f(n_e) = \frac{E_f}{k_B} = \frac{\hbar^2}{2m_e^* k_B} (3\pi^2 n_e)^{2/3} \quad (3.80)$$

$$K_e(T_e, n_e) = \frac{\pi^2 k_B^2}{3m_e^*} \tau_e T_e n_e \quad (3.81)$$

with  $k_B, \hbar$  being Boltzmann's constant and Planck's reduced constant, the Fermi temperature  $T_f$ ,  $E_f$  the Fermi energy and finally  $m_e^*$  the electron effective mass. For temperatures in the order of the Debye temperature  $T_D$  the electron phonon coupling  $G$  is given by [42, 59]:

$$G = \frac{\pi^2 m_e^* c_s^2 n_e}{6\tau_e T_e} \quad (3.82)$$

where  $c_s$  corresponds to the speed of sound of the material. The speed of sound depends on the mechanical properties and can be computed from the mass density  $\rho$ , Young's modulus  $E_y$  and the Poisson ratio

$\nu_{\text{poisson}}$ :

$$c_s = \sqrt{\frac{E_y(1 - \nu_{\text{poisson}})}{\rho(1 + \nu_{\text{poisson}})(1 - 2\nu_{\text{poisson}})}} \quad (3.83)$$

If the lattice temperature  $T_l$  is larger than  $T_l > 0.48T_D$  the error of eq. (3.82) is smaller than 6% [93]. Typical values of  $G$  for metals are ranging from  $2.6 \times 10^{16} \text{ W m}^{-3} \text{ K}^{-1}$  for gold and  $202 \text{ W m}^{-3} \text{ K}^{-1}$  for titanium, respectively [93]. Assuming incompressibility, the work due to changes of volume and pressure can be neglected. With the lattice specific heat capacity  $C_l$  the enthalpy obeys Kirchhoff's law:

$$dH_e = C_l dT \quad (3.84)$$

Typically, before melting or evaporation, the temperature  $T$  of a substance remains constant despite further addition of heat because the breakage of atomic or molecular bonds requires energy. While the temperature remains constant the enthalpy  $H_e$  exhibits a jump at the phase transition. This can be described by using the enthalpies for melting  $Q_l$  and evaporation  $Q_{\text{evap}}$  combined with Dirac's delta function  $\delta$  and the specific heat capacity for temperatures below melting temperature  $C_{l,0}$  [43, 94]:

$$C_l = C_{l,0} + Q_l \delta(T - T_{\text{melt}}) + Q_{\text{evap}} \delta(T - T_{\text{evap}}) \quad (3.85)$$

Typically, the melting enthalpies are much smaller compared to the enthalpies required for evaporation:  $Q_l \ll Q_{\text{evap}}$ . Hence, only the evaporation enthalpies are used. Numerically resolving the jump is achieved by assuming that the transition temperature  $\Delta T$  at the phase transition is smeared out with the solidus and liquidus temperatures:  $\Delta T = T_{\text{liq}} - T_{\text{sol}}$ . For different metallic glass systems ( $\text{MgO-SiO}_2$  and  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ ) the transition temperatures have been reported to be in the range of  $\Delta T = 50 \text{ K}$  to  $130 \text{ K}$  [95]. For thin ITO-films  $\Delta T = 100 \text{ K}$  has been proposed in [43]. Within the scope of this manuscript  $\Delta T = 50 \text{ K}$  is used to better represents the jump in material

parameters during the phase transition. Hence, the Dirac delta function in eq. (3.85) at the phase change becomes a gaussian [43, 94]:

$$C_1 = C_{1,0} + \frac{\rho Q_1}{\sqrt{\pi} \Delta T} \exp \left( - \left( \frac{T_1 - T_{\text{melt}}}{\Delta T} \right)^2 \right) \quad (3.86)$$

To bring equations eqs. (3.75) to (3.78) into dimensionless form the following scales are used:

$$t = t_{\text{sc}} \cdot \tau \quad (3.87)$$

$$z = l_{\text{sc}} \cdot \xi \quad (3.88)$$

$$T = T_{\text{sc}} \cdot \theta \quad (3.89)$$

$$q = q_{\text{sc}} \cdot \hat{q} \quad (3.90)$$

Thus, the scaled equations are given by:

$$\begin{aligned} \partial_\tau \theta_e + \frac{1}{C_e} \cdot \frac{q_{\text{sc}} t_{\text{sc}}}{T_{\text{sc}} l_{\text{sc}}} \partial_\xi \hat{q}_e = & - \frac{G}{C_e} \cdot t_{\text{sc}} (\theta_e - \theta_l) + \frac{t_{\text{sc}}}{C_e T_{\text{sc}}} \cdot S(\xi, \tau) \\ & - \frac{t_{\text{sc}}}{C_e T_{\text{sc}}} \cdot Q_{\text{e,ion}} \end{aligned} \quad (3.91)$$

$$\partial_\tau \hat{q}_e + \frac{K_e}{\tau_e} \cdot \frac{T_{\text{sc}} t_{\text{sc}}}{q_{\text{sc}} l_{\text{sc}}} \partial_\xi \theta_e = \frac{t_{\text{sc}}}{\tau_e} \hat{q}_e \quad (3.92)$$

$$\partial_\tau \theta_l + \frac{1}{C_l} \cdot \frac{q_{\text{sc}} t_{\text{sc}}}{T_{\text{sc}} l_{\text{sc}}} \partial_\xi \hat{q}_l = \frac{G t_{\text{sc}}}{C_l} \cdot (\theta_e - \theta_l) \quad (3.93)$$

$$\partial_\tau \hat{q}_l + \frac{K_l}{\tau_l} \cdot \frac{T_{\text{sc}} t_{\text{sc}}}{q_{\text{sc}} l_{\text{sc}}} \partial_\xi \theta_l = \frac{t_{\text{sc}}}{\tau_l} \hat{q}_l \quad (3.94)$$

#### 3.1.9 Pressure Waves

A rise in temperature due to heating causes matter to thermally expand. In the case of laser material processing, the heating is locally confined and happens faster than the heat can dissipate via heat conduction. This causes a lattice deformation, which can be modeled using the theory of linear elasticity.

Analogous to the previous section, a one-dimensional approach is going to be formulated because the lateral dimensions of the laser

beam ( $2 \cdot w_0 \approx 30 \mu\text{m}$ ) are much larger than the film thickness in the order of hundred nanometers. Thus, the time for the lateral waves to travel to the material boundary and reflect back is much larger than the time for the one-dimensional motion in the thickness direction and the assumption of a one-dimensional problem is appropriate for the mechanical equations [45, 96]. The timescale  $t_v$  during which the one-dimensional approach is valid is estimated by comparing the speed of sound (longitudinal waves)  $c_s$  to the beam diameter of the laser radiation  $2 \cdot w_0$ . For ITO, the speed of sound is  $c_s = 5845.03 \text{ m s}^{-1}$  (c.f. eq. (3.83) and table 6.1) and the laser beam diameters considered in this treatise are in the order of  $2 \cdot w_0 \approx 30 \mu\text{m}$ . Therefore, the mechanical wave needs  $t \approx 513.3 \text{ ps}$  to travel a lateral distance of 10% of the beam diameter. In addition to heat, intense laser radiation causes a local change of the free electron density in dielectrics that can lead to separation of negative and positive charges within the material. The resulting electric repulsion of lattice ions can be modeled using the hot-electron blast force [97]. During the laser matter interaction, the elastic equations of motion for the lattice deformation can then be modeled using the following equation [45]:

$$\rho \partial_t^2 u_z = (\lambda_1 + 2\mu_2) \partial_z^2 u_z - (3\lambda_1 + 2\mu_2) \alpha_{\text{th}} \partial_z T_l \quad (3.95)$$

Here  $\rho$  corresponds to the mass density, and  $u_z$  to the lattice displacement,  $\lambda_1, \mu_2$  to the first and second Lamé coefficients,  $\alpha_{\text{th}}$  to the thermal expansion coefficient and  $T_e, T_l$  the electron and lattice temperature, respectively.

The mechanical wave equation (eq. (3.95)) can be rewritten as a set of first order partial differential equations by introducing new variables, namely the velocity  $v_z$  and the strain in z-direction  $\varepsilon_{zz}$ :

$$\partial_t u_z = v_z \quad (3.96)$$

$$\partial_t v_z = \frac{\lambda_1 + 2\mu_2}{\rho} \partial_z \varepsilon_{zz} - \frac{3\lambda_1 + 2\mu_2}{\rho} \alpha_{\text{th}} \partial_z T_e \quad (3.97)$$

$$\partial_t \varepsilon_{zz} = \partial_z v_z \quad (3.98)$$

Analog to the previous section, the dimensionless form of eqs. (3.97) and (3.98) are obtained with the following scaling:

$$t = t_{\text{sc}} \cdot \tau \quad (3.99)$$

$$z = l_{\text{sc}} \cdot \xi \quad (3.100)$$

$$v_z = \frac{l_{\text{sc}}}{t_{\text{sc}}} \cdot \hat{v}_z \quad (3.101)$$

$$T = T_{\text{sc}} \cdot \theta \quad (3.102)$$

$$(3.103)$$

and therefore:

$$\partial_\tau \hat{v}_z - \frac{\lambda_1 + 2\mu_2}{\rho} \cdot \frac{t_{\text{sc}}^2}{l_{\text{sc}}^2} \partial_\xi \varepsilon_{zz} = - \frac{3\lambda_1 + 2\mu_2}{\rho} \alpha_{\text{th}} \cdot \frac{t_{\text{sc}}^2 T_{\text{sc}}}{l_{\text{sc}}^2} \partial_\xi \theta_1 \quad (3.104)$$

$$\partial_\tau \varepsilon_{zz} - \partial_\xi \hat{v}_z = 0 \quad (3.105)$$

The state of uniaxial strain in an isotropic material is considered [45]:

$$\varepsilon_{zz}(z, t) \neq 0 \quad (3.106)$$

$$\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{xy} = \varepsilon_{yz} = \varepsilon_{zx} = 0 \quad (3.107)$$

which leads to the stress-normal strain relations:

$$\sigma_{xx} = \sigma_{yy} = \lambda_1 \varepsilon_{zz} - (3\lambda_1 + 2\mu_2) \alpha_{\text{th}} (T_1 - T_0) \quad (3.108)$$

$$\sigma_{zz} = (\lambda_1 + 2\mu_2) \varepsilon_{zz} - (3\lambda_1 + 2\mu_2) \alpha_{\text{th}} (T_1 - T_0) \quad (3.109)$$

# 4 Model Development for Laser Ablation of Thin Films

Accurate models are essential for understanding, predicting and optimization of the ablation processes. They allow for identification of the relevant underlying physical processes, which are indispensable to explain the ablation process. Within this chapter, the physical mechanisms from chapter 3 are combined to formulate a mathematical model, which is able to predict the ablation crater shapes for thin semiconducting films. This chapter covers two approaches: The first approach is a threshold ablation model, which does not focus on the exact ablation mechanism but allows for fast and accurate prediction of the ablation crater shape in metals. The second approach consists of a more detailed model, that describes the absorption of the laser radiation and the subsequent heating of the electronic and the lattice subsystems with a two temperature model. The lattice heating causes a mechanical shockwave due to thermal expansion of the material which is described with an elastic wave equation.

## 4.1 Threshold Ablation Model

In ultrashort pulsed laser processing material is ablated if the absorbed fluence exceeds the material specific threshold fluence  $F_{\text{thr}}$ :

$$\mu_{\text{pro}} \cdot A \cdot F \geq F_{\text{thr}} \longrightarrow \text{Ablation} \quad (4.1)$$

$$\mu_{\text{pro}} \cdot A \cdot F \leq F_{\text{thr}} \longrightarrow \text{No ablation/material heating} \quad (4.2)$$

In general, the absorbed fluence depends on the projection of the radiation onto the material surface  $\mu_{\text{pro}} = \cos(\alpha_{\text{inc}})$ , where  $\alpha_{\text{inc}}$  is the

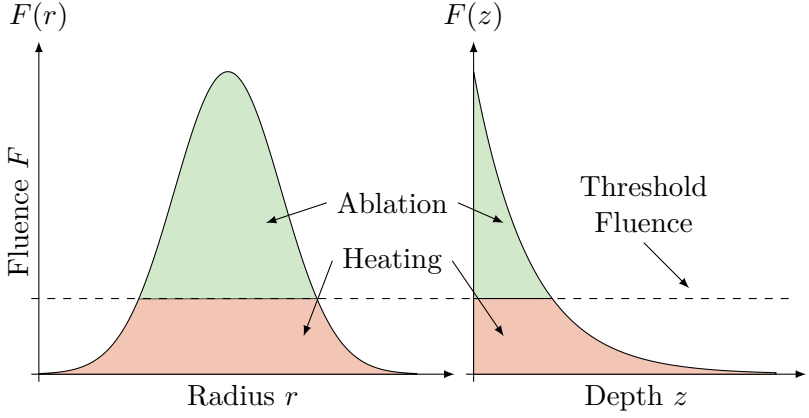


**Figure 4.1:** Schematic sketch of a gaussian fluence distribution  $F$  in radial direction  $r$  and into the depth  $z$  of the material. All fluence above the threshold fluence induces ablation (green area). The fluence below the threshold fluence is transformed into heat (red area).

angle of incidence. Additionally, the absorptivity also depends on the angle of incidence:  $A = A(\alpha_{\text{inc}})$ . Thus, the ablation condition becomes:

$$F = \mu_{\text{pro}} \cdot A(\alpha_{\text{inc}}) \cdot F(r, z) \geq F_{\text{thr}} \quad (4.3)$$

The fluence distribution  $F(r, z)$  for a Gaussian laser pulse (c.f. eq. (3.24)) that is absorbed by Lambert-Beer's law is given by:

$$F(r, z) = F_0 \exp\left(-\frac{2r^2}{w_0^2}\right) \exp\left(-\frac{z}{\delta_{\text{eff}}}\right) \quad (4.4)$$

A schematic sketch of the Gaussian fluence distribution  $F(r, z)$  is shown on the left in fig. 4.1. The radial region and depth in which the fluence  $F$  exceeds the threshold fluence  $F \geq F_{\text{thr}}$  is shown by the green areas. The remaining fluence below the threshold is transformed into heat within the material and colored with red.

The effective penetration depth  $\delta_{\text{eff}}$  depends on both, the optical penetration depth  $\delta_{\text{opt}}$  and the thermal penetration depth  $\delta_{\text{therm}}$  and is material dependent:

$$\delta_{\text{eff}} = \delta_{\text{opt}} + \delta_{\text{therm}} \quad (4.5)$$

In metals, the optical penetration depth for radiation in the visible and infrared (IR)-region is around a few tens of nanometers [98], whereas in dielectrics the optical penetration depth depends on the laser parameters. Due to intensity dependent changes of the free electron density, the optical and thermal properties of the material are altered during the laser pulse (c.f. sections 3.1.4, 3.1.6 and 3.1.8). The thermal penetration depth  $\delta_{\text{therm}}$  can be estimated by:

$$\delta_{\text{therm}} = 2\sqrt{D_{\text{th}} \cdot \tau_p} \quad (4.6)$$

Using eqs. (4.3) and (4.4), the ablation depth is described by the following analytical expression:

$$\delta_{\text{abl}} = \begin{cases} 0 & , F < F_{\text{thr}} \\ -\delta_{\text{eff}} \ln \left( \frac{F_{\text{thr}}}{F} \right) & , F \geq F_{\text{thr}} \end{cases} \quad (4.7)$$

Due to the analytical function for the ablation depth  $\delta_{\text{abl}}$ , this model allows for fast computation of the ablation crater shape.

## 4.2 Dual Hyperbolic Two Temperature Model

A more sophisticated description of the heating process is given by using the TTM. A full mathematical formulation to describe the ablation process is obtained by combining sections 3.1.8 and 3.1.9. The relevant equations are rewritten into conservational form. Hence, starting with the TTM, eqs. (3.75) to (3.78) become:

$$\partial_t \mathbf{Q} + \underline{\mathbf{A}} \partial_z \mathbf{Q} = \mathbf{RHS} \quad (4.8)$$

where  $\mathbf{Q}$  is the solution vector,  $\mathbf{A}$  is the system matrix and  $\mathbf{RHS}$  is the right-hand side of the equation:

$$\mathbf{Q} = (T_e, q_e, T_l, q_l)^T \quad (4.9)$$

$$\mathbf{A} = \begin{pmatrix} 0 & \frac{1}{C_e} & 0 & 0 \\ \frac{K_e}{\tau_e} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{C_l} \\ 0 & 0 & \frac{K_e}{\tau_l} & 0 \end{pmatrix} \quad (4.10)$$

$$\mathbf{RHS} = \begin{pmatrix} -\frac{1}{C_e}G(T_e - T_l) + S(z, t) \\ -\frac{1}{\tau_e}q_e \\ \frac{1}{C_l}G(T_e - T_l) \\ \frac{1}{\tau_l}q_l \end{pmatrix} \quad (4.11)$$

### 4.3 Mechanical Wave Equation

Analogous to the previous section, now the equations for the mechanical wave are rewritten into conservational form. Hence, eqs. (3.97) and (3.98) in conservational form become:

$$\partial_t \mathbf{Q} + \mathbf{A} \partial_z \mathbf{Q} = \mathbf{RHS} \quad (4.12)$$

$$\mathbf{Q} = (v_z, \varepsilon_{zz})^T \quad (4.13)$$

$$\mathbf{A} = \begin{pmatrix} 0 & \frac{\lambda_1 + 2\mu_2}{\rho} \\ 1 & 0 \end{pmatrix} \quad (4.14)$$

$$\mathbf{RHS} = \begin{pmatrix} -\frac{3\lambda_1 + 2\mu_2}{\rho} \alpha_{th} \partial_z T_e + 2\Lambda_{zz}(T_e \partial_z T_e) \\ 0 \end{pmatrix} \quad (4.15)$$

The displacement  $u_z$  is obtained by integration of  $v_z$  over time.

