

MECHANICAL STRESSES UPON PHASE TRANSITIONS

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vorgelegt von
cand.scient.
Tom Peder Leervad Pedersen
aus Aarhus, Dänemark

Berichter: Universitätsprofessor Dr.rer.nat.Matthias Wuttig
Prof. Dr.Scient. Arne Nylandsted Larsen

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Chapter 1

Introduction

The impact of functional coatings on the performance of many devices, tools and applications has been immense in recent years. For example, in microelectronics the use of special thin films has led to improvements of electronic devices, hard coatings have improved the performance of many tools, and optical coatings have been used to a large extent to improve the performance of windows. Additionally, new devices have been invented based on such coatings. The intelligent windows able to control the transmission of light into buildings, data storage media such as the CD and later the DVD, and water purification devices are known to most people nowadays.

The stability and the lifetime of such devices depend on the stability of the functional coatings. This parameter depends on the mechanical stresses in the films. The most dramatic consequence of such stresses is the cracking or delamination of the films. These processes can lead to a complete failure of the coating, and hence of the functionality of the device in which the coating is active. While such processes occur abruptly, slower stress-induced processes that lead to a degradation of the properties of the films are also possible. Hence the control and the understanding of the mechanical stresses in these functional coatings is crucial, and therefore this topic was chosen for this work. However, as not all functional coatings could be studied, a few groups of materials were selected for the studies here.

Transition metal oxides such as TiO_2 , ZrO_2 , HfO_2 , V_2O_5 , Nb_2O_5 , Ta_2O_5 , MoO_3 and WO_3 are among the most applied coatings today. These oxides have a wide spectrum of possible applications even though their main use is as optical coatings. In fact such thin oxide coatings used on normal windows can allow a higher transmission of the solar energy into a building and additionally allow a high reflectance in the infrared, which helps confine the heat inside the building. In a cold region, such coated windows help save energy. It is however in the warm regions of the world that coatings designed to have the opposite properties, i.e to hinder the transmission of solar energy into the building, have the biggest impact, as they help save considerable amounts of energy used for cooling. Additionally, the transition metal oxides find application also in laser mirrors, ionic conductors, broadband interference filters [77] as well transparent conductive coatings, hard coatings, etc. One of most exciting topics in recent years has been the photocatalytic and hydrophylic properties of TiO_2 which has opened a window of applications such as antibacterial and self-sterilizing coatings, self-cleaning clothes, windows, paint and street coatings, as well as anti-fogging glass, dishwashers, air- and water purification devices, etc.

Another technology that has entered the market in recent years, are optically switchable windows. In such devices that are based on particular metals or metal oxides, an apparently metallic surface can be made transparent and vice versa. The applications that can be imagined, some which have already been realized, include windows with switchable optical properties, rear-view mirrors that automatically reduce the intensity of the reflected light as well as displays with improved contrast ratios.

Phase change films have won a central position in another field of application of functional coatings: optical data storage technology. The principle of optical storage systems utilizes the properties of the phase change films. The significant difference in optical properties of two different physical states of the active material; the amorphous and the crystalline state is exploited. By heating microscopic volumes of the material by use of irradiation, a phase transition between the two states can be carried out. Thereby tiny areas with a reflection that differs from that of the surrounding matrix are formed, and thus the storage of information is allowed. In data storage media such as CD-RW and DVD-RW such phase change coatings are already employed.

These three interesting groups of materials are all applied in situations where it is crucial to guarantee a certain lifetime, meaning that it is highly important to understand their mechanical stress properties.

In this work, detailed studies of the stresses arising in the three mentioned classes of functional coatings are carried out. In the field of transition metal oxides, measurements of the deposition stresses arising in films deposited using the industrially applied DC-sputtering method were carried out. For optically switchable coatings, *in-situ* measurements were carried out during the switching process, leading to enhanced understanding of the nature of the behavior of the coatings. An improved understanding of the magnitude of the stresses involved and the mechanism responsible for the switching in certain materials was also realized. Finally, in the field of phase change materials, measurements of the mechanical stress associated with the phase transitions were carried out. Additionally, thorough investigations of the stress relaxation mechanisms in the amorphous phase of the phase change films were performed.

However, before the results of these measurements are presented, other important topics are described. To interpret and understand the findings of the measurements, it is necessary to have a fundamental understanding of the theory of mechanical stresses in thin films. Hence chapter 2 contains a description of the theory of mechanical stresses. The special situations that are encountered in the experiments are all treated in detail.

It is impossible to apply this theory to measurements of mechanical stresses though, if no experimental setup is available. To allow the investigations presented in this work, it was hence necessary to construct a system tailored to the projected measurements. This system is described and characterized in detail in chapter 3.

In chapter 4 a few supplementary methods are presented. These systems were used to measure parameters crucial for the determination of the mechanical stress, most notably the film thickness.

Finally, the results of the studies of the mechanical stresses for each of the material groups described above is presented in chapters 5 to 7.

Chapter 2

Theory of mechanical stresses

To understand the experimental results of chapters (5) to (7), it is important to comprehend the theory of mechanical stresses in thin film. This is the topic of this chapter. In the first section (2.1), a simple model for understanding the terms involved in the description of mechanical stress is given, while a thorough treatment of the theory of mechanical stresses is presented in sections (2.2)-(2.5). In sections (2.6)-(2.8) inelastic effects are treated. Because of its importance in understanding the findings of chapter 7, the topic of viscous flow is treated thoroughly (section 2.8.4).

2.1 Concepts and definitions

Mechanical stresses arise in thin films whenever they are exposed to externally applied forces. Generally, in one dimension, when a body is subjected to an applied force, F , it is deformed (figure 2.1). The application of opposite but equal forces results in a deformation called strain, which by convention denoted is ϵ and defined as the ratio of the length change Δl to the initial length l_0 :

$$\epsilon = \frac{\Delta l}{l_0} \quad (2.1)$$

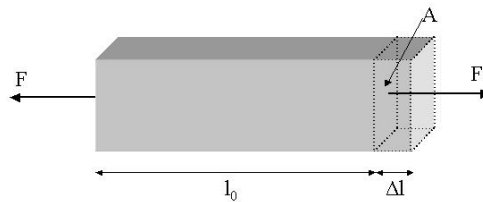


FIGURE 2.1: Schematic view of a force applied to a body and the resulting deformation of the body.



FIGURE 2.2: Schematic view of a the separation of stress into shear stress and orthogonal stress along an arbitrary section.

The applied forces place the body in a state of mechanical stress, as mechanical equilibrium must be upheld by internal stresses inside the body, hereby resulting in a stress σ defined as:

$$\sigma = \frac{F}{A} \quad (2.2)$$

where A is the surface on which the force F acts.

The strain and the stress are related through Hooke's law, which dates back to 1676:

$$\sigma = \frac{E}{(1 - \nu)} \cdot \varepsilon \quad (2.3)$$

and is applicable for elastic processes. The material dependent constant of proportionality E is called Young's modulus or elastic modulus, while ν describing the strain orthogonal to the applied stress is called Poisson's ratio. An interpretation of these constants is found in section 2.2.6.

In the situation where the forces place the body in a compressed state, the stress is called "compressive" and by convention attributed a negative sign. Similarly, in the case where the body is placed in an expanded state, the stress is by convention positive and called "tensile".

The deformation itself is called elastic or reversible, if the body returns to its original shape when the forces are removed. Similarly, it is called inelastic, plastic or irreversible, if the body shows a permanent change of shape after removal of the forces.

Making a section through the body at an arbitrary angle (figure 2.2) makes it necessary to resolve the stress into a transverse component τ called shear stress, and an orthogonal component σ_n , in order to sustain the mechanical equilibrium at the surface of the body.

The influence of shear stresses on a body can be understood from figure 2.3. The distortion of the body, which is called the shear strain, γ is related to the shear stress by:

$$\gamma = \frac{\tau}{G} \quad (2.4)$$

where G is the called the rigidity modulus of the material. It can be expressed as a function of the Young's modulus and the Poisson's ratio:

$$G = \frac{E}{2(1 + \nu)} \quad (2.5)$$

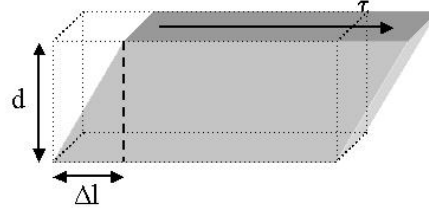


FIGURE 2.3: Schematic view of the effects of a shear stress on a body, resulting in a shear strain.

Additionally, the shear strain can be expressed as:

$$\gamma = \frac{\Delta l}{d} \quad (2.6)$$

where Δl is the change of length introduced by the shear stress at one side of the sample, and d is the thickness of the sample as seen in figure 2.3. Hence γ can be interpreted as a change of angle introduced in the body by the applied shear stress.

2.2 Elastic theory of mechanical stress

As thin films on substrates are three dimensional systems, the simple one-dimensional definitions from section 2.1 do not suffice to describe the state of mechanical stress in a thin film. Additional complications arise if the film or the substrate is anisotropic. Therefore, the description of mechanical stress in three dimensions is a rather complex matter. In this section, a thorough treatment of the theory of mechanical stress in three dimensions will be given. Even more details can be found for instance in references [94], [76] and [119].

2.2.1 The strain tensor

When a body is subjected to an applied force, the relative position of the atoms within it are altered, and the body is said to be strained or deformed. The initial position P of a point in the body can be described by a set of cartesian coordinates (x_1, x_2, x_3) , while the position P' in the strained body can be characterized by the coordinates (x'_1, x'_2, x'_3) (figure 2.4).

In the case of a linear transformation

$$x'_i = a_{i0} + x_i + \sum_{j=1}^3 (a_{ij}x_j) \quad (i = 1, 2, 3) \quad (2.7)$$

where the coefficients a_{ij} are constants, the positions of the points P and P' can be described by a vector $\vec{A}$, which has its origin in an arbitrary reference point (x_1^0, x_2^0, x_3^0) , and a vector $\vec{A}'$ whose

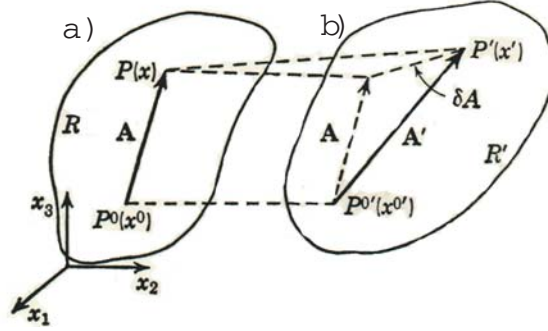


FIGURE 2.4: The change of the relative positions of the atoms between (a) an unstrained body, and (b) a strained body. From ref. [119].

origin is \$(x_1^{0'}, x_2^{0'}, x_3^{0'})\$. These vectors are related through

$$\vec{A}' = \vec{\delta A} + \vec{A} \quad (2.8)$$

where the single components of \$\vec{\delta A}\$ are given by

$$\delta A_i = A'_i - A_i = \sum_{j=1}^3 a_{ij} A_j \quad (i = 1, 2, 3) \quad (2.9)$$

From linear algebra, it is known that the components \$a_{ij}\$ may be expanded into a symmetric and a skew symmetric part in this way:

$$a_{ij} = \frac{1}{2}(a_{i,j} + a_{j,i}) + \frac{1}{2}(a_{i,j} - a_{j,i}) \quad (2.10)$$

Hence the components \$\delta A_i\$ can be expressed as:

$$\delta A_i = A'_i - A_i \quad (2.11)$$

$$= \sum_{j=1}^3 \left[\frac{1}{2}(a_{i,j} + a_{j,i}) + \frac{1}{2}(a_{i,j} - a_{j,i}) \right] A_j \quad (i = 1, 2, 3) \quad (2.12)$$

By introducing the coefficients \$\epsilon_{ij}\$ and \$\omega_{ij}\$:

$$\epsilon_{ij} = \epsilon_{ji} = \frac{1}{2}(u_{i,j} + u_{j,i}) \quad (2.13)$$

$$\omega_{ij} = -\omega_{ji} = \frac{1}{2}(u_{i,j} - u_{j,i}) \quad (2.14)$$

equation 2.12 can be written as

$$\delta A_i = \sum_{j=1}^3 [\epsilon_{ij} A_j + \omega_{ij} A_j] \quad (i = 1, 2, 3) \quad (2.15)$$

To interpret (2.15), it is useful to consider the implication of a pure translational motion. Such a rigid body motion is characterized by the fact that the length of any vector $\vec{A}$:

$$A = |\vec{A}| = \sqrt{\sum_{i=1}^3 A_i A_i} \quad (2.16)$$

is not changed. After an infinitesimal linear transformation like (2.7), the change in length δA can be expressed as:

$$A\delta A = \sum_{i=1}^3 [A_i \delta A_i] \quad (2.17)$$

where higher order terms in δA_i are neglected. Inserting the expression for δA_i , (2.9) one finds:

$$A\delta A = \sum_{i=1}^3 \sum_{j=1}^3 a_{ij} A_i A_j \quad (2.18)$$

For pure translation δA must vanish for all values of A_1 , A_2 and A_3 . Hence the following requirements must be satisfied:

$$a_{11} = 0 \quad (2.19)$$

$$a_{22} = 0 \quad (2.20)$$

$$a_{33} = 0 \quad (2.21)$$

$$a_{12} + a_{21} = 0 \quad (2.22)$$

$$a_{23} + a_{32} = 0 \quad (2.23)$$

$$a_{31} + a_{13} = 0 \quad (2.24)$$

$$(2.25)$$

This means that skew symmetry i.e. $a_{ij} = -a_{ji}$, is a sufficient condition for the transformation to be pure translation.

With this knowledge in hand, an interpretation of equation 2.15 is now possible: The term containing the skew symmetric coefficients ω_{ij} corresponds to pure translational motion, while the term containing the coefficients ε_{ij} represents pure deformation. Hence the coefficients ε_{ij} are defined as the components of the strain tensor $\bar{\varepsilon}$:

$$\bar{\varepsilon} = \begin{bmatrix} \varepsilon_{11} & \varepsilon_{12} & \varepsilon_{13} \\ \varepsilon_{21} & \varepsilon_{22} & \varepsilon_{23} \\ \varepsilon_{31} & \varepsilon_{32} & \varepsilon_{33} \end{bmatrix} \quad (2.26)$$

2.2.2 The components of strain: Geometrical interpretation

Diagonal elements, ε_{ii}

At the beginning of this chapter strain was defined as the normalized length increase of a one-dimensional body. By considering the geometrical interpretation of the components of the strain

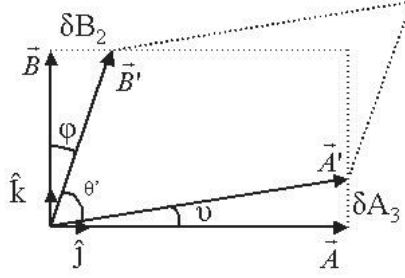


FIGURE 2.5: The increase of angle between vectors as a result of shear.

tensor, this result is reproduced if one considers the length increase δA of a vector $\vec{A}$, which is parallel to an axis i , after an infinitesimal transformation along this axis.

The original length of the vector $\vec{A}$ is given by (2.16), while the change of length after an infinitesimal transformation is given by (2.17). By use of the first term in equation 2.15 these observations can be summarized as:

$$A\delta A = \sum_{i=1}^3 \epsilon_{ij} A_i A_j \quad (2.27)$$

which can also be written as

$$\frac{\delta A}{A} = \frac{\sum_{i=1}^3 \epsilon_{ij} A_i A_j}{A^2} \quad (2.28)$$

In case of the vector $\vec{A}$ being parallel to the x-axis, this reduces to:

$$\frac{\delta A}{A} = \epsilon_{11} \quad (2.29)$$

Hence ϵ_{11} corresponds to the relative change of length of the vector along the x-axis.

This means that a cube which before the deformation has sides of length l , after the deformation has a side of length $(1 + \epsilon_{11})l$ in x-direction, while its dimensions in the y- and z-directions are left unchanged.

Similarly the components ϵ_{22} and ϵ_{33} correspond to the relative length change along the y- and z-axis.

Off-diagonal elements, ϵ_{ij}

To appreciate the geometrical meaning of the off-diagonal entries ϵ_{12} , ϵ_{23} and ϵ_{31} , a transformation of two points described by the vectors:

$$\vec{A} = \hat{j}A_2 \quad (2.30)$$

$$\vec{B} = \hat{k}B_3 \quad (2.31)$$

can be considered. $\hat{j}$ and $\hat{k}$ are the unit vectors in y- and z-direction (figure 2.5). After the deformation these vectors become:

$$\vec{A}' = \hat{i}\delta A_1 + \hat{j}(A_2 + \delta A_2) + \hat{k}\delta A_3 \quad (2.32)$$

$$\vec{B}' = \hat{i}\delta B_1 + \hat{j}\delta B_2 + \hat{k}(B_3 + \delta B_3) \quad (2.33)$$

While the angle between $\vec{A}$ and $\vec{B}$ is 90° , the angle θ' between $\vec{A}'$ and $\vec{B}'$ can be calculated from

$$\cos \theta' = \frac{\vec{A}' \cdot \vec{B}'}{|\vec{A}'||\vec{B}'|} \quad (2.34)$$

$$= \frac{A_2\delta B_2 + B_3\delta A_3}{A_2B_3} \quad (2.35)$$

$$= \frac{\delta B_2}{B_3} + \frac{\delta A_3}{A_2} \quad (2.36)$$

where the products of δA and δB have been neglected. This expression can be further reduced, as from equation 2.15 one has:

$$\delta B_2 = \varepsilon_{23}B_3 \quad (2.37)$$

$$\delta A_3 = \varepsilon_{23}A_2 \quad (2.38)$$

Inserting (2.37) and (2.38) into equation 2.36 yields:

$$\cos \theta' = 2\varepsilon_{23} \quad (2.39)$$

If one considers the change of the right angle between $\vec{A}$ and $\vec{B}$ ($\phi = 90^\circ - \theta'$) it follows that for small changes:

$$\cos \theta' = \sin(90^\circ - \phi) = \sin \phi = \phi = 2\varepsilon_{23} \quad (2.40)$$

Hence ε_{23} simply describes the change in the angle between the vectors $\vec{A}$ and $\vec{B}$ after the deformation (fig. 2.6)

From figure 2.5 it can be seen that for small angles:

$$\vartheta = \tan \vartheta = \frac{\delta A_3}{A_2} = \varepsilon_{23} \quad (2.41)$$

and

$$\varphi = \tan \varphi = \frac{\delta B_2}{B_3} = \varepsilon_{23} \quad (2.42)$$

A rotation of the parallelogram in figure 2.5 by an angle ε_{23} around the origin, yields the situation shown in figure 2.6. Hence the original rectangle has been transformed into a parallelogram by a so-called *shear*. The off-diagonal coefficients ε_{ij} therefore describe shear deformations of the body.

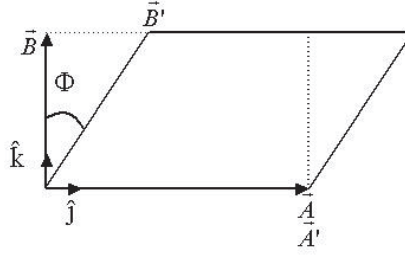


FIGURE 2.6: As a result of shear a rectangular shaped body is transformed into a parallelogram.

To distinguish between the diagonal elements of the strain tensor corresponding to length changes along the primary axis and the off-diagonal components, the shear strains are often denoted γ_{ij} . For the remainder of this work this practice is employed, meaning that the strain tensor takes on the form:

$$\bar{\bar{\epsilon}} = \begin{bmatrix} \epsilon_{11} & \gamma_{12} & \gamma_{13} \\ \gamma_{21} & \epsilon_{22} & \gamma_{23} \\ \gamma_{31} & \gamma_{32} & \epsilon_{33} \end{bmatrix} \quad (2.43)$$

2.2.3 Stress

The simple definition of stress given in section 2.1 is not an accurate one when it comes to describing a state of stress in a three-dimensional body. As it was the case for the strain as shown in section 2.2.1, a tensor notation of the stress is useful.

In figure 2.7 a body is shown which is subject to forces $\vec{S}_i$ acting on its surfaces. These surface forces are expressed as force per unit area of the surface at which they are acting. i denotes the normal of the surface. Resolving the components of $\vec{S}_i$ into components along the coordinate axis yields:

$$\vec{S}_i = \hat{e}_j S_{ij} \quad (2.44)$$

$$= \hat{e}_j \sigma_{ij} \quad (2.45)$$

where the definition

$$\sigma_{ij} = S_{ij} \quad (2.46)$$

was introduced. The elements σ_{ij} constitute a tensor $\bar{\bar{\sigma}}$ which is called the stress tensor. The indices i and j refer to the coordinate axis normal to the surface on which $\hat{S}$ acts and the direction of the components of $\hat{S}$, respectively.

In the case of a rhombic body as shown in figure 2.7, it can be seen that the diagonal entries σ_{11} , σ_{22} and σ_{33} correspond to normal stresses, while the remaining off-diagonal elements constitute shear stresses. Hence the shear stresses are sometimes denoted τ_{ij} . This convention is employed for the remainder of this work, meaning that the stress tensor takes on the form:

$$\bar{\bar{\sigma}} = \begin{bmatrix} \sigma_{11} & \tau_{12} & \tau_{13} \\ \tau_{21} & \sigma_{22} & \tau_{23} \\ \tau_{31} & \tau_{32} & \sigma_{33} \end{bmatrix} \quad (2.47)$$

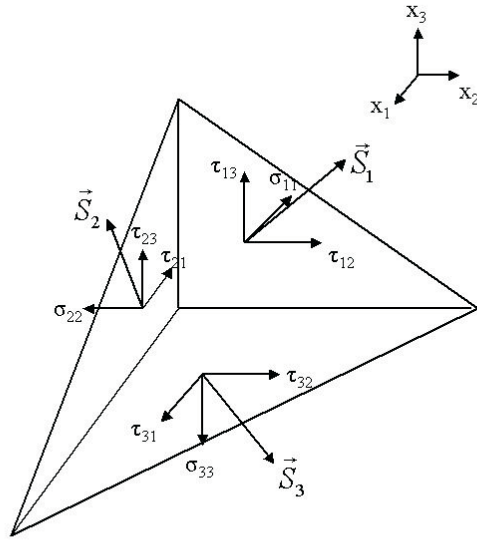


FIGURE 2.7: Forces $\vec{S}_i$ acting at the surfaces of a body can be resolved in coordinates along the coordinate axis. (See text for details.)

2.2.4 Hooke's law

Hooke's law (2.3) can be expressed by the strain and stress tensors $\bar{\bar{\epsilon}}$ and $\bar{\bar{\sigma}}$:

$$\sigma_{ij} = c_{ijkl} \epsilon_{kl} \quad (2.48)$$

As the indices i, j, k, l all range from 1 to 3, the tensor c_{ijkl} contains 81 elements. This number can be decreased substantially when considering that in an elastically homogeneous medium, where σ_{ij} is symmetric, c_{ijkl} is also symmetric. Therefore equation 2.48 can be simplified by the introduction of the so-called Voigt notation [94], which exchanges the indices of σ_{ij} to:

$$11 = 1 ; 22 = 2 ; 33 = 3 ; 23 = 4 ; 31 = 5 ; 12 = 6 \quad (2.49)$$

and introduces a factor of two in the off-diagonal elements of the strain tensor:

$$2\gamma_{23} = \gamma_4 ; 2\gamma_{31} = \gamma_5 ; 2\gamma_{12} = \gamma_6 \quad (2.50)$$

Using this equation, (2.48) reduces to:

$$\sigma_i = c_{ij} \epsilon_j \quad (i, j = 1, 2, \dots, 6) \quad (2.51)$$

The constants c_{ij} are defined as the elastic moduli of the material in question, and have the same unit as the stress elements σ_i , since the strain components are dimensionless.

Just as the stresses can be determined from the strains, the strains can be determined from the stresses in similar way by use of the moduli s_{ij} :

$$\varepsilon_j = s_{ij}\sigma_i \quad (i, j = 1, 2, \dots, 6) \quad (2.52)$$

For practical use however, the calculation of the strain and the stress components can be simplified by considering the expression of the elastic energy density of a material [4]:

$$f_{el} = \frac{1}{2} \sum_{i,j} c_{ij} \varepsilon_i \varepsilon_j \quad (2.53)$$

which can be shown to be related to the stress tensor components by [119]:

$$\sigma_i = \frac{\partial f_{el}}{\partial \varepsilon_i} \quad (2.54)$$

This helpful relation will be used in the following section.

2.2.5 Directional dependence of elastic properties

When the symmetry of the considered material increases, the number of independent elastic moduli decreases. For materials possessing a geometrical symmetry determined by their crystal structure etc., a degree of elastic symmetry is also given. Hence their elastic properties are identical along certain directions. In this section the structure of the matrix $\bar{c}$ for some common symmetry cases will be presented. Details can be found in for instance ref. [94].

A significant simplification of the $\bar{c}$ tensor is found for materials classified as orthotropic i.e. materials, that have three mutually orthogonal planes of elastic symmetry. If the set of coordinate axis is chosen such that the coordinate planes coincide with the planes of elastic symmetry, the elastic properties of the material can be characterized by only 9 independent components c_{ij} :

$$c_{ij}^{orthotropic} = \begin{bmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ c_{21} & c_{22} & c_{23} & 0 & 0 & 0 \\ c_{31} & c_{32} & c_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{66} \end{bmatrix} \quad (2.55)$$

This number is even further reduced in the case of a cubic system, where the symmetry leads to just 3 independent entries:

$$c_{ij}^{cubic} = \begin{bmatrix} c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{12} & c_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{44} \end{bmatrix} \quad (2.56)$$

In the case of elastically isotropic materials, such as an amorphous medium, the $\bar{c}$ matrix simplifies even further. The elastic properties of an isotropic medium are independent of the orientation of the coordinate axis. Hence the components c_{ij} are invariant to any rotation of these axis. By application of this concept, the $\bar{c}$ matrix reduces to:

$$c_{ij}^{isotropic} = \begin{bmatrix} c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{12} & c_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2}(c_{11} - c_{12}) & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{2}(c_{11} - c_{12}) & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{2}(c_{11} - c_{12}) \end{bmatrix} \quad (2.57)$$

where it has been applied that [94]:

$$c_{44} = \frac{1}{2}(c_{11} - c_{12}) \quad (2.58)$$

For crystalline materials the $\bar{c}$ matrix is reduced by the degree of symmetry of the crystal structure. As examples, a cubic system has the non-zero elements shown in equation 2.56, while the non-zero elements of the hexagonal crystal group are:

$$c_{ij}^{hexagonal} = \begin{bmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{13} & 0 & 0 & 0 \\ c_{13} & c_{13} & c_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{2}(c_{11} - c_{12}) \end{bmatrix} \quad (2.59)$$

As opposed to the isotropic case, only $c_{66} = \frac{1}{2}(c_{11} - c_{12})$ in the case of hexagonal symmetry.

By use of these matrices, the corresponding elastic energy densities can be calculated using equation 2.53, and the resulting strains and stresses can be derived from equation 2.54. An example is shown in the following section.

2.2.6 Elastic constants

In the case of cubic materials, the elastic energy density can be expressed by use of (2.53):

$$\begin{aligned} f_{el}^{cubic} &= \frac{1}{2} \sum_{i,j} c_{ij} \epsilon_i \epsilon_j \\ &= \frac{1}{2} c_{11} (\epsilon_1^2 + \epsilon_2^2 + \epsilon_3^2) + c_{12} (\epsilon_1 \epsilon_2 + \epsilon_2 \epsilon_3 + \epsilon_3 \epsilon_1) + \frac{1}{2} c_{44} (\gamma_4^2 + \gamma_5^2 + \gamma_6^2) \end{aligned}$$

The components of the stress tensor σ_i can now be evaluated from equation 2.54. As an example

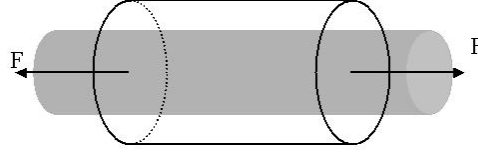


FIGURE 2.8: The example of an elastically stretched cylinder leads to important definitions of E , ν and μ .

σ_{11} is given by:

$$\sigma_{11} = \frac{\partial f_{el}^{cubic}}{\partial \epsilon_1} \quad (2.60)$$

$$= c_{11}\epsilon_{11} + c_{12}\epsilon_{22} + c_{12}\epsilon_{33} \quad (2.61)$$

$$= c_{12}(\epsilon_{11} + \epsilon_{22} + \epsilon_{33}) + (c_{11} - c_{12})\epsilon_{11} \quad (2.62)$$

$$= \lambda \delta_{ij} \epsilon_{ii} + 2\mu \epsilon_{11} \quad (2.63)$$

where the so-called Lamé constants [76]

$$\lambda = c_{12} \quad (2.64)$$

and

$$\mu = c_{44} \quad (2.65)$$

were introduced.

Similar expressions are found for the other components of the stress tensor. Hence σ_{ij} can generally be expressed as:

$$\sigma_{ij} = \lambda \delta_{ij} \epsilon_{ii} + 2\mu \epsilon_{ij} \quad (i, j = 1, 2, 3) \quad (2.66)$$

Solving for ϵ_{ij} yields:

$$\epsilon_{ij} = \frac{-\lambda}{2\mu} \delta_{ij} \epsilon_{ii} + \frac{1}{2\mu} \sigma_{ij} \quad (i, j = 1, 2, 3) \quad (2.67)$$

By now considering a simple example, a few very important definitions can be made: If a cylinder as shown in figure 2.8 is stretched elastically by an applied force F in the x -direction, a stress σ_{11} arises. Using the fact that all other stress components are zero, the non-zero strains become:

$$\epsilon_{11} = \frac{(\lambda + \mu)\sigma_{11}}{\mu(3\lambda + 2\mu)} = \frac{1}{E} \tau_{11} \quad (2.68)$$

$$\epsilon_{22} = \epsilon_{33} = \frac{-\lambda\sigma_{11}}{2\mu(3\lambda + 2\mu)} = \frac{-\nu}{E} \sigma_{11} = -\nu \epsilon_{11} \quad (2.69)$$

where

$$E = \frac{\mu(3\lambda + 2\mu)}{\mu + \lambda} \quad (2.70)$$

is called the Young's modulus, and represents the ratio of the stress σ to the strain ϵ in a certain direction. Similarly

$$\nu = \frac{\lambda}{2(\mu + \lambda)} \quad (2.71)$$

is called the Poisson's ratio. From equation 2.69 it can be appreciated, that ν represents the contraction or expansion of the body perpendicular to the axis of the applied force. By comparison with (2.52), it can be found that E and ν can be expressed as:

$$E = \frac{1}{s_{11}} \quad (2.72)$$

and

$$\nu = -\frac{s_{12}}{s_{11}} \quad (2.73)$$

In the case of a pure shear stress however, the only non-zero stress component as an example is σ_{23} . From equation 2.67, the corresponding strain element is then given by:

$$\gamma_{23} = \frac{-\tau_{23}}{2\mu} \quad (2.74)$$

As shown in section 2.2.2, the strain γ_{23} corresponds to an increase of the angle ϕ in figure 2.6. Hence by applying equation 2.40 μ is given by:

$$\mu = \frac{\tau_{23}}{\phi} \quad (2.75)$$

and can thus be interpreted as the ratio of the shear stress to the increase in angle introduced by the shear stress. Therefore μ (or G as it is sometimes denoted) is called the shear modulus or the rigidity modulus.

The three elastic constants, E , ν and μ are extremely important in the determination of stresses as shown below.

2.3 Substrate bending induced by mechanical stress

In a thin film, mechanical stresses can arise because the film is grown on and therefore fixed to a substrate. As it will be explained in detail below, a volume change in the film and heating of the sample amongst other processes, will result in stresses as the expansion or contraction of the film is constrained by the substrate. During growth so-called deposition stresses can arise. In

epitaxial films such stresses can arise as result of lattice mismatch etc., while in the production of amorphous films stresses can arise as a consequence of a variety of involved processes, which are further discussed in chapter 5.4.

One of the most amazing effects of mechanical stresses in thin films is the bending it induces in the entire sample including the substrate. In this section a derivation of this phenomenon based on the work of Timoschenko and Woineowsky-Krieger [126] is presented.

Mechanical stress in the thin film will tend to compress or expand the substrate dimensions, as a force corresponding to the mechanical stress in the film:

$$F = \sigma \cdot A \quad (2.76)$$

will be acting on the surface of the substrate at the interface. Additionally, the force induces bending moments in the plane along the x- and y-axis of system given by:

$$M_x = M_y = \vec{F} \times \vec{r} \quad (2.77)$$

Because of these bending moments, the substrate will bend and attain a given curvature along its x- and y-axis.