### 4.4 Combined Model

By combining the equations from sections 3.1.6, 4.2 and 4.3 a full mathematical description for the significant physical processes is achieved.

For convenience, the relevant equations are repeated here once more:

$$C_e(T_e)\partial_t T_e = -\partial_z q_e - G(T_e - T_l) + S \quad (4.16)$$

$$\tau_e \partial_t q_e + q_e = -K_e \partial_z T_e \quad (4.17)$$

$$C_l(T_l)\partial_t T_l = -\partial_z q_l + G(T_e - T_l) \quad (4.18)$$

$$\tau_l \partial_t q_l + q_l = -K_l \partial_z T_l \quad (4.19)$$

$$\rho \partial_t^2 u_z = (\lambda_1 + 2\mu_2) \partial_z^2 u_z - (3\lambda_1 + 2\mu_2) \alpha_{th} \partial_z T_l \quad (4.20)$$

$$\partial_t v_z = \frac{\lambda_1 + 2\mu_2}{\rho} \partial_z \varepsilon_{zz} - \frac{3\lambda_1 + 2\mu_2}{\rho} \alpha_{th} \partial_z T_e \quad (4.21)$$

$$\partial_t \varepsilon_{zz} = \partial_z v_z \quad (4.22)$$

As in the sections before, the above equations are written into conservation form:

$$\partial_t \mathbf{Q} + \underline{\mathbf{A}} \partial_z \mathbf{Q} = \mathbf{RHS} \quad (4.23)$$

$$\mathbf{Q} = (T_e, q_e, T_l, q_l, v_z, \varepsilon_{zz})^T \quad (4.24)$$

$$\underline{\mathbf{A}} = \begin{pmatrix} 0 & \frac{1}{C_e} & 0 & 0 & 0 & 0 \\ \frac{K_e}{\tau_e} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{C_l} & 0 & 0 \\ 0 & 0 & \frac{K_e}{\tau_l} & 0 & 0 & 0 \\ 0 & 0 & \frac{(3\lambda_1 + 2\mu_2)\alpha_{th}}{\rho} & 0 & 0 & -\frac{\lambda_1 + 2\mu_2}{\rho} \\ 0 & 0 & 0 & 0 & 1 & 0 \end{pmatrix} \quad (4.25)$$

$$\mathbf{RHS} = \begin{pmatrix} -\frac{1}{C_e} G(T_e - T_l) + \frac{\alpha_{abs}}{C_e} I(z, t) \\ -\frac{1}{\tau_e} q_e \\ \frac{1}{C_l} G(T_e - T_l) \\ -\frac{1}{\tau_l} q_l \\ 0 \\ 0 \end{pmatrix} \quad (4.26)$$

The intensity distribution  $I(z, t)$  on the right-hand side is given by a Gaussian pulse which is partially reflected at the sample surface ( $z = 0$ ). There, the reflectivity  $R$  depends on the electron density  $n_e$  present at the material surface:  $R = R(n_e(z = 0, t))$ . The absorption of the laser

radiation mostly occurs within the optical penetration depth  $\delta_{\text{opt}}$  which also depends on the free electron density  $\delta_{\text{opt}} = \delta_{\text{opt}}(n_e(z = 0, t))$ . To compute the intensity distribution within the sample multiple approaches are possible:

1. Solving Maxwells equations within the material with transient optical properties (eqs. (3.1) to (3.4))
2. Solve the electromagnetic wave equation (eq. (3.7))
3. Solve the transport equation for a Gaussian pulse (eq. (3.72))
4. Use Lambert-Beer's law

The first two approaches require sophisticated numerical methods (see. e.g. [8, 99]) and are not addressed within this work. The other two approaches are compared in section 6.5.

To numerically solve eq. (4.23) for  $z \in [0, L]$ , proper boundary and initial conditions are necessary. Heat losses through the front surface during the heating process are assumed to be negligible [45, 93, 100]:

$$q_e(z = 0, t) = 0 \quad (4.27)$$

$$q_l(z = 0, t) = 0 \quad (4.28)$$

Since the thickness of a sample exceeds the length  $L$  of the one-dimensional computational domain absorbing boundaries have to be set at  $z = L$ . The numerical realization of the absorbing boundary conditions is given by [101] and can be found in section 5.5. As for the mechanical problem, the front interface is a free surface, which can freely move. Thus, it is assumed to be stress-free:

$$\sigma_{zz}(z = 0, t) = 0 \quad (4.29)$$

which implies (c.f. eq. (3.109)) the boundary condition for  $\varepsilon_{zz}$ :

$$\varepsilon_{zz}(z = 0, t) = \frac{(3\lambda_1 + 2\mu_2)\alpha_{\text{th}}(T_1(z = 0, t) - T_0)}{\lambda_1 + 2\mu_2} \quad (4.30)$$

Furthermore, the following initial conditions are utilized:

$$I(z, t = 0) = (1 - R(n_e(z = 0, t = 0))) I_0 \exp(-16 \ln(2)) \quad (4.31)$$

$$T_e(z, t = 0) = T_0 \quad (4.32)$$

$$T_l(z, t = 0) = T_0 \quad (4.33)$$

$$\sigma_{xx}(z, t = 0) = \sigma_{zz}(z, t = 0) = \sigma_{yy}(z, t = 0) = 0 \quad (4.34)$$



# 5 Numerical Implementation

This chapter focusses on the algorithm, that is implemented to solve the hyperbolic set of partial differential equations given in eq. (4.23). Many numerical schemes have difficulties solving hyperbolic partial differential equations as they tend to cause oscillations in the solution. A way to deal with the oscillations is by introducing an artificial, numerical dissipation. This chapter covers a Lax-Friedrichs algorithm which is extended with a Predictor-Evaluate-Corrector scheme. Additionally, the implementation of absorbing boundary conditions after Gerrit Mur is provided.

## 5.1 Lax-Friedrichs Algorithm

Peter Lax and Kurt O. Friedrichs introduced a first order forward in time, centered in space (FTCS) scheme with a numerical dissipation which is particularly well-suited for solving partial differential equation (PDE)s involving shocks or discontinuities, as it can handle steep gradients without generating spurious oscillations.

Given the Hamiltonian-Jacobi equation:

$$\partial_\tau Q(\xi, \tau) + \underbrace{\underline{A} \cdot \partial_\xi Q(\xi, \tau)}_{:= H_{\mathbf{H}}(Q)} = 0 \quad (5.1)$$

where  $\xi \in [0, 1]$  is discretized by an uniform mesh  $\xi_i = i\Delta x$  into  $N$  increments. With the solution vector  $Q$  at position  $\xi_i$  being denoted

as  $Q_i = Q(\xi_i, \tau)$ , we can define:

$$\Delta_+ Q = Q_{i+1} - Q_i \quad (5.2)$$

$$\Delta_- Q = Q_i - Q_{i-1} \quad (5.3)$$

$$(5.4)$$

Then a numerical Hamiltonian  $\hat{H}_{\text{num}}$  can be defined with the left- and right-sided derivatives ( $u_-$  and  $u_+$ ) as:

$$H_{\text{H}}(Q) = \hat{H}_{\text{num}}\left(\frac{\Delta_+ Q}{\Delta x}, \frac{\Delta_- Q}{\Delta x}\right) = \hat{H}_{\text{num}}(u_-, u_+) \quad (5.5)$$

The simplest numerical Hamiltonian is the Lax-Friedrichs Hamiltonian [102]:

$$\hat{H}_{\text{LF}}(u_-, u_+) = H_{\text{H}}\left(\frac{u_- + u_+}{2}\right) - \frac{1}{2}\hat{\alpha}(u_+ - u_-) \quad (5.6)$$

$$\hat{\alpha} = \max|\partial_{\xi} H_{\text{H}}(Q)| \quad (5.7)$$

where  $\hat{\alpha}$  is the maximum eigenvalue of the Hamiltonian, which corresponds to the transport velocity of the information. Using the Lax-Friedrichs Hamiltonian eq. (5.1) can be solved using different time integration schemes.

## 5.2 Time Step Size Evaluation

To ensure numerical stability while solving hyperbolic partial differential equations, convergence criteria have to be met. In hyperbolic PDEs, information travels with a velocity  $\hat{\alpha}$  over a grid with a spacing of  $\Delta x$ . The necessary time step size  $\Delta t$  for convergence is then given by the Courant-Friedrichs-Lewy condition (CFL) [103]:

$$C_{\text{cfl}} = \frac{\hat{\alpha} \cdot \Delta t}{\Delta x} \quad (5.8)$$

where  $C_{\text{cfl}}$  is the Courant-Friedrichs-Lewy number which has to be smaller than 1 to ensure numerical stability. Within this treatise  $C_{\text{cfl}}$  is chosen to be fixed to  $C_{\text{cfl}} = 0.5$ .

## 5.3 Predictor-Evaluate-Corrector Scheme

Predictor-Evaluate-Corrector (PEC) schemes are numerical methods commonly used to solve an ordinary differential equation (ODE) or systems of ODEs. Depending on how often the corrector method is applied and how the corrections are weighted, there are different versions of a PEC. All versions are operating in two common steps [104]:

- The predictor step starts by anticipating the solution at the new time step (Often this is done by an explicit forward Euler method).
- Subsequently, the corrector step follows and refines the anticipated solution by using the predicted value and another method to compute the unknown solution at the same new time step with higher accuracy (e.g., by using an implicit method).

Thus, given the ODE:

$$\partial_t y = f(t, y) \quad (5.9)$$

$$y(t_0) = y_0 \quad (5.10)$$

and the time discretization  $y(t_i = i \cdot \Delta t) = y_i$  with the time step width  $\Delta t$ . Using Euler's method, we can write

$$\tilde{y}_{i+1} = y_i + \Delta t \cdot f(t_i, y_i) \quad (5.11)$$

$$y_{i+1} = y_i + \frac{1}{2} \Delta t (f(t_i, y_i) + f(t_{i+1}, \tilde{y}_{i+1})) \quad (5.12)$$

In general, to reach better accuracy the PEC corrector step can be repeated  $n$  times P(EC)<sup>n</sup>.

## 5.4 Solution for Layered Systems

To solve the equations given in chapter 4, a Lax-Friedrichs algorithm (c.f. section 5.1) is combined with the PEC method given in section 5.3. The materials considered in this thesis consist of multiple

layers with different physical properties and material laws. Therefore, different approaches are typically made to solve the equations on the computational domain:

- The computational domain is divided into subdomains (containing the different materials) on which the equations are solved individually. Then, the coupling of each domain has to be treated with appropriate boundary conditions
- The equations are solved on the full domain and the numerical scheme has to contain the different material properties.

Within this work, the second approach is chosen. Hence, the solution vector  $\mathbf{Q}$  and the system matrix  $\mathbf{A}$  are of dimension  $N \cdot N_s$  and  $(N \cdot N_s) \times (N \cdot N_s)$ , respectively. Here  $N$  corresponds to the number of increments in which the computational domain is divided and  $N_s$  to the number of solution variables. Consequently, the solution vector  $\mathbf{Q}$  and the system matrix  $\mathbf{A}$  are given by:

$$\mathbf{Q} = \underbrace{(a_0, \dots, a_N, b_0, \dots, b_N, \dots)}_{\# \text{ of Entries} = N \cdot N_s})^T \quad (5.13)$$

$$\mathbf{A} = \begin{pmatrix} a_{00} & a_{01} & \cdots & a_{0N_s} \\ a_{10} & a_{11} & \cdots & a_{1N_s} \\ \vdots & \vdots & \ddots & \vdots \\ a_{N_s 1} & a_{N_s 2} & \cdots & a_{N_s N_s} \end{pmatrix} \quad (5.14)$$

Each entry  $a_{ij}$  of the system matrix  $\mathbf{A}$  is a  $(N \times N)$  diagonal matrix with the corresponding material properties for each depth increment. Since all solution variables are contained in the solution vector  $\mathbf{Q}$ , special care has to be taken with the boundary conditions for each solution variable and while computing the left- and right-sided derivatives  $u_-$  and  $u_+$ . Therefore, the solution vector is divided into  $N_s$  sub-vectors where the derivatives and boundary conditions can be computed or set easily. The use of sparse matrices is recommended since the system matrix  $\mathbf{A}$  mostly contains zeros.

## 5.5 Absorbing Boundary Conditions

For a transport problem in one dimension, such as eq. (5.1) using finite differences time domain (FDTD) schemes, absorbing boundary conditions for the solution vector  $Q$  are easily implemented e.g., by using Mur boundary conditions [101, 105]. Let  $Q_i^n$  be the solution at  $x_i = i \cdot \Delta x$  and time step  $t_n = n \cdot \Delta t$  and consider the boundary at  $x = 0$  (i.e.,  $i = 0$ ), then:

$$u_s = \hat{\alpha} \cdot \Delta t / \Delta x \quad (5.15)$$

$$Q_0^{n+1} = Q_1^n + \frac{u_s - 1}{u_s + 1} \cdot (Q_1^n - Q_0^{n-1}) \quad (5.16)$$

where  $\hat{\alpha}$  is the maximum eigenvalue of  $A$  (c.f. eqs. (5.1) and (5.7)). The maximum eigenvalue  $\hat{\alpha}$  corresponds transport velocity of the problem.

## 5.6 Used Programming Libraries

The implementation of the threshold ablation model and the Lax-Friedrichs algorithm is based on the programming language Python. Table 5.1 summarizes the Python libraries, that were used for the implementation.

**Table 5.1:** Summary of the relevant Python package versions

| Name       | version |
|------------|---------|
| python     | 3.11.3  |
| lmfit      | 1.2.2   |
| matplotlib | 3.7.2   |
| numpy      | 1.25.1  |
| pandas     | 2.0.3   |
| pint       | 0.22    |
| scipy      | 1.11.1  |
| tmm        | 2.0.1   |
| tqdm       | 4.65.0  |

# 6 Analysis and Experimental Validation

In this chapter the physical models, developed in chapter 4, are compared to experimental results. Starting with the steady state optical properties the dielectric function of ITO is calibrated from UV-Vis measurements taken from [77]. Based on the steady state optical properties, the transient optical properties during laser excitation are investigated by consideration of ionization and free electron dynamics within the thin films. Next, the threshold ablation model, described in section 4.1, is extended to semiconducting thin films by using the transient optical penetration depth and compared to experimental ablation craters in ITO thin films (with thicknesses 50 nm, 100 nm & 180 nm) and 60 nm silicon nitride ( $\text{Si}_3\text{N}_4$ ) thin films [106, 107]. Furthermore, the influence of the peak fluence on the ablation mechanisms is analyzed with a combination of the two temperature-model and the elastodynamic model, as proposed in section 4.4. The solution of the combined model is obtained by utilization of the numerical implementation explained in chapter 5. Finally, a possible approach for damage-free processing of transparent thin films is given by changing the optical penetration depth of the material via free electron generation.

## 6.1 Material Properties

### 6.1.1 Sample Description

The ITO samples considered in this work consist of ITO films with different thicknesses over a 25 nm  $\text{SiO}_2$  passivation layer on top of a 1.1 mm float glass substrate and are produced by *Präzisions Glas &*

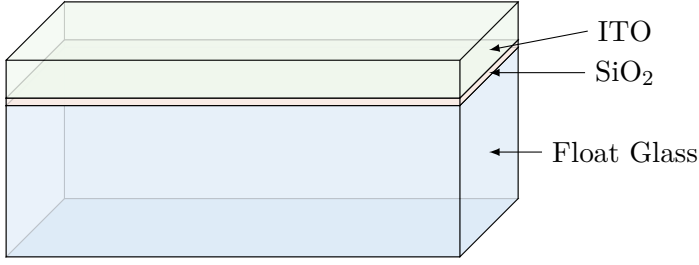


**Figure 6.1:** Schematic sketch of the ITO-samples. The actual thicknesses for the layers are: ITO 100 nm, SiO<sub>2</sub> 25 nm, float glass 1.1 mm.

*Optik GmbH, Iserlohn, Germany.* The investigated film thicknesses are 50 nm, 100 nm and 180 nm, respectively. A schematic sketch of the used 100 nm samples is shown in fig. 6.1 The sheet resistance of the 100 nm samples is specified to be smaller than  $20 \Omega/\square$  [108]. To successfully predict the interaction between laser radiation and thin films, a series of material parameters is required. The relevant material parameters, necessary to model the laser material interaction in ITO, SiO<sub>2</sub>, and the float glass substrate are summarized in tables 6.1 to 6.3.

## 6.2 Steady State and Transient Optical Properties of ITO

The material response to an external electromagnetic field and thus its optical properties can be modeled by use of the dielectric function. The dielectric function of the ITO films  $\varepsilon_{\text{ITO}}$  is utilized for the computation of the absorption, reflectivity, and transmission of the ITO film. For ITO, the dielectric function  $\varepsilon_{\text{ITO}}$  consists of three contributions: the bound electron contribution  $\varepsilon_{\text{TL}}$ , the free electron contribution  $\varepsilon_{\text{Drude}}$  and a dielectric background  $\varepsilon_{\infty}$  [77]:

$$\varepsilon_{\text{ITO}}(\omega, n_e) = \varepsilon_{\infty} + \varepsilon_{\text{TL}}(\omega, n_e) + \varepsilon_{\text{Drude}}(\omega, n_e) \quad (6.1)$$

**Table 6.1:** Relevant material parameters of ITO

| Name                       | Symbol               | Value                                                | Ref.  |
|----------------------------|----------------------|------------------------------------------------------|-------|
| Dielectric Background      | $\varepsilon_\infty$ | 1.96                                                 | [77]  |
| Resonator Strength         | $A$                  | 190.02 eV                                            | [77]  |
| Resonator Energy           | $E_{0,TL}$           | 5.07 eV                                              | [77]  |
| Resonator Broadening       | $C$                  | $1.20 \times 10^{-5}$ eV                             | [77]  |
| Intrinsic Bandgap          | $\Delta_0$           | 4.04 eV                                              | [77]  |
| Plasma Frequency           | $\omega_p$           | $2.02 \times 10^{15}$ rad s <sup>-1</sup>            | [77]  |
| El. Coll. Frequency        | $\gamma_{el}$        | $1.70 \times 10^{14}$ rad s <sup>-1</sup>            | [77]  |
| Param. for El. Coll. Freq. | $\beta$              | 0.1                                                  | [77]  |
| Max. El. Coll. Freq.       | $\gamma_{max}$       | $2.98 \times 10^{14}$ rad s <sup>-1</sup>            | [77]  |
| Electron Effective Mass    | $m_e^*$              | $0.53 \cdot m_e$                                     | [109] |
| Molecular Mass             | $M_{mole}$           | $7.14 \times 10^{-25}$ kg                            | [110] |
| Two Particle Rec. Rate     | $\eta_{2p}$          | $4.5 \times 10^{-17}$ m <sup>3</sup> s <sup>-1</sup> | [77]  |
| Auger Recombination Rate   | $\eta_{Auger}$       | $0.9 \times 10^{-45}$ m <sup>6</sup> s <sup>-1</sup> | [77]  |
| Latent Heat for Evap.      | $Q_{evap}$           | $5 \times 10^6$ J kg <sup>-1</sup>                   | [43]  |
| Poisson's Ratio            | $\nu_{poisson}$      | 0.31                                                 | [111] |
| Young's Modulus            | $E_y$                | $175 \times 10^9$ Pa                                 | [111] |
| Thermal Expansion Coef.    | $\alpha_{th}$        | $5.81 \times 10^{-6}$ K <sup>-1</sup>                | [112] |
| Density                    | $\rho$               | $7.1$ g cm <sup>-3</sup>                             | [113] |

**Table 6.2:** Relevant material parameters of SiO<sub>2</sub>

| Name                               | Symbol                 | Value                                          | Ref.  |
|------------------------------------|------------------------|------------------------------------------------|-------|
| Bandgap                            | $\Delta$               | 7.8 eV                                         | [50]  |
| Resonance Frequency                | $\omega_{\text{res}}$  | $20.59 \times 10^{15} \text{ rad s}^{-1}$      | [8]   |
| Bound Electron Density             | $n_{\text{b}}$         | $1.46 \times 10^{29} \text{ m}^{-3}$           | [8]   |
| Param. for El. Coll. Freq.         | $\beta$                | 0.1                                            | [8]   |
| Max. El. Coll. Freq.               | $\gamma_{\text{max}}$  | $1 \times 10^{16} \text{ rad s}^{-1}$          | [8]   |
| Electron Effective Mass            | $m_{\text{e}}^*$       | $m_{\text{e}}$                                 | [109] |
| Molecular Mass                     | $M_{\text{mole}}$      | $7.14 \times 10^{-25} \text{ kg}$              | [114] |
| Molar Mass                         | $M_{\text{mol}}$       | $60.0843 \times 10^{-3} \text{ kg mol}^{-1}$   | [115] |
| Two Particle Rec. Rate             | $\eta_{2\text{p}}$     | $2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ | [91]  |
| Latent Heat for Evap. <sup>a</sup> | $Q_{\text{evap}}$      | $8.014 \times 10^6 \text{ J kg}^{-1}$          | [116] |
| Poisson's Ratio                    | $\nu_{\text{poisson}}$ | 0.179                                          | [117] |
| Young's Modulus                    | $E_{\text{y}}$         | $73 \times 10^9 \text{ Pa}$                    | [118] |
| Thermal Expansion Coef.            | $\alpha_{\text{th}}$   | $5.24 \times 10^{-7} \text{ K}^{-1}$           | [119] |
| Density                            | $\rho$                 | $2.219 \times 10^3 \text{ kg m}^{-3}$          | [116] |

<sup>a</sup>Average of different values reported on p. 2083 [116]:  $(481 \text{ J mol}^{-1} + 484 \text{ J mol}^{-1} + 425 \text{ J mol}^{-1} + 536 \text{ J mol}^{-1})/4 = 481.5 \times 10^3 \text{ J mol}^{-1}$ . Using the molar mass  $M_{\text{mol}}$  given in the table, this equals  $8.014 \times 10^6 \text{ J kg}^{-1}$ .

**Table 6.3:** Relevant material parameters of float glass

| Name                    | Symbol                 | Value                                  | Ref.  |
|-------------------------|------------------------|----------------------------------------|-------|
| Bandgap                 | $\Delta$               | 3.2 eV                                 | [120] |
| Latent Heat for Evap.   | $Q_{\text{evap}}$      | $1.8 \times 10^6 \text{ J kg}^{-1}$    | [121] |
| Poisson's Ratio         | $\nu_{\text{poisson}}$ | 0.23                                   | [122] |
| Young's Modulus         | $E_{\text{y}}$         | $57.5 \times 10^9 \text{ Pa}$          | [122] |
| Thermal Expansion Coef. | $\alpha_{\text{th}}$   | $7.8975 \times 10^{-6} \text{ K}^{-1}$ | [123] |
| Density                 | $\rho$                 | $2.508 \times 10^3 \text{ kg m}^{-3}$  | [122] |

**Table 6.4:** Laser parameters for material processing of the ITO samples

| Name                            | Symbol                      | Value            | Ref. |
|---------------------------------|-----------------------------|------------------|------|
| Wavelength Pump                 | $\lambda_{\text{pump}}$     | 1056 nm          | [77] |
| Wavelength Probe                | $\lambda_{\text{probe}}$    | 528 nm           | [77] |
| Angle of Incidence Pump         | $\alpha_{\text{inc,pump}}$  | 38.7°            | [77] |
| Angle of Incidence Probe        | $\alpha_{\text{inc,probe}}$ | 0°               | [77] |
| Pulse Duration                  | $\tau_p$                    | 700 fs           | [77] |
| Beam Radius (1/e <sup>2</sup> ) | $w_0$                       | 15 $\mu\text{m}$ | [77] |

The dielectric function for the SiO<sub>2</sub> layer is a Drude-Lorentz model  $\varepsilon_{\text{SiO}_2} = \varepsilon_{\text{DL}}$  taken from [8]. The dielectric function for the float glass sample  $\varepsilon_{\text{Float}}$  is taken from [124], respectively. To obtain the parameters for the steady state optical properties, a calibration of the model parameters for the dielectric function of the ITO film  $\varepsilon_{\text{ITO}}$  is carried out. Therefore,  $\varepsilon_{\text{ITO}}$  is fitted to UV-Vis-measurements by using a Levenberg-Marquardt least-square optimization algorithm [77, 125]. The comparison between the measured and computed values for the reflectivity and transmission spectra for the ITO sample are shown in figs. 6.2 and 6.3, respectively. The measurement of the steady reflectivity  $R_{\text{meas}}$  is carried out at an angle of incidence of  $\alpha_{\text{inc}} = 8^\circ$  while the measurement of the transmission  $T_{\text{meas}}$  is performed at normal incidence  $\alpha_{\text{inc}} = 0^\circ$ . It is obvious from fig. 6.2 that the consideration of a single air-ITO-interface reflectivity by computation with the Fresnel reflectivity  $R_{\text{F}}$  (eqs. (3.26) to (3.28)) is not sufficient to describe the measured steady state reflectivity spectrum. In equilibrium, ITO has an optical penetration depth of  $\delta_{\text{opt}} = 1.17 \mu\text{m}$ . This is larger than the film thickness  $\delta_{\text{film}} = 100 \text{ nm}$ . Thus, thin film interferences dominate the measured and computed reflectivity and transmission spectra. Consequently, the transfer matrix method TMM has to be used to model the steady state optical properties. In the following, the origin of the maxima and minima in the reflectivity spectrum are explained. The first reflectivity maximum can be found

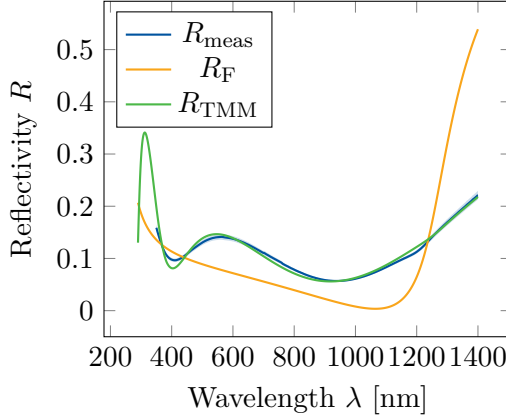


**Figure 6.2:** Measured and computed reflectivity  $R$  at an angle of incidence of  $\alpha_{\text{inc}} = 8^\circ$ . The measured data is depicted as the blue line while the computed values for the Fresnel reflectivity  $R_{\text{F}}$  and the reflectivity  $R_{\text{TMM}}$  computed from the TMM are shown as the orange and green lines, respectively [77].

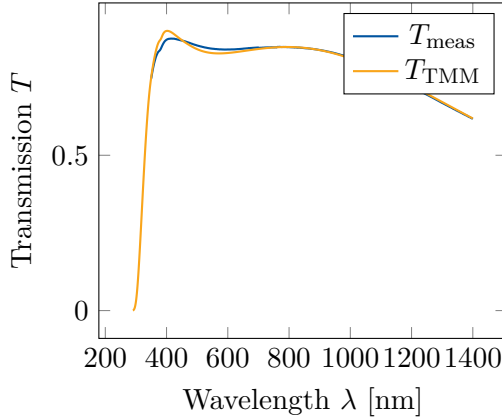


**Figure 6.3:** Measured and computed transmission  $T$  at an angle of incidence of  $\alpha_{\text{inc}} = 0^\circ$ . The measured data is depicted as the blue line while the computed values using the TMM are shown as the orange line [77].

at  $\lambda_{\max} = 321 \text{ nm}$  and is a result from a constructive interference within the ITO-layer. This explains the increase of reflectivity at the lower end of the measured wavelengths ( $\lambda = 350 \text{ nm}$ ). The optical path difference  $\Delta\lambda$  of the incoming and reflected wave from the ITO-SiO<sub>2</sub>-interface is given by  $\Delta\lambda = 2 \cdot \delta_{\text{film}} = 1.5 \cdot \lambda_{\max}/n_{\text{ITO}}(\lambda_{\max})$ . Here, the wavelength dependent refractive index of ITO  $n_{\text{ITO}}(\lambda_{\max})$  is given by  $n_{\text{ITO}}(\lambda) = \sqrt{\varepsilon_{\text{ITO}}(\omega = 2\pi c/\lambda, n_e = n_{e,\text{init}})}$  (c.f. eq. (6.1)). Due to the ratio of refractive indices  $n_{\text{ITO}} > n_{\text{Air}}$ , a total phase shift of  $\pi$  has to be taken into account for the reflection at the air-ITO-interface. The same phase shift of  $\pi$  has to be considered for the first reflectivity minimum at  $\lambda_{\min} = 411 \text{ nm}$ . Here, the path difference equals  $\Delta\lambda = 2 \cdot \lambda_{\min}/n_{\text{ITO}}(\lambda_{\min})$  leading to destructive interference. The last reflectivity minimum at  $\lambda = 937 \text{ nm}$  matches with the plasma frequency and free carrier absorption. Compared to a pure Drude model  $\varepsilon_{\text{Drude}}$ , the polarizability of the bound electrons (Tauc-Lorentz dielectric function  $\varepsilon_{\text{TL}}$ ) and the dielectric background  $\varepsilon_{\infty}$  result in a shift of the critical electron density to higher electron densities. Therefore, the effective plasma frequency becomes [55]:  $\tilde{\omega}_p = \sqrt{n_e e^2 / (\varepsilon_{\infty}^* \varepsilon_0 m_e^*)} \rightarrow \lambda_p = 935 \text{ nm}$  with  $\varepsilon_{\infty}^* = \varepsilon_{\infty} + \Re(\varepsilon_{\text{TL}})$ , where  $\Re$  corresponds to the real part of the dielectric function. At this wavelength, the light is transmitted through the ITO film and therefore reflected at the SiO<sub>2</sub>, and the float glass interfaces. This prevents the reflectivity from decreasing to zero as one would expect for bulk material. For smaller wavelengths the optical penetration depth increases in the plasma. Thin film interferences become less relevant as soon as the optical penetration depth  $\delta_{\text{opt}}$  becomes smaller than the film thickness  $\delta_{\text{opt}} < \delta_{\text{film}}$ . Then, the radiation is absorbed before reaching the material interfaces, which can lead to reflections and interferences. In equilibrium, due to the Sn doping, ITO already has a large free electron density of  $n_{e,\text{init}} \approx 1.32 \times 10^{27} \text{ m}^{-3}$ . Thus, the main ionization process is cascade ionization which drastically increases the free electron density during the laser pulse (c.f. section 3.1.6). The increase of the free electron density leads to a reduction of the optical penetration depth. For this reason, thin film interferences dominate the static optical properties, but become less important for electron

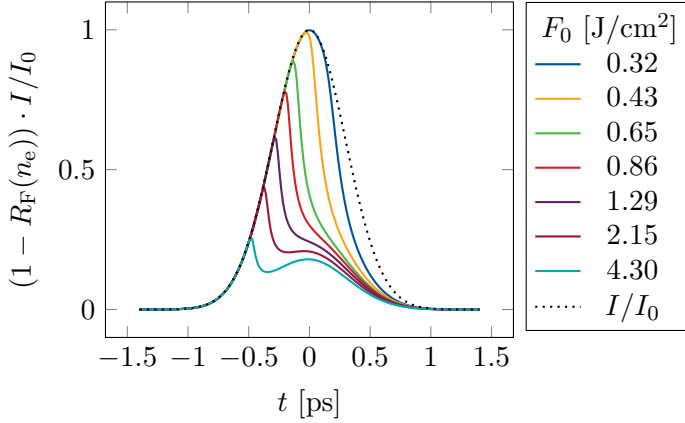


**Figure 6.4:** Temporal evolution of the normed effective intensity transmitted through the sample surface  $(1 - R_F(n_e)) \cdot I$  for a 700 fs laser pulse with different peak fluences  $F_0$ . The black dotted line shows the corresponding normalized intensity distribution without interaction with the sample.

densities larger than  $n_e = 4.254 \times 10^{27} \text{ m}^{-3}$ .

In the following, the influence of the electron generation on the optical properties during the laser pulse is demonstrated and used for the threshold ablation model later. The free electron density  $n_e$  itself is a function of the intensity  $I$  and is assumed to be constant over the depth within the ITO film. It is worth mentioning, that the electron density is still a function of the radial position as the laser spot dimension of some tens of micrometers is much larger than the film thicknesses and the radial intensity distribution follows a Gaussian distribution. Figure 6.4 shows the temporal evolution of the intensity which is transmitted through the sample surface  $(1 - R_F(n_e)) \cdot I$  for different peak fluences  $F_0$ . As a reference, the full incident intensity irradiating the sample is shown as the black dotted line in figs. 6.4 to 6.6, respectively. The change in free electron density changes the reflectivity  $R_F$  of the sample surface, leading to reflection of the incident intensity. Increasing the peak fluence  $F_0$  (i.e., increasing the peak intensity  $I_0$ )

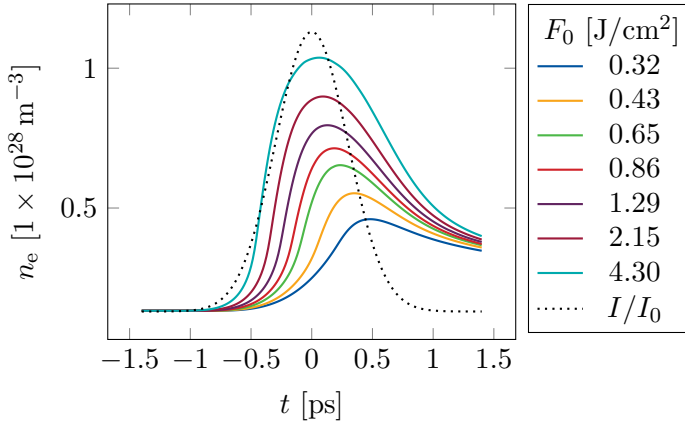


**Figure 6.5:** Temporal evolution of the free electron density  $n_e$  for a 700 fs laser pulse with different peak fluences  $F_0$ . The black dotted line shows the corresponding normalized intensity distribution without interaction with the sample.

results in stronger ionization which causes the surface to reflect more of the incident intensity. The corresponding free electron density  $n_e$  is computed by use of the rate eq. (3.59) described in section 3.1.6 with the use of the effective intensity  $(1 - R_F(n_e))I$ .