As the mechanical stress in the film σ_f gives rise to a force acting on the substrate as described above, it works as a shear stress τ on the substrate. In this case the bending moments can be calculated to [96]:

$$M_x = \frac{1}{2} \tau_x w d_f d_s \quad (2.78)$$

and

$$M_y = \frac{1}{2} \tau_y l d_f d_s \quad (2.79)$$

where l is the length of the sample and w is its width, while the substrate and film thicknesses are denoted d_s and d_f , respectively.

The relation between the bending moments and the radii of curvature of the substrate depends on the nature of the substrate. Anisotropy and the resulting directional dependence of the Young's modulus and the Poisson's ratio must be considered if anisotropic substrates are used. For substrates that are isotropic in the plane, such as ones of orientations hexagonal (0001), cubic (100) and (111), the following expressions are valid [76]:

$$M_x = \frac{E_s d_s^3 w}{12(1 - \nu_s^2)} \left(\frac{1}{R_x} - \nu_s \frac{1}{R_y} \right) \quad (2.80)$$

and

$$M_y = \frac{E_s d_s^3 l}{12(1 - \nu_s^2)} \left(\frac{1}{R_y} + \nu_s \frac{1}{R_x} \right) \quad (2.81)$$

Combining equations (2.78)-(2.81) yields:

$$\sigma_x = \frac{E_s d_s^2}{6(1 - \nu_s^2) d_f} \left(\frac{1}{R_x} + \nu_s \frac{1}{R_y} \right) \quad (2.82)$$

and

$$\sigma_y = \frac{E_s d_s^2}{6(1 - \nu_s^2) d_f} \left(\frac{1}{R_y} + \nu_s \frac{1}{R_x} \right) \quad (2.83)$$

These equations link the stress components σ_x and σ_y (by convention called in-plane stresses), which work as shear stresses τ_x and τ_y on the substrate, to the radii of curvature along the x- and y-axis. For cases where the stress is isotropic i.e. in cases of isotropic films such as in the amorphous and polycrystalline cases, σ_x equals σ_y . Therefore the equations (2.82) and (2.83) reduce to

$$\sigma = \sigma_x = \sigma_y = \frac{E_s d_s^2}{6(1 - \nu_s) d_f} \frac{1}{R} \quad (2.84)$$

Equation 2.84 is known as the Stoney equation [104]. It includes the term $(1 - \nu_s)$, which was not included by Stoney, as he did not consider the two-dimensional nature of the curvature. In literature there is also no consistency regarding this topic. Too often the term $E/(1 - \nu)$ is referred to as the "Young's modulus" even though it is correctly labelled as the "biaxial modulus", Y .

Additionally, in experiments one should consider the initial radius of curvature R_0 of the substrate. Perfectly flat substrates are not common. Hence, for measurements of exact stresses, the Stoney equation should include a term related to R_0 :

$$\sigma = \frac{E_s d_s^2}{6(1 - \nu_s) d_f} \left(\frac{1}{R} - \frac{1}{R_0} \right) \quad (2.85)$$

2.4 Volume changes and mechanical stress

When the film is subject to a volume change, the description of the mechanical stress is simple as long as the processes involved are elastic. From the following simple "Gedanken-experiment" [65], a complete set of equations describing such a scenario can be derived.

In figure 2.9.a, a system consisting of a substrate and a film is shown. The film is under no influence of stress. The first step in changing this is to remove the film from the substrate and subject it to a volume change. This volume change corresponds to a strain ε along the three major axis (figure 2.9.b):

$$\varepsilon = \frac{\Delta w}{w_0} = \frac{\Delta l}{l_0} = \frac{\Delta d}{d_0} \quad (2.86)$$

Fixing the expanded film to the substrate is impossible at this stage, as its area does not conform with the area of the substrate. Therefore the film area must be fitted to the area of the substrate by application of an external force in the x-y plane (figure 2.9.c). Hence a strain of

$$\varepsilon_x = \varepsilon_y = -\varepsilon \quad (2.87)$$

must be induced in the film. Associated with this strain in the x-y plane is an additional strain in the z direction:

$$\Delta \varepsilon_z = \frac{2\nu}{1 - \nu} \varepsilon \quad (2.88)$$

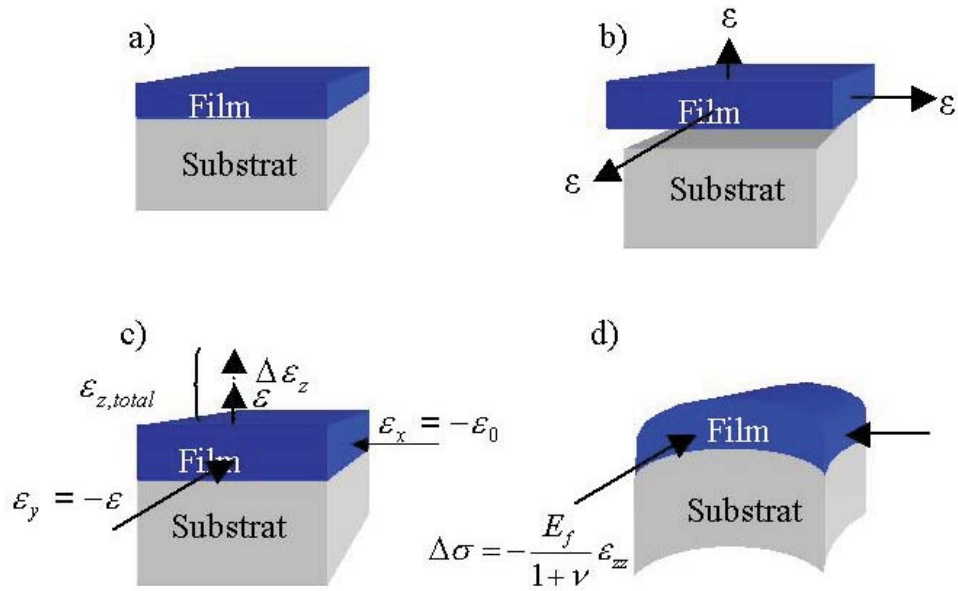


FIGURE 2.9: a) A substrate/film system which is under no influence of stress. b) The film is lifted of the substrate and it is subject to a volume change. c) The area of the film in the x-y plane is fitted to the dimensions of the surface of the substrate. d) As a result of the stress in the film, the whole system takes on a curved shape.

meaning that the total strain in z-direction is:

$$\epsilon_{z,total} = \epsilon_z + \Delta\epsilon_z = \left(\frac{1+\nu}{1-\nu} \right) \epsilon \quad (2.89)$$

Once the area of the film matches the area of the substrate, the film can be reattached, and the compressive force can be removed (figure 2.9.c). Now it is the substrate that prevents the film from expanding back to its shape in figure (2.9.b). This constraint on the film places it in a state of mechanical stress σ given by Hooke's law:

$$\sigma_x = \sigma_y \quad (2.90)$$

$$= - \left(\frac{E_f}{1-\nu} \right) \epsilon \quad (2.91)$$

$$= - \left(\frac{E_f}{1-\nu} \right) \left(\frac{1-\nu}{1+\nu} \right) \epsilon_{z,total} \quad (2.92)$$

$$= - \left(\frac{E_f}{1+\nu} \right) \epsilon_{z,total} \quad (2.93)$$

When the external force is removed the system takes on a curved shape (figure 2.9.d) as described in section 2.3.

The validity of this 'Gedanken-experiment' stems from the fact, that the effects of changes of physical quantities resulting in elastic transformations of the film only depend on the initial and final states of the system and not on any intermediate states. Therefore it is perfectly valid to consider an intermediary situation, where the film is removed from the substrate.

2.5 Thermal stress

Because of the constraint condition imposed on the film by the substrate on which it is fixed, temperature changes induce so-called thermal stresses in the film. The reason for this are the different coefficients of thermal expansion of film and substrate.

If the film-substrate system is subjected to a temperature change ΔT , the strains of the film (subscript f) and substrate (subscript s) are respectively:

$$\epsilon_f^i = \alpha_f \cdot \Delta T \quad (2.94)$$

and

$$\epsilon_s^i = \alpha_s \cdot \Delta T \quad (2.95)$$

if the film and substrate are considered isolated (superscript i) from each other. In reality however, the constraint condition applies and thus the film and the substrate cannot be considered isolated. Instead the difference between the thermal strains is imposed on the film by the substrate:

$$\epsilon_f = (\alpha_s - \alpha_f) \cdot \Delta T \quad (2.96)$$

Associated with this strain is a biaxial stress given by Hooke's law (2.3):

$$\sigma_f = \frac{E_f}{1 - \nu_f} (\alpha_s - \alpha_f) \cdot \Delta T = Y_f (\alpha_s - \alpha_f) \cdot \Delta T \quad (2.97)$$

As the coefficient of thermal expansion can vary significantly between substrate and film, large stresses can be induced by thermal changes. For instance, elevated temperatures during deposition will result in an introduction of thermal stresses in the film, when it is cooled to room temperature after growth.

2.5.1 Determination of elastic constants by exploiting thermal stresses

The nature of the relation describing thermal stresses (equation 2.97) implicates that the biaxial modulus and the coefficient of thermal expansion of an unknown film can be determined by a simple experiment: If identical films are deposited on two substrates with well-known coefficients of thermal expansion, measurements of their thermal stress as a function of a given temperature change will yield the desired information, as the thermal stresses in the two cases are:

$$\sigma_{f,s1} = \frac{E_f}{1 - \nu_f} (\alpha_{s1} - \alpha_f) \cdot \Delta T_{s1} \quad (2.98)$$

and

$$\sigma_{f,s2} = \frac{E_f}{1 - \nu_f} (\alpha_{s2} - \alpha_f) \cdot \Delta T_{s2} \quad (2.99)$$

Solving the coupled equations yields:

$$Y_f = \frac{\left(\frac{\Delta \sigma_{f,s1}}{\Delta T_{s2}} \right) - \left(\frac{\Delta \sigma_{f,s2}}{\Delta T_{s1}} \right)}{\alpha_{s1} - \alpha_{s2}} \quad (2.100a)$$

$$\alpha_f = \frac{\alpha_{s2} \cdot \left(\frac{\Delta \sigma_{f,s1}}{\Delta T_{s1}} \right) - \alpha_{s1} \cdot \left(\frac{\Delta \sigma_{f,s2}}{\Delta T_{s2}} \right)}{\left(\frac{\Delta \sigma_{f,s1}}{\Delta T_{s1}} \right) - \left(\frac{\Delta \sigma_{f,s2}}{\Delta T_{s2}} \right)} \quad (2.100b)$$

Hence, the elastic constants of an unknown film can be determined without knowledge of its structure or identity.

2.6 Stress relaxation

This section treats the topic of irreversible deformations in materials. When the mechanical stress becomes too large i.e. when it surpasses the material dependent elastic limit (or proportional limit), the deformation is no longer elastic and reversible. Above this threshold, plastic flow or yielding is observed, and the bonds of the material are broken or irreversibly rearranged. This can be understood from fig. 2.10. As long as the relation between stress and strain is linear, elastic

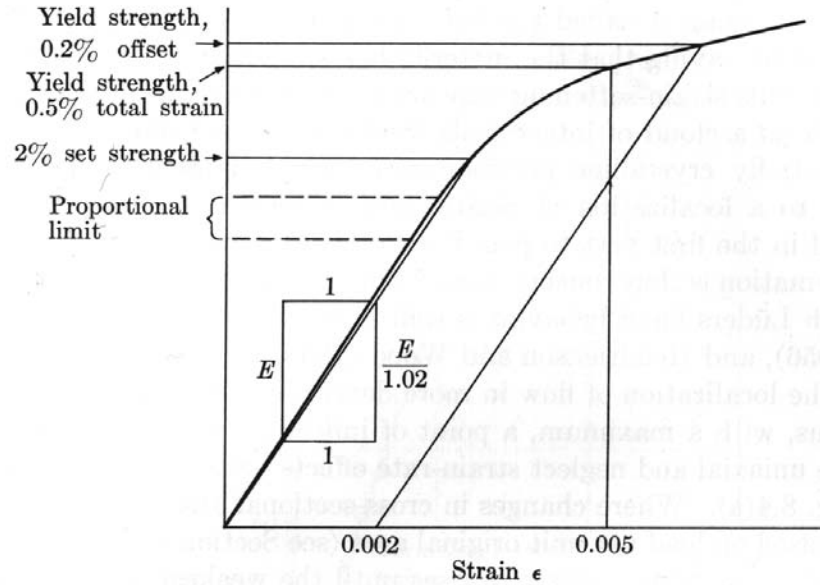


FIGURE 2.10: A stress versus strain curve shows the transition from the elastic deformation regime to the region of plastic flow above the proportionality limit. At low strains the stress increases proportional to the strain. However, at higher strains the material begins to yield and the stress does not show a proportional response. From ref. [76].

processes rule, and the elastic theory of the preceding sections, in which the bonds of the material are only stretched or shortened in response to the applied stress, must be applied. However, this linear relationship is lost above the proportional limit, and the theory of stress relaxation which is described in this section applies.

As a note of caution, the often used term "yield strength" is normally defined in relation to a certain deviation from the linear behavior. In figure 2.10 the yield strength for definitions of 0.2% offset and 0.5% total strain offset respectively, are shown [76].

In the region of plastic flow, several types of processes are possible. One distinguishes between plastic deformations, where at a certain threshold force the material suddenly strains, and the original shape is not recovered upon removing the force, and the so-called creep mechanisms. Creep are processes in which the material slowly strains irreversibly under the application of a constant force. Within the regime of creep deformations one additionally distinguishes between time-dependent and time-independent creep.

For plastic flow to occur, the magnitude of the stress must surpass the cohesive strength of the material. Considering a perfect crystal one can estimate the stress required to break the crystal bonds. This stress corresponds to the atomic force shown in fig. 2.11. As a rule of thumb, the theoretical cohesive strength is [23]:

$$\sigma_b = \frac{E}{10} \quad (2.101)$$

Similarly, the theoretical shear strength is of the order of $\tau_b = G/10$ [23]. In reality though, crystals are not perfect. The imperfections reduce the values for σ_b and τ_b that are usually found. In fact,

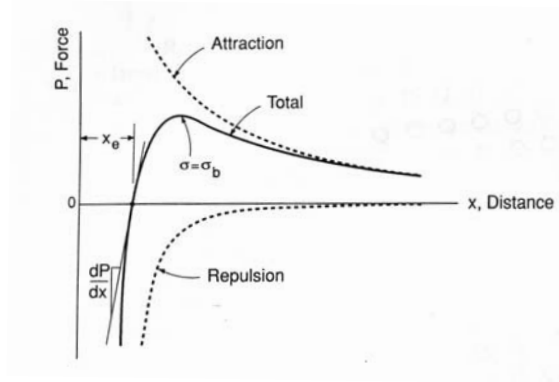


FIGURE 2.11: The balance between attractive and repulsive forces between atoms. The maximum force σ_b corresponds to the cohesive strength of the considered crystal. From ref. [23].

the cohesive and shear strengths are often a factor of 10-1000 lower than the theoretical limits [23], [76]. The reason for this arise from the lattice defects present in the crystal. These lattice defects play a crucial role in the description of the mechanisms for plastic flow, which are described below.

Additionally one has to consider the thickness of the film. The reason is seen in the definition of the stress (2.2). Stress is defined as force normalized to the area on which the force works. Hence the force can be expressed as

$$F = \sigma \cdot d_f \cdot w \quad (2.102)$$

where d_f is the thickness of the film and w its width. This means that for a given value of the biaxial stress σ , the force on the interface increases linearly with the thickness of the film. Hence thicker film are more prone to cracking and delamination than thin films.

2.7 Plastic deformations in crystalline materials

When a crystal undergoes time-independent permanent deformations, it is said to "yield". Such plastic deformations can be explained by dislocation mechanics, which in turn explains why real crystalline materials yield at relatively low stresses compared to the theoretical limits calculated in section 2.6.

Plastic deformations occur by a shear stress induced motion of dislocations through the crystal. This motion of the dislocation takes place by passing one atom at a time instead of happening simultaneously over an entire plane, as assumed in the calculation of the theoretical strength of the crystal. Therefore the dislocation can move through the crystal at stresses that are much lower than its theoretical strength.

Origin for the plastic deformations are the well-known characteristic types of dislocations, for instance the edge dislocation and the screw dislocation (see e.g. [4] for details). As an example, the edge dislocation present where a partial atomic plane is terminated (figure 2.12) can be considered. Its motion through a crystal can be understood from figure 2.13. In figure 2.13.a, the atom A is attracted to the atoms B and C in the neighboring plane. When a shear stress τ is applied, atom

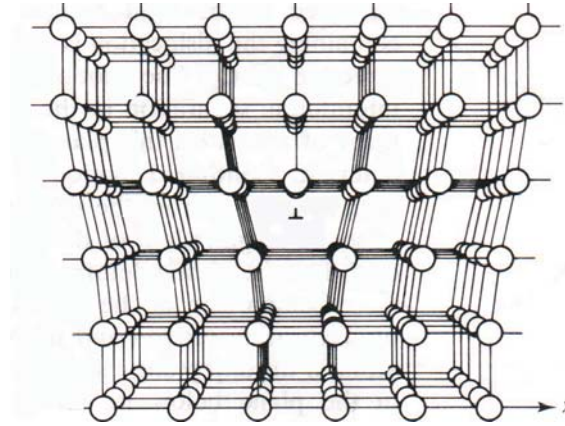


FIGURE 2.12: The edge dislocation ($\perp$) in a cubic structure is situated where the partial plane terminates. From ref. [16].

A is preferentially attracted to atom C. As a result, the atomic rearrangement seen in figure 2.13.b arises. It can be seen that the dislocation has just moved one atom to the right. As this process is repeated, the dislocation moves towards the surface (fig. 2.13.c), and as it moves out of the crystal, it can be seen from fig. 2.13.d, that the surface of the crystal is displaced. The plane on which the dislocation line moves is labelled "the slip plane", while the direction of the dislocation movement is called the "slip direction".

In a similar way, the screw dislocation can move through the crystal, as its Burgers vector also lies in the slip direction. Hence the edge and screw dislocations are labelled "glide dislocations".

Other dislocations whose Burgers vector does not lie in the slip direction do not glide through the crystal. As an example one can consider the dislocation loop shown in fig. 2.14 which consist of a group of vacancies. Its Burgers vector $\vec{AF}$ that does not lie in the slip direction, and therefore the dislocation cannot glide with ease through the crystal. The orientation of dislocations vary depending on the crystal structure. Usually the dislocations are found in characteristic crystallographic planes depending on the structure considered. The properties of these planes can be understood when considering the force τ_f required for dislocation motion in the case of an edge dislocation (fig. 2.12) [16]:

$$\tau_f = G \cdot \exp\left(\frac{-2\pi a}{(1-\nu)b}\right) \quad (2.103)$$

where a is the vertical distance between slip planes and b is the slip distance. It is seen, that τ_f is small when a is large and b is small, meaning that dislocations are found in close-packed planes with a large separation distance between adjacent planes. Hence these are the planes along which slip occurs the easiest. For different crystal structures the planes in which dislocations and slip are usually found are listed in table 2.1, while some examples are shown in figure 2.15.

Even though glide dislocations move easily through the crystal, they can be obstructed by obstacles. Such obstacles increase the strength of the materials by a factor of 10 or more [23], and hence stabilize the materials with respect to slip deformation. Grain-boundaries have this effect, as do the different sized atoms in alloys. Slip deformation is also difficult in materials of covalent

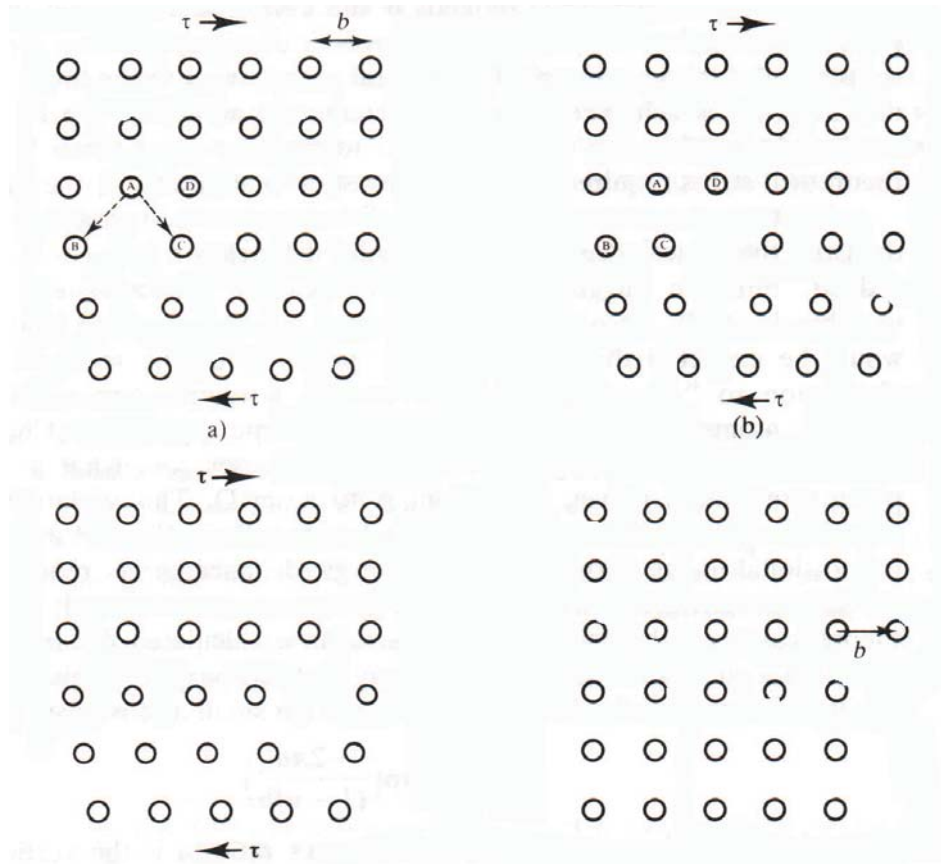


FIGURE 2.13: The atomic rearrangement resulting in dislocation motion in the case of an edge dislocation. a) Before the motion, b) The atomic rearrangement arising as a result of the applied shear stress τ , c) Further movement of the dislocation to the right, and d) As the dislocation arrives at the surface of the crystal, a displacement of the top part of the crystal is seen. From ref. [16].

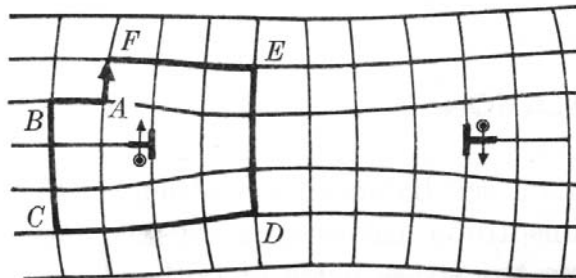


FIGURE 2.14: The Burgers vector $\vec{AF}$ of a dislocation loop does not lie in the slip direction. Hence the dislocation cannot move through the crystal and is known as a sessile dislocation. From ref. [76].

Structure	Slip plane	Slip direction
FCC	$\{111\}$	$\langle\bar{1}10\rangle$
BCC ¹	$\{110\}$	$\langle\bar{1}11\rangle$
	$\{112\}$	$\langle11\bar{1}\rangle$
	$\{123\}$	$\langle11\bar{1}\rangle$
	$\{0001\}$	$\langle11\bar{2}0\rangle$
HCP	$\{10\bar{1}0\}$	$\langle11\bar{2}0\rangle$
	$\{10\bar{1}1\}$	$\langle11\bar{2}0\rangle$

TABLE 2.1: Slip planes and direction in common crystal structures. ¹ In the bcc system, the presence of slip systems other than type $\{110\} \langle\bar{1}11\rangle$ depends upon the temperature and the specific system. After Ref. [16]

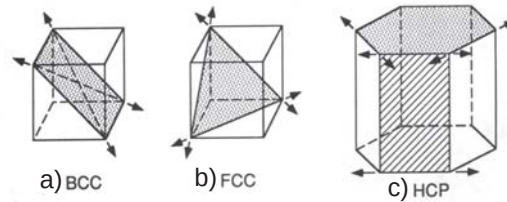


FIGURE 2.15: Typical slip planes and directions (indicated by arrows) for different crystal structures. a) BCC $\{110\}$, $\langle\bar{1}11\rangle$, b) FCC $\{111\}$, $\langle1\bar{1}0\rangle$, and c) HCP $\{0001\}$ and $\{10\bar{1}0\}$, $\langle11\bar{2}0\rangle$. After ref. [76].

bonding such as C and Si as well as metal-oxides, -carbides and -nitrides, because of the directional nature of the bonds. The strength of these materials can on the other hand be reduced by microscopic cracks found in their structures [23].

Even though obstacles make slip deformation difficult, the dislocations have means to circumvent them. The edge dislocation is known to make a "climb", when atoms move out of the slip plane by interchanging position with a neighboring vacancy. Hence a dislocation that has encountered an obstacle can climb to an adjacent plane, but as this process requires diffusive motion of atoms, it is temperature activated.

Additionally, dislocations can undergo "twinning" and "kinking" processes, when the dislocation slip is blocked. In twinning a mirror image of a part of the crystal is created across a "twin plane" in a process involving the motion of an edge dislocation. Twinning is usually found in hcp and bcc crystal structures as seen in the example of twinning shown in fig. 2.16.

Kinking is normally only found in crystals having only one set of planes in which slip occurs easily. When such crystals are compressed or extended, so-called crystallographic buckling known as "kinking" takes place. In this process dislocation pairs are formed on parallel planes and are separated to produce a region in which the lattice is rotated.

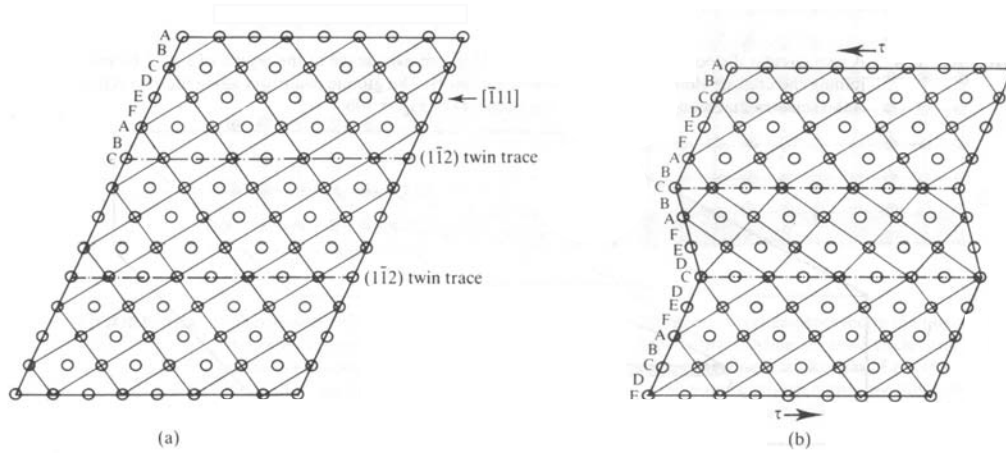


FIGURE 2.16: A mirror image of the initial crystal structure (a) is produced across the twinning plane (b). From ref. [16].

2.8 Creep in crystalline materials

When a crystalline material undergoes a time-dependent inelastic deformation, it is said to "creep". Creep mechanisms involve dislocation motion similar to that described in section 2.7, but also include processes based on diffusion of material. While the processes based on motion of dislocations are limited to crystalline materials, the processes based on diffusion mechanisms can be active both in crystalline and amorphous materials. Hence the topic of creep is closely related to the topic of viscous flow in amorphous material which is treated in section 2.8.4.

Within the time-dependence of creep, several regimes are found (fig. 2.17):

- Transient creep refers to a situation where the strain rate $\dot{\epsilon}$ decreases with time. Within this regime, structural changes are found as the density of dislocations increases as the strain becomes larger.
- Steady state creep is the scenario of a strain rate $\dot{\epsilon}$ which is constant in time. In this regime an invariant steady-state structure is formed, in which formation of new dislocations is countered by the disappearance of others for instance by dislocation annihilation.
- Tertiary creep covers the state in which $\dot{\epsilon}$ increases with time. Hence tertiary creep leads to fracture of the material.

Additionally, different creep mechanisms dominate the creep process under the conditions given in the sample. The regions and mechanisms are seen in fig. 2.18. $\sigma/G = 0.1$, where G is the shear modulus, can be taken as an approximate value of the theoretical strength of the material. At high stress levels (σ_4) the dislocation glide mechanism described in section 2.7 dominates. At lower stress levels, the creep mechanisms described in this section are dominant. Depending on the exact stress level and temperature of the sample, either the dislocation creep, the Coble creep or the Nabarro-Herring creep mechanism dominates. These mechanisms are described below.

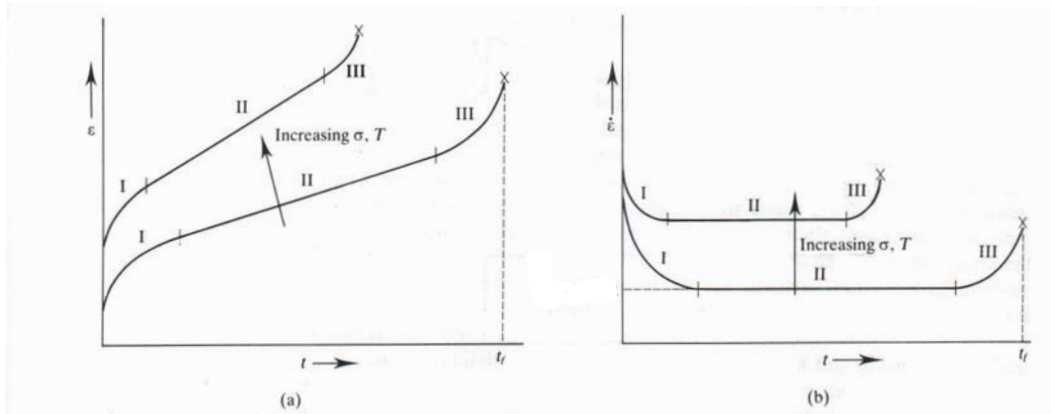


FIGURE 2.17: Depending on the time-dependence of a) the strain and b) the strain rate, three different regimes of creep can be identified: I) Transient creep, II) Steady-state Creep, and III) Tertiary creep. From ref. [16].

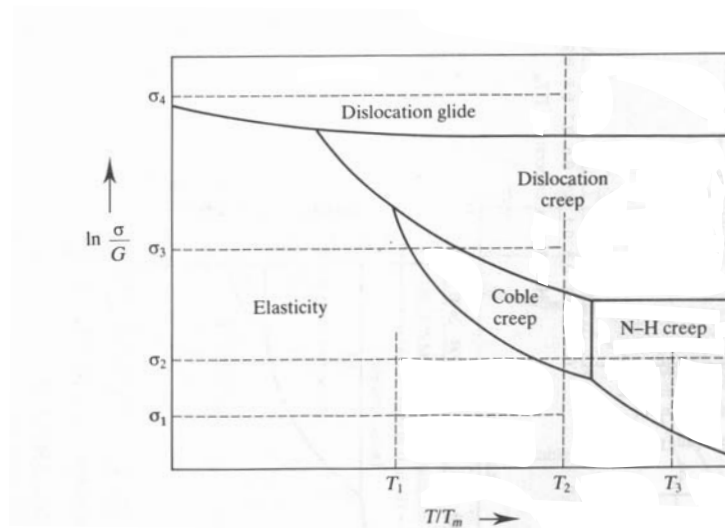


FIGURE 2.18: Depending on the stress level and the temperature of the sample, different creep mechanisms dominate the creep process. See text for further details. From ref. [16].

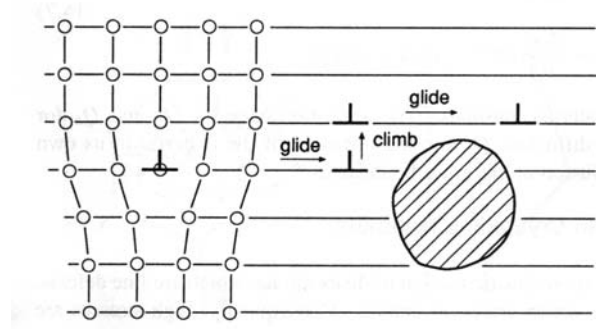


FIGURE 2.19: Dislocation climb to circumvent an obstacle enables the dislocation glide to continue. From ref. [23].

2.8.1 Creep by dislocation glide

The mechanism in which a dislocation glide motion is hindered by an obstacle and hence has to overcome it to be able to proceed, is labelled "dislocation glide" creep (figure 2.19). This process is temperature dependent: In a stress free crystal the dislocation needs a certain energy U_0 , which can be thermally supplied, to pass the obstacle. However, in the case of a stressed crystal, the stress tends to push the dislocation past the obstacle and hence reduces the energy necessary to pass it by an amount δU . It can be shown that the strain rate of dislocation glide creep is [16]:

$$\dot{\epsilon}_{dg} = \dot{\epsilon}_0 \cdot \exp\left(-\frac{U_0}{kT}\right) \exp\left(\frac{\delta U}{kT}\right) \quad (2.104)$$

where $\dot{\epsilon}_0$ is a material parameter, and δU increases with the applied stress and thus can be regarded as an external work reducing the barrier to circumvent the obstacle. Hence it can be seen that the creep rate increases with increasing stress.