The maximum free electron density  $n_{e,\max}$  is reached after the intensity of the laser pulse reaches its peak because ionization of electrons is not instantaneous but takes time (c.f section 3.1.6 and eq. (3.64)). The material parameters of ITO which are used for the computation can be found in table 6.1. The maximum free electron density  $n_{e,\max}$  depends on multiple effects and process parameters: The peak intensity  $I_0$  of the laser pulse, the recombination rate  $w_{\text{rec}}$  and the bandgap  $\Delta$  of the material. Due to the Burstein-Moss-effect, the bandgap increases with a higher degree of ionization (see fig. 3.5 and eq. (3.67)). This is used in solving the rate equation for the free electron density and the dielectric function of ITO (c.f. eq. (6.1)). If the Burstein-Moss-effect would be neglected Additionally, the electron collision time reduces with increasing the free electron density (c.f. eq. (3.39)). Analogous

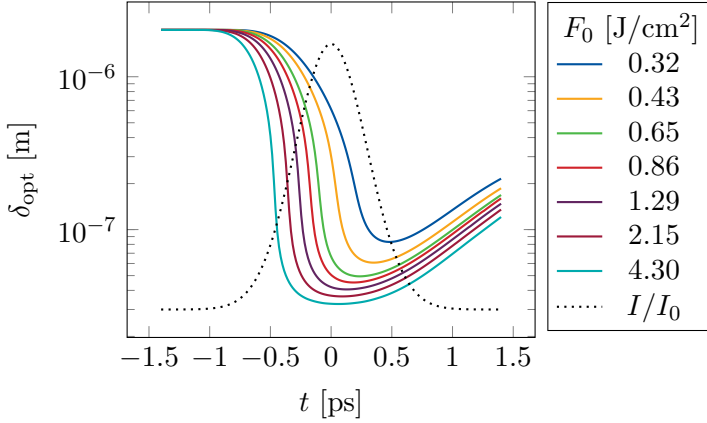


**Figure 6.6:** Temporal evolution of the optical penetration depth for different peak fluences  $F_0$ . The used laser pulse duration and wavelength is  $\tau_p = 700$  fs and  $\lambda = 1056$  nm, respectively. The black dotted line shows the corresponding normalized intensity distribution without interaction with the sample.

to the reflectivity, the optical penetration depth depends on the free electron density  $n_e$  because the dielectric function depends on the free electron density  $\delta_{\text{opt}} = \delta_{\text{opt}}(n_e)$ . Figure 6.6 shows the temporal evolution of the optical penetration depth during the laser pulse with a wavelength of  $\lambda = 1056$  nm and a pulse duration  $\tau_p = 700$  fs for different peak fluences  $F_0$ . In the beginning of the 1056 nm laser pulse the optical penetration depth  $\delta_{\text{opt}}$  equals the static value  $\delta_{\text{opt}} = 1.17 \mu\text{m}$ . As soon as the free electron density increases to its maximum, the optical penetration depth decreases until it reaches a minimum during the pulse duration. Depending on the peak fluence  $F_0$ , the minimum value ranges from 17 nm to 80 nm. Higher peak fluences lead to smaller optical penetration depths due to the generation of larger free electron densities.

## 6.3 Threshold Ablation Model - ITO

The threshold ablation model has been extensively used to model and predict ablation crater widths and depths for metals and other materials [126–128]. For semiconductors and insulators (e.g. Si, SiO<sub>2</sub> and other glasses) however, there exist a few more sophisticated models to describe the ablation craters and damage regions by consideration of free electron dynamics, electromagnetic wave propagation, and TTM [9, 49, 50, 91]. In glasses, if the free electron density exceeds the critical electron density ( $n_e \geq n_{e,\text{crit}}$ ) the material is assumed to be ablated. For this purpose, either beam propagation methods or the wave equation for the electric field are solved numerically. The electron density is computed as a function of the intensity, resulting from the electric field amplitude [8, 9]. A big advantage of the threshold model (see section 4.1) is that it does not require sophisticated numerical methods and solution algorithms such as the beam propagation method or Maxwell equation solvers, used for glasses.

Within this section, the threshold model will be extended to be applicable to dielectrics by consideration of the change in optical properties due to free electron generation. As described in section 3.1.4, the material becomes metal-like if the electron density of the material exceeds the critical electron density  $n_{e,\text{crit}}$ . For this reason, for some dielectrics the threshold fluence matches with the fluence, which is required to excite enough electrons to reach the critical electron density  $n_{e,\text{crit}}$ . However, reaching the critical electron density cannot be considered as an universal ablation criterion in semiconductors [6].

As already described, the optical and thermal properties of semiconductors depend on the temperature and the free electron density which both depend on the laser parameters (see sections 3.1.4 and 3.1.8). The optical penetration depth can decrease around several orders of magnitude during an intense ultrashort laser pulse. Within this section, the threshold ablation model is compared to experimental ablation craters. All crater profiles are measured by the use of an atomic force microscope (AFM) and are measured at Hochschule München [106]. Figures 6.7 to 6.9 show selected ablation craters for 700 fs laser pulses

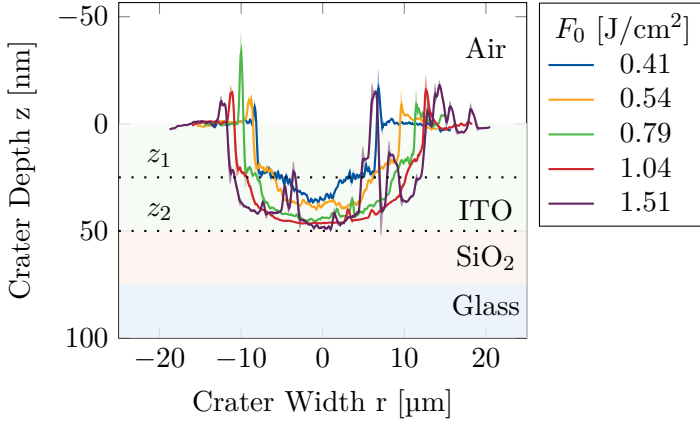


**Figure 6.7:** Experimental single pulse ablation craters for 50 nm ITO films for different peak fluences at a pulse duration of 700 fs. There are two depth plateaus visible at  $z_1 \approx 25$  nm and  $z_2 \approx 50$  nm, of which the latter matches with the film thickness. Each plateau is indicated by the black dotted lines. The measurement is taken from [106].

with varying peak fluences on ITO-samples with the thicknesses 50 nm, 100 nm and 180 nm. Sharp vertical transitions to a first plateau are observable at the radial positions where the Gaussian fluence equals the threshold fluence  $F(r) = F_{\text{thr}}$ . The sharp vertical transitions are found for all peak fluences  $F_0$  and film thicknesses. For small fluences, the ablation crater depths are almost constant at the depth plateau  $z_1$  indicated in figs. 6.7 to 6.9, respectively. While increasing the peak fluence for a film thickness of  $\delta_{\text{film}} = 50$  nm results in ablation of the full film, a second plateau is reached at  $z_2 \approx 70$  nm at a peak fluence of  $0.79 \text{ J cm}^{-2}$ , and a film thickness of  $\delta_{\text{film}} = 100$  nm. Increasing the peak fluence even further ( $F_0 \geq 2.15 \text{ J cm}^{-2}$ ) results in full ablation of the 100 nm film. Full ablation of the ITO films with a film thickness of 180 nm could not be achieved in the investigated fluence regime. The maximum ablation depth achieved for a peak fluence  $F_0 = 4.11 \text{ J cm}^{-2}$  is 135 nm. Ridge formation can be found

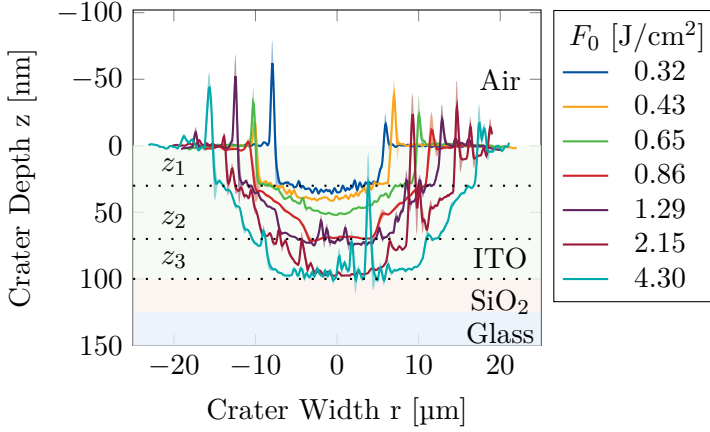


**Figure 6.8:** Experimental single pulse ablation craters for 100 nm ITO films for different peak fluences at a pulse duration of 700 fs. There are three depth plateaus visible at  $z_1 = 30$  nm,  $z_2 = 70$  nm and  $z_3 = 100$  nm. Each plateau is indicated by the black dotted lines. The first two plateaus originate from the first and second spallation and the third equals the film thickness  $z_3 \approx \delta_{\text{film}}$ . The measurement is taken from [106].

around all craters with heights ranging from 15 nm to 120 nm. For each peak fluence, the maximum ridge height and the corresponding plateau depths  $z_i$  are summarized in table 6.5. A comparison of the measured ablation depths for the film thicknesses of 50 nm, 100 nm and 180 nm as a function of the peak fluence  $F_0$  is shown in fig. 6.16. For each peak fluence, the measured ablation depth in the center of the ablated crater is obtained by averaging the depth-values in the region  $|r| \leq 3 \mu\text{m}$ , where the standard deviation is used as the corresponding error. The film thicknesses for the 50 nm and 100 nm films are shown with the dotted lines as a guide to the eye. The threshold ablation model, which is described in section 4.1, can be used to compute the ablation depths of the craters. The crater depths as a function of the peak fluence are computed by the use of eq. (4.7) and are shown in fig. 6.16 as well. The threshold fluence  $F_{\text{thr}} = 0.22 \text{ J cm}^{-2}$  is found by

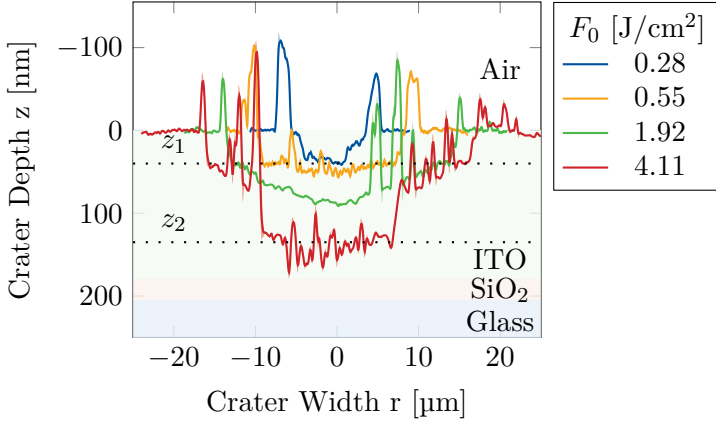


**Figure 6.9:** Experimental single pulse ablation craters for 180 nm ITO films for different peak fluences at a pulse duration of 700 fs. There are two depth plateaus visible at  $z_1 \approx 40$  nm and  $z_2 \approx 135$  nm. Each plateau is indicated by the black dotted lines. The ITO layer is not fully ablated. The measurement is taken from [106].

calibrating the computed ablation crater shapes to the measured ablation craters using a Levenberg-Marquardt least-square optimization algorithm [125]. The effective penetration depth  $\delta_{\text{eff}}$  is assumed to equal the optical penetration depth  $\delta_{\text{opt}}$  while neglecting the thermal penetration depth  $\delta_{\text{therm}}$ .

The Gaussian spatial intensity distribution of the laser pulse with a beam radius of  $w_0 \approx 14.8 \mu\text{m}$  leads to an uneven distribution of the free electron density in radial direction. The generated electron densities in the center are larger compared to the outer regions. Thus, both the reflectivity  $R_F$  and the optical penetration depth  $\delta_{\text{opt}}$  are both dependent on the radial position in the laser beam. Using the maximum free electron density that is excited by the laser pulse at each position, the optical penetration depths  $\delta_{\text{opt}} = \delta_{\text{opt}}(n_{e,\text{max}}(r))$  at the respective positions are computed using eq. (3.36). Then, the single pulse ablation crater shape is obtained by evaluation of eq. (4.7) with

**Table 6.5:** Crater depths and plateau depths for ITO samples with a film thickness of 50 nm, 100 nm and 180 nm, which are processed with 700 fs laser pulses and different peak fluences

| Layer Thickness [nm] | 50    | 100   | 180    |
|----------------------|-------|-------|--------|
| $z_1$ [nm]           | 25    | 30    | 40     |
| $z_2$ [nm]           | 50    | 70    | 100    |
| $z_3$ [nm]           | -     | 100   | -      |
| Ridge Height [nm]    | 15-50 | 15-80 | 50-120 |
| Fully Ablated?       | ✓     | ✓     | -      |

$F(r)$  and  $\delta_{\text{opt}}(n_{\text{e,max}}(r))$ . A comparison of the model and measured AFM-craters for a 100 nm and a 180 nm ITO film is shown in fig. 6.10. There is a good agreement between the overall shapes and depths of the computed and measured single pulse ablation craters. The decreasing electron distribution in radial direction results in an increase of the optical penetration depth for larger distances from the center of the beam. This causes the first plateau  $z_1$ , already mentioned in table 6.5 and fig. 6.8. For large fluences, the model slightly overestimates the crater width, while the overall modeled shape still agrees well with the measured crater shapes. While the presented extension to the threshold ablation model is able to successfully describe the crater shape, the underlying ablation mechanisms are not covered. The ablation mechanisms during thin film ablation are either photothermal or photomechanical in nature. Which mechanism is dominant depends on the used laser fluence and is discussed for the ablation of ITO layers in detail in section 6.6.

## 6.4 Threshold Ablation Model - $\text{Si}_3\text{N}_4$

$\text{Si}_3\text{N}_4$  films are often used as passivation layers for wafer structures or thin film photovoltaic solar cells [129]. For this reason, the applicability of the threshold ablation model (section 4.1) to  $\text{Si}_3\text{N}_4$  films is proven

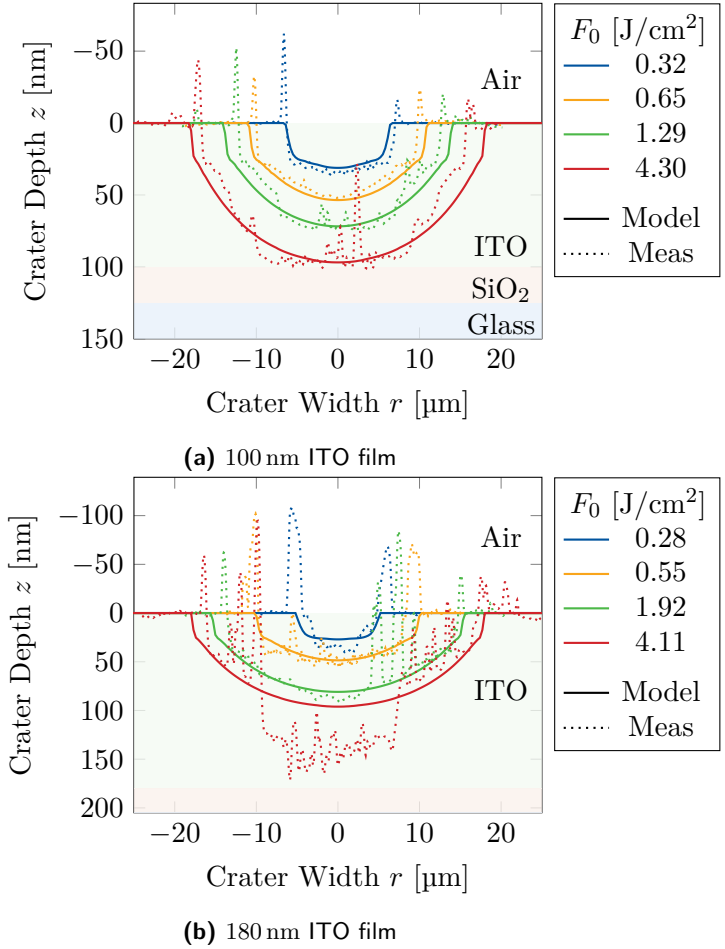


**Figure 6.10:** Comparison of the threshold ablation model (solid lines) and measured single pulse ablation crater shapes (dotted lines) in fig. 6.10a 100 nm and fig. 6.10b 180 nm ITO films for selected peak fluences.