2.8.2 Nabarro-Herring creep

In contrast to dislocation glide creep, Nabarro-Herring creep relies solely on diffusional flow of material. Hence, it is important at elevated temperatures and in materials where dislocation creep is intrinsically difficult, such as ceramics and oxides. The mechanism of Nabarro-Herring creep can be intuitively understood from figure 2.20. When the depicted grain is subjected to an applied stress σ as shown, the grain changes shape as vacancies diffuse from the horizontal sides to the vertical sides of the grain, and a net flux of atoms is observed in the opposite direction (figure 2.20.b).

The strain rate associated with this mechanism can be found to [16]:

$$\dot{\epsilon}_{NH} = A_{NH} \cdot \left(\frac{D_L}{d^2}\right) \left(\frac{\sigma \Omega}{kT}\right) \quad (2.105)$$

where A_{NH} is a geometrical factor of the order of 10, D_L is the lattice self-diffusion coefficient, d is the grain size (fig. 2.20) and Ω is the atomic volume.

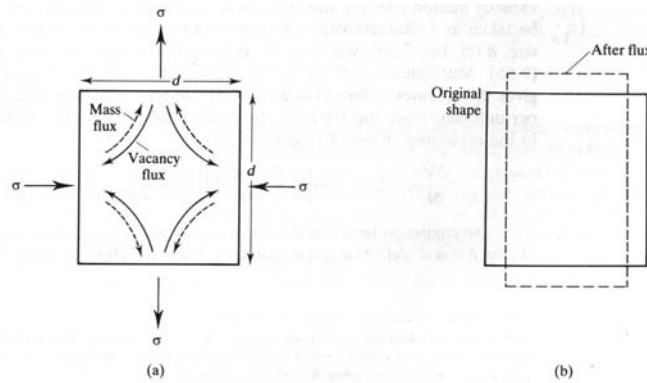


FIGURE 2.20: Nabarro-Herring creep involves the diffusion of vacancies and material in opposed direction to cope with an applied stress (a). The result is a change of shape of the grain as seen in (b). From ref. [16].

2.8.3 Coble Creep

Using a similar diffusional mechanism, Coble creep is akin to Nabarro-Herring creep. The difference is that in Coble creep, the atoms diffuse along the surface of the single crystal or along the grain-boundaries in the polycrystal. Hence Coble creep is sensitive to the size of the grains. Therefore this process only becomes important in materials which have very small grains, though in general one must consider Coble creep and Nabarro-Herring creep as parallel processes in the regime of diffusional creep.

The rate of strain change can in the case of Coble creep be found to [16]:

$$\dot{\epsilon}_C = A_C \left(\frac{D_{GB} \delta'}{d^3} \right) \left(\frac{\sigma \Omega}{kT} \right) \quad (2.106)$$

where A_C is a geometrical factor of the order of 10, D_{GB} is the effective grain-boundary diffusivity and δ' is the thickness of the grain boundary.

2.8.4 Viscous flow

The topic of viscous flow is important for the inelastic deformations taking place in amorphous materials. Viscous flow describes the plastic relaxation of stress towards a state of zero biaxial stress. The viscosity η , which is more correctly called the "shear viscosity", is defined as the resistance of a body to an applied shear stress τ . This shear stress in turn causes permanent changes to the shape of the body. The rate at which this process takes place is called the shear strain rate $\dot{\gamma}$ and is given by [85]:

$$\tau = \eta \cdot \dot{\gamma} \quad (2.107)$$

Typically, an undercooled liquid undergoes its glass transition when its viscosity is of the order of $10^{12} \text{ Pa} \cdot \text{s}$ [58]. Hence, for a material with such a viscosity, the strain rate imposed by a stress of 1 MPa is $10^{-6}/\text{s}$. This means that the shape of glasses is very resistant to applied stresses, at least at low temperatures. At elevated temperatures glasses can flow considerably easier, as the viscosity

changes by several orders of magnitude upon heating. The viscosity itself can vary drastically between different materials. Examples of viscosities are (at 25°C): 0.890 mPa·s (Water), 1.526 mPa·s (Hg) and 809 mPa·s (Triethanolamine) [17].

Relation between stress and viscosity

As thin films are fixed to a substrate, they are constrained by its dimension. This means that the total biaxial strain, irrelevant of the history of the film with respect to stress relaxation, is a constant of time:

$$\epsilon_{total} = \epsilon_{elastic} + \epsilon_{plastic} = const \quad (2.108)$$

or

$$\dot{\epsilon}_{total} = \dot{\epsilon}_{elastic} + \dot{\epsilon}_{plastic} = 0 \quad (2.109)$$

where $\epsilon_{elastic}$ is the elastic strain and $\epsilon_{plastic}$ is the plastic strain.

While the elastic contribution can be expressed using Hooke's law (equation 2.3):

$$\dot{\epsilon}_{elastic} = \frac{\dot{\sigma}}{Y_f} \quad (2.110)$$

the derivation of the the plastic contribution is not as simple. As viscous flow occurs when shear stresses are acting on the film, the choice of the coordinate basis must be considered, as the size of the shear stresses depend on the basis (section 2.2.3). It is even possible to choose a basis for which the off-diagonal entries of the stress tensor vanish. As it is clear that viscous flow must be independent of this choice of basis, the approach of equivalent stresses, σ_{eq} and strains, ϵ_{eq} as suggested by von Mises [76] is taken. Here σ_{eq} is shown to introduce an equivalent plastic strain rate $\dot{\epsilon}_{eq}$. The equivalent stresses and strains do not depend on the choice of basis:

$$\sigma_{eq} = \sqrt{\frac{1}{2}[(\sigma_{22} - \sigma_{33})^2 + (\sigma_{33} - \sigma_{11})^2 + (\sigma_{11} - \sigma_{22})^2] + 3(\tau_{23}^2 + \tau_{13}^2 + \tau_{12}^2)} \quad (2.111a)$$

$$\dot{\epsilon}_{eq} = \sqrt{\frac{2}{9}[(\dot{\epsilon}_{22} - \dot{\epsilon}_{33})^2 + (\dot{\epsilon}_{33} - \dot{\epsilon}_{11})^2 + (\dot{\epsilon}_{11} - \dot{\epsilon}_{22})^2] + \frac{1}{3}(\dot{\gamma}_{23}^2 + \dot{\gamma}_{13}^2 + \dot{\gamma}_{12}^2)} \quad (2.111b)$$

If one considers two special cases i.e. the case of pure biaxial stress and the case of pure shear stress respectively, a relation between the biaxial stress, the biaxial plastic strain rate and the viscosity can be found.

1) Biaxial stress. The scenario of pure biaxial stress is characterized by a biaxial stress

$$\sigma = \sigma_{11} = \sigma_{22},$$

and a biaxial plastic strain rate

$$\epsilon_{plastic} = \epsilon_{11} = \epsilon_{22}$$

with $\epsilon_{33} = -2\epsilon_{plastic}$.

All other entries of the stress tensor $\bar{\bar{\sigma}}$ and the strain tensor $\bar{\bar{\epsilon}}$ are zero.

When inserting these values, the equivalent stress and strain compute to

$$\sigma_{eq} = \sigma$$

and

$$\dot{\epsilon}_{eq} = 2\dot{\epsilon}_{plastic}.$$

2) Shear stress. In the case of pure shear stress, $\tau = \tau_{12}$ can be characterized by a shear strain $\gamma = \gamma_{12}$, while the other components of $\bar{\sigma}$ and $\bar{\epsilon}$ are zero. In this case, the equations (2.111) yield

$$\sigma_{eq} = \sqrt{3}\tau$$

and

$$\dot{\epsilon}_{eq} = \frac{\dot{\gamma}}{\sqrt{3}}.$$

By use of these two scenarios and equation 2.107, a relation between viscosity and the equivalent stress and plastic strain rates can be found:

$$\eta = \frac{\tau}{\dot{\gamma}} = \frac{\sigma_{eq}}{3\dot{\epsilon}_{eq}} = \frac{\sigma}{6\dot{\epsilon}_{plastic}} \quad (2.112)$$

which can be rearranged to give the important relation:

$$\dot{\epsilon}_{plastic} = \frac{\sigma}{6\eta} \quad (2.113)$$

From combining equations (2.109), (2.110) and (2.113), a description of viscous flow in the case of an applied biaxial stress at a constant temperature is found:

$$\frac{\sigma}{6\eta} + \frac{\dot{\sigma}}{Y_f} = 0 \quad (2.114)$$

The time-dependence of the viscosity can now be found by substituting the Stoney equation (2.85) into (2.114):

$$\eta(t) = -\frac{Y_f}{6} \frac{\kappa(t) - \kappa(0)}{\dot{\kappa}(t)} \quad (2.115)$$

where $\kappa=1/R$ is the curvature of the sample.

Temperature dependence of the viscosity

The viscosity has a dramatic dependence on the temperature. The characteristics of this behavior is shown in figure 2.21. Not shown is that upon crystallization of the liquid at the melting temperature T_m , the viscosity increases abruptly and discontinuously by several orders of magnitude. In contrast, in the case of an undercooled liquid the viscosity increases continuously. This behavior in the liquid and undercooled liquid phases can be approximated by the Fulcher-Vogel equation [36],[122],[137]:

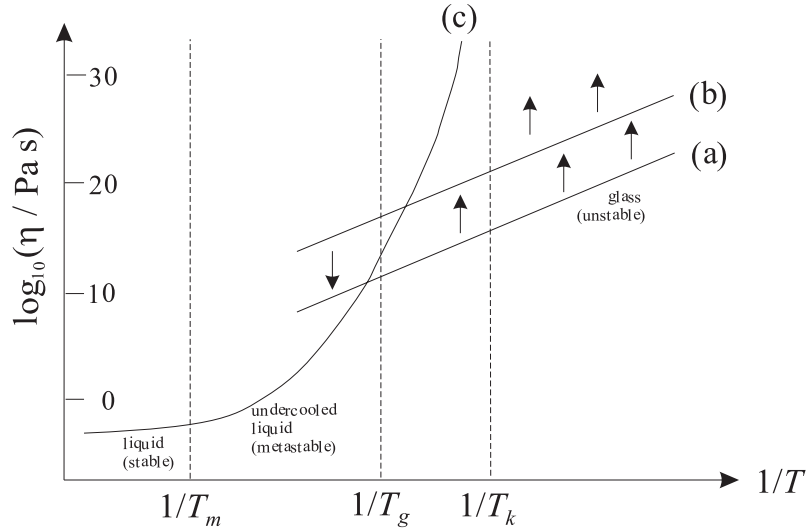


FIGURE 2.21: The viscosity of different phases as a function of temperature. The curves represent a) fast cooling, b) slow cooling and c) infinitively slow cooling. From ref. [53].

$$\eta_{eq}(T) = \eta_0 \cdot \exp\left(\frac{A}{T - T_0}\right) \quad (2.116)$$

where η_0 and A are constants. T_0 is a temperature very close to the Kauzmann temperature [54]. At the Kauzmann temperature, the undercooled liquid possesses perfect order, and no flow defects (see below) are present. This means that viscous flow is impossible, and hence the viscosity approaches infinity.

As described in detail in section 7.4, the undercooled liquid is in a state of internal equilibrium until it approaches the glass transition temperature T_g . At this stage it is configurationally frozen into an isoconfigurational state. The viscosity of an isoconfigurational state increases at a smaller rate upon further cooling, than that of the undercooled liquid as seen in fig. 2.21. As the glass transition depends on the cooling rate as found in section 7.4, the viscosity of the isoconfigurational states also depends on the cooling rate. This can be seen in the paths (a) representing fast cooling, and (b) representing slow cooling in figure 2.21.

As the isoconfigurational states with time will tend to relax towards their equilibrium structure, the viscosity will also increase with time. This is indicated by the vertical arrows in figure 2.21. For the same reason, heating of the glass to a temperature above T_g results in a decrease of the viscosity, as the viscosity of the equilibrium structure is lower above this temperature.

Description of viscous flow

Viscous flow occurs by the mechanism of irreversible shear rearrangements occurring at sites called flow defects. These flow defects can be assumed to be free volume fluctuations in the case of metallic glasses [121], [130], and dangling bonds in the case of glasses with covalent bonds [14],[122],[132]. In any case the concentration of flow defects is by convention denoted as n_f . The

strain rate induced by an applied shear stress can be expressed by [129], [138] [121]:

$$\dot{\gamma} = \omega_f \cdot \gamma_0 \cdot V_0 \cdot n_f \quad (2.117)$$

Here ω_f is the jump frequency for a flow defect under the influence of the stress, γ_0 is the local shear strain induced by the rearrangement of one defect, and V_0 is the volume of a defect.

The jump frequency ω_f can be expressed as [121]:

$$\omega_f = k(f) \cdot \beta(\tau) \quad (2.118)$$

where $k(f)$ is the thermally activated jump rate in the situation where no stress is applied i.e. in a situation where the defect jumps at equal rates between a unstrained and a strained position. $\beta(\tau)$ represents the biasing of the jump into the strained position in the presence of a stress τ . In a stress free situation $k(f)$ can be expressed as:

$$k_f = k_f^0 \cdot \exp\left(-\frac{\Delta G_b}{k_B T}\right) \quad (2.119)$$

where k_f^0 is called the attempt frequency, and ΔG_b is the activation energy barrier for motion.

However, in the situation of an applied stress, the energy barriers ΔG_b for forward and backward defect jumps are not equal. From rate theory, ω_f can be expressed as the difference between the forward and backward rates, which both have an exponential dependence on the energy barrier, hence resulting in a sinh dependence for ω_f [43], [138]:

$$\omega_f = k_f \cdot \sinh\left(\frac{\gamma_0 \cdot V_0 \cdot \tau}{k_B T}\right) \quad (2.120)$$

Here, the activation energy was expressed as a function of V_0 and γ_0 as defined in equation 2.117.

Combining equations (2.117), (2.120) and (2.119) yields:

$$\dot{\gamma} = k_f \cdot \gamma_0 \cdot V_0 \cdot n_f \cdot \sinh\left(\frac{\gamma_0 \cdot V_0 \cdot \tau}{k_B T}\right) = k_f \cdot \gamma_0 \cdot V_0 \cdot n_f \cdot \frac{\gamma_0 \cdot V_0 \cdot \tau}{k_B T} \quad (2.121)$$

where the last equality is true for small shear stresses, in which case the sinh function can be approximated by a Taylor series.

From a comparison of equations (2.107) and (2.121), it becomes evident that the viscosity is independent of the shear stress itself, as it can be expressed as:

$$\eta = \frac{k_B T}{(\gamma_0 \cdot V_0)^2 \cdot k_f \cdot n_f} \quad (2.122)$$

This regime of small shear stresses, where the viscosity does not depend on the shear stress, is labelled the "region of Newtonian viscous flow". As every isoconfigurational state has a specific flow defect concentration, which in the Newtonian case is constant, the temperature dependence of the viscosity can be given by:

$$\eta = \frac{k_B T}{(\gamma_0 \cdot V_0)^2 \cdot k_f^0 \cdot n_f} \cdot \exp\left(\frac{Q_{iso}}{k_B T}\right) \quad (2.123)$$

where the isoconfigurational activation energy Q_{iso} was introduced as a measure for the activation energy. Hence the slope of the viscosity of the isoconfigurational states in figure 2.21 is just Q_{iso}/k_B .

Modelling viscous flow

In the theory of structural relaxation in glasses, simple models have been proposed for the case of a decrease in the concentration of flow defects. This decrease can be induced by several processes; normally one distinguishes between flow defect annihilation involving either one or two defects. The interaction between two flow defects can be interpreted as the recombination of two dangling bonds in the case of covalent glasses and the recombination of two free volume fluctuations in the case of metallic glasses. Depending on the number of flow defects involved in the annihilation process, the resulting decrease in the flow defect concentration can be expressed by [102], [121], [130], [148]:

$$\dot{n}_{f,u} = -k_{r,u} \cdot (n_f - n_{eq}) \quad (2.124a)$$

$$\dot{n}_{f,b} = -k_{r,b} \cdot (n_f - n_{eq})^2 \quad (2.124b)$$

$$\dot{n}_{f,i} = -k_{r,i} \cdot n_f (n_f - n_{eq}) \quad (2.124c)$$

First order terms in n_f describe annihilation of defects at the site of a single defect, while quadratic terms in n_f describe flow defect annihilation by the interaction of two defects. Therefore, equation (2.124a) is said to be based on unimolecular (subscript u) and equation (2.124b) on bimolecular (subscript b) relaxation kinetics. The combination of the two (equation 2.124c) is based on a combination of the two annihilation processes i.e. intermediate (subscript i) kinetics.

The rate equation constants k_r are assumed to have the following dependence on temperature:

$$k_r = k_r^0 \cdot \exp\left(-\frac{Q_{rel}}{k_B T}\right) \quad (2.125)$$

Time dependence of the viscosity at temperatures well below T_g

At a fixed temperature well below the glass transition temperature, the concentration of flow defects is generally orders of magnitudes larger than the concentration of flow defects of the equilibrium structure $n_{f,eq}$ at this temperature. Hence

$$(n_f - n_{f,eq}) \approx n_f. \quad (2.126)$$

Using this approximation, the relations (2.124) describing the flow defect concentration reduce to

$$\dot{n}_{f,u} = -k_{r,u} \cdot n_f \quad (2.127a)$$

in the case of unimolecular relaxation kinetics, and

$$\dot{n}_{f,b} = -k_{r,b} \cdot n_f^2. \quad (2.127b)$$

for bimolecular relaxation kinetics. Solving the differential equations (2.127a) and (2.127b) yields the following time-dependence of n_f in the two cases:

$$n_{f,u}(t) = n_f(0) \cdot \exp(-k_{r,u} t) \quad (2.128a)$$

and

$$n_{f,b}(t) = \frac{n_f(0)}{1 + n_f(0)k_r t} \quad (2.128b)$$

where the constant $n_f(0)$ describes the flow defect concentration at $t = 0$.

Using equation 2.122, the following expressions of the viscosity as a function of time at constant temperature can be obtained:

$$\eta(t) = \eta_0 \cdot \exp(k_{r,u} t) \quad (2.129a)$$

for the unimolecular model, and

$$\eta(t) = \eta_0 + n_0 \eta_0 k_{r,b} t = \eta_0 + k_b t \quad (2.129b)$$

in the bimolecular case, where

$$k_b = n_0 \eta_0 k_{r,b} = \text{constant} \quad (2.130)$$

Hence, unimolecular relaxation kinetics predict a viscosity that increases exponentially with time, while a linear increase of the viscosity as a function of time is characteristic for bimolecular relaxation kinetics at a constant temperature well below T_g .

Time dependence of the viscosity at T close to T_g

At temperatures close to the glass transition temperature, the approximation (2.126) no longer applies, as n_f is of the same order as $n_{f,eq}$ in this regime. Hence the differential equations (2.124) must be solved. This results in the following expressions for unimolecular, bimolecular and intermediate relaxation kinetics, respectively:

$$n_{f,u}(t) = n_{f,eq} + (n_0 - n_{f,eq}) \cdot \exp(-k_{r,u} t) \quad (2.131a)$$

$$n_{f,b}(t) = \frac{n_0 + k_{r,b} n_{f,eq} (n_0 - n_{f,eq}) \cdot t}{1 + k_{r,b} (n_0 - n_{f,eq}) \cdot t} \quad (2.131b)$$

$$n_{f,i}(t) = \frac{n_0 n_{f,eq}}{n_0 + (n_{f,eq} - n_0) \cdot \exp(-k_{r,i} n_{f,eq} t)} \quad (2.131c)$$

Using equation 2.122, the expressions for the time-dependence of the viscosity now become:

$$\eta_u(t) = \frac{\eta_{f,eq}}{1 + \left(\frac{\eta_{f,eq}}{\eta_0} - 1 \right) \cdot \exp(-k_{r,u} t)} \quad (2.132a)$$

$$\eta_b(t) = \frac{\left(\frac{\eta_{f,eq} - \eta_0}{\eta_{f,eq}} \right) \cdot k_{r,b} t + \eta_0}{1 + \left(\frac{\eta_{f,eq} - \eta_0}{\eta_{f,eq}^2} \right) \cdot k_{r,b} t} \quad (2.132b)$$

$$\eta_i(t) = \eta_{f,eq} - (\eta_{f,eq} - \eta_0) \cdot \exp\left(-\frac{k_{r,i}}{\eta_{f,eq}} t\right) \quad (2.132c)$$

where the equilibrium viscosity η_{eq} is described by the Fulcher-Vogel-equation (2.116).

The temperature dependence of the rate equation constants k in equation 2.132 can be computed using equations (2.123), (2.125), (2.122) and (2.130):

$$k = \frac{k_B T}{(\epsilon_0 \cdot V_0)^2} \cdot \frac{k_r^0}{k_f^0} \cdot \exp\left(\frac{Q_{rate}}{k_B T}\right) \quad (2.133)$$

where

$$Q_{rate} = Q_{iso} - Q_{rel} \quad (2.134)$$

Hence the rate equation constants show an Arrhenius dependence on temperature.

Using the expressions (2.131) and (2.132) for the viscosity, the stress evolution as a function of time at a fixed temperature can be calculated using equation 2.114 in each of the situations:

- Constant viscosity

In the case where the viscosity does not depend on time, solving equation 2.114 yields:

$$\sigma(t) = \sigma_0 \cdot \exp\left(-\frac{Y_f}{6\eta} t\right) \quad (2.135a)$$

or

$$\ln\left(\frac{\sigma(t)}{\sigma_0}\right) = -\frac{Y_f}{6\eta} t \quad (2.135b)$$

where σ_0 is the initial stress at $t = 0$. In this case $\ln\left(\frac{\sigma(t)}{\sigma_0}\right)$ will decrease linearly with time.

- Viscosity behavior as found far from equilibrium

Using the expressions (2.129) for the time-dependence of the viscosity as found at temperatures far below T_g i.e. far away from equilibrium, the solutions of equation 2.114 become:

a) unimolecular relaxation kinetics far away from equilibrium:

$$\ln\left(\frac{\sigma(t)}{\sigma_0}\right) = -\frac{Y_f}{6k_{r,u}\eta_0} [1 - \exp(-k_{r,u}t)] \quad (2.136a)$$

b) bimolecular relaxation kinetics far away from equilibrium:

$$\ln\left(\frac{\sigma(t)}{\sigma_0}\right) = -\frac{Y_f}{6k_{r,b}} \ln\left(1 + \frac{k_{r,b}}{\eta_0} t\right) \quad (2.136b)$$

- Viscosity behavior as found close to equilibrium.

The time-dependence of the viscosity as found at temperatures close to T_g (equations 2.132) induce the following solutions of equation 2.114:

a) unimolecular relaxation kinetics close to equilibrium:

$$\ln \left(\frac{\sigma(t)}{\sigma_0} \right) = -\frac{Y_f}{6\eta_{f,eq}} \left(t + \frac{\eta_{f,eq} - \eta_0}{k_{r,u}\eta_0} \cdot [1 - \exp(-k_{r,u}t)] \right) \quad (2.137a)$$

b) bimolecular relaxation kinetics close to equilibrium:

$$\ln \left(\frac{\sigma(t)}{\sigma_0} \right) = -\frac{Y_f}{6} \cdot \left(\frac{1}{k_{r,b}} \cdot \ln \left[1 + \left(\frac{1}{\eta_0} - \frac{1}{\eta_{f,eq}} \right) \cdot k_{r,b}t \right] + \frac{t}{\eta_{f,eq}} \right) \quad (2.137b)$$

c) intermediate relaxation kinetics close to equilibrium:

$$\ln \left(\frac{\sigma(t)}{\sigma_0} \right) = -\frac{Y_f}{6k_{r,i}} \cdot \ln \left(1 + \left[\exp \left(\frac{k_{r,i}}{\eta_{f,eq}} t \right) - 1 \right] \cdot \frac{\eta_{f,eq}}{\eta_0} \right) \quad (2.137c)$$

2.9 Summary

In the description of mechanical stress one distinguishes between elastic and inelastic behavior. In elastic processes, the original shape of a strained body is recovered when the strain-inducing mechanical stress is removed. This is not the case for inelastic behavior, where the deformations induced by the mechanical stresses are not reversible. Hence the changes to the shape of the body are permanent in this regime.

In the elastic regime it is possible to describe the situation of volume changes of a thin film deposited on a substrate. This allows a prediction of the mechanical stresses expected for such a process. Hence this description allows a comparison between experimentally measured stresses upon volume changes and theoretical predictions. In this work, this is exploited in the case of phase change materials as described in chapter 7 and for optically switchable film (chapter 6).

Elastic theory also describes thermal stresses arising in thin films that are subjected to temperature changes. It was shown (section 2.5) how this feature can be exploited to determine the elastic constants of materials for which these are not already known. This is an interesting application of the elastic theory, and in this work such determination of elastic constants was carried out for the phase change materials (chapter 7).

In the inelastic regime, mechanical stress can be relieved by several processes. The processes involved depend on the structure of the film i.e dislocation glide and creep mechanisms in crystalline materials and viscous flow mechanisms in amorphous films. During the course of this work such processes were observed quite often, and specific findings are described for optically switchable coatings in chapter 6 and for phase change films in chapter 7.

Chapter 3

Experimental details

The theoretical description of mechanical stress in thin films presented in the preceding chapter described many interesting situations in which mechanical stresses can be exploited to gather information on the properties and nature of thin films. However, the theory does not allow any direct statements on such properties. Such conclusions can be only be made with the help of experimental measurements of mechanical stresses. As a experimental setup was not available at the start of this work, one had to constructed.

The decision on the method on which such stress measurements should be based is not quite simple, though. There are a variety of methods available for measurements of mechanical stresses in thin films. Each has its advantages and drawbacks, which should be considered before selecting the method suitable for a given experiment. Certain methods offer a large versatility and can be applied in many situations. Others are only applicable in special scenarios, but on the other hand might offer superior properties for such particular cases. In this chapter, a brief comparison of the most widespread methods for stress measurements is given in section 3.1. Then in sections (3.2) - (3.6), the setup chosen for the measurements presented in this work is characterized and described in detail. Finally, in section 3.7 a second system having a special application is presented.

3.1 Stress measurement methods

The methods of measuring mechanical stresses in thin films are many and can seem difficult to comprehend for non-specialists in the field. However, even though they sometimes carry quite adventurous names such as "wafer curvature method", "nano-indentation" and "critically refracted longitudinal wave method", they only describe simple approaches to measurement of mechanical stresses. In this section the principle of the most widespread methods will be briefly presented along with their advantages and drawbacks.

3.1.1 Diffraction based methods

All methods based on diffraction in the thin film exploit that the interplanar spacing d_{hkl} can be determined via the Bragg equation:

$$2d_{hkl}\sin\theta = \lambda \quad (3.1)$$

From the change in lattice spacing compared to the stress-free value $d_{hkl,0}$, the strain can be determined by use of:

$$\varepsilon = \frac{\Delta d}{d_{hkl,0}} \quad (3.2)$$

$$= -\cot\theta_0\Delta\theta \quad (3.3)$$

where $\Delta\theta$ is the change in the Bragg scattering angle, θ_0 .

To characterize the stress state in a given thin film, it is necessary to know the complete stress tensor. However, as seen in chapter 2.2.5, this tensor is dramatically simplified in cases of high symmetry. Indeed, in cases where only in-plane biaxial stress is measured, it is only necessary to determine the in-plane strain, ε_{11} . In this case the biaxial stress is given by Hooke's law:

$$\sigma_{11} = \frac{E_{hkl}}{1 - \nu_{hkl}} \varepsilon_{11} \quad (3.4)$$

A number of methods make use of diffraction to measure mechanical stresses. These include X-ray diffraction also employing synchrotron radiation, and electron- and neutron diffraction. However, independent of the method, certain properties of the film must be known. As the methods are based on the determination of lattice spacings, only crystalline films can be characterized. Additionally, the use of Hooke's law implies that the elastic properties of the film must be known. Otherwise successful stress measurements are not possible. Another drawback of the methods is that they are not suited for in-situ measurements as the measuring time is too long to get acceptable resolution, with the possible exception of synchrotron experiments.

For the determination of stresses in thin films, neutron diffraction measurements are not particularly well suited. The reason is that the penetration depth associated with this method in typical materials is several centimeters. For film thicknesses of the order of 100 nm, this seems a little exaggerated [147].

The electron diffraction method can however be quite useful, as it combines focus diameters of about 10 nm with a penetration depth of less than 100 nm [147]. This combination allows a high resolution in local stress measurements. However the method does not make any direct statement about the macroscopic stresses in the film.

The best suited method for stress measurements is X-ray diffraction. By use of either the $\Theta - 2\Theta$ mode or the grazing incidence mode, direct determination of the in-plane strains are possible. Details on these modes of measurement can be found in chapter 4.

3.1.2 Curvature based methods

As seen in section 2.3, the biaxial stress in the film introduces a constant curvature of the entire sample. The Stoney equation (2.84) relates the radius of curvature R to the biaxial stress σ :

$$\sigma = \frac{E_s d_s^2}{6(1 - \nu_s) d_f} \frac{1}{R} \quad (3.5)$$

It is obvious that methods based on measuring the curvature of the sample yield a direct determination of the biaxial stress in the sample. This is even possible when only the elastic modulus and the Poisson's ratio of the substrate are known. No information on the elastic constants of the film is necessary, and stresses in films that are not crystalline can also be measured.

Methods based on the wafer curvature approach are based a very accurate determination of curvatures. The most widespread ones are the capacitive deflection method, the curvature determination using a scanning laser beam, and methods based on profilometry. While the two former methods are well-suited for in-situ measurements upon variation of stress, the latter method requires removal of the sample and placement in the profilometer.

Curvature measurements based on capacitance changes are realized by metallizing the substrate on the non-film side and having this metal surface form a capacitor with a stiff electrode. When the sample is supported at its edge(s), a change of curvature will thus lead to a change of capacitance.

The measurement of stress based on a curvature determination utilizing a laser has the additional advantage, that it can be applied in a variety of setups without too many complications. In fact all that is required is that the surface of the sample that faces the laser is reflective. Hence the laser based system can be used whenever a window allows the laser to access the sample.

In the profilometry based approach, the topography of the sample is measured, and a mean curvature is determined, from which the stress can be calculated.

3.1.3 Spectroscopic methods

Another approach for measuring mechanical stresses is the application of spectroscopy. Photoluminescence (PL) and in particular Raman spectroscopy have been applied in the literature for this purpose. They exploit the fact that the characteristic peaks show a shift that depends linearly on the stress. However, the application of these method is limited to cases where the sample can be positioned in the spectrometer. Hence in-situ measurements of stress changes are difficult to implement.

3.1.4 Comparison

An overview of the advantages and disadvantages of the methods suited for analysis of stresses in thin films as mentioned above is given in Table 3.1.

Method	Accuracy/MPa	in-situ	Comments
XRD	20 ^a	-	crystalline films
Capacitance	1	X	only applicable when capacitance possible
Laser (Radius)	5	X	very versatile, reflection required
Raman	50 ^b	-	Film must allow good Raman signal

TABLE 3.1: A comparison of the properties of the most wide-spread methods of measuring mechanical stresses. The accuracy depends on the properties of the sample. The numbers given here are typical for normal samples. ^a depends on surface condition [147]. ^b From ref. [147].

The difference of measurements that a system should allow at the I. Institute of Physics, called for utmost versatility and accuracy. Therefore the method based on the scanning laser was chosen. The setups that were constructed based on this method are presented in the sections below along with the modules for sample manipulation that were constructed for them.

3.2 System 1 - The scanning laser beam system

This system is based on the scanning of a laser beam across the surface of the sample. A photograph of the setup is shown in figure 3.1. The 5 mW HeNe laser(1), which is situated in the top part of the system, emits a monochromatic beam with a wavelength of 633 nm and a beam radius of 0.81 mm with a divergence of 1.0 mrad. Since the laser light is polarized, its intensity can be adjusted with a rotatable polarizing filter(2), which is placed in front of the laser. A mirror(3) directs the beam onto the galvanoscanner(4) - a component which allows the controlled tilting of a mirror by the application of a current. From here the beam is reflected through 90° by a beam-splitter(5) and passes a plano-convex lens(6) before being directed to the sample(7) by additional mirrors(8). After being reflected by the sample, the beam returns through the plano-convex lens and the beamsplitter before falling onto the detector unit(9). This purpose-built unit consists of a one-dimensional position sensitive detector (PSD) in front of which a cylindrical lens and a 633nm band pass filter are placed. This design allows the perfect alignment of all the components with respect to the optical axis. Hence by use of the PSD, the relative position of the beam can be determined.