**Table 6.6:** Laser parameters for material processing of the  $\text{Si}_3\text{N}_4$  samples [107]

| Name                    | Symbol                | Value              |
|-------------------------|-----------------------|--------------------|
| Wavelength Pump         | $\lambda$             | 1030 nm            |
| Angle of Incidence Pump | $\alpha_{\text{inc}}$ | $0^\circ$          |
| Pulse Duration          | $\tau_p$              | 200 fs             |
| Beam Radius ( $1/e^2$ ) | $w_0$                 | $13.5 \mu\text{m}$ |

in this section, by applying it to 60 nm  $\text{Si}_3\text{N}_4$  films. The experimental craters and corresponding laser parameters (see fig. 6.11 and table 6.6) are taken from [107]. Analogous to section 6.3, the optical properties of the  $\text{Si}_3\text{N}_4$  film are described by the dielectric function:

$$\varepsilon_{\text{Si}_3\text{N}_4} = \varepsilon_\infty(\omega) + \varepsilon_{\text{Drude}}(\omega, n_e) \quad (6.2)$$

where  $\varepsilon_\infty(\omega)$  corresponds to the equilibrium dielectric function for a given angular frequency  $\omega$  of the laser light and  $\varepsilon_{\text{Drude}}(\omega, n_e)$  to the free electron contribution (c.f. section 3.1.4). The equilibrium dielectric function for  $\text{Si}_3\text{N}_4$   $\varepsilon_\infty(\omega)$  is taken from [130]. Again, the rate equation for the free electron density (c.f. eq. (3.59)) is used to compute the temporal evolution of the free electron density and the optical penetration depth. In order to achieve good agreement between the threshold ablation model and the measured ablation craters in  $\text{Si}_3\text{N}_4$ , an electron density dependent bandgap (i.e., the Burstein-Moss effect) and electron collision time had to be considered. Due to the Burstein-Moss effect the bandgap (c.f. fig. 3.5) increases according to eq. (3.67) with increasing electron density. The intrinsic bandgap  $\Delta_0$  of  $\text{Si}_3\text{N}_4$  equals  $\Delta_0 = 2.71 \text{ eV}$  [130]. Similar to ITO, in  $\text{Si}_3\text{N}_4$  the electron collision time  $\tau_e$  decreases with increasing electron density since it is more likely to collide with other free electrons. However, the model for the electron collision time of ITO (c.f. eq. (3.39)) does not produce good agreement of the computed crater shapes with the experimentally observed crater shapes. For this reason, the following

calibration function for the electron collision time is introduced:

$$\tau_e(n_e) = \tau_{e,0} \cdot \frac{1}{\exp\left(\frac{n_e - n_{e,\text{crit}}}{n_{e,\text{crit}}}\right) + 1} + \tau_{e,\text{min}} \quad (6.3)$$

Here,  $\tau_{e,\text{min}}$  is the minimum electron collision time and  $n_{e,\text{crit}}$  is the critical electron density of  $\text{Si}_3\text{N}_4$ , respectively. The minimum collision time  $\tau_{e,\text{min}}$  corresponds to the inverse maximum electron collision frequency  $1/\gamma_{\text{max}}$  (see also eq. (3.39)). With the effective electron mass of  $m_e^* = 0.5 \cdot m_e$ , the critical electron density (at  $\lambda = 1030 \text{ nm}$ ) is given by  $n_{e,\text{crit}} = \omega^2 \varepsilon_\infty(\omega) \varepsilon_0 m_e^* / e^2 = 5.25 \times 10^{26} \text{ m}^{-3}$  [55, 131, 132]. The calibration function eq. (6.3) is chosen in such a way that it saturates at the equilibrium value  $\tau_{e,0}/(\exp(-1) + 1) = 3.39 \text{ fs}$  for small electron densities and at the minimum value of  $\tau_{e,\text{min}}$  after the electron density exceeds the critical electron density  $n_{e,\text{crit}}$ . Similar approaches with different calibration functions for (bulk) transparent dielectrics can be found in [8, 50]. According to Matthiessen's rule, the effective electron collision time can be estimated:  $1/\tau_e = \sum 1/\tau_i$  where the collision times  $\tau_i$  originate from different scattering mechanisms (e.g.  $\tau_{\text{phonon}}, \tau_{\text{impurities}}, \tau_{\text{defects}}, \dots$ ). In contrast to the bulk materials considered in [8, 50], for thin semiconducting films, surface scattering  $\tau_{\text{surface}}$  has to be considered [133]. Surface scattering and impurity scattering are considered to prevent the collision time from increasing to unphysically large values for small electron densities (as in [8]) and rather saturate at a maximum value. The exponential function in eq. (6.3) was introduced to describe a smooth transition between  $\tau_{e,0}$  and  $\tau_{e,\text{min}}$ . The calibration of the relevant parameters by use of a nonlinear optimization using a Nelder-Mead algorithm [125] results in  $\tau_{e,0} = 4.11 \text{ fs}$ ,  $\tau_{e,\text{min}} = 0.39 \text{ fs}$  and  $F_{\text{thr}} = 0.87 \text{ J cm}^{-2}$ . Note that the calibrated threshold fluence  $F_{\text{thr}} = 0.87 \text{ J cm}^{-2}$  slightly differs from the value  $F_{\text{thr}} = 0.82 \text{ J cm}^{-2}$  reported in [107]. A comparison between the computed and the measured craters can be found in fig. 6.11. The craters are measured by the use of a white light interferometer (WLI). Overall, there is a good agreement between the shapes of the computed and measured craters for all peak fluences. For a peak fluence of

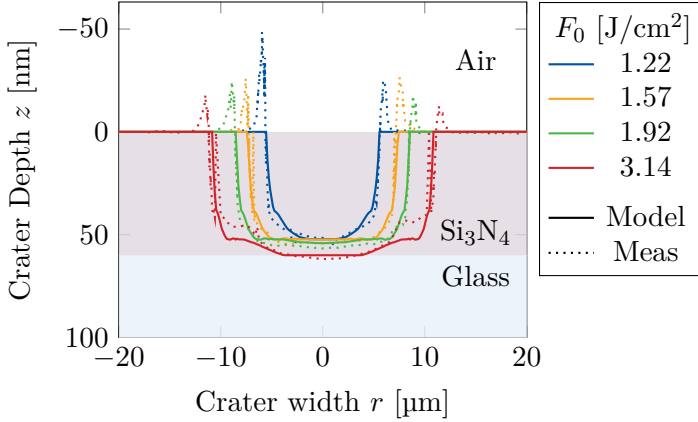


**Figure 6.11:** Comparison of the threshold ablation model (solid lines) and measured single pulse ablation crater shapes (dotted lines) in a 60 nm- $\text{Si}_3\text{N}_4$  film for selected peak fluences. There is good agreement between the model and the craters. The experimental craters are measured with a white light interferometer and are taken from [107].

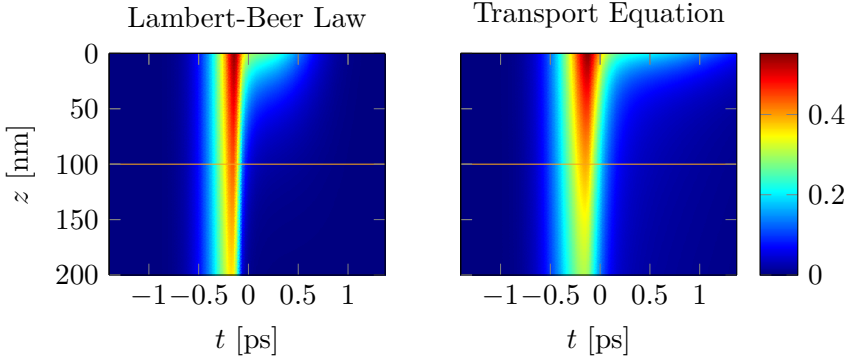
$3.14 \text{ J cm}^{-2}$ , there is a deviation between the measured depth and the computed depth in the outer regions of the ablation crater. However, the quantitative crater shape for the model and the WLI measurement are very similar. It has to be noted, that for thin transparent ITO films, with film thicknesses  $\delta_{\text{film}} \approx 0 \text{ nm}$  to  $180 \text{ nm}$ , WLI measurements are not as accurate as AFM measurements [106].

## 6.5 Comparison of Absorption Coefficient Models

So far two different models have been proposed to describe the absorption process of intense ultrashort laser pulses in transparent media: The first model is deduced from the dielectric function where the absorption coefficient is proportional to the imaginary part  $\Im$  of the dielectric function:  $\alpha_{\text{abs}} = 2\omega/c_0 \Im(\sqrt{\varepsilon(\omega, n_e)})$  (c.f. section 3.1.4). Then, the laser intensity as a function of depth  $z$  and time  $t$ , can be described by Lambert-Beer's law with transient optical properties:

$$I(t, z) = (1 - R_F) I_0 \exp \left( -4 \ln(2) \frac{t^2}{\tau_p^2} \right) \exp(-\alpha_{\text{abs}} z) \quad (6.4)$$

where  $R_F$  corresponds to the reflectivity of the sample surface. Both the reflectivity  $R_F = R_F(n_e(t))$  and the absorption coefficient  $\alpha_{\text{abs}} = \alpha_{\text{abs}}(n_e(t))$  depend on the transient electron density  $n_e(t)$ . Here, the electron density is only considered at the sample surface (i.e.,  $n_e(t) = n_e(z = 0, t)$ ). In the second model, the temporal and spatial intensity distribution within the material and hence its absorption is described by a one-dimensional transport equation eq. (3.72). The absorption is modeled by multiphoton ionization and cascade ionization while the laser pulse propagates through the material (see eq. (3.73)). Figure 6.12a shows the resulting intensity distributions  $I(t, z)$  of the transient Lambert-Beer law, given in eq. (6.4), and are compared to the transport equation eq. (3.72) in ITO for a laser pulse with a peak fluence of  $F_0 = 0.86 \text{ J cm}^{-2}$ . As shown in fig. 6.12b, during the rising time of the Gaussian intensity distribution both models show the same behavior for all depths ( $z = 0 \text{ nm}$ ,  $100 \text{ nm}$  and  $200 \text{ nm}$ ). The intensity



(a) Comparison of the normed intensity distributions

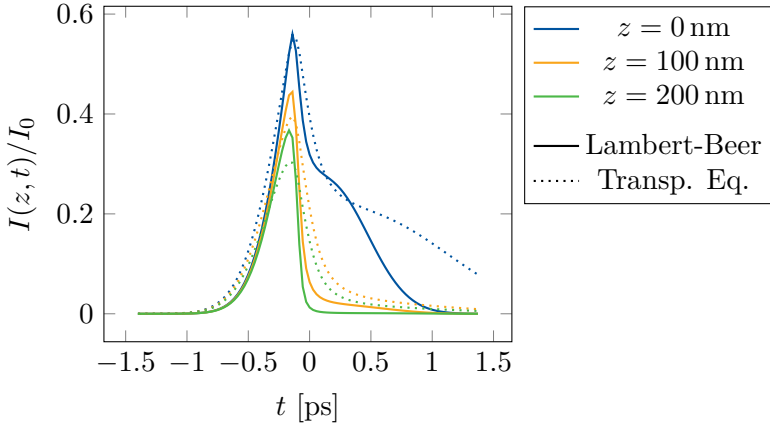

 (b) Comparison at the depths  $z = 0$  nm, 100 nm and 200 nm

**Figure 6.12:** Comparison of the normalized intensity distribution  $I(z, t)/I_0$  for the transport equation (eq. (3.72)) and the Lambert-Beer law (eq. (6.4)) in ITO with transient optical properties for a laser pulse with a peak fluence of  $F_0 = 0.86 \text{ J cm}^{-2}$ . The orange horizontal lines in fig. 6.12a at  $z = 100$  nm correspond to the orange lines in fig. 6.12b.

maxima for the transport equation at the depths  $z = 100\text{ nm}$  and  $200\text{ nm}$  are reached slightly later than for the Lambert-Beer law. This is reasonable because the transport equation takes the propagation time of the light into account, which is neglected in Lambert-Beer's law. The predictions by the transport equation result in lower peak intensities for larger depths. The propagation speed of the light depends on the local refractive index and therefore on the local free electron density. This leads to a broadening of the laser pulse for larger propagation depths. For this reason, the reached peak intensity is slightly lower for the intensity distributions computed from the transport equation in comparison to the Lambert-Beer law. The time when the material surface becomes reflective matches for both models.

However, the computation times strongly differ due to the stability criterion for the transport equation. According to the CFL-condition, the high spatial resolution to resolve light propagation in ITO films with film thicknesses ranging from  $\delta_{\text{film}} = 50\text{ nm}$  to  $180\text{ nm}$  requires very small time steps in the order of  $\Delta t = 1 \times 10^{-18}\text{ s}$ . Therefore, several million time steps are required to compute the laser pulse propagation for ultrashort laser pulses with a pulse duration of several hundreds of femtoseconds through the ITO films. In order to reduce the computational cost, the Lambert-Beer law is used for further computations, because the overall results for the intensity distribution for both models are very similar. It should be noted that for larger film thicknesses and bulk material the assumption of an evenly distributed electron density over the film thickness no longer holds. Then the transport equation should be used to compute the electron density and intensity distributions.

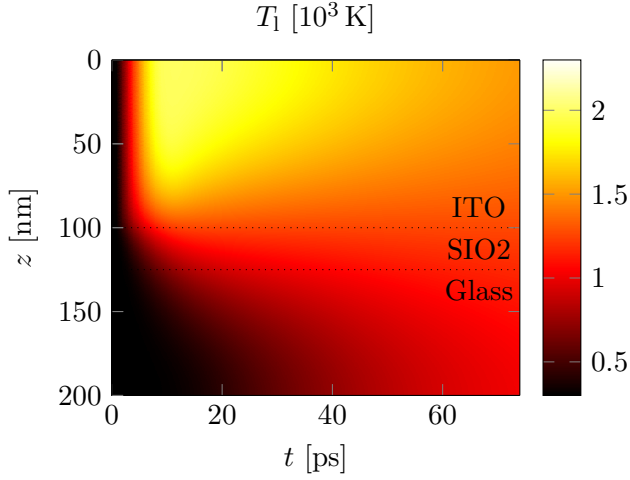
### 6.6 Influence of Fluence on Ablation Mechanisms

Depending on the peak fluence, different ablation crater shapes are observed in ITO layers (see section 6.3 and figs. 6.8 and 6.10). Small fluences (i.e., fluences close to the threshold fluence  $F_{\text{thr}} = 0.22\text{ J cm}^{-2}$ ) result in ablation craters with relatively constant ablation depths, while

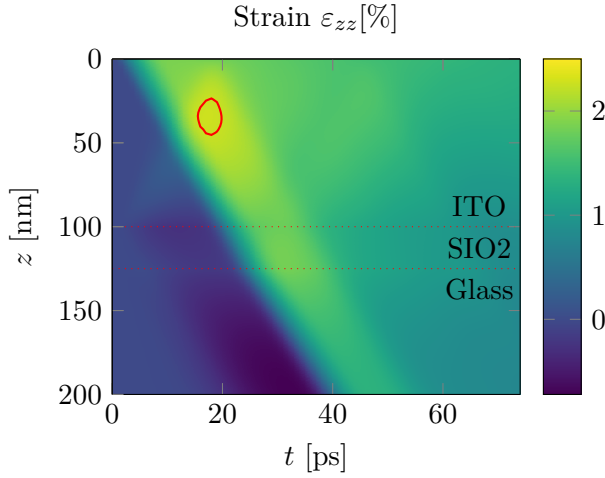
large fluences lead to ablation of the complete film. The peak fluence which is required for ablation of the complete film increases with the film thickness. For a 100 nm ITO film, the flat ablation crater shape becomes parabolic for peak fluences around  $F_0 = 0.43 \text{ J cm}^{-2}$  to  $0.65 \text{ J cm}^{-2}$ . Therefore, a different ablation behavior is expected around peak fluences of  $F_0 \approx 0.43 \text{ J cm}^{-2}$ . To identify the relevant ablation mechanisms, the model derived in section 4.4 is utilized.

The laser pulse excites free electrons (see section 3.1.6) and heats the electronic subsystem, which transfers the stored energy to the lattice system. This is described by the two temperature model (see section 4.2). The lattice heating causes the lattice to expand thermally and thereby induce strains and stresses within the layer stack. The stresses propagate as mechanical waves within the materials. In a first approximation, neglecting plastic deformation and hydrodynamics, these waves can be described by elastodynamics (see section 4.3).

Some results of the combined model (see section 4.4) for 100 nm ITO samples for peak fluences  $F_0 = 0.22 \text{ J cm}^{-2}$ ,  $0.65 \text{ J cm}^{-2}$  and  $1.29 \text{ J cm}^{-2}$  of the combined TTM-mechanical model are exemplarily shown in figs. 6.13, 6.14a and 6.14b. Figure 6.13 shows the computed lattice temperature  $T_l(z, t)$  and uniaxial strain distributions in  $z$ -direction  $\varepsilon_{zz}(z, t)$  for a laser pulse with a peak fluence  $F_0 = F_{\text{thr}} = 0.22 \text{ J cm}^{-2}$ . The maximum predicted lattice temperature in fig. 6.13a is  $T_l = 1908 \text{ K}$  and is thus close to but does not reach the melting temperature  $T_{\text{melt}}$  of ITO. The rise of the lattice temperature around  $t \approx 8 \text{ ps}$  causes the lattice to thermally expand leading to a pressure wave within the ITO-layer. The corresponding computed thermally induced strains  $\varepsilon_{zz}(z, t)$  are shown in fig. 6.13b. The pressure wave is reflected at the ITO-air interface and at the ITO-substrate interface around  $t \approx 10 \text{ ps}$ . The reflected fraction from the ITO-substrate interface travels towards the film surface at  $z = 0$  where it is reflected again at  $t \approx 17 \text{ ps}$ . At this time, the total strain, given by the sum of the resulting strains, reach a maximum  $\varepsilon_{zz} = 2.45\%$  at a depth  $z \approx 31 \text{ nm}$ . The maximum strain value is close to the yield strain of  $\varepsilon_{\text{yield}} = 2.2\%$  reported for 100 nm ITO films on flexible PET substrates [134]. The depth where  $\varepsilon_{zz} \geq \varepsilon_{\text{yield}}$  ( $z \approx 31 \text{ nm}$ ) matches with the



(a) Lattice temperature  $T_l$



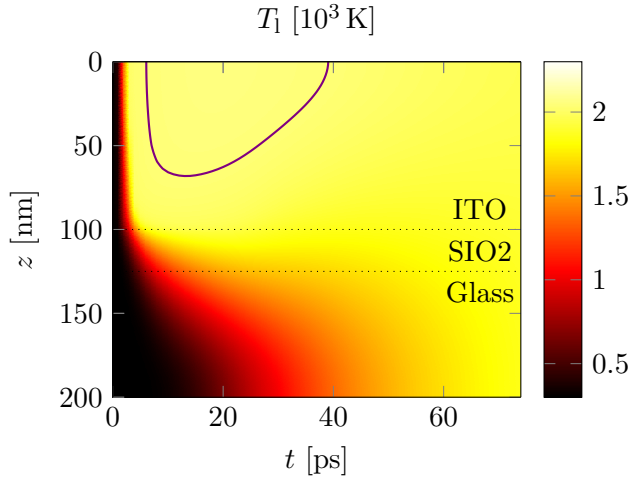
(b) Uniaxial strain  $\epsilon_{zz}$

**Figure 6.13:** Computation of the lattice temperature  $T_l$  and uniaxial strain  $\epsilon_{zz}$  for a 700 fs laser pulse with a peak fluence of  $F_0 = 0.22 \text{ J cm}^{-2}$  in a 100 nm ITO film. The area where  $\epsilon_{zz} \geq \epsilon_{\text{yield}}$  is indicated by the red contour line.