The design of the system in combination with thorough efforts guided towards reducing the noise of the relevant signals (see section 3.6) means that upon scanning across just a centimeter, the system can accurately measure curvatures of 10^{-3} m^{-1} . Using a standard sample consisting of a film of 100-200 nm thickness and a substrate of 150-200 μm thickness, the minimum detectable stress changes are of the order of 2 MPa. This resolution can be improved even further if it is demanded, by choosing thicker films, etc. for reasons explained in section 3.6.

The principle of the measurement can be appreciated from the principle sketch in figure 3.2. The use of a beamsplitter allows both the galvanoscanner and the PSD to be positioned at the focal distance of the plane convex lens, but at different locations. This means, that even though the laser beam is moved through an angle α by the galvanoscanner, each angle will result in a beam parallel to the optical axis, once the beam passes the lens.

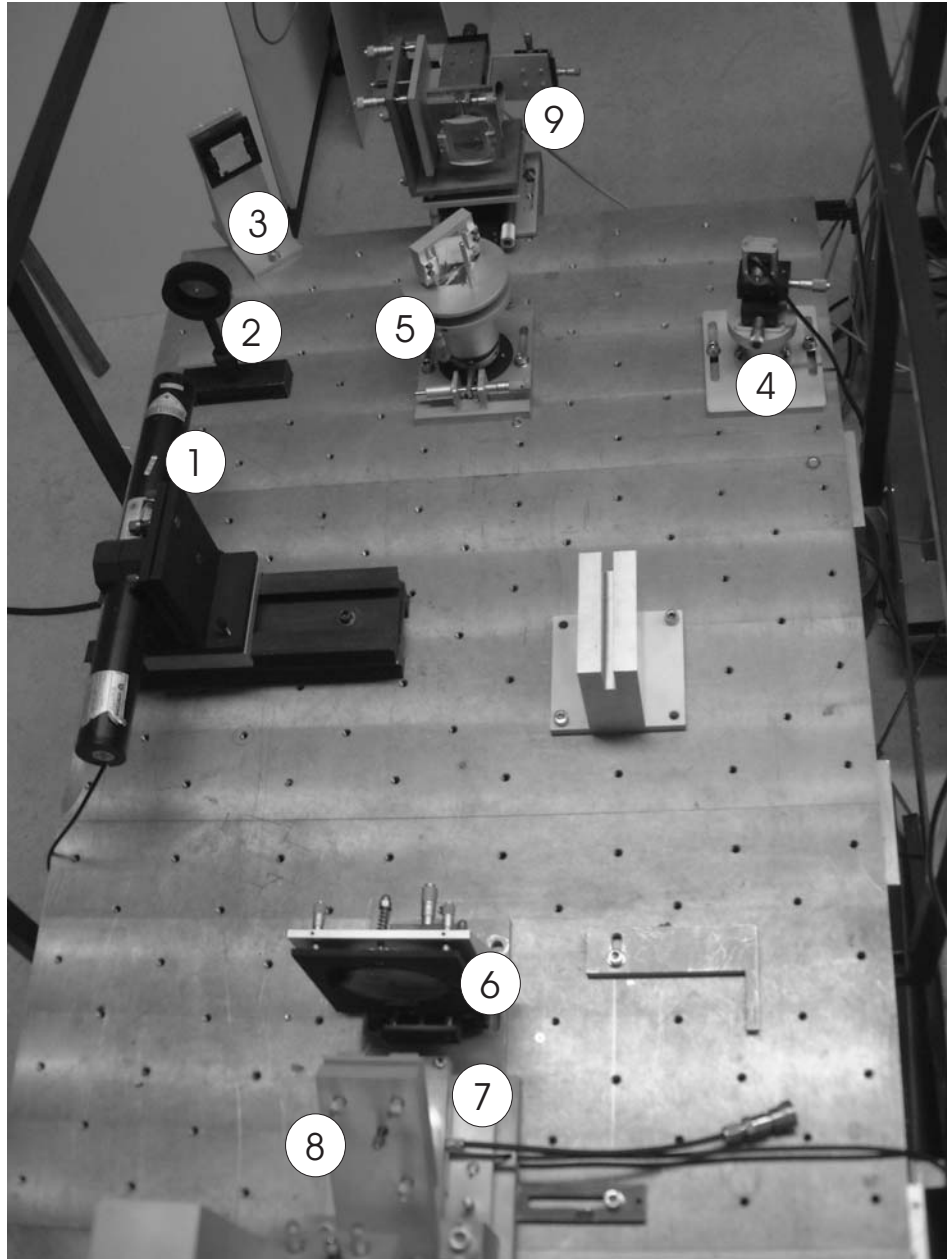


FIGURE 3.1: A photograph of the stress measuring unit. The picture shows the optical components of the system (See text for details)

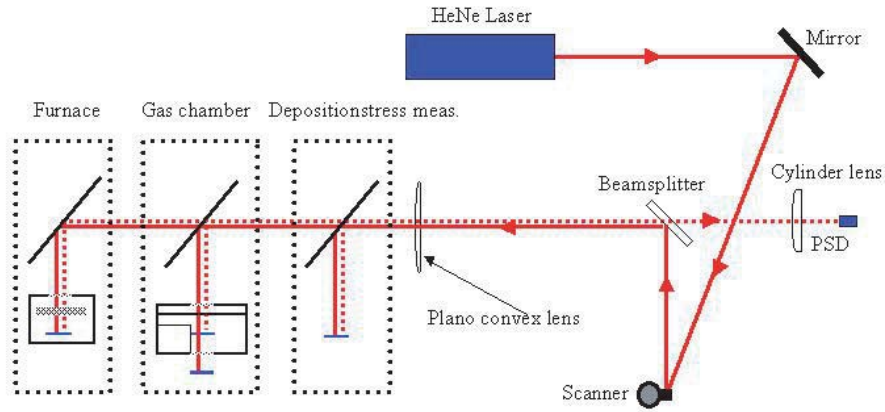


FIGURE 3.2: Schematic diagram of the stress measurement system. See text for details.

The system exploits the fact that the behavior of the reflected beam depends dramatically on the curvature of the sample. This can be appreciated from figure 3.3, where two different situations are shown.

A flat sample (figure 3.3.a) reflects the beams back along the path of the incident beams, and hence no movement of the beam is measured by the PSD, when the beam is scanned across the sample. For a curved sample (figure 3.3.b) the beam is reflected to a path slightly different to the path of the incoming beam. As a result the beam moves across the PSD, when it is scanned across the sample. The movement of the beam on the PSD, which can be determined very precisely (as described in section 3.8.3) is linked to the radius of curvature R of the sample by the following equation:

$$\frac{x}{s} = \frac{2f}{R} \quad (3.6)$$

where x is the distance the beam moves on the PSD, s is the length of the scan i.e. the distance the beam travels on the sample surface upon scanning, while $f=1.0165$ m is the focal length of the plano-convex lens at the laser wavelength. This formula arises as a result of the geometry of the system. It is derived in Appendix 3.9 at the end of this chapter. However, in reality the term $2f$ in equation 3.6 must be determined experimentally i.e. the system must be calibrated. The reason is that the optical components (beamsplitter, cylinder lens, band pass filter, plano-convex lens as well as additional components like mirrors and windows used depending on the type of measurement), which are inserted in the path of the beam alter the properties of the system. Hence the system is calibrated using two mirrors with radii of 20.0 ± 0.2 m and ∞ , respectively. The calibration is done in two steps. In the first step, the perfectly flat mirror is placed at the sample position. Scanning

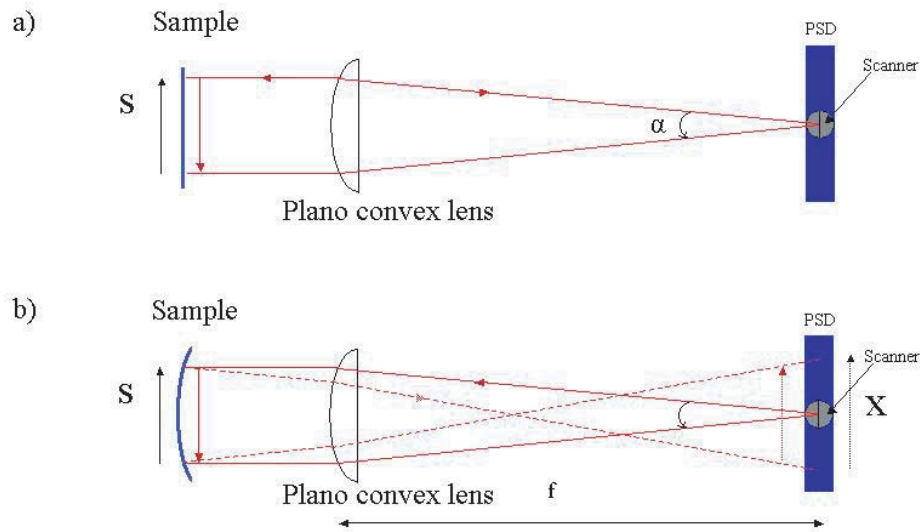


FIGURE 3.3: Samples of different curvature reflect the beam in different manners. In a) the behavior of a flat sample is shown, while in b) the reflection of a curve sample is sketched.

across it allows the perfect positioning of the PSD. In the second step, the mirror with a radius of 20 m is placed at the sample position. Using software (see section 3.5) the motion of the laser beam on the PSD corresponding to this radius is recorded as the mean value of 25 measurements. Then the calibration constant (i.e the term $2f$) can be determined using equation 3.8.

The entire setup is placed on a heavy table and rests on sand cushions to reduce vibrations. During the development of the system experiments with other vibration reducing supports were carried out. Air cushions were found to have the best level of noise reduction, followed by inflatable tubes. Regrettably these supports had severe drawbacks such as costs and short lifetime respectively, and hence the sand cushions whose damping properties are not particularly good were used. Additionally, a box-like structure was build around the system to reduce air motion, which was found to induce noise in the measurements also (see section 3.6.1 for details). The use of the box also secures a constant background signal in the intensity measurements, as it eliminates the influence of changing light conditions in the laboratory.

3.3 Measurement types

The use of the scanning laser system allows three general types of measurements, which are described in this section:

- Deposition stress measurements are determined using the simple setup described in section 3.3.1

- *in-situ* stress measurements in optically switching gasochromic films are done using a special gas chamber, which is described in section 3.3.2.
- *in-situ* stress measurements during thermal cycling are carried out using a furnace, whose details are explained in section 3.4.

3.3.1 Deposition stress measurements

When carrying out deposition stress measurements there are a few important practices to consider. Most of these arise because the commercially available substrates, which are used for these measurements are not perfectly flat i.e they do not possess an infinite radius of curvature. Instead they are equipped with an intrinsic radius which often even is inhomogeneous across the substrate. As this influence cannot be ignored, the Stoney equation [104] includes a term describing the effect of the original curvature R_s of the substrate:

$$\sigma = \frac{Y_f d_s^2}{6d_f} \left[\frac{1}{R_{f,s}} - \frac{1}{R_s} \right] \quad (3.7)$$

This means, that the curvature of the substrate has to be measured before deposition. After the growth of the film, the new curvature $R_{f,s}$ of the film/substrate combination is then measured. From the change of curvature, the deposition stress can be calculated using equation 3.7.

The difficulty of deposition stress measurements arises from the inhomogeneity of substrate curvatures. As a result, the measured curvature depends on the exact location on the sample at which the scanning is carried out. Therefore the sample holder for these measurements was designed to ensure that the sample is positioned in the same way every time: As seen in fig. 3.4, the sample can be pushed into a corner formed by the three vertical pins. Using this system the measured radii can be reproduced very well, as evidenced by the 10 measurements of the same sample, removed and replaced after each measurement, seen in fig. 3.5.

Additionally the scientist carrying out these measurements should preferably carry a degree in bookkeeping, as only a perfect marking of the samples as well as monitoring the scan parameters (see section 3.5) ensure, that exactly the same position on the sample is scanned across before and after deposition.

3.3.2 The gas chamber

For carrying out *in-situ* investigations of the stress build-up in switchable gasochromic films, a special chamber was designed. Its overall position can be seen in figure 3.1. It is placed at the same position as the deposition stress unit(7), which can be removed to make space for the gas chamber.

The largest difference between the gas chamber unit and the setup for deposition stresses is the support of the sample. During initial experiments it was found, that the flow of gas into and out of the gas chamber resulted in vibrations of the sample when it was just supported at its edges.

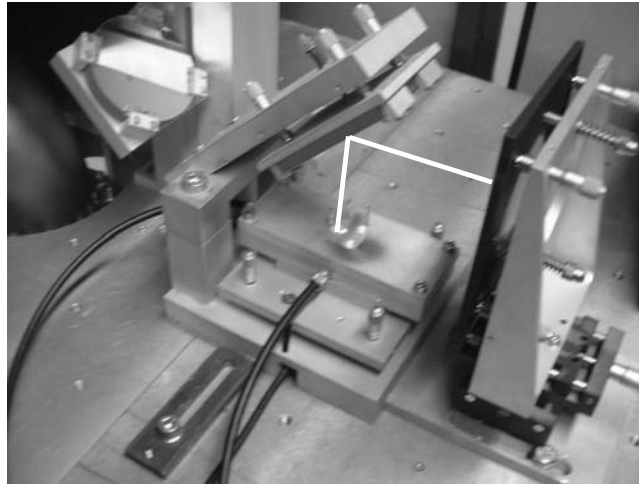


FIGURE 3.4: Photograph of the sample holder for deposition stress measurements. The mirror at the top directs the laser beam onto the supporting platform, where the sample is placed. To allow the sample to behave freely, it is supported by three balls arranged in a triangular pattern. Furthermore, three pins forming a corner into which the samples fit are placed on the platform, ensuring a consistent positioning of the sample every time. To ease the adjustment, the entire platform can be tilted along two axis by use of micrometer screws, allowing the easy adjustment of the direction of the reflected laser beam. The white line schematically depicts the laser path.

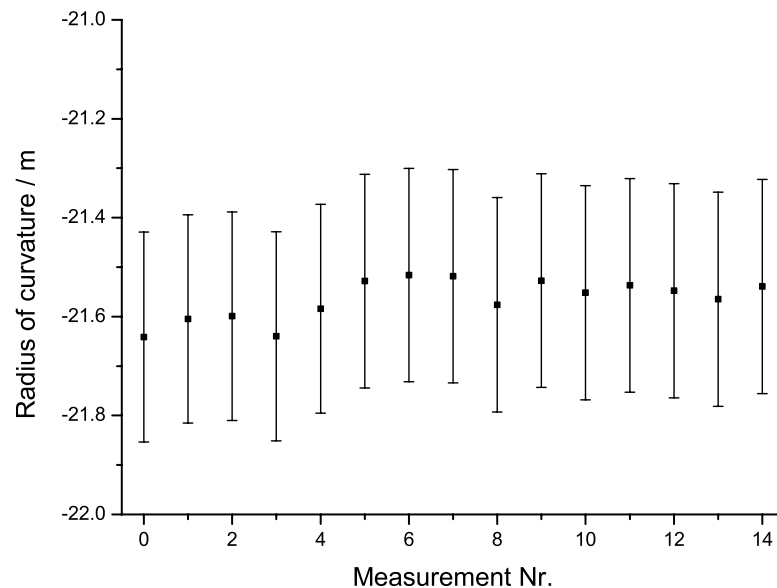


FIGURE 3.5: The radius of curvature of a sample is reproduced nicely, after removal and replacement after each of the 15 measurements shown.

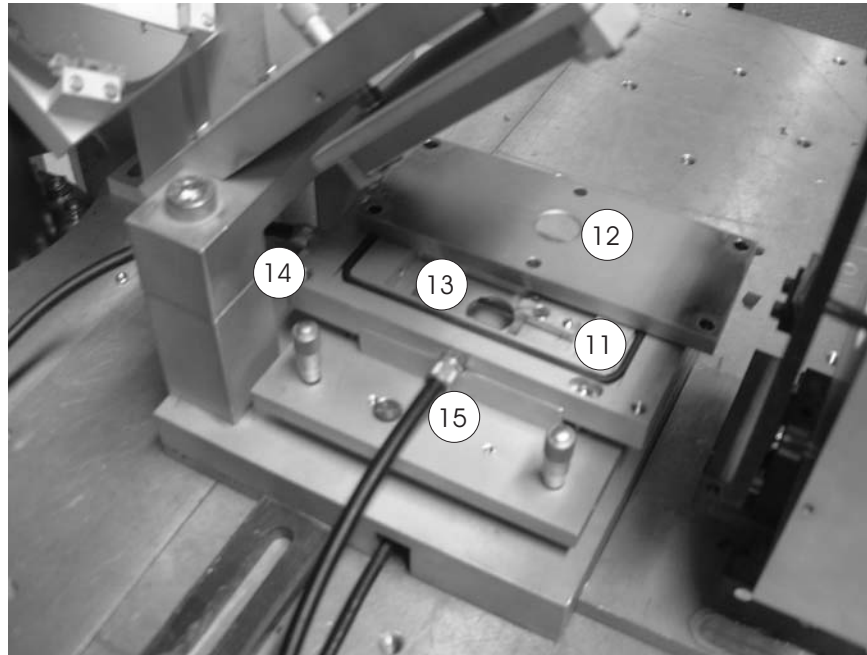


FIGURE 3.6: The clamping of the sample in the gas chamber. The lid of the chamber is moved to allow a look at the clamping site.

Therefore it was decided to clamp the sample at one end. This approach eliminates vibrations within a timescale of a few seconds, but as a result, special care must be taken with respect to the dimensions of the substrate. As found by use of finite elements analysis [18], the relationship between the length and the width of the sample must be larger than 2:1 to guarantee that the part of the sample which is farther than a distance equal to its width away from the clamping behaves like a sample which is not clamped. Hence the region farthest away from the clamping must be chosen for the scanning. Because of these findings, the 24 mm x 24 mm substrates that are used for compatibility reasons in the gas chamber, the deposition stress measurement unit and the sputtering system, are cut into rectangular pieces of 6 mm x 24 mm before being clamped at one end(11) (figure 3.6). As the clamping takes place on a region 4 x 6 mm, and as the scanning cannot be performed to the edge of film because of the changing curvatures upon switching, a path of only approximately 6-8 mm along the long axis of the samples can be scanned across.

The cell is equipped with two anti-reflection coated windows(12,13). One is situated at the top of the cell, while the other sits at its bottom. While the first window is mandatory, the second window allows the option of measuring the intensity of the laser beam after it has passed through the sample by use of a detector situated below the cell, i.e. the transmission of the sample can be determined.

Just as the deposition stress unit, the gas chamber unit can be tilted to direct the path of the reflected laser beam onto the PSD.

For introducing gas into the chamber, it is connected to two tubes. Through the one tube(14) connected at the rear end of the unit, the chamber can be evacuated to a base pressure of less than 10 mbar. A specific gas can be added to the chamber through the tube(15) attached to the side of the

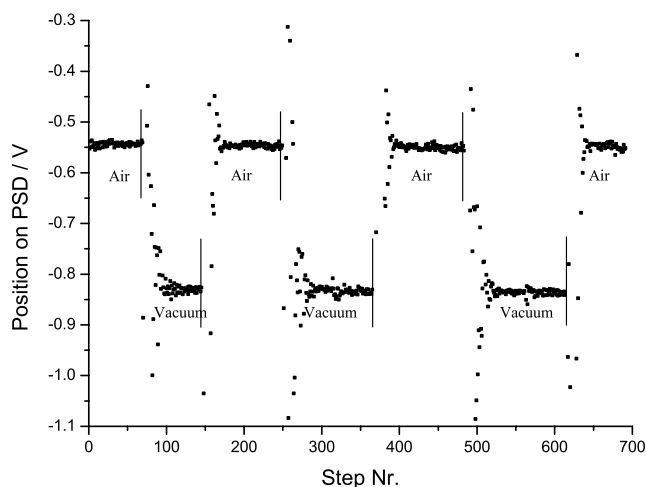


FIGURE 3.7: The stability of the position on the PSD as measured from the reflection of a silver mirror clamped in the gascell. The gas atmosphere was changed as indicated in the figure.

chamber. This configuration of the positions of the inlet and outlet connections, proved favorable with respect to reducing vibrations of the sample during the first few time steps of evacuation and gas inlet, respectively. This can be seen from the measurement shown in figure 3.7. Upon loading the cell with hydrogen, oxygen and argon, the position of the beam on the PSD only changes within the first 20-25 measuring steps i.e. 4-5 s, before remaining constant for the remainder of the phase (- that a slight shift of position unexpectedly can be observed, is attributed to the minor change of the index of refraction upon changing the gas atmosphere in the cell).

The evacuation and gas inlet into the gas chamber is controlled by a separate system. This system is transportable and also applicable to other measurement types i.e. spectroscopy, ellipsometry etc. By using computer-controlled mass flow controllers, it is possible to mix any desired composition of argon, hydrogen and oxygen, before letting it into the gas chamber. Additionally, the system allows the measurement of the gas pressure in the chamber. Details of the system can be found in the work of Theofilos Eleftheriadis [28].

3.4 The furnace

The furnace(10) was constructed to allow the *in-situ* study of mechanical stresses during heating and cooling of samples. Its overall position in the system can be seen in figure 3.1 and on the left of figure 3.2. As the entrance window of the furnace chamber is at a different height than the standard operational height of the laser beam ($h=15$ cm), the laser beam has to be redirected into the furnace by use of the periscope-like configuration of the mirrors, which is shown in figure 3.8.

The furnace consists of a vacuum chamber in which a cooling cylinder is placed. Inside this cylinder the sample is placed on a blackened 20 mm x 60 mm copper piece(17) of 200 μm thick-

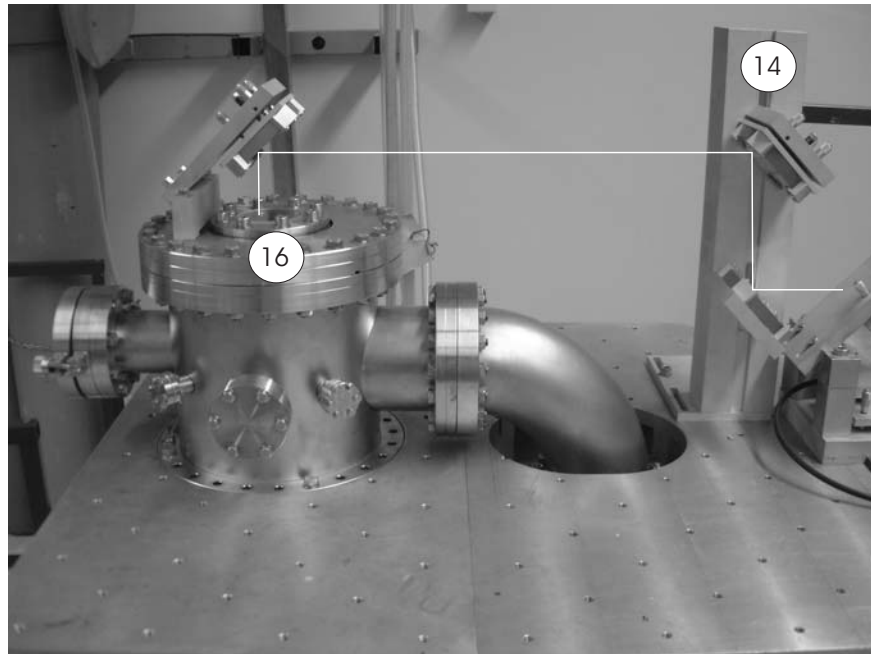


FIGURE 3.8: The furnace seen from the outside. The laser beam (schematically depicted by the white line) is directed into the furnace by the periscope-like arrangement of the mirrors seen to the left.

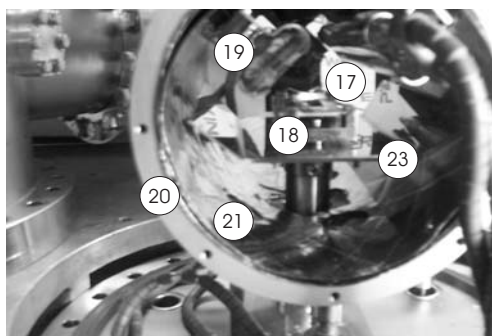


FIGURE 3.9: The platform of the furnace. The blackened Cu-piece is supported by two Al₂O₃ cylinders. The UV-lamps are positioned above the sample at angles $\pm 45^\circ$

ness, which is supported towards its ends by two horizontal hollow ceramic Al_2O_3 cylinders(18) with a radius of 1 mm (fig 3.9). The use of thin Al_2O_3 supports minimizes the loss of heat by thermal conduction to other components of the sample holder. At the far end of the copper piece, a reference sample, to which a thermocouple is glued, is fixed to the copper piece. This setup secures a reliable and precise measurement of the sample temperature. The heating itself is carried out by use of two UV-radiation lamps(19) which are positioned at angles of $\pm 45^\circ$ above the sample (fig 3.9). Their radiation is absorbed by the sample and also by the blackened copper piece, which helps achieving a homogeneous temperature profile across the sample. A temperature gradient across the sample could therefore almost be eliminated as can be appreciated from figure 3.10.a. Here a phase change sample (see chapter 7) was heated. Upon the phase transition the sample changes its optical properties, and the reflected signal increases. For a homogeneous temperature in the film, the reflectance should increase by a constant amount at every point of the scan. As can be seen in fig. 3.10.a, this is almost the case. For comparison a support of the sample by stainless steel cylinders resulted in the thermal profile shown in figure 3.10.b: In the vicinity of the supporting steel pins at positions -0.2 cm and 1.1 cm, large temperature gradients can be observed.

As mentioned above, the platform is placed inside a cooling cylinder(20) (figure 3.9). This double walled cylinder is filled with slowly flowing water and equipped with equally spaced layers of highly reflective tungsten foil(21) on its inner side. Additionally, the cylinder ends are closed by copper pieces coated with layers of tungsten foil on their inside only having small openings for sample positioning, thermocouple wires etc. To complete the confinement of the heat, the platform is shielded from below by a stainless steel radiation shield. Hereby the heated region is confined to the region in the vicinity of the sample.

This design of furnace has three main advantages:

1. It allows heating rates of more than 30 K/min and cooling rates of more than 10 K/min (above 100°C).
2. The platform is very stable during thermal cycling. As a result, the sample is very stable and does not tilt during heating. This is important, as early experiments showed, that a sideways movement of the reflected laser beam result in slight variations of the determined stress. This can only be explained by slightly different optical properties of a changed optical path, meaning that the calibration constant determined as explained in section 3.2, is only accurate for the beam path used when calibrating, and has a slightly different value when this path is changed. Hence the path chosen upon calibration should be kept constant throughout the measurement. Thus, the achieved stability of the platform is of crucial importance for viscosity measurements, where very small and slowly emerging stress changes are detected.
3. The path of the reflected beam can be adjusted by hand from the outside using two micrometer screws, by which the entire platform(23), on which the sample is situated, can be tilted.

The vacuum chamber is evacuated by a turbomolecular pump, which is attached to a mechanical pump. Hereby, a base pressure of less than 10^{-6} mbar can be achieved. At present, the maximum temperature which can be achieved is around 550°C depending on the heating rate.

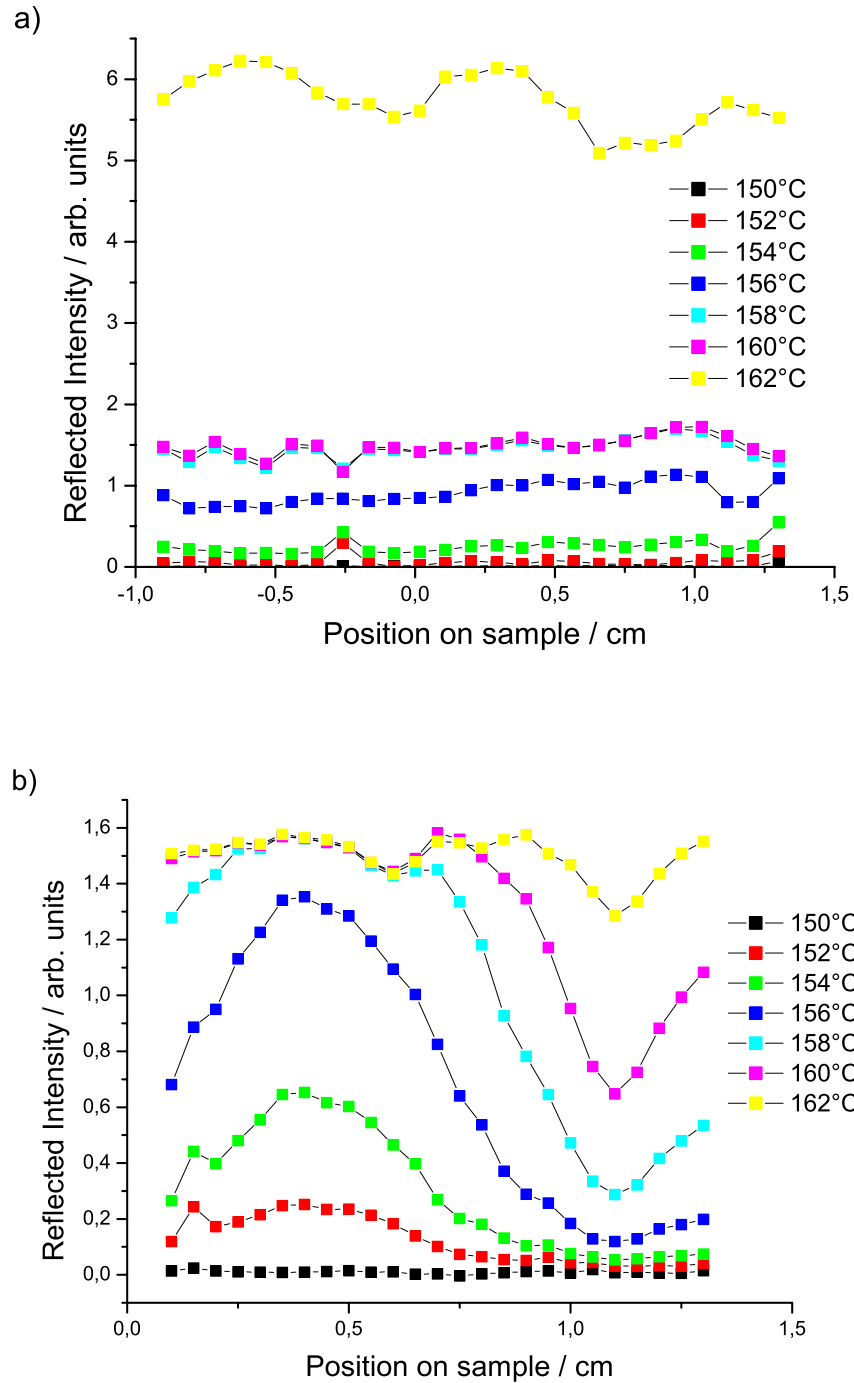


FIGURE 3.10: The homogeneity of the temperature across the sample can be seen from the change of reflectance of a phase-change sample. a) When the sample is supported by sapphire pins, the change of reflection occurs at the same temperature across the sample. b) When the sample is supported by stainless steel pins, the change of reflectance occurs at lower temperatures around the supporting pins. Hence a temperature gradient in the vicinity of the stainless steel pins is detected, while the use of the sapphire pins results in a homogeneous temperature across the sample.

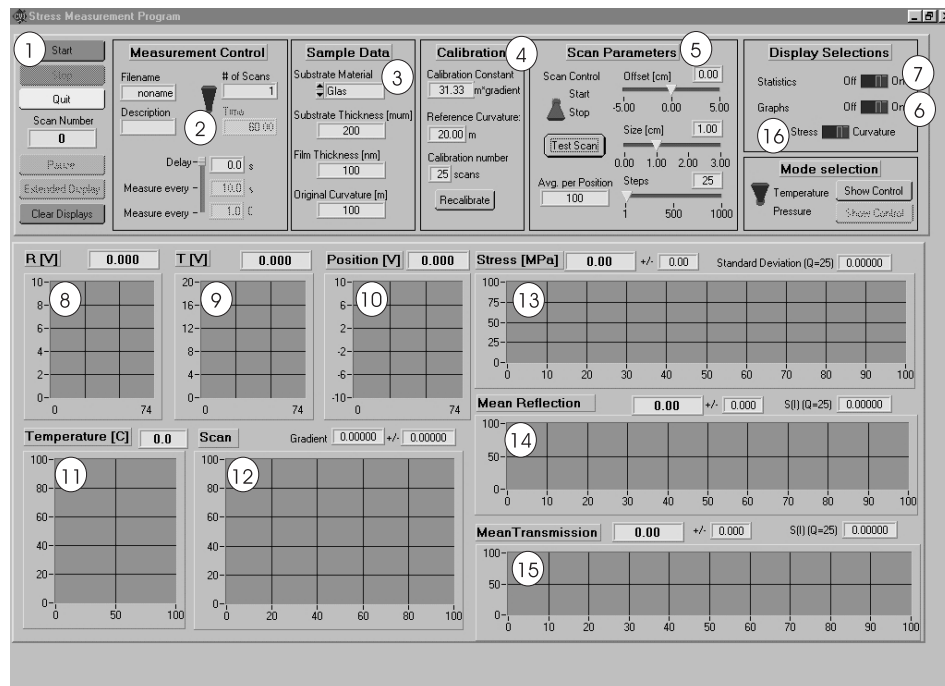


FIGURE 3.11: Screenshot of the user interface of the software for controlling the scanning laser beam system

3.5 Software

When the sample has been positioned and the adjustment of the path of the reflected beam has been carried out, the measurements are completely software controlled. Within the programming environment "Lab-Windows" [87] which is a C-based scientific platform for the development of scientific software, a program was developed, which enables the measurement and direct display of mechanical stresses. Additionally, the program allows the control of the laser, the heating of the furnace, the gas conditions in the gas chamber as well as the monitoring of all necessary control parameters.