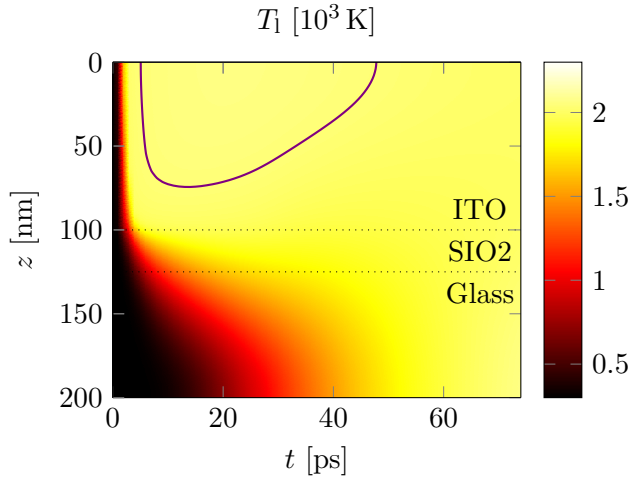
first plateau depth  $z_1$  in the measured ablation craters (c.f. table 6.5 and fig. 6.8). This depth equals to the depth where the maximum forces act on the lattice atoms predicted by MD simulations [6, 51]. Increasing the peak fluence results in larger peak lattice temperatures exceeding the melting temperature of ITO. Figures 6.14a and 6.14b exemplarily show the computed lattice temperature distributions  $T_l(z, t)$  for laser pulses with peak fluences  $F_0 = 0.65 \text{ J cm}^{-2}$  and  $1.29 \text{ J cm}^{-2}$ . The maximum depth where melting temperature is reached increases with increasing fluence and also depends on the film thickness. For comparison, the temperature distributions for different fluences in an ITO film with a film thickness of  $\delta_{\text{film}} = 50 \text{ nm}$  are shown in fig. 6.15. Similar to the 100 nm ITO sample, small fluences result in temperatures slightly below melting temperature and the computed strains exceed the yield strain at the first plateau depth around  $z \approx 25 \text{ nm}$ . For the peak fluences of  $F_0 = 0.41 \text{ J cm}^{-2}$  and  $F_0 = 0.54 \text{ J cm}^{-2}$  the computed depths where melting temperature is reached are slightly smaller with the experimental measurements (c.f. figs. 6.7 and 6.16.) Increasing the peak fluence results in melting of the entire ITO film.

In fig. 6.16 the maximum computed depths where melting temperature is reached (i.e.,  $T_l(z, t) = T_{\text{melt}}$ ) for different peak fluences are compared with the measured ablation depths. This comparison is reasonable because evaporation in the center of the ablation crater leads to expulsion of most of the molten material. For reference, the ablation depths, computed by the threshold ablation model are also plotted. For peak fluences  $F_0 \geq 0.43 \text{ J cm}^{-2}$  and film thicknesses of  $\delta_{\text{film}} = 50 \text{ nm}$  and  $100 \text{ nm}$  the  $z$ -values predicted by the TTM-model are in good agreement with the measured ablation depths. For larger film thicknesses, (i.e.,  $\delta_{\text{film}} = 180 \text{ nm}$ ) the TTM predicts ablation depths exceeding the measured values. There are multiple reasons why the TTM predicts too large depths in which melting temperature is reached. Firstly, the parameters used for the dielectric function are calibrated from the 100 nm sample.

A change of the film thickness results in different calibrated material parameters. This can be explained by the fact, that the initial free electron density, the grain size, and the chemical composition

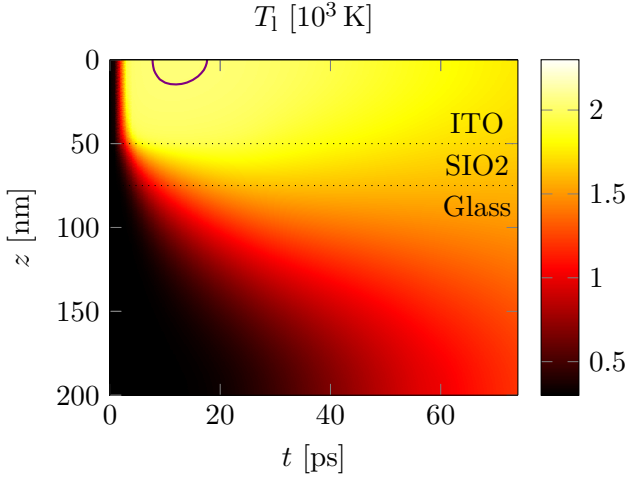


(a)  $F_0 = 0.65 \text{ J cm}^{-2}$

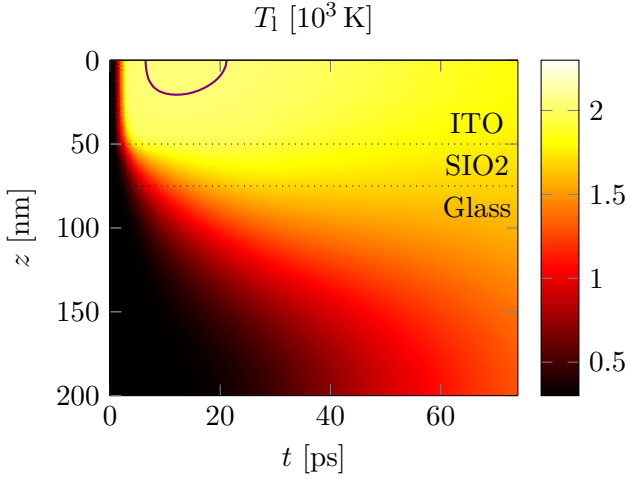


(b)  $F_0 = 1.29 \text{ J cm}^{-2}$

**Figure 6.14:** Computation of the lattice temperature  $T_1$  for a peak fluence of  $F_0 = 0.65 \text{ J cm}^{-2}$  and  $F_0 = 1.29 \text{ J cm}^{-2}$ . The violet contour line indicates the region where the melting temperature of ITO is reached  $T_1 = T_{\text{melt}}$ .



(a)  $F_0 = 0.41 \text{ J cm}^{-2}$



(b)  $F_0 = 0.54 \text{ J cm}^{-2}$

**Figure 6.15:** Computation of the lattice temperature  $T_l$  for a peak fluence of  $F_0 = 0.41 \text{ J cm}^{-2}$  and  $F_0 = 0.54 \text{ J cm}^{-2}$  in a 50 nm ITO-film. The violet contour line indicates the region where the melting temperature of ITO is reached  $T_l = T_{\text{melt}}$ .

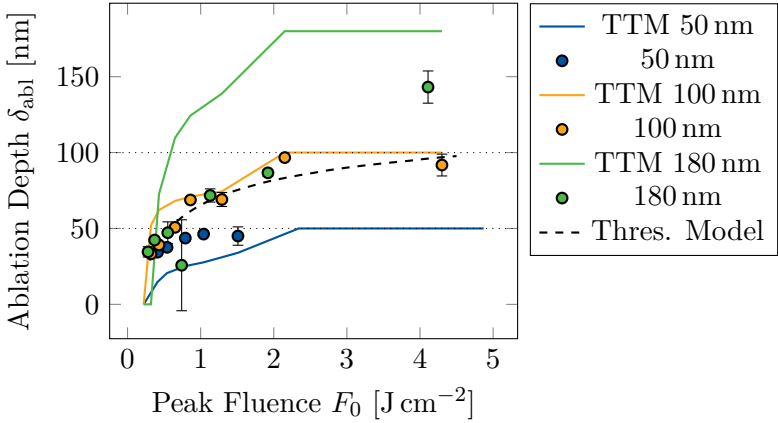


**Figure 6.16:** Comparison of the measured ablation depth  $\delta_{\text{abl}}$  for ITO-samples at the center of the pulse and the computed ablation crater depths by use of the threshold ablation model (c.f. section 4.1). The ITO-samples have film thicknesses of  $\delta_{\text{film}} = 50$  nm, 100 nm and 180 nm. The dotted lines indicate the film thickness for  $\delta_{\text{film}} = 50$  nm and 100 nm, respectively.

of the films change if the film thickness is increased [25, 135, 136]. Furthermore, it is assumed that the electron density is constant over the whole film thickness [77]. This no longer holds for larger film thicknesses because an increase of the electron density at the sample surface increases the absorption in the top part of the film. The minimum optical penetration depths during the laser pulse for different pulse energies range from 17 nm to 80 nm for fluences between  $0.32 \text{ J cm}^{-2}$  to  $4.3 \text{ J cm}^{-2}$ , where larger fluences result in lower optical penetration depths (see e.g. fig. 6.6). According to Lambert-Beer's law, the intensity at the surface of the ITO-film is larger compared to depths close to the interface to the  $\text{SiO}_2$  layer. For ITO the average mean free path of an electron equals 8.3 nm [137] which is much smaller than the film thickness but still leads to a homogenisation of the free electron distribution  $\tau_{\text{ehom}}$  in two dimensions within the films is can be esti-

mated by  $\tau_{\text{ehom}} = \delta_{\text{film}}^2 / (2D_e)$ . Here  $D_e$  corresponds to the diffusivity of the free electrons (For ITO  $D_e = 2.77 \times 10^{-3} \text{ m}^2 \text{ s}^{-1}$  [137]). For film thicknesses  $\delta_{\text{film}}$  of 100 nm and 180 nm this leads to  $\tau_{\text{ehom}} = 0.9 \text{ ps}$  and  $\tau_{\text{ehom}} = 2.92 \text{ ps}$ , respectively. This is larger than the pulse duration of  $\tau_p = 500 \text{ fs}$ . Consequently, this results in a non-homogeneous electron distribution along the  $z$ -direction for larger film thicknesses. Assuming a constant electron density within the whole 180 nm-film therefore leads to an overestimation of the absorbed energy. Then the simple Lambert-Beer law in the source term for the TTM is not applicable anymore. Hence, if the absorption for larger film thicknesses is overestimated, then the absorbed energy is overestimated, leading to too high predicted temperatures.

## 6.7 Double Pulse Ablation

After production, 12-inch Si- and gallium nitride (GaN)-wafers can carry around  $2.6 \cdot 10^{12}$  transistors which are connected to ICs and spatially separated by low- $\kappa$  materials [138]. To effectively cut the ICs without damaging the substrate or the complex layered structures within the individual ICs, laser grooving is used to introduce trenches in the low- $\kappa$  materials left and right of the actual cut (section 1.1). Transmission of the laser radiation into lower low- $\kappa$  layers or the substrate may cause cracks or delamination, which can damage an IC. The exact composition and thickness of the individual films on the wafer is often confidential. A typical combination of materials present in the dicing street of *imec* is given in fig. 6.17 [139]. To give a proof of concept, the simulations are carried out on a simplified reference model system. This model system consists of a  $\text{SiO}_2$  layer on top of a Si-substrate. The thickness of the low- $\kappa$  layers is typically in the order of several  $\mu\text{m}$ . Hence, the thickness of the  $\text{SiO}_2$  film is set to be  $\delta_{\text{film}} = 5 \mu\text{m}$ . Section 6.2 demonstrated that the transient optical properties of transparent semiconductors during laser excitation can drastically differ from the steady state optical properties. The generation of free electrons leads to a reduction of the optical penetration

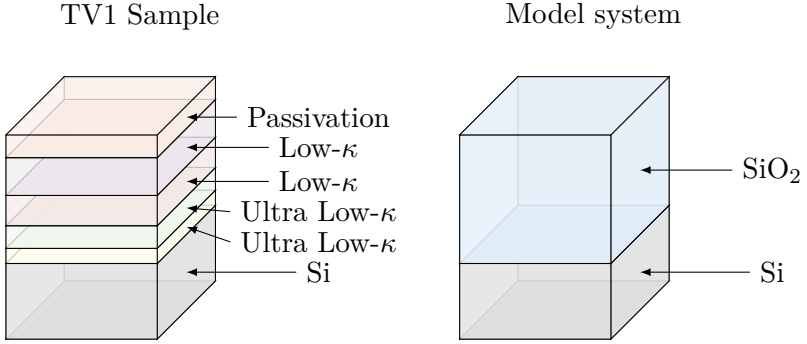


**Figure 6.17:** Schematic structure of imec's TV1 sample [139]. Due to the unknown composition of the individual layers a simplified model system is used in this work.

depth and an increase of reflectivity. This section explores the opportunity to individually remove the topmost transparent low- $\kappa$  films without transmission of the laser radiation by utilizing the free electron generation. Thereby, the introduction of heat into the substrate is reduced and delamination can be avoided.

The intensity distribution  $I(z, t)$  of a 700 fs IR laser pulse for different initial free electron densities  $n_{e, \text{init}}$  is calculated using eq. (6.4) and is shown in fig. 6.18. To model the optical properties within the  $\text{SiO}_2$  layer, the following dielectric function is used:

$$\varepsilon_{\text{SiO}_2}(\omega, n_e) = \varepsilon_{\infty}(\omega) + \varepsilon_{\text{Drude}}(\omega, n_e) \quad (6.5)$$

where the functional relationship  $\varepsilon_{\infty}(\omega)$  is taken from [140]. For a laser wavelength of  $\lambda = 1056 \text{ nm}$  the equilibrium term is given by  $\varepsilon_{\infty} = 2.1281 + 0.0029 \cdot i$  and the free electron contribution is modeled by the Drude term  $\varepsilon_{\text{Drude}}$ . While the IR laser pulse is fully transmitted through the  $\text{SiO}_2$  layer when there are no initial free electrons present, most of the radiation gets absorbed within the first  $3 \mu\text{m}$  with an initial free electron density of  $1 \times 10^{25} \text{ m}^{-3}$ . The peak intensity of the laser pulse is reached at  $t = 0 \text{ s}$ . At this time, the reflectivity of the sample surface increases strongly and prevents the laser radiation from

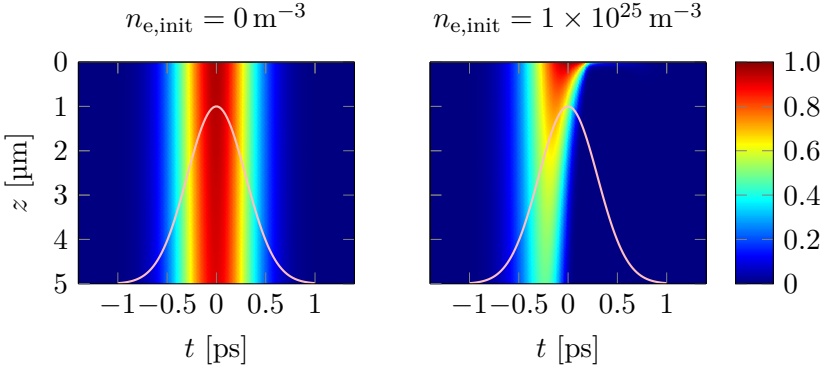


**Figure 6.18:** Comparison of the intensity distribution  $I(z, t)$  of an ultrashort laser pulse ( $\lambda = 1056 \text{ nm}$ ,  $\tau_p = 700 \text{ fs}$ ,  $I_0 = 1 \times 10^{16} \text{ W m}^{-2}$ ,  $w_0 = 10 \mu\text{m}$ ) in a  $\text{SiO}_2$  film with a film thickness of  $\delta_{\text{film}} = 5 \mu\text{m}$  for different initial electron densities  $n_{e,\text{init}}$ . The pink lines indicate the temporal evolution of the incident laser pulse. Larger initial electron densities lead to a reduction of the optical penetration depth.

entering the  $\text{SiO}_2$  layer.