A screen shot of the graphical user interface is shown in figure 3.11. In the top portion, all control parameters are collected, while the bottom part contains graphic displays of all the important measured quantities as well as some desired control parameters.

1. In the top left corner a measurement is started <START>, paused <PAUSE> or stopped <STOP>. The pause button is especially useful if an unexpected minor problem occurs during the measurement and a check of some system components has to be carried out.
2. In this field, a filename and a description of the measurement must be typed. Additionally the mode of the measurement must be defined. There are three options: Continuous scanning, scanning separated by time steps and scanning separated by temperature steps. The most common choice is the continuous scanning to gather as much information as possible.

3. For calculations of stresses the necessary sample parameters must be set. The substrates include Si (100) and glass. Furthermore, the thickness of film and substrate must be entered, to ensure correct calculation of the mechanical stress.
4. When switching between types of measurement and hence different sample holders, the calibration constant must be determined, as it varies slightly depending on the included optical components in the three measurement units. An average value of typically 25 measurements is saved with date and time at the end of the file `<calibrat.dat>`.
5. The scan parameter panel is used to choose the scanning path on the sample. `<Offset>` sets the center of the scan. `<Scan Size>` sets the length of the scan, while `<Steps>` defines in how many steps the path will be scanned. With `<Average>` the number of measurements used to average the position on the PSD can be set (see section 3.6 for details).
6. As the monitoring of all parameters and the drawing of the graphs takes up a considerable time (about 1 s after each scan), the update of the graphs can be switched off. This does not influence the data acquisition.
7. To get a better idea of the quality of the measurements a statistical package can be switched on. Hereby one can display the precision of the measurements.

In the graphs in the lower portion of the user interface the following parameters are displayed:
 8. The reflected intensity of the laser beam for the last four scans.
 9. The transmitted intensity of the laser beam for the last four scans (only for gas chamber measurements)
 10. The position of the beam on the PSD for the last four scans (any unwanted vertical beam movement can be monitored here).
 11. The temperature for the last 100 scans.
 12. Display of the last scan. The position of the beam on the PSD is plotted versus the relative position on the sample. Any deviation from a homogeneously curved sample, which would yield a constant slope behavior can be spotted directly.
 13. This display shows either the radius of curvature or the stress change in the film for the last 200 scans. The quantity which is actually displayed is chosen by switch (16).
 14. The reflected intensity of the last 200 scans is shown.
 15. The transmitted intensity of the last 200 scans is displayed (only applies for gas chamber measurements).
 16. The display of either stress or radius of curvature in display 13 can be chosen.

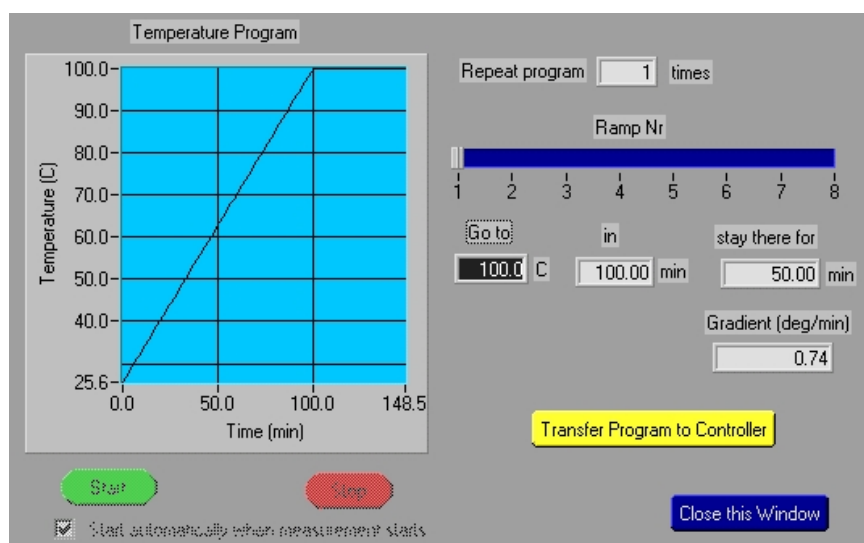


FIGURE 3.12: Screenshot of the User interface window allowing the programming the ramps for the temperature cycling using the furnace.

The heating and cooling is controlled in a separate window (figure 3.12). Here the desired temperature and heating time can be set. From these entries, a heating rate is calculated and displayed. For cooling the same procedure applies. A total number of 7 ramps can be programmed like this. All parameters set in this window must then be transferred to an external temperature controlling unit from Eurotherm [31]. Once the parameters arrive at this unit, the measurement is started by pressing its <START> button. The Eurotherm controller now monitors the power flowing from the external power supply into the lamps inside the furnace. Simultaneously the temperature is measured by the Eurotherm controller and the power is adjusted to conform with the desired heating rate. Additionally the temperature is fed to the software and shown in display 11 (figure 3.11).

To limit the risk of data loss in the case of the computer stalling, the storage files are closed and reopened for every 100 scans. There are two files for every measurement. The first file (*.dat) contains the following informations of the measurement: Start time, end time, date, description, scanning parameters, number and relative time of scan, temperature during scan, gradient of scan, curvature of scan, averaged reflected intensity of laser beam and averaged transmitted intensity of laser beam

The second file (*.da2) contains all information of each and every scan: Additionally to the scan number, all relative positions on the sample, all positions on the PSD, all reflected intensities as well as all transmitted intensities are recorded. Normally this file is not used, but it can be quite useful in controlling temperature homogeneity across the sample, beam movement etc.

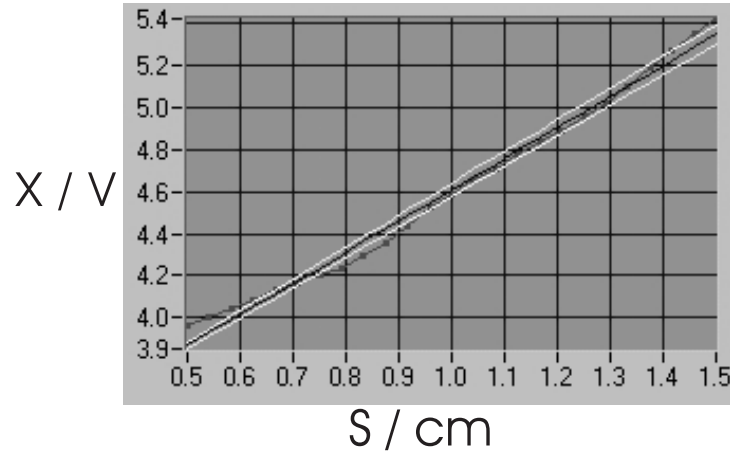


FIGURE 3.13: Gradient of a scan. The black line is the fit to the data points which are found not to lie exactly on this straight line.

3.6 Characterization of the scanning laser apparatus

As described in the previous section and in appendix 3.9, a scan of a sample of constant curvature will yield a slope - a straight line - when the position on the PSD, P_i is plotted versus the position on the sample, x_i . An example is shown in figure 3.13. From this measurement the gradient G of the slope can be deduced. Subsequently, the radius of curvature R can be calculated by:

$$R = \frac{C_{calibration}}{G} \quad (3.8)$$

where $C_{calibration}$ is the calibration constant, which is determined with the help of calibration mirrors as described in section 3.2.

During the development of the scanning laser system, a premium was put on increasing its sensitivity. In order to make improvements within this field, two factors must be considered. The first is to increase the signal i.e. the change of curvature or the sensitivity to curvature changes, while the other is to reduce the noise of the signal. Both points are of equal importance and both must be considered in order to achieve satisfactory results.

As can be appreciated from the Stoney equation (eq. 3.7), the signal can be improved by increasing the thickness of the film or by decreasing the thickness or the nature - and thereby the biaxial modulus - of the substrate. As an example one can switch from 1 mm Si ($Y_s=180.7$ GPa) to 150 μm glass ($Y_s=92.05$ GPa). Another approach is to use a detector with smaller dimensions. The standard PSD, which yields sufficiently high signals for most applied film and substrate parameters, measures 1 mm x 12 mm. However, in demanding situations where the stress changes are very small, for instance in viscosity measurements, PSDs of dimensions 1 mm x 6 mm or 1 mm x 3 mm, can be installed. Hereby, the signal can be increased by a factor of 2 or 4, respectively (see section 3.8.3 for details on the PSD).

On the other hand a large signal can be of relatively little use, if it shows a large intrinsic noise. Therefore it is of great importance to minimize the noise of the signal. To understand where the

noise arises, the considerations below are useful. Further details on the concepts of precision and accuracy can be found in [9].

A scan consists of a number of steps, M , at each of which the position, P_j on the PSD is determined as an average of N measurements of the position, $p_{i,j}$, as described in section 3.8.3. The averaged position is denoted $P_{N,j}$. For each $p_{i,j}$ the difference to $P_{N,j}$ is given by:

$$p_{i,j} - P_{N,j} = \delta_{p_{i,j}} \quad i = (1, 2, \dots, N) \quad (3.9)$$

The best estimate of the standard deviation of the position, $\sigma_N(P_j)$, is given by [9]:

$$S_N(P_j) = \sqrt{\frac{\sum_{i=1}^N \delta_{p_{i,j}}^2}{N(N-1)}} \quad (3.10)$$

Hence for every one of the M steps of the scan, the position on the PSD is determined with an accuracy of:

$$P_j = P_{N,j} \pm S_N(P_j) \quad j = (1, 2, \dots, M) \quad (3.11)$$

From the position determination of the M steps the gradient, G_M , is calculated:

$$G_M = \frac{M \sum_{j=1}^M x_j P_j - \sum_{j=1}^M x_j \sum_{j=1}^M P_j}{M \sum_{j=1}^M x_j - \left(\sum_{j=1}^M x_j \right)^2} \quad (3.12)$$

The points on the slope, $P_{G,j}$, described by the gradient corresponding to the positions of the M steps are given by:

$$P_{G,j} = G_M x_j + B \quad (3.13)$$

where B is a constant. Using (3.11) the difference between the measured points P_j and the points on the slope $P_{G,j}$ can be expressed as:

$$P_j - P_{G,j} = \delta_{G,j} \pm S_N(P_j) \quad (3.14)$$

where $\delta_{G,j} = P_{N,j} - P_{G,j}$.

The best estimate of the standard deviation $\sigma_M(G)$ of the gradient can now be written as:

$$S_M(G_M) = \frac{M \sqrt{M^{-1} \sum_{j=1}^M (P_j - P_{G,j})^2}}{\sqrt{(M-2) \left(M \sum_{j=1}^M x_j^2 - \left(\sum_{j=1}^M x_j \right)^2 \right)}} \quad (3.15)$$

$$= \frac{M^{1/2} \sqrt{\sum_{j=1}^M [\delta_{G,j} \pm S_N(P_{N,j})]^2}}{\sqrt{(M-2) \left(M \sum_{j=1}^M x_j^2 - \left(\sum_{j=1}^M x_j \right)^2 \right)}} \quad (3.16)$$

Evaluating the sums over the position on the sample, x , using a scan size of x_L yields:

$$\sum_{j=1}^M x_j^2 = x_L^2 \frac{M(2M-1)}{6(M-1)} \quad (3.17)$$

and

$$\left(\sum_{j=1}^M x_j \right)^2 = x_L^2 \frac{M^2}{4} \quad (3.18)$$

Equation 3.16 can now be written as:

$$S_M(G_M) = \frac{\sqrt{\sum_{k=1}^M [\delta_{G,k} \pm S_N(P_N, k)]^2}}{x_L} \cdot \left(\frac{M}{(M-2) \frac{M^2(2M-1)}{6(M-1)} - \frac{M^2}{4}} \right)^{1/2} \quad (3.19)$$

Hence the gradient, G , is measured as:

$$G = G_M \pm S_M(G_M) \quad (3.20)$$

When measuring the radius of curvature, which is calculated from equation 3.8, it is given as a mean value from Q measurements:

$$R = R_Q \pm S_Q(R_Q) \quad (3.21)$$

$S_Q(R_Q)$ and $S_M(G_M)$ are related through the following equation:

$$\frac{S_Q(R_Q)}{R_Q} = \frac{1}{\sqrt{Q}} \cdot \frac{S_M(G_M)}{G_M} \quad (3.22)$$

Therefore $S_Q(R_Q)$ can be written as

$$S_Q(R_Q) = \frac{S_M(G_M) \cdot R_M \cdot R_Q}{C_{calibration} \cdot \sqrt{Q}} \simeq \frac{S_M(G_M) \cdot R_Q^2}{C_{calibration} \cdot \sqrt{Q}} \quad (3.23)$$

where $R_M \simeq R_Q$ is the radius of curvature corresponding to G_M as calculated by equation 3.8.

Inserting expression 3.19 of $S_M(G_M)$ yields

$$S_Q(R_Q) = \frac{R_M^2}{x_L \cdot C_{calibration}} \cdot \sqrt{\frac{M}{Q}} \left(\frac{\sum_{j=1}^M [\sigma_{G,j} \pm S_N(P_N, j)]^2}{(M-2) \frac{M^2(2M-1)}{6(M-1)} - \frac{M^2}{4}} \right)^{1/2} \quad (3.24)$$

Similarly, when measuring the mechanical stress, which is calculated by the Stoney equation (eq. 3.7), it is often given as a mean value from Z measurements:

$$\sigma = \sigma_Z \pm S_Z(\sigma_Z) \quad (3.25)$$

Similar to $S_Q(R_Q)$ and $S_M(G_M)$, $S_Z(\sigma_Z)$ and $S_Q(R_Q)$ are related through:

$$\frac{S_Z(\sigma_Z)}{\sigma_Z} = \frac{1}{\sqrt{Z}} \frac{S_Q(R_Q)}{R_Q} = \frac{6d_f S_Q(R_Q) \sigma_Q}{Y_s d_s^2 \sqrt{Z}} \quad (3.26)$$

where $\sigma_Q \simeq \sigma_Z$ corresponds to R_Q by use of the Stoney equation. This means that $S_Z(\sigma_Z)$ can be written as

$$S_Z(\sigma_Z) = \frac{6 \cdot \sigma_Z^2 \cdot d_f}{M_s \cdot d_s^2 \cdot x_L \cdot C_{calibration}} \cdot \sqrt{\frac{M}{ZQ}} \left(\frac{\sum_{j=1}^M [\delta_{G,j} \pm S_N(P_{N,j})]^2}{(M-2) \frac{M^2(2M-1)}{6(M-1)} - \frac{M^2}{4}} \right)^{1/2} \quad (3.27)$$

From this equation the direct implication of the parameters which influence the noise of the stress measurement can be seen. For instance a doubling of the length of the scan, x_L , will halve the value of $S_Z(\sigma_Z)$.

3.6.1 Noise of signals

It is obvious from equations (3.24) and (3.27) that $S_Q(R_Z)$ and $S_Z(\sigma_Z)$ are heavily affected by the homogeneity of the curvature, which is represented in the equation by the parameter $\delta_{G,j}$, and the accuracy with which the position on the PSD can be measured, represented by $S_N(P_N, j)$. While the former parameter is easy to control as homogeneously curved substrates can be chosen before deposition, the accuracy of the position determination on the PSD can only be reduced to a minimum by investigating the parameters affecting it. Hence significant efforts were put into such investigations, as presented below.

As described in detail in appendix 3.8.3, the output voltage V_0 describing the position on the PSD is determined from the following equation:

$$V_0 = 10 \cdot \frac{V_1 - V_2}{V_1 + V_2} = 10 \cdot \frac{V_B}{V_A} \quad (3.28)$$

where V_1 and V_2 are the amplified voltages corresponding to the photocurrents produced when the laser beam hits the detector, and V_A and V_B are their sum and difference, respectively. As can be seen from equation 3.28, the noise of the signals V_A and V_B will be transferred directly into the noise of the signal V_0 .

The efforts to minimize the noise in the signals V_A and V_0 , which are the reflected intensity and the position on the detector, respectively, included analysis of the influence of every component of the optical setup as well as the electronic components used in the data acquisition and -evaluation. Below, the results from these investigations are presented.

The analysis of the influence of the components used in the setup focused on the laser itself, the galvanoscanner, the used lenses, mirrors and other optical components as well as the influence from the surroundings.

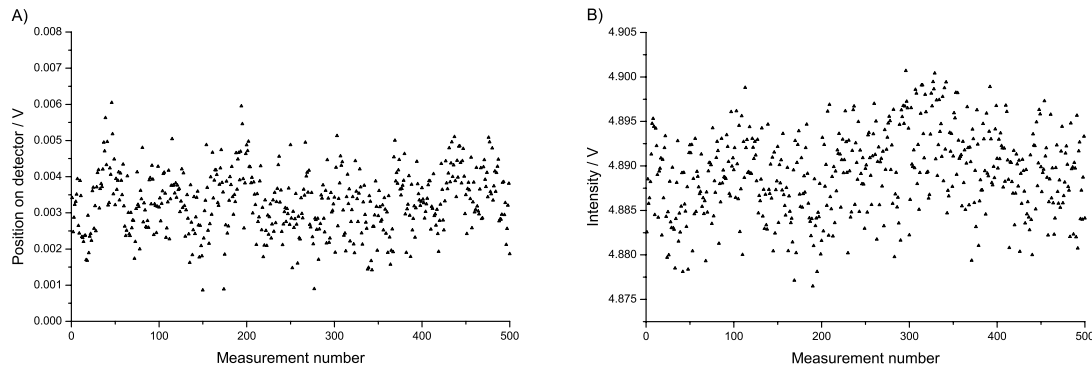


FIGURE 3.14: Noise of the used HeNe laser. a) Noise of the position. b) Noise of intensity. Open symbols represent single measurements, while averages of 100 measurements are represented with filled symbols.

To investigate the influence of the laser, four different lasers were tested. For each laser the position on the PSD, V_0 , and the intensity, V_A , were measured. The diameter of the laser beam was roughly constant among the lasers. The results for the HeNe laser which is used in the system can be seen in figure 3.14. Averaged over 100 measurements, the signals have values of $V_0 = 0.013 \pm 0.003$ V and $V_A = 4.888 \pm 0.005$ V.

Other lasers behaved differently. The lasers whose properties were investigated were:

- Uniphase HeNe laser
- Other HeNe laser
- Intensity stabilised HeNe laser
- Semiconductor laser ($\lambda = 670\text{nm}$)

The resulting position noise and the intensity noise of these lasers are plotted in figure 3.15 for constant intensity and position on the detector (open symbols). It is seen, that the semiconductor laser by far has the lowest noise values. The inferiority of the HeNe lasers can by large be compensated, though. Using software options, it is possible to make an average over a number of values of the position signal V_0 . This reduces the performance gap between the laser types as shown by the filled symbols in figure 3.15. In spite of the superior performance of other lasers, the Uniphase HeNe laser was kept in use, as it shows a very good directional stability and low divergence. Additionally, the noise level achieved with it when performing an averaging, is only slightly worse than the noise found for the other lasers, and only has a significance in the most demanding experimental situations.

The influence from any vibrations of the building was investigated by making comparable experiments using an air-cushion supported table that eliminates vibrations. No difference in position noise was found as can be seen from table 3.2. The intrinsic noise of the position output at the center of the PSD is 5.0 mV without averaging in either of the two situations.

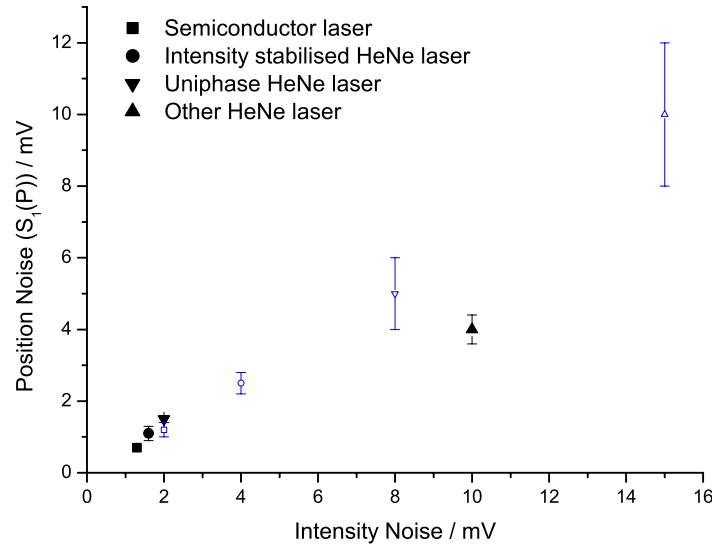


FIGURE 3.15: Comparison of the noise introduced by different lasers. It is seen that averaging the signal almost eliminates the differences in performance between the lasers.

Additional measurements of the noise of the position output of the PSD was investigated in detail as a function of the included optical components. In all setups it was ensured that the beam hit the PSD at its center, to allow a comparison of the values. In one setup, the beam was directed from the beamsplitter directly onto the PSD. This mode was achieved by turning the beamsplitter 90° . Additionally the noise of this configuration was determined in the cases where the galvanoscanner was on and off. As can be seen in table 3.2, the noise of the signal increases slightly compared to the previous situation. This can be explained by larger spot size of the beam hitting the detector arising because of the divergence of the laser. However the noise of the position signal showed no dependence on the status of the galvanoscanner.

The influence of the pumps used to evacuate the furnace was studied using the reflected signal of a 20 m mirror placed inside it. As shown in table 3.2, the noise increases to 6.5 mV in this configuration, while the operation of the pumps adds a minor contribution, resulting in a value of 7.0 mV. This rather small contribution was achieved by using rubber tubes rather than metal tubes between the mechanical pump and the turbomolecular pump. Additionally a vibration absorber was installed between the furnace chamber and the turbomolecular pump.

Finally the influence of the motion of the surrounding air was investigated. In all of the experiments described above, an external box-like structure surrounded the system. Using the setup where the 20 m is placed inside the furnace, which was shown to result in a noise level of 6.5 mV, the box-like structure was removed. As a result the noise of the position signal of the PSD increased to 8.0 mV (table 3.2). This showed the importance of using the box-like structure for all measurements.

As a consequence of these findings it was decided to carry out a certain number of averages per

System configuration	$S_1(P)/\text{mV}$
Laser onto detector	5.0
Laser onto detector on air cushion table	5.0
PSD/Scanner OFF	5.3
PSD/Scanner ON	5.3
20 m mirror in furnace/Pumps OFF	6.5
20 m mirror in furnace/Pumps ON	7.0
20 m mirror in furnace/Pumps OFF/Box removed	8.0

TABLE 3.2: Noise of the position output of the PSD depending on the used optical and system components. The laser beam was adjusted to hit the PSD at the center for each measurement.

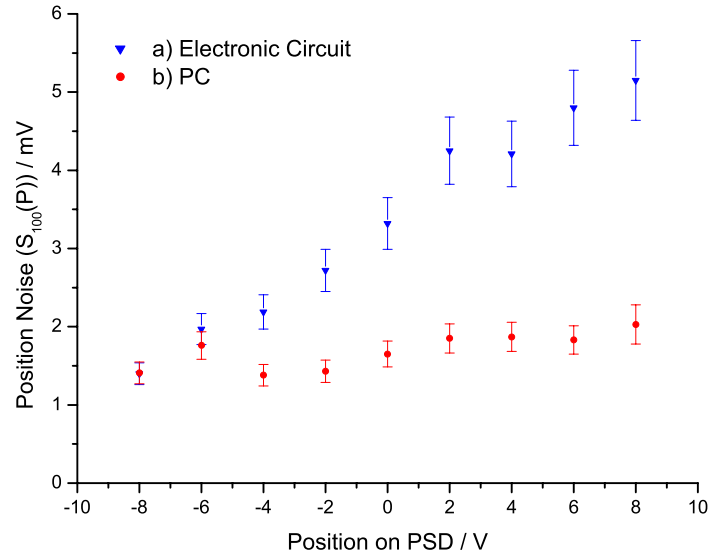


FIGURE 3.16: Noise of the position Signal as a function of the position itself. a) Electronic Circuit. b) PC

position on the PSD, when performing the scanning. Hereby the inferiority of the HeNe laser can largely be compensated. The disadvantage of this approach is an increase in the duration of a scan. A scan with no averaging has a duration of 3.5 s while a scan using an averaging over 100 values per position lasts about 5 s.

The most significant noise reduction was realized, when the calculation of the position on the detector was moved from the signal procession circuit of the PSD to the PC. The reason for this move is shown in figure 3.16.a. Here it can be appreciated, that the noise of the position signal depends dramatically on the position itself. The reason for this rather peculiar behavior is a component on the signal processing circuit [47] - the analogue computational unit AD538 from Analog Devices [3], which calculates the position based on equation 3.28. The dramatic difference between the two outer positions on the PSD, $V_0 = -10$ V and $V_0 = +10$ V is shown in figure 3.17. Even though the noise of V_A and V_B is the same in the two cases, the noise of V_0 differs dramatically in

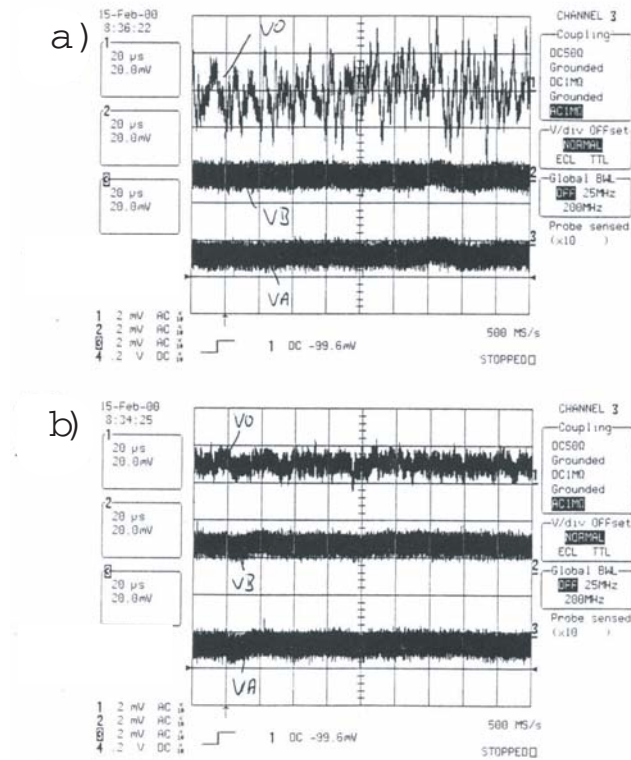


FIGURE 3.17: Noise difference between the two extreme position on the PSD when the electronic circuit is used for evaluation. a) At position $V_0 = +10$ V i.e at the top of the detector and b) at position $V_0 = -10$ V i.e at the bottom of the detector. The signals V_A and V_B have similar noise, while the calculated position V_0 has far larger noise at $V_0 = +10$ V.

the two cases. As this dependence is a result of the short-comings of the AD538 unit used on the circuit designed to be used with the PSD, the computation of V_0 was integrated in the software, resulting in a position noise which is symmetric around the center of the PSD as shown in figure 3.16.b.

The real noise found when measuring curvatures can be appreciated from figure 3.18. For 100 subsequent measurements a result of $R = 20.07 \pm 0.02$ m is found. Additionally, the influence of movements in the laboratory can be seen. In the first few hours as well as at end of the measurement, there were people moving around in the lab, illustrating the sensitivity of the system even with the use of sand cushions to reduce the vibrations.

3.7 System 2 - the two-beam system

The three methods described above are all used to determine stresses in film that were produced using sputtering (see Chapter 5.2). To gather insight in the stress evolution during the deposition itself, another system for stress measurements was designed. The necessity for a new system arises

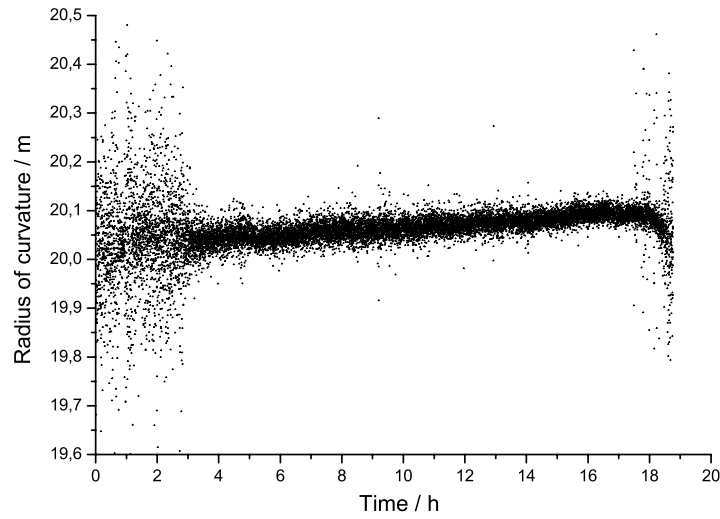


FIGURE 3.18: Curvature measurement on a 20 m calibration mirror. At the beginning and at the end of the experiment, the noise is far larger than during the remainder of the measurement. This was correlated by motion and movements of workers in the laboratory.

because of the sheer dimension of the laser scanning apparatus. The application of an awkward to handle system measuring about 1.5 m x 0.5 m and weighing several hundred kg to a sputter deposition system is extremely difficult. Therefore another approach was taken in developing an easy to handle system for such applications.

A side view of the two beam system can be seen in figure 3.19. Its physical dimension is just 30 cm x 20 cm x 10 cm, and it is very easy to attach to different deposition systems. The applied semiconductor laser [103] emits a laser beam at 670 nm, and has an adjustable focus length. The beam is divided by a beamsplitter into two parts, which are directed parallelly onto the sample by mirrors 1-3. From the sample surface, the two beams are reflected onto two sensitive split photodiodes [105]. As the curvature of the sample changes during deposition, the beams will move on the photodiodes, which can detect motions of less than 0.1 μm . From this movement, the stress can be calculated using the approach given below.

3.7.1 Calculating stresses using the two-beam system

The calculation of the stress using the two beam system can be understood by the following derivation:

Consider two parallel beams as shown in figure 3.20. They are reflected to angles θ_A and θ_B at a surface of constant curvature. In this situation the following expressions are valid:

$$\sin\left(\frac{\theta_B}{2}\right) = \frac{D \cdot n}{R} \quad (3.29)$$

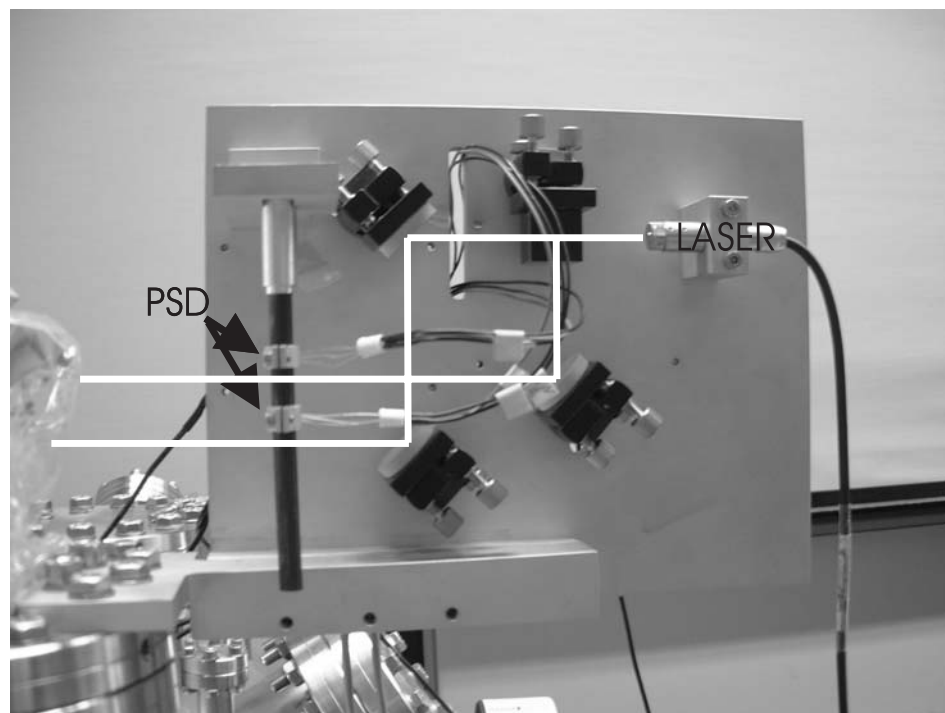


FIGURE 3.19: A photograph of the two-beam system. The Laser path is schematically depicted by the white line (See text for explanation).

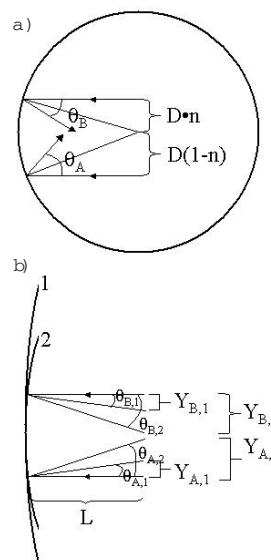


FIGURE 3.20: Principle sketch for stress determination using the two-beam system. a) The reflection from a circle of radius R . b) The reflection of two stationary beams from circles of different radii.

$$\sin\left(\frac{\theta_A}{2}\right) = \frac{D(1-n)}{R} \quad (3.30)$$

where D is the distance between the two laser beams hitting the sample, while n determines the position of the laser beams relative to the center of a circle of radius R .

Adding these expressions yields:

$$\sin\left(\frac{\theta_B}{2}\right) + \sin\left(\frac{\theta_A}{2}\right) = \frac{D}{R} \quad (3.31)$$

which for small angles approaches:

$$\frac{\theta_B}{2} + \frac{\theta_A}{2} = \frac{D}{R} \quad (3.32)$$

In a situation where the radius of the circle changes from R_1 to R_2 , the following expressions are valid:

$$\tan(\theta_{B,1}) = \frac{Y_{B,1}}{L} \quad (3.33)$$

and

$$\tan(\theta_{B,2}) = \frac{Y_{B,2}}{L} \quad (3.34)$$

where $Y_{B,1}$ and $Y_{B,2}$ are the displacements of the reflected beams at a distance L from the surfaces 1 and 2 respectively. $\theta_{B,1}$ and $\theta_{B,2}$ are the angles of reflection.

For small angles these expressions reduce to:

$$\theta_{B,1} = \frac{Y_{B,1}}{L} \quad (3.35)$$

$$\theta_{B,2} = \frac{Y_{B,2}}{L} \quad (3.36)$$

Combining equations (3.35) and (3.36) yields for beam B:

$$\theta_{B,2} - \theta_{B,1} = \frac{Y_{B,2} - Y_{B,1}}{L} \quad (3.37)$$

Similarly one gets the following expression for beam A:

$$\theta_{A,2} - \theta_{A,1} = \frac{Y_{A,2} - Y_{A,1}}{L} \quad (3.38)$$

From the Stoney equation (eq. 3.7)

$$\Delta\sigma = \frac{M_s d_s^2}{6d_f} \left(\frac{1}{R_2} - \frac{1}{R_1} \right) \quad (3.39)$$

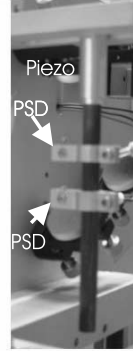


FIGURE 3.21: The detectors and Piezo translator.

it now follows (when applying equations (3.32),(3.37) and (3.38)):

$$\Delta\sigma = \frac{M_s d_s^2}{6d_f} \frac{1}{D} \left(\frac{\theta_{B,2}}{2} + \frac{\theta_{A,2}}{2} - \frac{\theta_{B,1}}{2} - \frac{\theta_{A,1}}{2} \right) \quad (3.40)$$

$$= \frac{M_s d_s^2}{6d_f} \frac{1}{D} \left(\frac{\theta_{B,2} - \theta_{B,1}}{2} - \frac{\theta_{A,2} - \theta_{A,1}}{2} \right) \quad (3.41)$$

$$= \frac{M_s d_s^2}{6d_f} \frac{1}{D} \left(\frac{Y_{B,2} - Y_{B,1}}{2L} - \frac{Y_{A,2} - Y_{A,1}}{2L} \right) \quad (3.42)$$

$$= \frac{M_s d_s^2}{6d_f} \frac{1}{D} \left(\frac{\Delta Y_B}{2L} - \frac{\Delta Y_A}{2L} \right) \quad (3.43)$$

$$= \frac{M_s d_s^2}{6d_f} \frac{1}{D} \left(\frac{\Delta Y_B - \Delta Y_A}{2L} \right) \quad (3.44)$$

This means, that the stress is directly determined from the difference of the beam motion on the two split photodiodes.

The calibration of the split photodiodes is realized by an ingenious design of its holder: The diodes are attached to a very light carbon tube, which itself hangs freely from the bottom of a piezo translator [101] as can be seen in figure 3.21. This uniaxial piezoelement allows the controlled movement of the entire carbon tube, and hereby the diodes, in a direction perpendicular to the axis at which the diodes are split. This movement mirrors the shifting of the laser beams by change of stress in the film. Hence the signal change of a set movement of a few micrometers is measured, and the calibration necessary for deriving the distances ΔY_A and ΔY_B from the voltage signal supplied by the split photodiodes can now be performed. From this signal the stress can be determined by equation 3.44.

The application of the system has not yet been fully realized, as a sputtering chamber designed to take full advantage of its virtues has not yet been taken into use.

3.8 Appendix: Components of the setup

In this appendix the details of the crucial components in the laser scanning setup will be presented along with important points to keep mind when using or making changes to them.

3.8.1 HeNe Laser

The 5 mW HeNe Laser model 1125P from the company "Uniphase" emits polarized monochromatic light at 633 nm. The beam diameter is specified to 0.81 mm ($1/e^2$ of TEM_{00}) with a divergence of 1.0 mrad. The spot size at larger distances, z , is hence given by [80]

$$w(z) = \frac{\lambda \cdot z}{\pi \cdot w_0} \quad z \gg z_0 \quad (3.45)$$

where $w_0=0.405$ mm is the spot size at the beam waist length of the laser, and λ is the laser wavelength. Thus it is found that the laser beam has a radius of 1.0 mm at the deposition stress unit and gas chamber, and 1.5 mm at the sample holder inside the furnace.

3.8.2 Galvanoscanner

The galvanoscanner which is used to move the laser beam through an angle, thus creating the scanning motion of the beam, operates by the same principle as a galvanometer used for measurements of currents. This means that the axis to which the mirror is attached rotates a given angle depending on the applied current. The scanner is controlled by an external electronics unit, which can be programmed from the software.

3.8.3 Position Sensitive Detector (PSD)

Photodetectors such as the PSD, which is employed in the scanning laser system, operates based on simple diode principles. The ones employed here are p-i-n type diodes, which use an intrinsic layer of high resistivity as the active layer (figure 3.22). When hit by photons an absorption takes place. The absorption at depth z , $N_{ph}(z)$ is given by the relation [75]:

$$N_{ph}(z) = N_{ph}(0) \exp(-\alpha z) \quad (3.46)$$

where $N_{ph}(0)$ is the number of incident photons, and α is the optical absorption coefficient. To guarantee a high absorption, semiconductors featuring a direct band gap or ones allowing an indirect transition must be employed. As the photons are absorbed, they generate electron-hole pairs in the region of the diode featuring a high electric field. This field will extend across the intrinsic region, when the p-i-n diode is placed under reverse bias. Hence the carriers are swept out of this region and therefore generate an electrical current in the external electrical circuit.

The standard PSD used here has an active area of 1 mm x 12 mm, but it can be substituted by smaller PSDs with active areas of 1 mm x 6 mm or 1 mm x 3 mm. The latter is not recommendable though, except for measurements of extremely small stress changes.

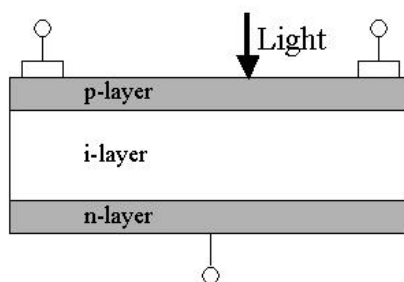


FIGURE 3.22: The principle of operation of the PSD.

3.8.4 Gas chamber

The gas chamber was constructed from aluminum. In its top and in its bottom anti-reflex coated windows are placed. The use of anti-reflection coatings is absolutely crucial in order to eliminate reflections, which can hit the detectors. The clamping of the sample was realized by having the sample rest on the polished aluminium surface and from above holding it into place by pressing a 2 mm Teflon layer glued to an aluminium lever onto it. The Teflon was used to exploit its slight spring effect, thus allowing a tight clamping of the sample.

3.8.5 Transmission detector

The transmission detector which is employed to measure the laser intensity, that is transmitted through a sample placed in the gas chamber, is a simpler version of the PSD. When hit by the laser beam, photocurrents are produced. These are amplified by an external amplifying unit, which yields a voltage proportional to the intensity. When no sample is in the gas chamber, the amplification factor can be calibrated to realize a direct proportionality between the output voltage of 0-10 V and the transmission of 0-100 percent.

3.8.6 Furnace

The furnace is equipped with a hatch for easier loading and unloading of samples. The hatch also has a build-in quartz window, which allows the direct monitoring of the sample during thermal cycling. As the window is specified to 420°C, a protective radiation shield which can be placed directly in front of the window was designed.

In order to obtain good absorption of the radiation in the copper piece supporting the sample, it was manually coated by black carbon dust. Additionally, it was equipped with a series of drilled through holes of 1 mm diameter in the vicinity of the reference sample. This was done to allow the ceramic cement used for gluing the reference sample to the copper piece to get proper hold. For all designs of the copper plate without these holes, the reference sample and the ceramic cement failed to stick to the copper support.

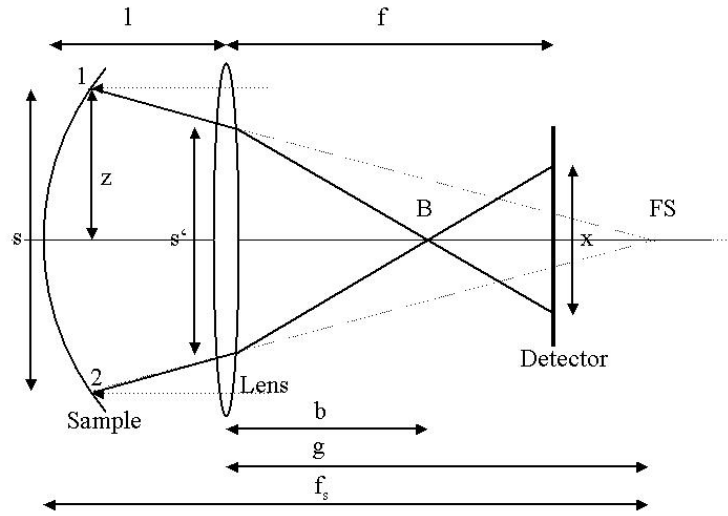


FIGURE 3.23: Schematic view of the optical setup which is used to determine the curvature.

The copper piece is supported by two horizontal ceramic Al_2O_3 tubes, which proved to have worse thermal conductivity than all other supporting materials, which were considered. A temperature gradient across the sample could therefore be widely avoided as explained in section 3.4.

3.9 Appendix: Geometry of the scanning laser system

As mentioned in section 3.2, the geometry of the scanning laser system yields a simple relation between the position on the sample, x , the position on the PSD, s , and the radius of curvature, R :

$$\frac{x}{s} = \frac{2f}{R} \quad (3.47)$$

where f is the focal length of the plane-convex lens.

The proof of this equation is based on the geometry shown in figure 3.23. In a real measurement, the beam will be scanned from position 1 to position 2, which have a spacing s . At these positions the beams will be reflected back through the plano-convex lens, which is placed at a distance l from the sample. They will cross each other in the point B, located at a distance b from the lens and fall onto the detector, which is placed at the focal distance f of the lens. On the PSD the beams will be spaced by a distance x . In the absence of the lens, the two beams can additionally be imagined to cross in the focal point of the sample, FS, which is located at a distance f_s from the sample and a distance g from the lens.

The following relations are now valid:

$$fs = \frac{R}{2} \quad (3.48)$$

and

$$\frac{1}{f} = \frac{1}{g} + \frac{1}{b} \quad (3.49)$$

The relationship between x and s can be expressed as:

$$\frac{x}{s} = \frac{x}{s'} \cdot \frac{s'}{s} \quad (3.50)$$

where the distance between the laser beams at the lens is s' . Denoting the height difference between the point on the sample hit by the beam and the center of the sample by z means that:

$$\frac{s'}{s} = \frac{g}{f_s - z} = \frac{f_s - l}{f_s - z} \quad (3.51)$$

$$= f \left(\frac{1}{f} - \frac{1}{g} \right) - 1 \quad (3.52)$$

$$= \frac{f}{g} \quad (3.53)$$

$$= \frac{f}{f_s - l} \quad (3.54)$$

Similarly,

$$\frac{x}{s'} = \frac{f - b}{b} = \frac{f}{b} - 1 \quad (3.55)$$

$$= f \left(\frac{1}{f} - \frac{1}{g} \right) - 1 \quad (3.56)$$

$$= \frac{f}{g} \quad (3.57)$$

$$= \frac{f}{f_s - l} \quad (3.58)$$

Inserting equations (3.54) and (3.58) in equation (3.50) and applying equation (3.48) now yields:

$$\frac{x}{s} = \frac{x}{s'} \cdot \frac{s'}{s} \quad (3.59)$$

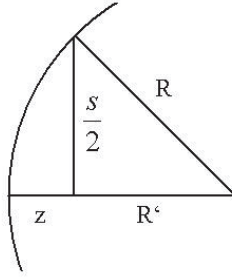
$$= \frac{f}{f_s - l} \cdot \frac{f_s - l}{f_s - z} \quad (3.60)$$

$$= \frac{f}{f_s} \cdot \frac{1}{1 - \frac{z}{f_s}} \quad (3.61)$$

$$= \frac{f}{f_s} \quad (z \ll f_s) \quad (3.62)$$

$$= \frac{2 \cdot f}{R} \quad (2z \ll R) \quad (3.63)$$

Equation 3.63 is in fact only valid for $2z \ll R$. This means that there is a restriction on the scan size depending on the radius of curvature, as can be seen from the following considerations.

FIGURE 3.24: Geometrical understanding of R and R' .

In figure 3.24, R and z are shown. They are related to each other through R' . From simple geometry one gets:

$$R^2 = \frac{s^2}{4} + R'^2 \quad (3.64)$$

Using equation 3.64 in the expression of z yields:

$$z = R - R' \quad (3.65)$$

$$= R - \sqrt{R^2 - \frac{s^2}{4}} \quad (3.66)$$

which can be rearranged to:

$$\frac{2z}{R} = 2 - \sqrt{4 - \frac{s^2}{R^2}} \quad (3.67)$$

This means that the restriction on the scan size is:

$$s \ll R \quad (3.68)$$

or

$$2z \ll R \quad (3.69)$$

As the radius of curvature is always larger than 1 m and the scan size less than 2 cm, this requirement on s is in fact always met.

3.10 Summary

The construction of an experimental setup for accurate stress measurements was a complicated task. However, once realized and fully operational, it worked reliable and allowed the study of some very interesting topics. In the following sections (5)-(7), these topics are described in detail. Coincidentally, each topic made use of special unique parts of the system: The study of deposition stress made use of the sample holder for deposition stress measurements; the study of the mechanical behavior of switchable coatings was carried out with use of the gas chamber, while the study of mechanical stresses in phase change materials employed the furnace for measurements. Hence the potential of the entire system can be understood from these studies.

Chapter 4

Supplementary experimental methods

4.1 Introduction

During the course of the investigations of the mechanical stresses in the films studied here, additional methods were utilized in order to obtain information crucial to the analysis of the stress measurements. The most important quantity of these is the film thickness, which enters directly into the Stoney equation (eq. 2.84), and hence must be measured with high precision. Moreover, a study of thickness changes upon phase changes and transitions, information which is helpful in studying the elastic/inelastic nature of these processes through equation 2.93 and related *in-situ* stress measurements, could be carried out using the X-ray reflection method (section 4.2.2). Optical spectroscopy which is described in section 4.3 additionally served as a reference for the optical transmission and reflectivity data obtained simultaneously to the stress measurements in the case of optically switchable coatings. X-ray measurements also helped determine the density of a variety of films. This proved to be especially important in the case of tungsten oxide, where several properties were shown to depend directly on the film density. Moreover, measurements of electrical resistivity upon heating were used to calibrate the temperature measurements in the furnace belonging to the stress measurement system. In this section spectroscopy and X-ray based methods will be briefly presented. A description of electrical resistivity measurements upon heating can be found in ref. [90]. References for further details are given in the relevant sections.

4.2 X-ray measurements

X-ray measurements allow the determination of several important film properties. Most important for this work was the precise film thickness determination, which can be carried out with an accuracy of 1 % or better. Additionally, the density of the films can be determined to better than 1 % as can the surface roughness of the samples. Structural properties such as crystallinity and texture can also be measured.

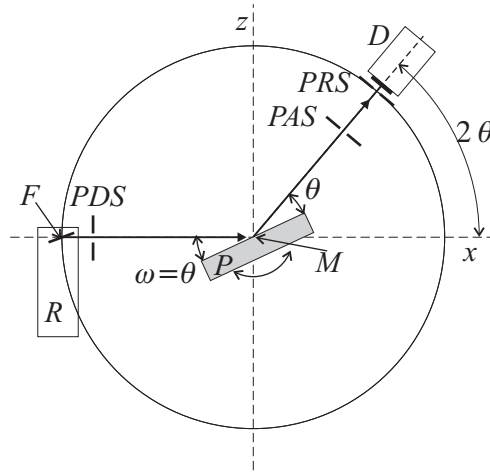


FIGURE 4.1: The geometry of a θ - 2θ scan. From Ref. [141].

4.2.1 Principle

The X-ray technique utilizes the interaction between the highly energetic X-rays and electrons in the investigated material. Hence the method is very sensitive to changes in the electron density in the sample. Even though this is described by a complex theory, the concepts can be explained using simple geometric arguments.

Conventionally, one distinguishes between three modes of measurements using the X-ray system. In all cases, the sample is irradiated by a monochromatic X-ray beam, which in the system used has a wavelength of $1.54 \text{ \AA}$.

- In one case the beam hits the sample (P) at an angle θ . As the detector (D) is placed at an identical angle θ to the sample, it is placed at an angle of 2θ to the incoming beam (Fig. 4.1). The sample and the detector are automatically turned through the desired angle interval. Hence, the method is conventionally referred to as a θ - 2θ scan, and the detector measures reflections from planes parallel to the sample surface.
- In the "grazing incidence" mode, the sample is irradiated under a constant angle ω , while the detector scans across an angular range (Fig. 4.2). This method allows measurements on thin films, as the beam does not penetrate as deep into the sample as it is the case in the θ - 2θ scan.
- In the third mode, the detector is fixed at a certain position, and the sample is tilted along both axes. This mode is called "rocking-curve" measurement, and allows the determination of texture. It wasn't used for this work and hence is not described in detail here.

A thorough description of all measurement modes can be found in [90]. The X'PERT PRO system used at the I. Institute of Physics allows the tilting of sample and detector with an accuracy of 0.0001° .

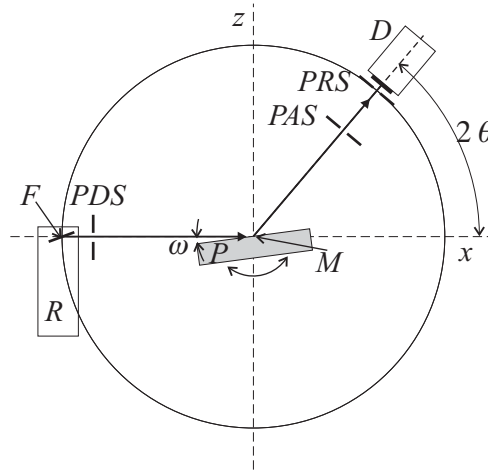


FIGURE 4.2: The setup of a grazing incidence measurement. From Ref. [141].

4.2.2 X-ray reflection

In the case of X-ray reflection (XRR) measurements, the θ - 2θ scan is applied in all cases. From XRR measurements important film properties such as density, thickness and roughness can be deduced. The theory of these procedures can be found in references [141] and [90]. Here only a brief look into the determination of these properties is given.

In fig. 4.3 typical θ - 2θ scans are shown. Several features are evident. At low angles the so-called total reflection edge is seen. Its position θ_{TR} is closely related to the density, ρ , of the film through

$$\Theta_{TR} \sim \rho^{1/2} \quad (4.1)$$

At higher angles, an interference pattern from the reflection of the X-ray at the surface of the film and the interface between film and substrate can be seen. The distance between the interference oscillations is closely related to the thickness d of the film:

$$d \approx \frac{\lambda}{2} \frac{1}{\Theta_{n+1} - \Theta_n} \quad (4.2)$$

where Θ_n and Θ_{n+1} are the angles of subsequent maxima, and λ is the wavelength of the X-ray. Additionally, statements about the sample roughness can be made using XRR measurements. The extinction of the interference oscillations at lower angles as seen in fig. 4.3.c indicates that the sample has higher roughness than the samples shown in fig. 4.3.a and fig. 4.3.b.

4.2.3 X-ray diffraction

X-ray diffraction (XRD) is used for the characterization of crystalline samples. The method is based on the well-known Bragg condition. In figure 4.4 the scattering from different lattice planes is shown. The Bragg condition for constructive interference is:

$$2d_{hkl} \sin\theta = \lambda \quad (4.3)$$

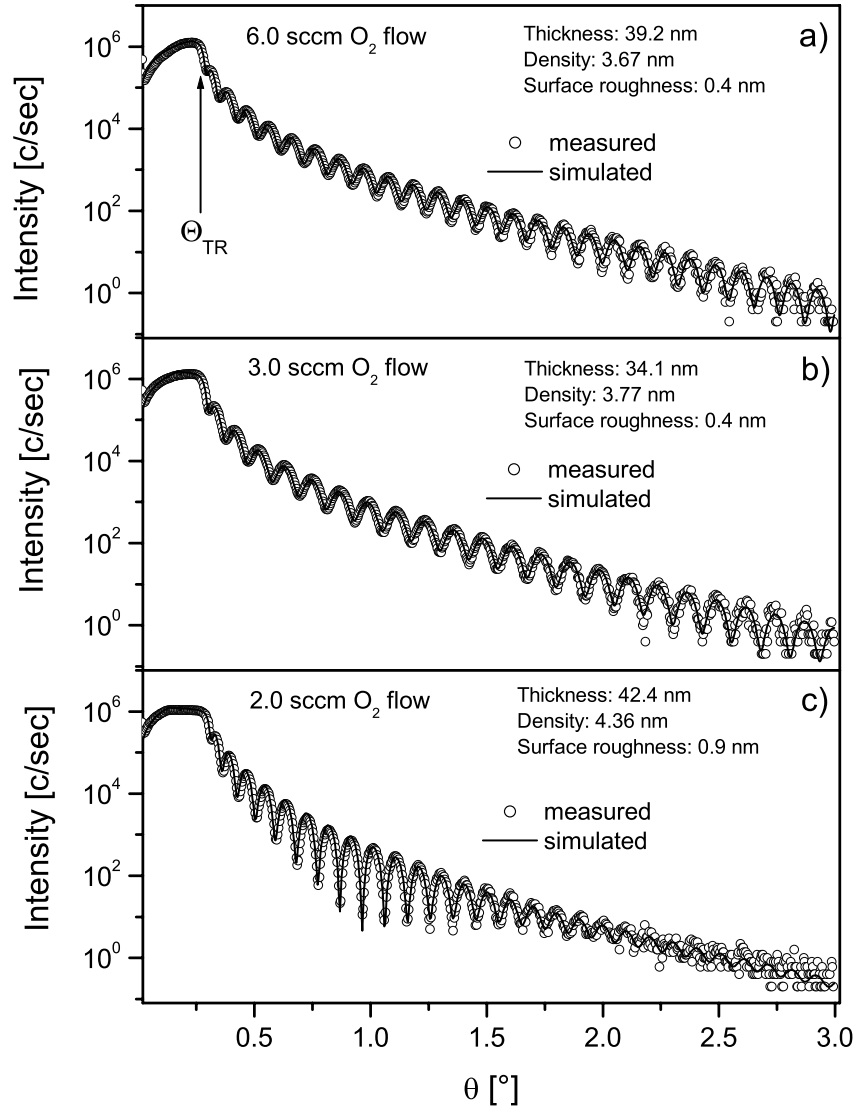


FIGURE 4.3: Typical θ - 2θ scans: a) a TiO_2 sample deposited at 6 sccm O_2 flow, b) a TiO_2 sample deposited at 3 sccm O_2 flow, and c) a $(\text{TiO}_{1.2})_{0.787}$ sample deposited at 2 sccm O_2 flow. From the total reflection edge the density of the film can be determined, while the film thickness can be determined from the spacing between the oscillations at higher angles. Additionally, statements about the roughness can be made from the angle to which the oscillations continue to be observed.

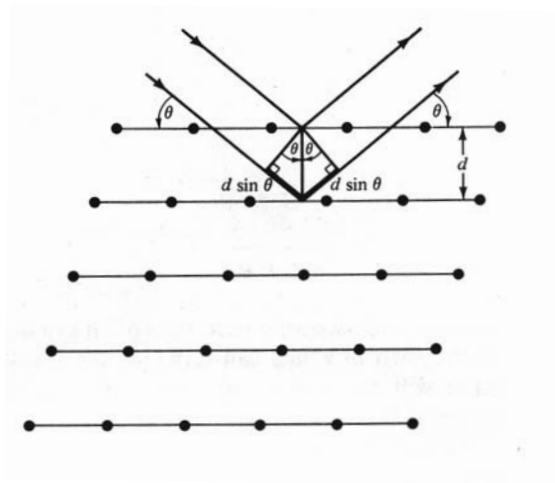


FIGURE 4.4: The well-known Bragg scattering from different planes. Constructive interference is obtained when the Bragg-condition (4.3) is satisfied.

where d_{hkl} is the lattice plane spacing, θ is the angle between the X-ray beam and the planes, and λ is the wavelength of the X-ray beam. In XRD measurements the intensity, shape and position of the reflection peaks yield detailed information on the structural properties of the film.

When carrying out XRD measurements, the choice of mode is associated with certain advantages and drawbacks. The grazing incidence setup has the disadvantage, that it only penetrates a thin region at the top of the film. On the other hand, it has the advantage of being extremely sensitive. The alternative θ - 2θ scan is not quite as sensitive as the grazing incidence measurement, but the beam penetrates deeper into the sample. Hence the choice of setup must be based on the properties of the sample.

The degree of crystallinity of the samples can be divided into four categories, each of which has their own "fingerprint" XRD profile (some of which are shown in fig. 4.5). The amorphous sample (a) show no well-defined peaks, while the spectrum of a polycrystalline sample (b) shows all allowed diffraction peaks. A special case of this, the textured polycrystalline sample (c) shows peaks of very high intensity as some crystallite orientations are dominant. Finally, a monocrystalline shows only sharply defined peaks associated with the crystallite orientation of the sample, but none were available for measurement.

4.3 Optical spectroscopy

For transparent films, optical spectroscopy can also be used for determination of the film thickness. As this method is much quicker than the X-ray based methods, it was applied whenever it was possible. Additionally, optical spectroscopy was used for measurements of the switching of optically switchable coatings, which give further insight in the behavior of such films. These measurements also served as a reference for the experiments carried out using the mechanical stress measurement setup. In this brief presentation only the determination of the thickness shall be explained. Further

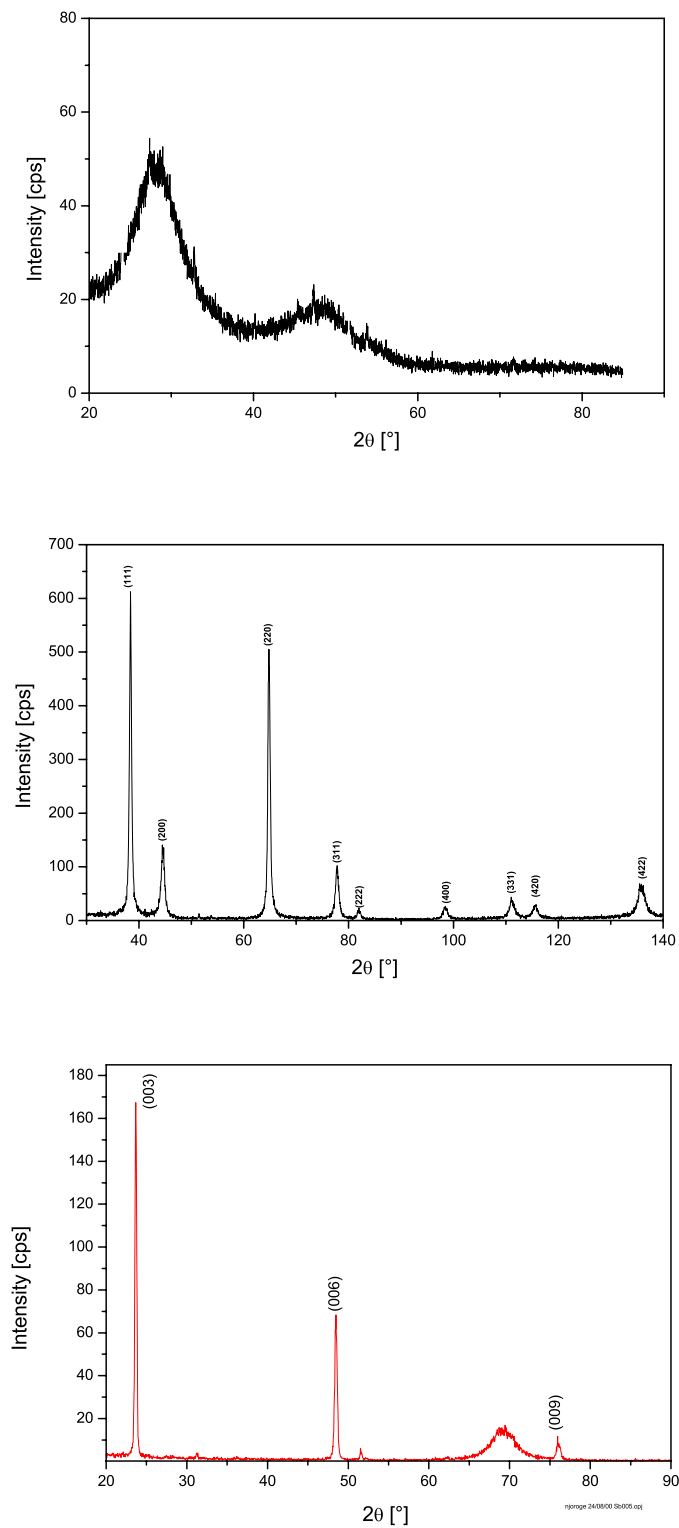


FIGURE 4.5: Typical XRD scans for 3 different cases of crystallinity. a) An amorphous sample shows no well-defined peaks, b) a polycrystalline sample shows all of the allowed diffraction peaks, c) a textured polycrystalline sample shows peaks of very high intensity for the orientations that are dominant.

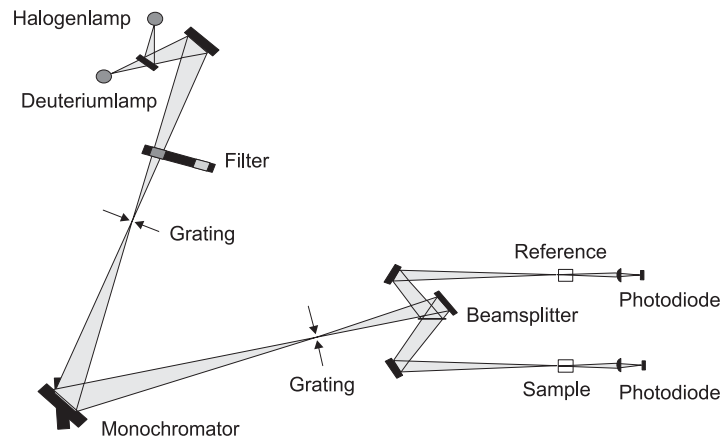


FIGURE 4.6: The principle of the spectrometer. See text for details. After ref. [141].

details on the virtues of optical spectroscopy can be found in ref. [141].

4.3.1 Principle

The main purpose of optical spectroscopy is the determination of the transmission and reflection properties of a given film. At the I. Institute of Physics this was carried out using a LAMBDA-25 spectrometer from Perkin-Elmer. This instrument allows investigations of optical properties in the wavelength region of $\lambda = 190\text{--}1100\text{ nm}$. The principle of the measurement is shown in fig. 4.6. For transmittance measurements the monochromatic light is simultaneously directed through the sample and a reference sample, while the reflectivity of the sample is compared with the reflection of a reference sample in the case of reflectivity measurements. In a measurement, the reflectivity and transmission is measured step-wise across the desired wavelength region (typically $190\text{--}1100\text{ nm}$) with a resolution of 960 nm/min .

To obtain the thickness (and the index of refraction) the measured behavior of reflectivity and transmission is simulated. The simulation is carried out in the SCOUT 2 programme by application of the Fresnel equations. By this procedure the film is characterized by its thickness and its dielectric function. It is beyond the scope of this work to describe this method in detail, but a thorough treatment of optical spectroscopy and the simulations using SCOUT 2 can be found in ref. [141].