To generate a free electron density of  $1 \times 10^{25} \text{ m}^{-3}$  at the time when the “ablation” laser pulse irradiates the film surface, another “excitation” laser pulse can be used, which precedes the ablation pulse. The pulse energy of the excitation pulse should be chosen such that the pulse does not induce damage within the material. Additionally, it is beneficial if the photon energy exceeds the bandgap of the material. Thus, strong absorption and minimal transmission to lower layers or the substrate is ensured. Low- $\kappa$  dielectrics have a bandgap of  $\Delta = 7.7 \text{ eV}$  [141], which is comparable to  $\text{SiO}_2$  ( $\Delta = 7.8 \text{ eV}$  [50]). However, defects and impurities in the crystalline lattice cause bandgap narrowing in low- $\kappa$  materials, such that bandgaps range from  $6.1 \text{ eV}$  to  $6.8 \text{ eV}$  [142]. This corresponds to wavelengths ranging from  $203 \text{ nm}$  to  $182 \text{ nm}$ , respectively. Consequently, excimer lasers with a wavelength of  $182 \text{ nm}$  to  $203 \text{ nm}$  should be used for the excitation process of low- $\kappa$  materials.

In industrial applications however, there are other materials within

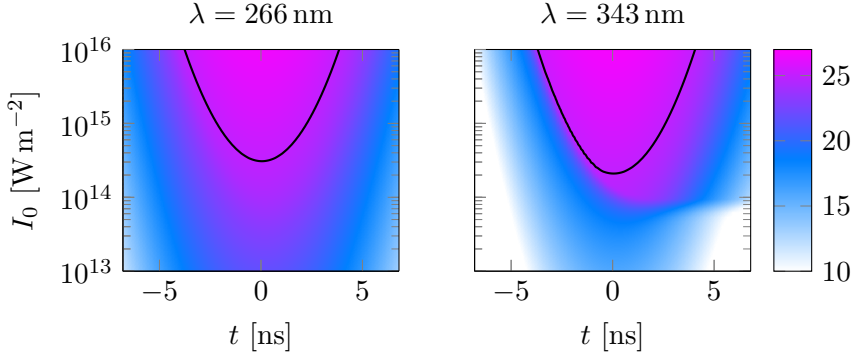


**Figure 6.19:** Temporal evolution of the free electron distribution  $\log_{10}(n_e(t))$  at the surface of a  $5\text{ }\mu\text{m}$   $\text{SiO}_2$  film for an UV nanosecond laser pulse with different peak intensities  $I_0$ . The black contour line indicates the regions where the electron density exceeds  $n_e \geq 1 \times 10^{25} \text{ m}^{-3}$  (c.f. fig. 6.18).

the cutting line, which have smaller bandgaps than  $\text{SiO}_2$  and therefore provide seed electrons to reduce the optical penetration depth. Hence, electron generation for wavelengths of 266 nm and 343 nm are now studied in detail. Frequency tripled and quadrupled IR lasers are able to produce wavelengths of 343 nm and 266 nm respectively. Typical pulse durations range from picoseconds to several nanoseconds. For these wavelengths, the respective photon energies are 3.6 eV and 4.7 eV. Thus, two-photon-absorption via MPI is the driving absorption process. Consequently, the steady state optical penetration depth  $\delta_{\text{opt}}$ , computed via the dielectric function eq. (6.5) and eq. (3.36), for laser pulses with a wavelength of  $\lambda = 266 \text{ nm}$  and  $\lambda = 343 \text{ nm}$  results in  $\delta_{\text{opt}} = 4.94 \text{ }\mu\text{m}$  and  $\delta_{\text{opt}} = 8.53 \text{ }\mu\text{m}$ , respectively. For 266 nm the optical penetration depth  $\delta_{\text{opt}}$  is smaller than the  $\text{SiO}_2$  film thickness. The temporal evolution of the free electron density  $n_e(t)$  for 3.4 ns laser pulses with both wavelengths and different peak intensities  $I_0$  is shown in fig. 6.19. The black contour lines indicate the regions where the electron density exceeds  $1 \times 10^{25} \text{ m}^{-3}$ . For  $\lambda = 266 \text{ nm}$  the temporal evolution of the free electron density follows the temporal intensity

distribution. In contrast to  $\lambda = 266 \text{ nm}$ , for  $\lambda = 343 \text{ nm}$  the temporal evolution of the electron density is asymmetric for peak intensities larger than  $I_0 \geq 1 \times 10^{14} \text{ W m}^{-2}$ . Then, the multiphoton ionization leads to an electron density of  $n_e \approx 1 \times 10^{15} \text{ m}^{-3}$  and avalanche ionization sets in. Electrons are still generated due to avalanche ionization during the fading tail of the laser pulse which leads to the asymmetric shape.

To efficiently reduce the optical penetration depth for the IR ablation pulse, the required free electron density is  $1 \times 10^{25} \text{ m}^{-3}$  (see fig. 6.18). The obligatory peak intensities and delay times with in which the UV excitation pulse generates the free electron density of  $1 \times 10^{25} \text{ m}^{-3}$  is shown by the black contour line in fig. 6.19. Thus, the optical penetration depth of the IR ablation pulse is reduced if the peak intensity of the UV laser pulse is larger than  $I_0 \geq 1.2 \times 10^{14} \text{ W m}^{-2}$ . Increasing the peak intensity of the UV excitation pulse results in a longer process window for possible the delay times for the IR ablation pulse. However, it should be noted that increasing the peak intensity for the excitation pulse might induce substrate damage.

Similar approaches with excitation in the UV and visible regime and ablation pulses in the visible and IR regime already proved an increase of absorption and a decrease of ablation threshold for silicon carbide and fused silica [143, 144]. Moreover, there are already approaches to model double pulse excitation with time-dependent density functional theory (DFT) [145]. Here, it is shown, that the absorbed energy is the largest if the excitation pulse and the ablation laser pulse irradiate the sample simultaneously. However, due to the numerical complexity, the used pulse durations are ranging from 30 fs to 70 fs and therefore complicate the experimental handling of the beneficial delay time between the two pulses. Therefore, the experimental feasibility with nanosecond UV laser pulses is proven here.



# 7 Summary and Outlook

## 7.1 Summary

This thesis presents a comprehensive numerical process model for the ablation of transparent semiconducting thin films by means of ultrashort pulsed laser radiation. The model considers the relevant physical mechanisms to describe the shapes of the ablation craters and gives insight about the dynamics during the ablation process. The equilibrium optical properties are determined based on static UV-Vis measurements by use of the dielectric function. For intense ultrashort laser pulses, the optical properties of semiconductors change drastically due to ionization of bound electrons during the laser pulse. To adequately describe the optical properties (i.e., reflectivity, absorption, and optical penetration depth) during the laser pulse, free electron dynamics are considered by the use of rate equations for the free electron density within the semiconducting films. Despite not explicitly shown in this manuscript, it is found that bandgap widening due to the Burstein-Moss effect and an electron density dependent electron collision time needs to be incorporated for adequately predicting the experimental results [77]. Moreover, this work extends the threshold fluence ablation model, which so far could only be used to describe the ablation crater shape for pulsed material ablation in metals [7, 128, 146], to accurately describe ablation craters in semiconducting materials like ITO and dielectrics like  $\text{Si}_3\text{N}_4$ . This is achieved by utilization of the transient optical penetration depth for the energy penetration depth in the threshold model.

At a microscopic level, the ablation process is modeled by simulation of the relevant underlying physical processes induced by intense laser pulses. The developed model considers the absorption of the ultrashort-

pulsed laser radiation, the subsequent heating of the material stack and mechanical pressure waves, that are caused by thermal expansion due to the increase of temperature. The heating of the material stack is modeled by a hyperbolic TTM, where the heat source is based on the transient optical properties. The TTM is extended by an enthalpy method to prevent an overestimation of the lattice temperatures and account for phase changes. Due to the lattice heating thermal strains and stresses are induced within the layer stack, that propagate as mechanical waves. The latter are described using an elastic wave equation. Considering the thickness of the thin films and the lateral dimensions of the laser beam, the proposed model could be reduced from three dimensions to one dimension. By simulating the underlying physical processes mentioned above, the relevant ablation mechanisms are identified to be a combination of mechanical spallation for regions in the crater where the fluences are close to the threshold fluence and thermal melting and melt expulsion for larger fluences.

### 7.1.1 Research Questions

With the model developed in this work, it is finally possible to answer the initially posed research questions.

#### Research Question 1

- For which parameter values is the laser ablation of a thin transparent layer photo-thermally and for which is it photo-mechanically dominated?
- Is the ablation mechanism controllable, e.g., via the effective energy penetration depth  $\delta_{\text{eff}}$  and the film thickness  $\delta_{\text{film}}$ ?

$$\delta_{\text{eff}} > \delta_{\text{film}} \quad \text{photo-mechanical?}$$

$$\delta_{\text{eff}} \leq \delta_{\text{film}} \quad \text{photo-thermal?}$$

## Answer to Research Question 1

- In ITO, the ablation process is photo-mechanically dominated for 700 fs laser pulses with peak fluences  $F_0 \leq 0.43 \text{ J cm}^{-2}$  (this corresponds to  $2 \cdot F_{\text{thr}}$ ). For larger peak fluences  $F_0 > 0.43 \text{ J cm}^{-2}$  the ablation mechanism is photothermal.
- In ITO, the ablation mechanism for 700 fs laser pulses is not controllable by the effective penetration depth  $\delta_{\text{eff}}$  since it roughly equals the optical penetration depth  $\delta_{\text{opt}}$ . The optical penetration depth  $\delta_{\text{opt}}$  itself is in the order of the film thickness for a local fluence of  $F = F_{\text{thr}} = 0.22 \text{ J cm}^{-2}$ . Increasing the fluence results in decreasing the optical penetration depth while simultaneously increasing the induced heat. However, if stress confinement is present in the regions where the induced heat is not sufficient for melting or phase explosion, the ablation mechanism is photomechanical and photothermal otherwise.

## Research Question 2

- Is it possible to model the ablation crater of thin semiconducting films with a phenomenological ablation criterion?
- Can exceeding of a critical electron density be defined as a phenomenological ablation criterion for the ablation of thin semiconducting films?

## Answer to Research Question 2

Exceeding the critical electron density could not be identified as a phenomenological ablation criterion. However, the ablation craters can be modeled using the threshold fluence  $F_{\text{thr}} \approx 0.22 \text{ J cm}^{-2}$  as a phenomenological ablation criterion instead of the critical electron density. Therefore, the threshold ablation model is combined with transient optical properties which result from the free electron dynamics.

## 7.2 Outlook

The models that were developed within the scope of this work are able to describe the ablation crater shapes (c.f. section 4.1) of thin semiconducting films and give insights about the underlying ablation mechanisms (see section 4.4). Some assumptions and simplifications have been made during the development of the models and can be used for further improvement of the model:

- **Electron dynamics:** For the modelling of the free electron dynamics it was assumed, that the densities and effective masses of the electrons and the holes are equal. Further, it was assumed that the valence and conduction bands have a parabolic shape. This allows the simplified computation of the bandgap widening due to the Burstein-Moss effect. For other materials with more complex band structures, such as GaN or organic semiconductors, a quantum mechanical approach has to be made. One possible approach could be the use of DFT.
- **Interference and beam propagation:** The modelling of the laser radiation propagation in the film stack and its absorption is done by use of the TMM and a Lambert-Beer law until the optical penetration depth becomes smaller than the film thickness. The use of the TMM is only valid if the refractive index of the layers does not change drastically within the individual

layers. Especially for transparent insulators with a small electron mobility and film thicknesses larger than 100 nm this assumption is no longer valid. In this case, the wave equation for the electric field within the materials has to be solved explicitly (c.f. eq. (3.7)) with a time dependent charge carrier density and dipole moment density. Due to interference of the electromagnetic waves within the thin films the local intensity can exceed the incident peak intensity.

- **Absorption:** The absorption for the threshold ablation model and the TTM is modeled by the use of the nonlinear Lambert-Beer law. For the materials, considered in this thesis mostly absorb the laser radiation in the topmost layer. This no longer holds for more complex layered film systems. Thus, the absorption should be either computed by solving the electromagnetic wave equation or by computation of the Poynting vector within the film stack [78].
- **Plasticity:** The presented one-dimensional model for the mechanical waves in the film system are considered to be fully elastic. To get a more comprehensive model, hardening laws should be implemented to describe plastic deformations. There are several types of hardening, including isotropic hardening and kinematic hardening. Isotropic hardening corresponds to the uniform increase of the material's yield strength into all directions as it is deformed. Kinematic hardening accounts for the material's response to deformation based on the history of deformation. In kinematic hardening, the yield surface shifts due to the prior loading cycles. The description of the hardening laws is typically described using linear or nonlinear equations for the stress-strain relationship.
- **Delamination and cracks:** Due to the one-dimensional elastic model delamination and cracks in radial direction cannot be described. In order to do so, the model has to be extended to two or three dimensions. Then, the stress-strain relationship

becomes more complex due to the tensor properties of the elastic modulus tensor  $\underline{C}_{\text{el}}$ . With Einstein's sum convention the stress-strain relationship in an isotropic material thus reads:

$$\sigma_{ij} = C_{\text{el}ijkl}(\varepsilon_{kl} - \alpha_{\text{th}}\Delta T\delta_{kl}) \quad (7.1)$$

$$C_{\text{el}ijkl} = \frac{E_y}{2(1 + \nu_{\text{poisson}})}(\delta_{il}\delta_{jk} + \delta_{ik}\delta_{jl}) + \frac{E_y\nu_{\text{poisson}}}{(1 + \nu_{\text{poisson}})(1 - 2\nu_{\text{poisson}})}\delta_{ij}\delta_{kl} \quad (7.2)$$

where  $E_y$  corresponds to Young's modulus and  $\nu_{\text{poisson}}$  to Poisson's ratio of the material, respectively. Since every material in the stack of thin films has a different thermal expansion heating leads to stresses at the film interfaces. If the stress exceeds a material specific threshold this can be used as a criterion for damage or delamination.

- **Phase transitions and melt expulsion:** The current model describes the phase transitions by introducing the enthalpy required for melting in the TTM. However, the interaction between the mechanical pressure wave and the molten material is neglected. To introduce this interaction the formulae for the elastic wave equation have to be exchanged by a hydrodynamic description. This is described by Euler equations. A combination of the Euler equations with a TTM in metals can be found in [52]. To describe semiconductors, the model from [52] should be extended by use of electron dynamics and the transient optical properties in order to model the heat source.

Finally, the considerations regarding the double pulse excitation of transparent materials presented in section 6.7 require experimental validation. Therefore, an UV nanosecond laser should be synchronized with an IR femtosecond laser source. Then the feasible process window can be analyzed by a variation of the delay times and peak intensities. Furthermore, it should be noted, that the excitation pulse should spatially encompass the ablation pulse to prevent too large optical penetration depths in the peripheral region of the ablation pulse.

# Acronyms

|                                |                                    |
|--------------------------------|------------------------------------|
| AFM                            | atomic force microscope            |
| BPM                            | beam propagation method            |
| CAGR                           | compound annual growth rate        |
| Cd                             | cadmium                            |
| CFL                            | Courant-Friedrichs-Lewy condition  |
| CVD                            | chemical vapor deposition          |
| DFT                            | density functional theory          |
| DOS                            | density of states                  |
| FDTD                           | finite differences time domain     |
| FTCS                           | forward in time, centered in space |
| FWHM                           | full width at half maximum         |
| GaN                            | gallium nitride                    |
| IC                             | integrated circuit                 |
| In                             | indium                             |
| In <sub>2</sub> O <sub>3</sub> | indium oxide                       |
| IR                             | infrared                           |
| ITO                            | indium tin oxide                   |
| MD                             | molecular dynamics                 |
| MPI                            | multiphoton ionization             |

## Acronyms

|                                |                                             |
|--------------------------------|---------------------------------------------|
| ODE                            | ordinary differential equation              |
| OLED                           | organic light-emitting diode                |
| PDE                            | partial differential equation               |
| PEC                            | Predictor-Evaluate-Corrector                |
| PET                            | polyethylene terephthalate                  |
| PMOLED                         | passive matrix organic light-emitting diode |
| SHG                            | second harmonic generation                  |
| Si                             | silicon                                     |
| Si <sub>3</sub> N <sub>4</sub> | silicon nitride                             |
| SiO <sub>2</sub>               | silicon dioxide                             |
| Sn                             | tin                                         |
| SnO <sub>2</sub>               | tin dioxide                                 |
| TCO                            | transparent conducting oxide                |
| TEM                            | transverse electro-magnetic                 |
| TMM                            | transfer matrix method                      |
| TTM                            | two temperature model                       |
| UV                             | ultraviolet                                 |
| WLI                            | white light interferometer                  |
| Zn                             | zinc                                        |

# List of Symbols

|                   |                                            |                      |
|-------------------|--------------------------------------------|----------------------|
| $0$               | Null Vector                                |                      |
| $A_T$             | Tauc Resonator Strength                    | J                    |
| $A$               | Absorption                                 |                      |
| $A$               | System Matrix                              |                      |
| $A$               | Tauc Lorentz Resonator Strength            | J                    |
| $B$               | Magnetic Induction                         | T                    |
| $C_{\text{cfl}}$  | CFL Number                                 |                      |
| $C_{\text{el}}$   | Elastic Modulus Tensor                     |                      |
| $C_e$             | Electron Specific Heat Capacity            | J/(m <sup>3</sup> K) |
| $C_{\text{l},0}$  | Equilibrium Lattice specific Heat Capacity | J/(m <sup>3</sup> K) |
| $C_{\text{l}}$    | Lattice specific Heat Capacity             | J/(m <sup>3</sup> K) |
| $C_l$             | Characteristic Transfer Matrix             |                      |
| $C$               | Tauc Lorentz Resonator Broadening          | J                    |
| $D_e$             | Electron diffusivity                       | m <sup>2</sup> /s    |
| $D_e$             | Density of Electron States                 | m <sup>-3</sup>      |
| $D_h$             | Density of Hole States                     | m <sup>-3</sup>      |
| $D_{\text{th}}$   | Thermal Diffusivity                        | m <sup>2</sup> /s    |
| $D$               | Electric Displacement Field                | F/m                  |
| $E_0$             | Electric Field Amplitude                   | V/m                  |
| $E_{0,\text{TL}}$ | Tauc Lorentz Resonance Energy              | J                    |
| $E_{\text{av}}$   | Average Electron Energy                    | J                    |
| $E_{\text{crit}}$ | Critical Energy for Collision Ionization   | J                    |
| $E_{\text{f}}$    | Fermi Energy                               | J                    |
| $E_{\text{ph}}$   | Photon Energy                              | J                    |
| $E_{\text{p}}$    | Pulse Energy                               | J                    |