Chapter 5

Deposition stresses in transition metal oxides

5.1 Introduction

Understanding and controlling mechanical stresses is of great importance in the field of transition metal oxides. The group of transition metals consists of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W. These metals form the stoichiometrically stable oxides TiO_2 , ZrO_2 , HfO_2 , V_2O_5 , Nb_2O_5 , Ta_2O_5 , CrO_3 , MoO_3 and WO_3 .

These oxides have a wide array of possible applications and are used as functional coatings in many devices. Their main application is however optical coatings. Thin films based on these oxides can be used to design coatings that allow a high transmission of the solar energy into a building and also has a high reflectance in the infrared, helping confine the heat in a building. Hence energy used for heating can be saved, by application of window equipped with such coatings. In warm regions of the world the coatings are designed in the opposite way to hinder the transmission of solar energy into the building. Thus energy used for cooling can be saved.

Additionally, such transition metal oxides find application in laser mirrors, ionic conductors, broadband interference filters [77] as well transparent conductive coatings, hard coatings etc. In recent years TiO_2 has attracted particular interest as its anatase phase has photocatalytic and hydrophilic properties, which have been exploited in devices such as antibacterial and self-sterilizing coatings, self-cleaning clothes, self-cleaning windows and anti-fogging glass, dishwashers, self-cleaning house and street coatings [35] and air- and water purification devices [99] especially in Japan.

As these films are applied in situations where it is crucial to guarantee a certain lifetime, it is important to understand and control their level of mechanical stress. Stress induced effects can lead to a partly or complete loss of functionality in case of a serious failure such as delamination or the formation of cracks. As the films in most cases do not undergo any transformations in their application, but just deliver a given function, the source of mechanical stresses in the films arise during deposition. Hence it is the objective of this study to investigate and understand the origin of deposition stresses in such transition metal oxides.

In industrial applications, these oxides are often deposited using sputter deposition (see section 5.2). Therefore this method of deposition was chosen for this study, which was carried out using the setup for deposition stress measurements described in section 3.3.1.

In section 5.2 the properties of sputter deposition is described along with the parameters used for deposition of the transition metal oxides (section 5.3). Section 5.4 contains theoretical descriptions of deposition stresses, while the results of the deposition stress measurements are shown and explained in detail in section 5.5.

It should be noted that chromium which also belongs to this group of transition metals was omitted from the study as it forms hazardous oxide compounds.

5.2 Sputter deposition

The films studied in this work were all exclusively produced by sputtering. In this process which is classified as a physical vapor deposition (PVD) process, the film is grown on substrates by a process in which the desired material by bombardment with energetic ions is placed in its gas phase, and directed onto the substrate where it is condensed.

Normally sputtering is used for deposition of metals and other conducting materials. Substances such as oxides and nitrides can be produced by sputtering by increasing the partial pressure of oxygen or nitrogen in the surrounding gas atmosphere. The sputtering method has the advantage compared to other deposition methods, that it allows homogeneous large scale deposition i.e. the coating of architectural glass, plastic substrates etc., Hence it is important from the perspective of industrial application.

A detailed description of the principle of the process is given in section 5.2.1, the systems used at the RWTH Aachen are presented in Section 5.2.2, while details on deposition of the materials studied here are given in sections 5.3.1 and 5.3.2.

5.2.1 Principle of DC-magnetron sputtering

The principal setup of a sputter system is shown in figure 5.1. A circular target material welded onto a magnetron is placed inside a vacuum chamber. A constant current and a negative potential of several hundred Volt is applied to the target. The substrate is positioned above the target. To allow the flooding of the chamber by a sputtering gas such as Ar, Xe or Kr and reactive gases such as O₂ or N₂, gas inlets are installed.

The plasma shown in fig. 5.1 is produced by flooding the evacuated chamber with a sputtering gas (typically Ar) to a pressure of 0.8-12 Pa. The applied potential now accelerates the naturally present Ar⁺ ions onto the target. Hereby metal as well as secondary electrons are released from the target. The latter induce further ionization of the sputtering gas. Depending on the distance between the electrodes, d , and the pressure of the sputter gas p_{tot} , a break-down voltage U_D at which a glow-discharge occurs is given by [33]:

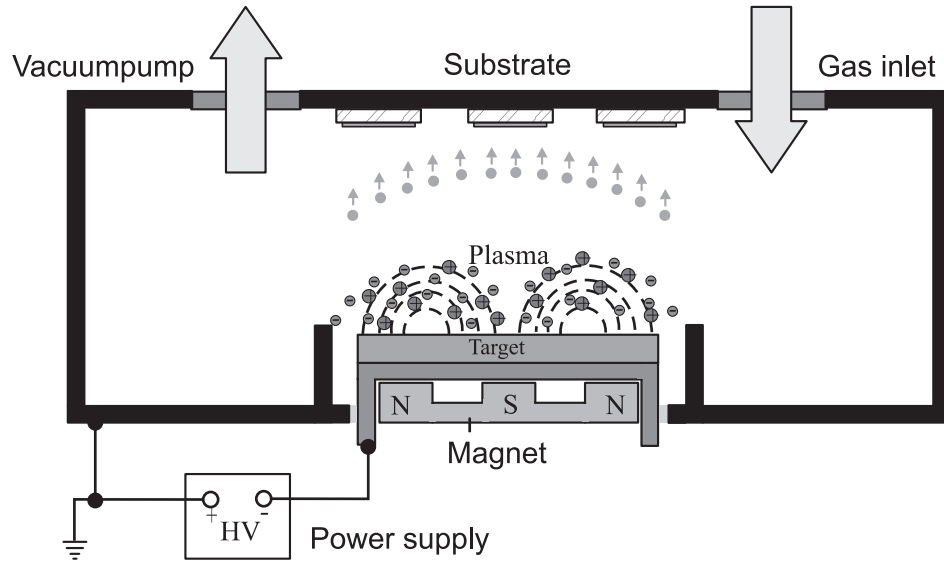


FIGURE 5.1: Principle setup of a sputter system. The argon ions are accelerated onto the target where material is sputtered away. Parts of the sputtered material hits the substrate where the film is grown. See text for further details. After ref. [141]

$$U_D = \frac{A \cdot p_{tot} \cdot d}{\ln(p_{tot} \cdot d) + B} \quad (5.1)$$

where A and B are material constants. Hence, when the ionization rate produced by the secondary electrons is above a certain threshold, a stable glowing plasma is created.

To reduce the necessary gas pressure required for stable plasma operation, in magnetron sputtering a circular magnet is placed below the target. Due to its radial north-south characteristics, the electrons now travel in paths above the target as seen in figure 5.1. Therefore the electrons travel in the sputter gas for a longer duration and thus have a larger possibility of ionizing it. As a result, the pressure of the sputtering gas can be reduced by up to a factor of 100 and still suffice for stable plasma operation. This reduction of the pressure additionally implies, that the material released from the target is subject to less collisions with the sputter gas atoms on its path to the substrate. Hence it possesses larger kinetic energy upon arrival at the substrate, and also the sputter rate is increased. The disadvantage of the use of a magnet below the target is, that the electron-density in the plasma is largest where the magnetic field is parallel to the target surface. Hence the majority of the released material from the target, originates from a circular area on it. This leads to the formation of a so-called erosion pit on the target mirroring the magnetic field. As a result the target material is not used efficiently, as the target must be exchanged once the target material has been removed in the region of the erosion pit.

Because of the nature of the sputtering process, only conducting materials can be used as a target material in the case of direct current (DC) sputtering. In the case of a non-conductive target material, the bombardment by positive ions would result in a build-up of charge at its surface. This would result in a screening the applied electrical field, and thus the process would quickly stop.

The deposition of non-conductive films can only be made possible by applying special sputter-configurations. Oxides and nitrides can easily be prepared by addition of oxygen and nitrogen, respectively, to the gas atmosphere in the sputter chamber. This configuration is called "reactive sputtering" and was used to deposit the oxides and nitrides studied in this work. Another configuration allowing the deposition of non-conductive materials is radio frequency (RF) sputtering, in which an alternating potential is applied to the target. In this case, the sputter process has two phases: In the first phase the deposition takes place, while in the second phase the charge is removed from the target surface.

The properties of the resulting deposited films depend on a variety of parameters of the sputter process. The most important ones are:

- Sputter current (I_s): The sputter current determines the current flowing in the target i.e. the number of impinging ions. The main contribution stems from the Ar^+ ions. In the most frequently used sputter modes, the sputter current is held constant to ensure a constant rate of material removal.
- Sputter voltage (V): As mentioned above, a voltage can be applied to the target. This voltage determines the maximum energy with which the ions of the sputter gas can hit the target. As the gas ions do not transfer all their energy to single target atoms, the energy of the released atoms will have a distribution within a certain energy range (typical energies are 1-10 eV [56], [123]). Additionally, the sputter voltage determines the sputter yield Y_s i.e. the number of atoms released per incoming sputter gas ion by the relation [24]:

$$Y_s = \text{const} \cdot (V - V_0)^{2/3} \quad (5.2)$$

where V_0 is a material constant which typically lies in the range 10-50 eV.

- Target to substrate distance (d): Along with the total pressure, the distance between the target and the substrate determines the number of collisions with the atoms of the sputter gas, which the sputtered particles are subject to on their path from the target to the substrate and hence their kinetic energies upon arrival at the substrate.
- Total pressure (p_{tot}): The total pressure determines the mean free path length and hence the kinetic energy of the sputtered particles travelling towards the substrate. The mean free path is proportional to $1/p_{tot}$ (von Paschen law) [33].
- Partial pressures of reactive gases ($p_{specimen}$): By adding reactive gases such as O_2 and N_2 to the gas atmosphere of the sputter chamber, oxides and nitrides can be produced. Their stoichiometry can be tuned by varying the pressure of the reactive gases at a constant total pressure. The addition of reactive gases additionally affects the sputter yield and the rate of removal from the target, as they can cover the target surface. The implications of these phenomena on the sputter conditions and film properties are further elaborated in section 5.3.2.
- Substrate temperature (T_s): The temperature of the substrate affects the density and also the degree of crystallinity of the growing film, as elevated temperatures will assist diffusion

in the growing film. Additionally an elevated substrate temperature can lead to mechanical stresses through (2.97).

- Substrate bias: By biasing the substrate, ions and electrons can be directed onto it, and additionally be accelerated or decelerated. The density, crystallinity and other film properties can be manipulated using this approach [24], [144].
- Angle of deposition: Even though the system employed at the RWTH Aachen uses a parallel positioning of target and substrate, other geometries can be used. As a result, a thickness gradient across the film as well as anisotropic effects can be produced.
- Size and geometry of target: Depending on the target size and the depth of the erosion pit, the degree of (in)homogeneity of the film properties across the substrate can be (in)voluntary changed.

5.2.2 Sputter systems used

For the production of the films investigated in this work two sputter systems were used. The first system was custom-built at the I. Institute of Physics (Fig. 5.2) [123]. It possesses six target positions placed inside a cylindrical chamber. The targets have a diameter of 76 mm. Above them at a distance of 55-78 mm, the substrates are positioned on a rotatable platform carrying 24 spaces for substrates. The sputtering is carried out in a stationary mode i.e. the desired substrate is rotated to a position above the target of choice, and the film is deposited. Before deposition the chamber is evacuated to a base pressure of 1×10^{-3} Pa before being flooded with an argon sputter gas of 99.999% purity and in some cases a reactive gas (O_2 or N_2) of 99.999% purity to a total pressure of 0.8-12 Pa. Voltage is applied to the target by an external power supply yielding a max. output of 600 V at 1.2 A. During sputtering the current is always kept constant.

The second system in use is a commercial system LS320S from Pfeiffer/von Ardenne (Fig 5.3). It is constructed for the sole purpose of sputtering films for optical data storage applications. It allows the production of four samples per sputter run. The samples are positioned at a distance of 40 mm above the targets on a rotatable platform. There are four target positions. Upon sputtering, the system is evacuated to a pressure of less than 3×10^{-6} mbar. An argon gas of 99.999% purity is used as a sputter gas at a flow rate of 30 sccm, yielding a total pressure of 7.3×10^{-3} mbar. After a pre-sputter process, which serves to clean the target, the sputtering is carried out in either of two modes:

- Stationary sputtering, where the substrate is placed above the target and the film is deposited.
- Sputtering during rotation, where the platform carrying the substrates is rotated at a rate of approximately 20 rpm.

The phase change material targets used with this system included $Ag_{5.5}In_{6.5}Sb_{59}Te_{29}$, $Ge_2Sb_2Te_5$, and $Ge_4Sb_1Te_5$, which were all deposited using DC-sputtering at rates of 0.5 nm/s, 0.5 nm/s and 0.4 nm/s respectively. In some cases films of either SiO_2 , Si_3N_4 or $ZnS-SiO_2$ were sputtered on top of the phase change films to protect them against oxidation - all these cap layers were deposited using the RF-method at rates of 0.010 nm/s, 0.013 nm/s and 0.018 nm/s, respectively.

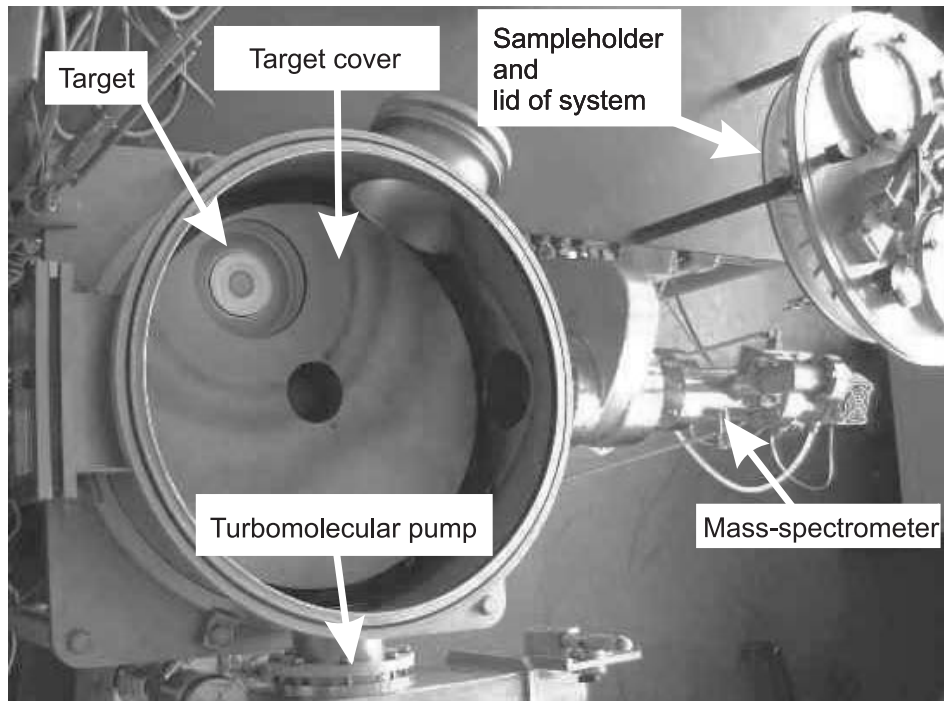


FIGURE 5.2: Photo of the sputter system used at the I. Institute of physics (see text for details). After ref. [141].

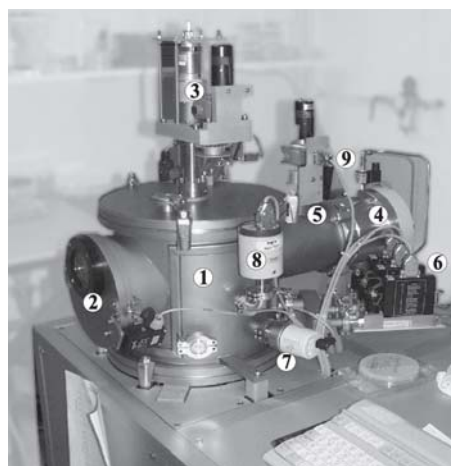


FIGURE 5.3: Photo of the sputter system used at the I. Institute of physics for the deposition of phase change films exclusively. From ref. [90].

Material	Sputter current [mA]	p_{tot} [Pa]	d [mm]	$p \cdot d$ [Pa·mm]
TiO _x	900	1.0	78	78
ZrO _x	900	0.8	70	56
HfO _x	500	0.8	65	52
VO _x	750	0.8	78	62
NbO _x	900	0.8	70	56
TaO _x	300	0.8	78	62
MoO _x	800	1.0	78	78
WO _x	667	0.8	78	62

TABLE 5.1: The invariant sputter parameters for oxidic mode sputtering of transition metal oxides.

5.3 Sputter parameters for growth of transition metal oxides

5.3.1 Parameters for metallic films

The sputtering of the metallic films investigated here was straightforward. Most films were deposited at a total argon pressure of 0.8 Pa, while the sputter current ranged from 300 mA to 900 mA. The distance between film and target was between 65 mm and 78 mm. The complete details of the sputtering are listed in table 5.1.

5.3.2 General parameters for sputtering of oxide films

To guarantee a successful deposition of an oxide (or a nitride), a thorough characterization of its sputter behavior must be carried out. Upon flooding the chamber with the oxygen gas to a certain partial pressure, the process slowly changes its character from metallic to oxidic. The characterization of the sputter behavior is hence associated with an investigation of the result of the sputter deposition process at a variety of different oxygen partial pressures. Additionally, the resulting film properties depend on the order in which the experiments are carried out. Films deposited upon step-wise increasing oxygen partial pressure differ in their properties from films grown upon step-wise decreasing the oxygen partial pressure. This phenomenon is referred to as a hysteresis-effect. The reason for it lies in the different coverage of the target found in the two cases: At low partial pressures the target coverage is low, and the removed particles are mainly metallic. However, because of the geometry of the chamber, these metallic particles will not only be deposited on the substrate, but also on the walls of the chamber. The produced metallic areas on the walls can thus getter oxygen from the gas atmosphere, and hence reduce the partial pressure of oxygen. At high oxygen partial pressures, the target coverage is large, and the removal of metal particles becomes more rare. As the rate of removal of the target material decreases, less metal particles arrive at the walls of the chamber. Thus the walls become inactive in removing oxygen from the gas atmosphere. If the partial pressure of oxygen is reduced at this stage, the point at which the target coverage is reduced (and where the rate of sputtered metal particles increases again) is shifted to a slightly lower oxygen partial pressure. Therefore a hysteresis effect arises as it is seen in for ZrO_x in fig. 5.4. Conventionally, the mode of high rate and low oxygen

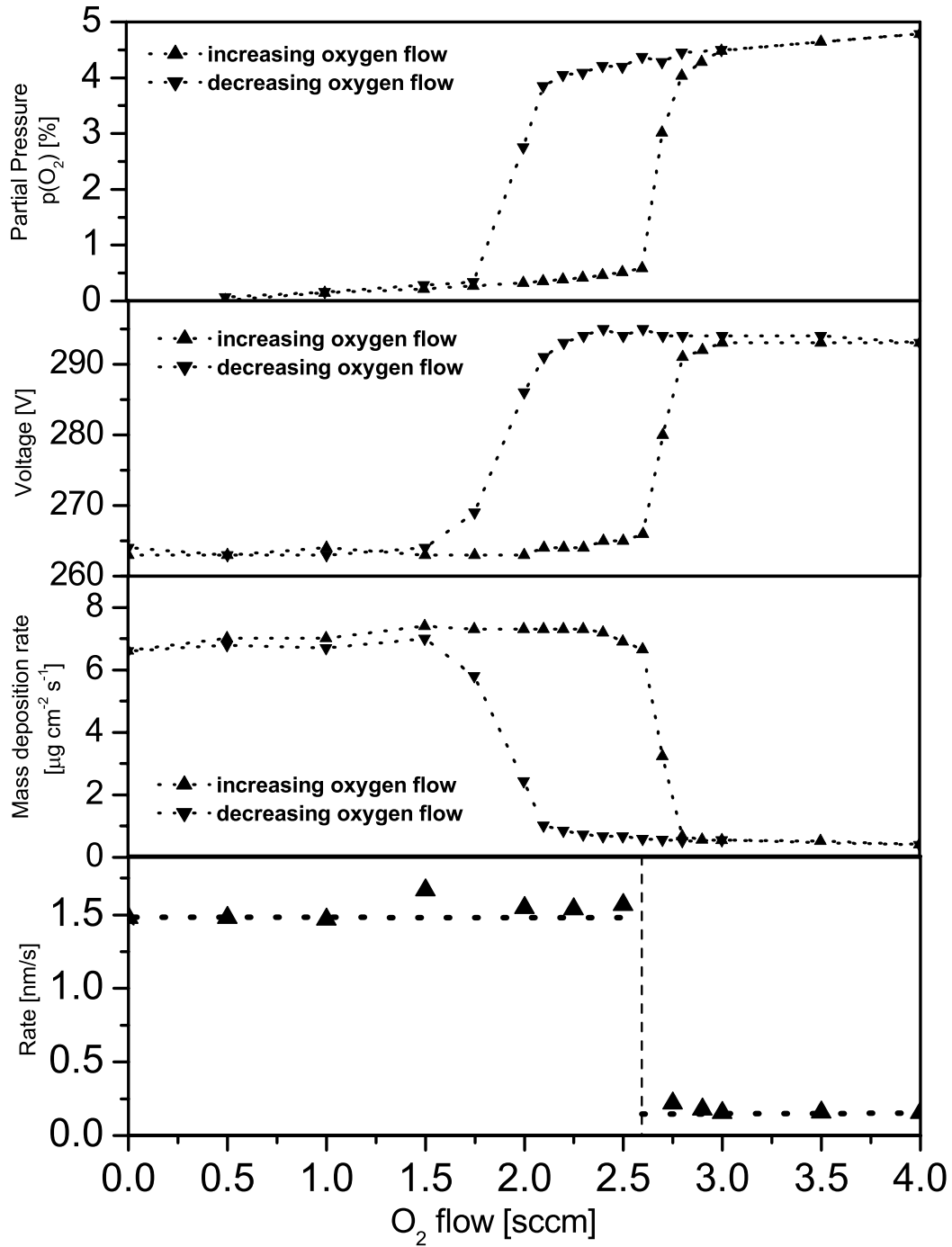


FIGURE 5.4: The properties of the deposition of zirconium oxide as a function of the oxygen flow. a) The oxygen partial pressure showing a pronounced hysteresis effect, b) the sputter voltage, c) the mass deposition rate, and d) the sputter rate as determined from ex-situ XRR measurements on samples produced using increasing oxygen flow. (See text for details). From ref. [136].

pressure is called "metallic mode" (0-1.5 sccm), the hysteresis region (1.5-3.0 sccm) is referred to as "transition mode", while the region of low rate and high oxygen partial pressure (3.0 sccm and higher) is labelled "oxidic mode" or "compound mode".

For other transition metal oxides the behavior is similar. However, the sputter regions are shifted towards lower or higher oxygen partial pressures. The reason for this is, that when the reactivity of the metal is high (like in Ti), the oxygen flow required for the realization of the stoichiometric oxide is lower. For less reactive metals (like W) the oxygen flow required is much higher.

In the following, the sputter behavior of all the investigated oxides will be shown. The system of tungsten oxide will be characterized in more detail, as it was subject to the most thorough mechanical stress investigations of all the deposited oxides. As an additional example, the sputter properties of titanium oxide are explained in section 5.3.4.

5.3.3 Sputtering of tungsten oxide

The tungsten oxide films studied here were deposited at total pressures ranging from 0.8 Pa to 12 Pa. For every value of the total pressure, the sputter properties as a function of the oxygen partial pressure was studied. This work was carried out by H. Weis [141] and C. Salinga [111]. As an example the characteristics of the sputtering at total pressures of 0.8 and 6 Pa are shown in fig. 5.5. Samples produced at a total pressure of 6 Pa were shown to have very quick switching kinetics and hence were studied in detail. Using a constant sputter current of 400 mA (6 Pa) and 667 mA (0.8 Pa) and fixed substrate to target distance of 78 mm, the oxygen partial pressure, the voltage and the sputter rate was monitored for oxygen flows of 0 to 50 sccm in both cases. Below, the features of the sputtering at 6 Pa is described. The sputtering at 0.8 Pa is very similar. However oxygen flows for the metallic mode, the transition region and the oxidic mode are shifted to slightly higher values, as it is indicated in figure 5.5.a.

In fig. 5.5.a the different domains of sputtering can be identified. The changes seen in the O_2 partial pressure as a function of the O_2 flow mirror significant changes in the sputter conditions. In region I at oxygen flows less than 10 sccm, the sputtering is metallic i.e. the oxygen gettering by the walls is predominant. Hence a linear increase of the O_2 partial pressure is seen. Domain II is the transition region. In this region the target surface is increasingly covered by oxygen, and the oxygen gettering by the walls begins to lose its significance. In this region it is evident that the deposition rate rapidly decreases because of the target coverage.

This trend continues in domain III above 25 sccm, where the target is completely oxidized, and the oxygen gettering by the walls can be neglected. Hence the gradient linking the O_2 partial current to the O_2 flow becomes steeper than in domain I. The behavior of the voltage can also be understood in terms of the coverage of the target. The oxidized top layer on the target works as an insulator, and hence increases the target resistance. At a constant sputter current the voltage must thus increase. Once the target is fully covered at an oxygen flow of 25 sccm, the voltage becomes largely constant.

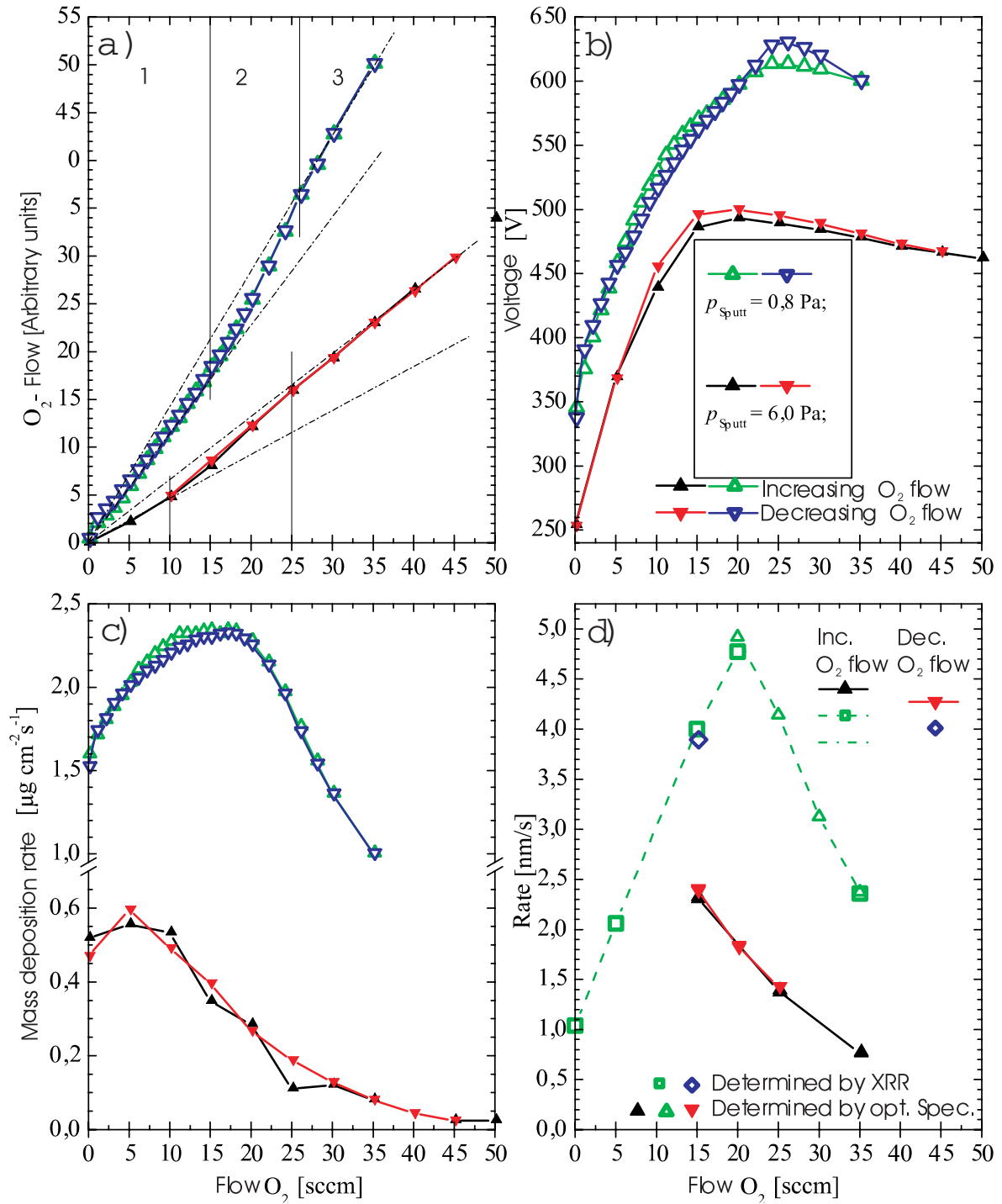


FIGURE 5.5: The properties of the deposition of tungsten oxide as a function of the oxygen flow at total pressures of 0.8 Pa and 6 Pa. a) The oxygen partial pressure, b) the sputter voltage, c) the mass deposition rate and d) the sputter rate. From ref. [141].

5.3.4 Deposition of titanium oxide

As the hysteresis behavior is not particularly evident in the case of tungsten oxide sputtering, the deposition parameters of titanium oxide are also described in detail as seen in this section.

The titanium oxide films were deposited at a total pressure of 1.0 Pa. At this pressure, important characteristic properties of the sputter process such as oxygen partial pressure, target voltage, mass deposition rate and the sputter rate as determined ex-situ by XRR were monitored as a function of the oxygen flow during deposition. In the case of titanium oxide stable oxidic mode sputtering is achieved at a flow of 3 sccm. Therefore in figure 5.6 the sputter parameters are shown in the range of 0 to 9 sccm.

The behavior of titanium oxide highlights the hysteresis behavior of reactive sputtering as mentioned in section 5.3.2. The sharp increase in oxygen partial pressure upon increasing O₂ flow, and the abrupt decrease in oxygen partial pressure upon decreasing O₂ flow mirrors the getter function of the surrounding walls.

5.3.5 Sputtering of other metal oxides

In figures 5.7 to 5.11, the sputter parameters of all the investigated oxides are shown. In some cases not all of the four sputter properties of oxygen partial pressure, target voltage, mass deposition rate and sputter rate were measured, and hence the figures are not complete. In all cases however, the voltage was determined.

5.4 Theory of deposition stress

In this section a description of mechanical stresses arising in thin films upon sputter deposition will be given. As sputtering is an extremely complex process involving a variety of parameters as seen above, this description can only be based on general considerations and cannot take into account influences that are only present in very specific scenarios, yet might still have significant influence on the deposition stress.

The origin of mechanical stresses in sputtered films can be understood from a theory based on the bombardment of the growing film by energetic atoms and ions. In sputtering, the film may be bombarded by the sputtered atoms themselves, back-reflected neutrals of the sputter gas (in this case Ar neutrals), as well as ions produced and extracted from the plasma or the reactive sputter gas. Depending on the energy and flux of such impinging particles, the deposition stresses arising in the grown films can be understood.