## List of Symbols

|                    |                                         |                      |
|--------------------|-----------------------------------------|----------------------|
| $E_y$              | Young's Modulus                         | Pa                   |
| $E$                | Electric Field                          | V/m                  |
| $F_0$              | Peak Fluence                            | J/m <sup>2</sup>     |
| $F_{\text{thr}}$   | Threshold Fluence                       | J/m <sup>2</sup>     |
| $F$                | Fluence                                 | J/m <sup>2</sup>     |
| $G$                | Electron Phonon Coupling Constant       | W/(m <sup>3</sup> K) |
| $H_H$              | Hamiltonian                             | J                    |
| $H_e$              | Enthalpy                                | J                    |
| $H$                | Magnetic Field                          | A/m                  |
| $I_0$              | Peak Intensity                          | W/m <sup>2</sup>     |
| $I$                | Intensity                               | W/m <sup>2</sup>     |
| $J_f$              | Current Density of Free Charge Carriers | A/m <sup>2</sup>     |
| $K_e$              | Electron Thermal Conductivity           | W/(mK)               |
| $K_l$              | Lattice Thermal Conductivity            | W/(mK)               |
| $K_{\text{th}}$    | General Thermal Conductivity            | W/(mK)               |
| $K$                | # of Photons to Overcome Bandgap        |                      |
| $L$                | Length of the Computational Domain      | m                    |
| $M^2$              | Beam Quality Factor                     |                      |
| $M_{\text{mole}}$  | Molecular Mass                          | kg                   |
| $M_{\text{mol}}$   | Molar Mass                              | kg/mol               |
| $M$                | Magnetization                           | A/m                  |
| $N_s$              | Number of Solution Variables            |                      |
| $N$                | Number of Increments                    |                      |
| $P$                | Polarization Density                    | C/m <sup>2</sup>     |
| $Q_{\text{e,ion}}$ | Ionization Energy                       | J                    |
| $Q_{\text{evap}}$  | Latent Heat of Vaporization             | J                    |
| $Q_l$              | Latent Heat                             | J                    |
| $Q$                | Solution Vector                         |                      |
| $R_F$              | Fresnel Reflectivity                    |                      |
| $R_{\text{TMM}}$   | TMM Reflectivity                        |                      |
| $R_c$              | Curvature of the Wavefront              | m                    |
| $R_{\text{meas}}$  | Measured Reflectivity                   |                      |

|                             |                                                  |                                   |
|-----------------------------|--------------------------------------------------|-----------------------------------|
| $R$                         | Reflectivity                                     |                                   |
| $S$                         | Source                                           | $\text{W/m}^3$                    |
| $T_0$                       | Environment Temperature                          | K                                 |
| $T_D$                       | Debye Temperature                                | K                                 |
| $T_{\text{TMM}}$            | TMM Transmission                                 |                                   |
| $T_{\text{evap}}$           | Evaporation Temperature                          | K                                 |
| $T_e$                       | Electron Temperature                             | K                                 |
| $T_f$                       | Fermi Temperature                                | K                                 |
| $T_{\text{liq}}$            | Temperature Liquidus                             | K                                 |
| $T_l$                       | Lattice Temperature                              | K                                 |
| $T_{\text{meas}}$           | Measured Transmission                            |                                   |
| $T_{\text{melt}}$           | Melting Temperature                              | K                                 |
| $T_{\text{sc}}$             | Temperature Scale                                | K                                 |
| $T_{\text{sol}}$            | Temperature Solidus                              | K                                 |
| $T$                         | Temperature                                      | K                                 |
| $T$                         | Transmission                                     |                                   |
| $V$                         | Volume                                           | $\text{m}^3$                      |
| $\Delta T$                  | Transition temperature Width<br>(Solid-Liquid)   | K                                 |
| $\Delta\lambda$             | Path Difference for Interferences                | m                                 |
| $\Delta_0$                  | Intrinsic Bandgap                                | J                                 |
| $\Delta_{\text{BM}}$        | Burstein-Moss Bandgap Widening                   | J                                 |
| $\Delta t$                  | Time Step Size                                   | s                                 |
| $\Delta x$                  | Grid Spacing                                     | m                                 |
| $\Delta$                    | Bandgap                                          | J                                 |
| $\Lambda_{zz}$              | Electron Blast Force                             | $\text{J}/(\text{m}^3\text{K}^2)$ |
| $\Phi_D$                    | Dawson Function                                  |                                   |
| $\Phi$                      | Phase                                            |                                   |
| $\alpha_{\text{TL}}$        | Constant for Tauc Lorentz Dielectric<br>Function | J                                 |
| $\alpha_{\text{abs}}$       | Absorption Coefficient                           | $1/\text{m}$                      |
| $\alpha_{\text{casc}}$      | Cascade Ionization Rate Prefactor                | $1/\text{s}$                      |
| $\alpha_{\text{inc,probe}}$ | Angle of Incidence Probe Pulse                   | deg                               |
| $\alpha_{\text{inc,pump}}$  | Angle of Incidence Pump Pulse                    | deg                               |

## List of Symbols

|                          |                                                |                         |
|--------------------------|------------------------------------------------|-------------------------|
| $\alpha_{\text{inc}}$    | Angle of Incidence                             | deg                     |
| $\alpha_{\text{th}}$     | Thermal Expansion Coefficient                  | 1/m                     |
| $\delta_{\text{abl}}$    | Ablation depth                                 | m                       |
| $\delta_{\text{eff}}$    | Effective Penetration Depth                    | m                       |
| $\delta_{\text{film}}$   | Film Thickness                                 | m                       |
| $\delta_{\text{opt}}$    | Optical Penetration Depth                      | m                       |
| $\delta_{\text{therm}}$  | Thermal Penetration Depth                      | m                       |
| $\delta_{ij}$            | Kronecker Delta                                |                         |
| $\delta$                 | Dirac Delta Function                           |                         |
| $\eta_0$                 | Impedance of Free Space                        |                         |
| $\eta_{2p}$              | Two Particle Recombination Rate                | $\text{m}^3/(\text{s})$ |
| $\eta_{\text{Auger}}$    | Auger Recombination Rate                       | $\text{m}^6/(\text{s})$ |
| $\eta_{\text{casc}}$     | Cascade Ionization Rate Non-Retarded Prefactor | 1/s                     |
| $\gamma_K$               | Keldysh Parameter                              |                         |
| $\gamma_{\text{TL}}$     | Constant for Tauc Lorentz Dielectric Function  | J                       |
| $\gamma_{\text{el}}$     | Angular Collision Frequency of Electrons       | rad/s                   |
| $\gamma_{\text{max}}$    | Max. Angular Collision Frequency of Electrons  | rad/s                   |
| $\hat{E}$                | Energy                                         | J                       |
| $\hat{H}_{\text{LF}}$    | Lax Friedrichs Hamiltonian                     | J                       |
| $\hat{H}_{\text{num}}$   | Numerical Hamiltonian                          | J                       |
| $\hat{\alpha}$           | Eigenvalue                                     |                         |
| $\hat{q}_{\text{e}}$     | Scaled Electron Heat Flux                      |                         |
| $\hat{q}_{\text{l}}$     | Scaled Lattice Heat Flux                       |                         |
| $\hat{q}$                | Scaled Heat Flux                               |                         |
| $\hat{v}_z$              | Scaled Velocity                                |                         |
| $\hbar$                  | Reduced Planck's constant                      | J/s                     |
| $\lambda_1$              | Lame First Parameter                           | Pa                      |
| $\lambda_{\text{probe}}$ | Wavelength of the Probe Pulse                  | m                       |
| $\lambda_{\text{pump}}$  | Wavelength of the Pump Pulse                   | m                       |
| $\lambda$                | Wavelength                                     | m                       |

|                              |                                      |                      |
|------------------------------|--------------------------------------|----------------------|
| $\mathcal{H}$                | Hermite Polynomial                   |                      |
| RHS                          | Right Hand Side                      |                      |
| $\mu_0$                      | Vacuum magnetic permeability         | N/A <sup>2</sup>     |
| $\mu_2$                      | Lame Second Parameter                | Pa                   |
| $\mu_{\text{ch}}$            | Charge Carrier Mobility              | m <sup>2</sup> /(Vs) |
| $\mu_{\text{pro}}$           | Projection onto Inclined Surface     |                      |
| $\mu$                        | Magnetic Permeability                | N/A <sup>2</sup>     |
| $\nu_{\text{poisson}}$       | Poisson's Ratio                      |                      |
| $\omega_{\text{T}}$          | Tunneling Frequency                  | rad/s                |
| $\omega_{\text{res}}$        | Resonance Frequency of Photons       | rad/s                |
| $\omega_p$                   | Plasma Frequency                     | rad/s                |
| $\omega$                     | Angular Frequency of Photons         | rad/s                |
| $\rho$                       | Mass Density                         | kg/m <sup>3</sup>    |
| $\sigma_{\text{el}}$         | Charge Carrier Density               | S/m                  |
| $\sigma_{xx}$                | Uniaxial Stress in x-direction       | Pa                   |
| $\sigma_{yy}$                | Uniaxial Stress in y-Direction       | Pa                   |
| $\sigma_{zz}$                | Uniaxial Stress in z-direction       | Pa                   |
| $\sigma$                     | Mechanical Stress                    | Pa                   |
| $\tau_{\text{e},0}$          | Initial Electron Collision Time      | s                    |
| $\tau_{\text{e},\text{min}}$ | Min. Electron Collision Time         | s                    |
| $\tau_{\text{ehom}}$         | Electron homogenisation time         | s                    |
| $\tau_{\text{e}}$            | Electron Collision Time              | s                    |
| $\tau_{\text{l}}$            | Lattice Collision Time               | s                    |
| $\tau_p$                     | Pulse Duration                       | s                    |
| $\tau$                       | General Collision Time               | s                    |
| $\tau$                       | Scaled Time                          |                      |
| $\theta_{\text{e}}$          | Scaled Electron Temperature          |                      |
| $\theta_{\text{l}}$          | Scaled Lattice Temperature           |                      |
| $\theta_{\text{opt}}$        | Angle to Optical Axis                | deg                  |
| $\theta$                     | Scaled Temperature                   |                      |
| $\tilde{\omega}_p$           | Shifted Plasma Frequency             | rad/s                |
| $\tilde{n}$                  | Generalized Complex Refractive Index |                      |
| $\tilde{r}$                  | Field Reflectivity                   |                      |
| $\tilde{t}$                  | Field Transmission                   |                      |

|                         |                                                    |       |
|-------------------------|----------------------------------------------------|-------|
| $\varepsilon_0$         | Vacuum Relative Permittivity                       | F/m   |
| $\varepsilon_\infty$    | Constant Dielectric Background                     |       |
| $\varepsilon_{DL}$      | Drude Lorentz Dielectric Function                  |       |
| $\varepsilon_{Drude}$   | Drude Dielectric Function                          |       |
| $\varepsilon_{Float}$   | Dielectric Function of Float Glass                 |       |
| $\varepsilon_{ITO}$     | Dielectric Function of ITO                         |       |
| $\varepsilon_{Si_3N_4}$ | Dielectric Function of $Si_3N_4$                   |       |
| $\varepsilon_{SiO_2}$   | Dielectric Function of $SiO_2$                     |       |
| $\varepsilon_{T,2}$     | Imag. Part of the Tauc Dielectric Function         |       |
| $\varepsilon_{TL,1}$    | Real Part of Tauc-Lorentz Dielectric Function      |       |
| $\varepsilon_{TL,2}$    | Imag. Part of the Tauc-Lorentz Dielectric Function |       |
| $\varepsilon_{TL}$      | Tauc Lorentz Dielectric Function                   |       |
| $\varepsilon_{pol}$     | Dielectric Function of bound electrons             |       |
| $\varepsilon_{yield}$   | Uniaxial Yield Strain                              |       |
| $\varepsilon_{xx}$      | Uniaxial Strain in x-Direction                     |       |
| $\varepsilon_{xy}$      | Uniaxial Strain in xy-Direction                    |       |
| $\varepsilon_{yy}$      | Uniaxial Strain in y-Direction                     |       |
| $\varepsilon_{yz}$      | Uniaxial Strain in yz-Direction                    |       |
| $\varepsilon_{zx}$      | Uniaxial Strain in zx-Direction                    |       |
| $\varepsilon_{zz}$      | Uniaxial Strain in z-Direction                     |       |
| $\varepsilon$           | Mechanical Strain                                  |       |
| $\varepsilon$           | Dielectric Function                                |       |
| $\xi_{TL}^4$            | Constant for Tauc Lorentz Dielectric Function      | $J^4$ |
| $\xi$                   | Scaled Spatial x-Coordinate                        |       |
| $\zeta$                 | Gouy-Phase                                         |       |
| $a_B$                   | Bohr Radius                                        | m     |
| $a_{atan}$              | Constant for Tauc Lorentz Dielectric Function      | $J^4$ |
| $a_{ln}$                | Constant for Tauc Lorentz Dielectric Function      | $J^4$ |

|                     |                                                   |                                    |
|---------------------|---------------------------------------------------|------------------------------------|
| $c_0$               | Vacuum Speed of Light                             | m/s                                |
| $c_s$               | Speed of Sound                                    | m/s                                |
| $c$                 | Speed of Light                                    | m/s                                |
| $e$                 | Electron Charge                                   | C                                  |
| $g_{\text{diff}}$   | Diffusion Rate Factor                             | 1/(s)                              |
| $h$                 | Planck's Constant                                 | J/s                                |
| $i$                 | Imaginary Unit                                    |                                    |
| $k_B$               | Boltzmann's Constant                              | $\text{m}^2\text{kg/s}^2/\text{K}$ |
| $k$                 | Wave Vector                                       | $\text{m}^{-1}$                    |
| $l_{\text{sc}}$     | Length Scale                                      | m                                  |
| $m_e^*$             | Electron Effective Mass                           | kg                                 |
| $m_e$               | Electron Mass                                     | kg                                 |
| $m_h^*$             | Hole Effective Mass                               | kg                                 |
| $n_b$               | Bound Electron Density                            | $1/\text{m}^3$                     |
| $n_{\text{ch}}$     | Charge Carrier Density                            | $\text{m}^{-3}$                    |
| $n_{\text{e,crit}}$ | Critical Electron Density                         | $1/\text{m}^3$                     |
| $n_{\text{e,init}}$ | Initial Electron Density                          | $1/\text{m}^3$                     |
| $n_{\text{e,max}}$  | Maximum Electron Density                          | $1/\text{m}^3$                     |
| $n_{\text{e,tot}}$  | Bound Electron Density                            | $1/\text{m}^3$                     |
| $n_e$               | Free Electron Density                             | $1/\text{m}^3$                     |
| $n_h$               | Density of Holes                                  | $\text{m}^{-3}$                    |
| $n$                 | Refractive Index                                  |                                    |
| $q_e$               | Electron Heat Flux                                | $\text{W}/\text{m}^2$              |
| $q_l$               | Lattice Heat Flux                                 | $\text{W}/\text{m}^2$              |
| $q_{\text{sc}}$     | Scaled Heat Flux                                  | $\text{W}/\text{m}^2$              |
| $q$                 | General Heat Flux                                 | $\text{W}/\text{m}^2$              |
| $r$                 | Radius                                            | m                                  |
| $t_0$               | Temporal Pulse Offset                             | s                                  |
| $t_{\text{ret}}$    | Retardation Time for Cascade Ion-<br>ization Rate | s                                  |
| $t_{\text{sc}}$     | Time Scaling                                      | s                                  |
| $t$                 | Time                                              | s                                  |
| $u_s$               | Numerical Velocity                                |                                    |
| $u_z$               | Displacement                                      | m                                  |
| $v_z$               | Velocity                                          | m/s                                |

## *List of Symbols*

|                   |                              |                          |
|-------------------|------------------------------|--------------------------|
| $w_0$             | Beam Radius                  | m                        |
| $w_{\text{MPI}}$  | Multiphoton Ionization Rate  | $1/(\text{m}^3\text{s})$ |
| $w_{\text{SFI}}$  | Strong Field Ionization Rate | $1/(\text{m}^3\text{s})$ |
| $w_{\text{casc}}$ | Cascade Ionization Rate      | $1/(\text{m}^3\text{s})$ |
| $w_{\text{diff}}$ | Diffusion Rate               | $1/(\text{m}^3\text{s})$ |
| $w_{\text{rec}}$  | Recombination Rate           | $1/(\text{m}^3\text{s})$ |
| $w$               | Depth Depending Beam Radius  | m                        |
| $x$               | x-Coordinate                 | m                        |
| $y$               | y-Coordinate                 | m                        |
| $z_{\text{R}}$    | Rayleigh Length              | m                        |
| $z$               | z-Coordinate                 | m                        |

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