5.4.1 Properties of bombarding particles

In sputtering, the film is bombarded by energetic particles as it grows. Depending on the exact sputter parameters, these particles will possess a low or high energy and be incident on the film

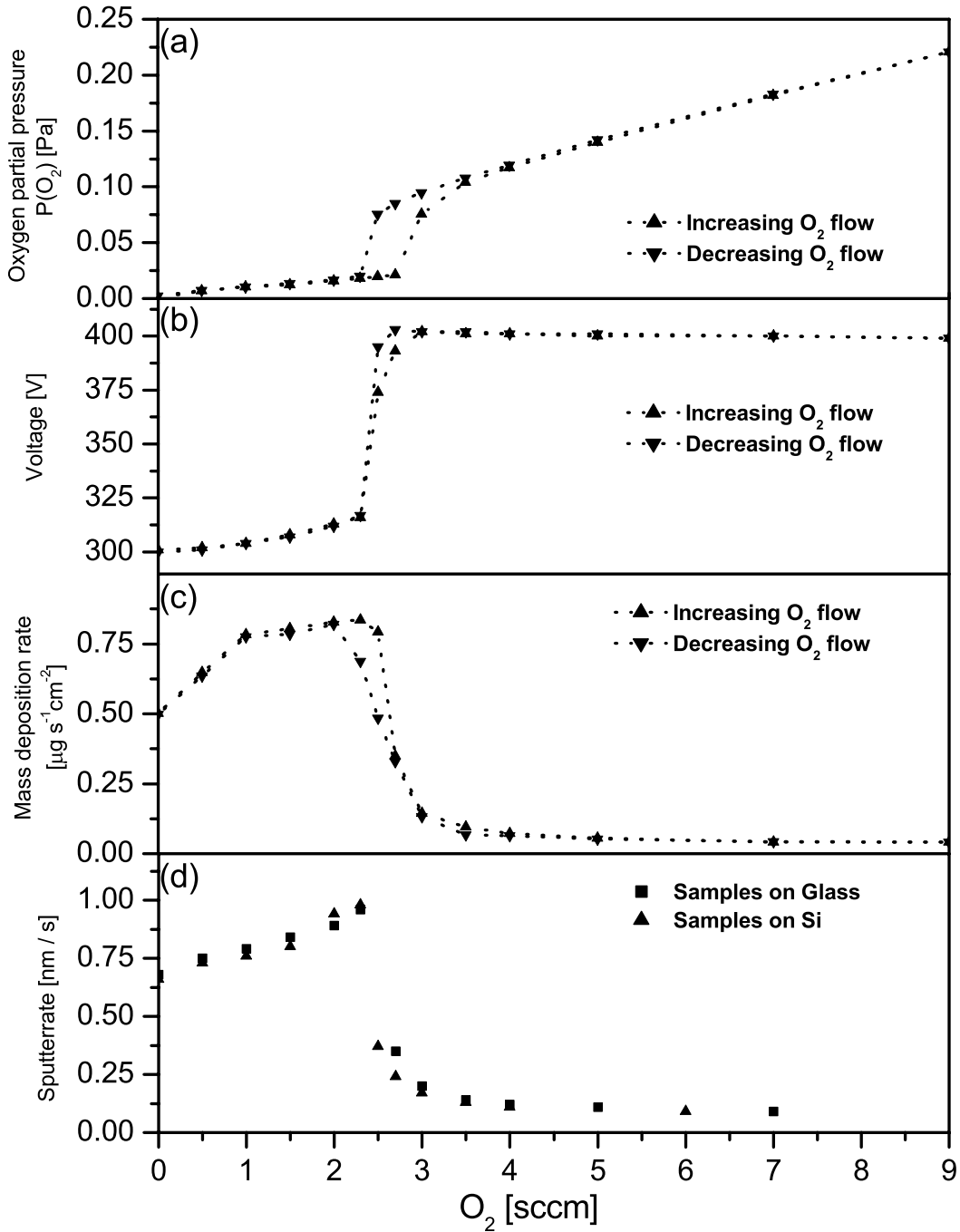


FIGURE 5.6: The properties of the deposition of titanium oxide as a function of the oxygen flow. a) The oxygen partial pressure, b) the sputter voltage c) the mass deposition rate d) the sputter rate as determined from ex-situ XRR (from samples produced using increasing oxygen flow). From ref. [81]

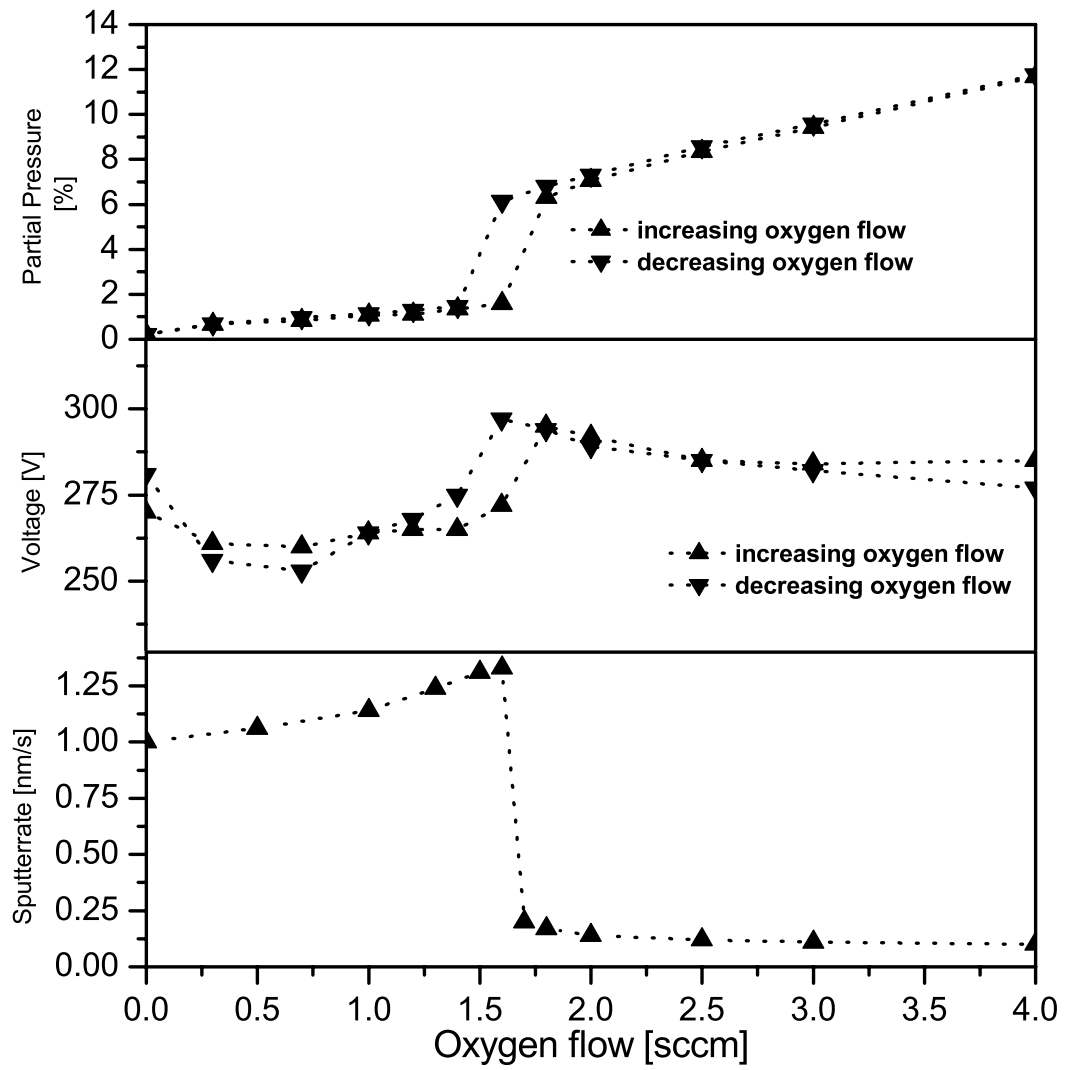


FIGURE 5.7: The properties of the deposition of hafnium oxide as a function of the oxygen flow. a) The oxygen partial pressure, b) the sputter voltage and d) the sputter rate as determined from ex-situ XRR (all samples produced using increasing oxygen flow).

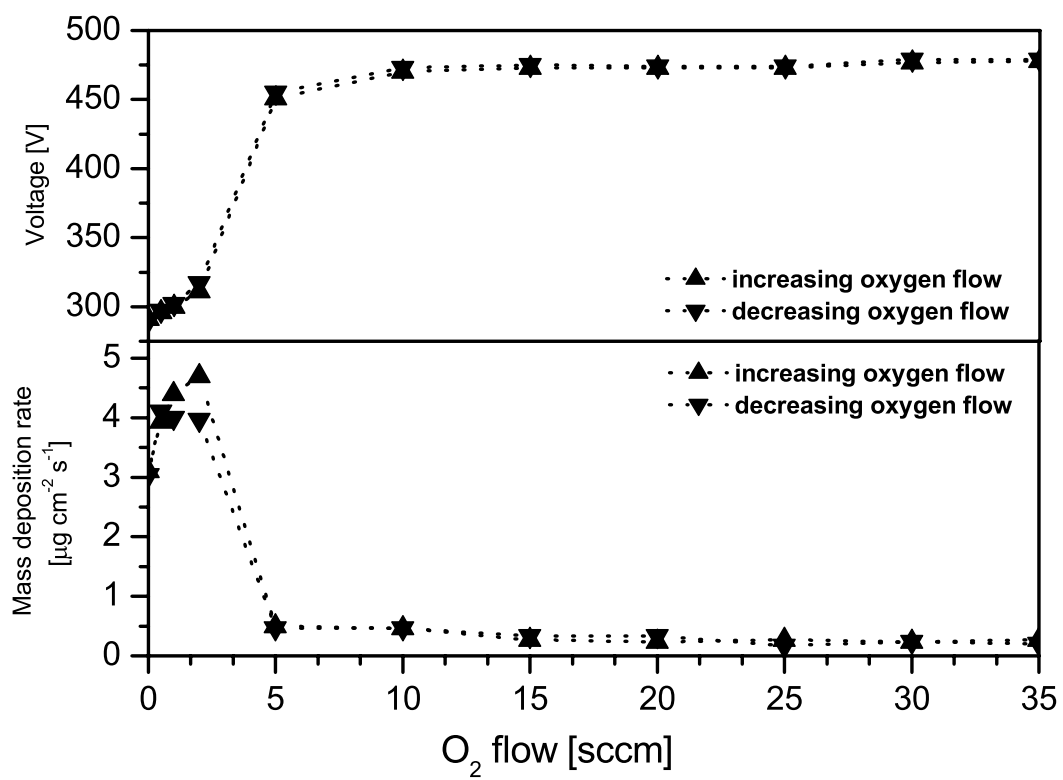


FIGURE 5.8: The properties of the deposition of vanadium oxide as a function of the oxygen flow. a) the sputter voltage and b) the mass deposition rate.

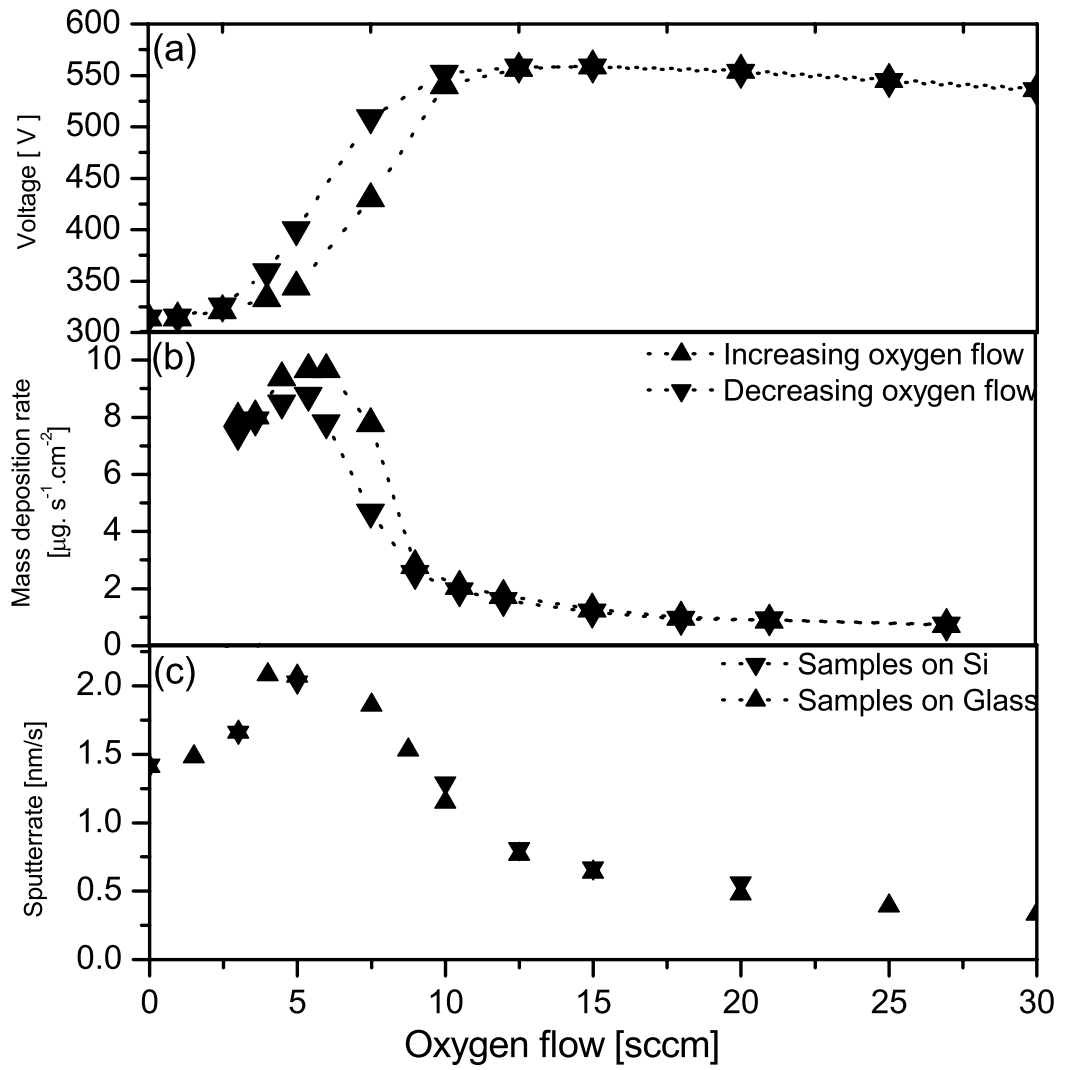


FIGURE 5.9: The properties of the deposition of niobium oxide as a function of the oxygen flow. a) the sputter voltage, b) the mass deposition rate, and c) the sputter rate as determined from ex-situ XRR (all samples produced using increasing oxygen flow). From ref. [135].

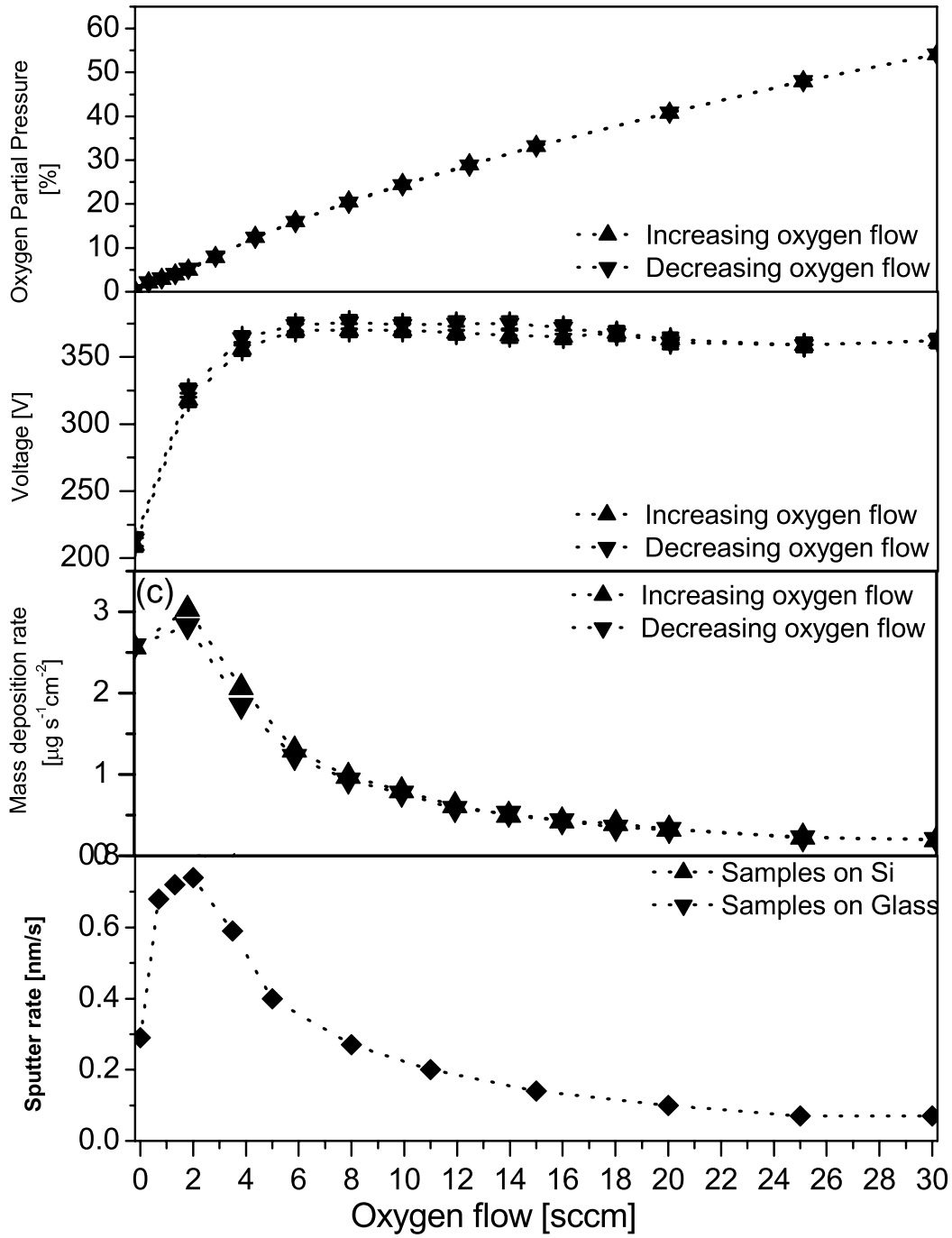


FIGURE 5.10: The properties of the deposition of tantalum oxide as a function of the oxygen flow. a) the oxygen partial pressure, b) the sputter voltage, c) the mass deposition rate, and d) the sputter rate as determined from ex-situ XRR (all samples produced using increasing oxygen flow). From ref. [93].

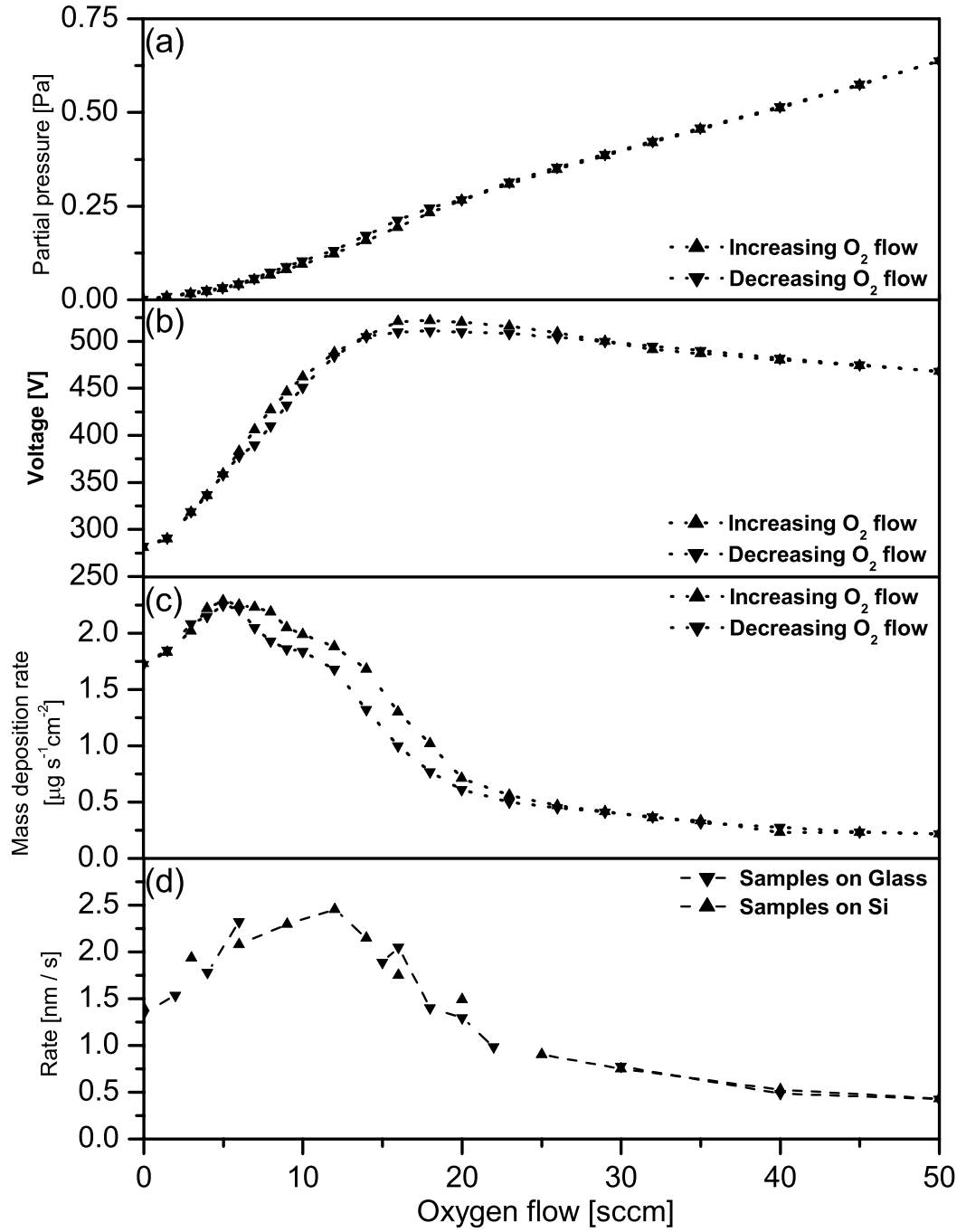


FIGURE 5.11: The properties of the deposition of molybdenum oxide as a function of the oxygen flow. a) the oxygen partial pressure, b) the sputter voltage, c) the mass deposition rate, and d) the sputter rate as determined from ex-situ XRR (all samples produced using increasing oxygen flow). From ref [82].

with a given flux. At the target three types of particles mainly arise: Secondary emitted electrons, sputtered particles and back-reflected Ar neutrals. The fraction of reflected Ar^+ is very small i.e. of the order of 10^{-4} [145]. Hence the influence of such Ar^+ ions can mostly be neglected because of their low number.

Considering the mass of the particles, it is evident that the Ar neutrals and the sputtered atoms have the biggest impact. Hence the total energy arriving at the substrate can be expressed as [145]:

$$E_{total} = \frac{R_j \varepsilon_r + Y_s \varepsilon_s}{\alpha} \quad (5.3)$$

where ε_r and ε_s are the average energies of the reflected Ar particles and sputtered atoms respectively. α is the sputter efficiency, Y_s is the sputter yield, while R_j is the particle reflection coefficient of the Ar neutrals, which has been shown to follow:

$$R_j \sim \left(\frac{M_T}{M_{Ar}} \right)^2 \quad (5.4)$$

where M_T is the atomic mass of the target and M_{Ar} is the Ar atomic mass.

The average energy of the sputtered particles is rather independent on the mass ratio $M=M_T/M_{Ar}$, while the energy reflection coefficient for the argon neutrals can be expressed by:

$$\varepsilon_r \sim \left(\frac{M_T}{M_{Ar}} \right)^{1/3} \quad (5.5)$$

The sputter efficiency scales with $M^{-1/2}$, while the sputter yield has an M^{-1} dependence. Hence the total energy incident on the substrate can be expressed as:

$$E_{total} \sim K_R M^2 + K_S M^{-1.5} \quad (5.6)$$

where K_R and K_S are constants for reflected and sputtered particles, respectively. It can be seen that for target masses larger than the Ar mass i.e. $M > 1$, the contribution from the reflected particles is dominant, while for light target materials the sputtered atoms contribute the most.

Based on these atom-energies and fluxes, the two borderline cases of tensile and compressive stress can be explained as given below, while a model linking the two cases together is also available (see section 5.4.3).

5.4.2 Tensile stress

When the bombardment of the growing film occurs by ions of low energies i.e. less than a few eV per atom, the deposited film can contain a considerable amount of voids [151]. Other experiments have associated tensile stress with a growth of columns perpendicular to the substrate [59]. Depending on the structure of the film, these voids or columns will result in a state of tensile stress in the film. A model relating the structure of the sputtered film to the temperature and the Ar pressure (which directly influences the particle energies) is seen in figure 5.12 [125], [78]. Under

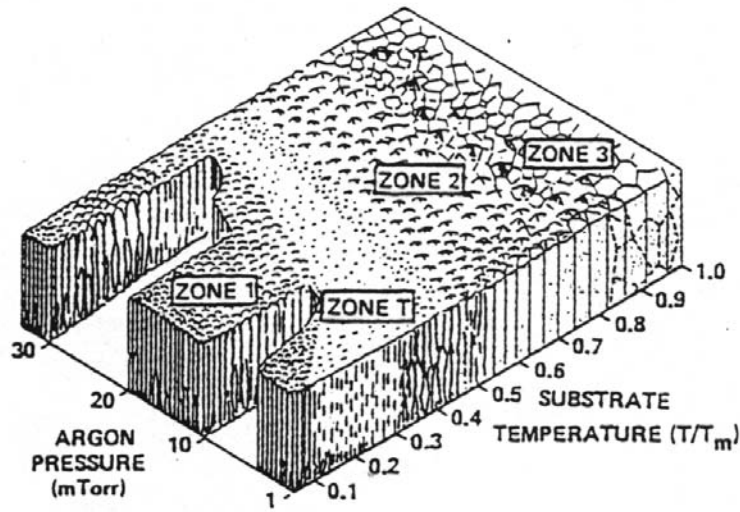


FIGURE 5.12: When the film is deposited at a low temperature and a relatively high pressure, it will contain significant amounts of voids and columnar growth can arise. At higher temperatures columnar growth is no longer possible, and the film becomes increasingly crystalline. From ref. [125].

conditions of low temperature and relatively high pressures, i.e. low impinging particle energies, film structures having voids and columnar features arise. These structures lead to tensile stresses.

In polycrystalline films tensile stresses can be explained by the grain boundary relaxation model. The tensile stress arises as atomic forces acting across the gap between neighboring grains force the grain walls to deform. This deformation on the other hand is balanced by opposing forces inside the grain. A combination of the forces leads to a tensile stress in the film, whose magnitude can be estimated by:

$$\sigma = \frac{E_f}{1 - \nu_f} \frac{\Delta}{\Theta} \quad (5.7)$$

where Θ is the final grain size, and Δ is the so-called relaxation distance given by:

$$\Delta = \frac{ar_0 - r_0^2}{a - r_0} \quad (5.8)$$

where a is the bulk lattice constant, and r_0 is the ionic radius.

In amorphous films, tensile stress can arise by a similar mechanism, if special sputter conditions create voids and cavities in the structure.

5.4.3 Transition from tensile to compressive stress

As seen from figure 5.12, the columnar structure is lost, when the energy of the incident particles increases above a certain limit i.e. at low pressures. This limit is moved to lower energies at higher temperatures, but during the deposition of the films studied here, the temperature did not increase substantially.

When the impinging ions have energies of tens to hundreds of eV, their collision with the growing film will result in a displacement of atoms into the film i.e. into spaces smaller than the normal volume per atom. As a result the film will be placed in a state of compressive stress. This transition from tensile to compressive stress has been modelled by the following expression for the deposition stress [59]:

$$\sigma = Y_f \frac{1}{d_0} (\Delta_{shad} - d_{depl,0}) - \frac{1}{3} Y_f f_{an} n_V \frac{j}{R} \quad (5.9)$$

where the first term represents the tensile stress, and the second term is the compressive stress. The tensile stress term is found by comparing the dimensions of the columnar growth features with the spaces between the columns. d_0 is the total width of a square column and a neighboring void, while Δ_{shad} and $d_{depl,0}$ are widths of the space between columns related to shadowing and surface energy minimization. When no columnar growth is observed, Δ_{shad} and $d_{depl,0}$ are zero, and no tensile stress is found.

The second term of equation 5.9 corresponds to compressive stress. f_{an} is a constant related to anisotropy effects, n_V is a dimensionless parameter that increases with increasing ion energy, and also depends on point defect properties and the defect density of the material. j is the flux of ions incident on the growing film, R is the growth rate, while Y_f is the biaxial modulus as introduced in section 2.3.

Examination of the term associated with compressive stresses shows, that the compressive stress contribution increases for increasing ion energies (through n_V), for an increasing ion flux j , and for a decreasing sputter rate R .

Contrary to intuitive considerations, the natural incorporation of an amount of the sputter gas atoms has on the other hand been shown not to have any significant influence on the compressive stress. In fact it has been shown that compressive stress and the amount of gas in the film are independent of each other as found by Thornton *et al.* [124]. The entrapment of argon in the growing film is hence a concurrent process, but it is not origin of the compressive stresses.

5.4.4 Compressive stress

A successful description of the origin of compressive mechanical stress in sputtered films has been put forward by C.A. Davis [19]. This model explains the magnitude and origin of the compressive stress by a balance between stress induced by so-called "knock-on implantation" of film atoms, and stress relieved by "thermal spike migration".

Build up of stress - knock-on implantation

Compressive stress is assumed to originate from atoms that are implanted below the surface of the film by an incident particle, in a process labelled "knock-on implantation". The displacement of an atom into a position below the surface of the film only occurs, when the impinging ion has an energy above a certain threshold E_{koi} , which depends on the nature of the film. Using the theory of

knock-on cascades, the rate of atoms per area $\partial n_i / \partial t$ that are moved to sites below the film surface is given by [145]:

$$\frac{\partial n_i}{\partial t} \sim jE^{1/2} \quad (5.10)$$

where j and E is the flux and energy respectively of the incident particles.

As the volume occupied by the displaced atoms is smaller than the normal atomic volume, the film is placed in a strained state by the knock-on implantation. Associated with this strain is a compressive stress as given by Hooke's law (eq. 2.3).

Relaxation of stress - Thermal spikes

When the film is placed in a strained state by the implantation of atoms, it is energetically favorable to move the implanted atoms to its surface. To do so, an implanted atom must acquire a certain threshold energy E_{is} to overcome the energy from the surrounding atoms, that confine it in its position, and be close to the surface. As some atoms are trapped deep in the film, not all atoms that acquire sufficient energy will move to the surface of the film, an aspect that should be considered when estimating the magnitude of E_{is} . The required energy can be received from the bombarding energetic particles. When these hit the surface of the film, their energy is transferred to the atoms surrounding the site of impact. This produces a local heating, which is referred to as a thermal spike (or a displacement spike in the case of higher particle energies) [84]. For energies less than 1 keV only one thermal spike occurs per particle impact. This means that the energy Q , which is distributed in the process can be approximated by the kinetic energy of the impinging particle. This energy is distributed to the atoms in the volume of the thermal spike and allows them to diffuse.

The number of atoms per area that receive sufficient energy to overcome E_{is} during a single thermal spike, when the energy is distributed at the impact site can be expressed by [117]:

$$n_{is} = 0.016\rho \left(\frac{Q}{E_{is}} \right)^{5/3} \quad (5.11)$$

where ρ is a material constant of the order of 1, which expresses the ratio of the diffusion coefficients of atoms in the film to the diffusion coefficient of the heat [117].

The rate at which atoms are moved to the surface can hence be seen as a relaxation rate. It is proportional to n_{is} , the fraction of the density of displaced atoms n to the density of the material N , and to the flux of impinging particles j :

$$\frac{\partial n_R}{\partial t} = n_{is} j \frac{n}{N} = 0.016\rho j \frac{n}{N} \left(\frac{E}{E_{is}} \right)^{5/3} \quad (5.12)$$

where the energy Q distributed in the thermal spike was approximated by the kinetic energy E of the ions.

Equilibrium theory

The assumption on which Davis' theory is based is that the density of implanted atoms, n , is constant with time. As the film is growing, the net rate per area at which displaced atoms are build into the film is then given by:

$$\frac{dn_{i,net}}{dt} = R \frac{n}{N} \quad (5.13)$$

where R is the total rate at which addition of atoms to the film takes place.

Additionally the net implantation rate can be regarded as the balance of the rates of implantation n_i , and relaxation, n_R :

$$\frac{dn_{i,net}}{dt} = \frac{dn_i}{dt} - \frac{dn_R}{dt} \quad (5.14)$$

The fraction of implanted atoms can now be found by combining equations (5.10), (5.12), (5.13) and (5.14):

$$\frac{n}{N} = \frac{E^{1/2}}{\frac{R}{j} + 0.016\rho \left(\frac{E}{E_{is}}\right)^{5/3}} \quad (5.15)$$

By assuming that the strain of the film is proportional to the fraction of displaced atoms n/N , the stress can be computed [146]. By use of Hooke's law (eq. 2.3) the following expression for the compressive stress in the film can be found:

$$\sigma(E) = Y_f \frac{E^{1/2}}{\frac{R}{j} + 0.016\rho \left(\frac{E}{E_{is}}\right)^{5/3}} \quad (5.16)$$

$$= Y_f \frac{E^{1/2}}{\frac{R}{j} + kE^{5/3}} \quad (5.17)$$

where $k = 0.016\rho E_{is}^{5/3}$

In the general case, the incident particles have energies spanning a range of energies. Hence an integration over all energies above E_{is} must be carried out:

$$\sigma = \int_{E_{is}}^E \sigma(E) f(E) dE \quad (5.18)$$

where $f(E)dE$ is the number of incident particles with energies in the interval $E+dE$.

The contents of equation 5.17 can be intuitively understood, if one plots the stress as a function of the kinetic energy of the incident particles for different values of R/j (figure 5.13). It can be seen that the compressive stress in all cases initially increases as the ion energy increases. For even higher values of E , the compressive stress slowly decreases (Region II). However, the magnitude of the maximum compressive stress is highly dependent on R/j (Region I). The largest compressive stress is found for low values of R/j , while the lower values of compressive stress at these energies are found for high values of R/j .

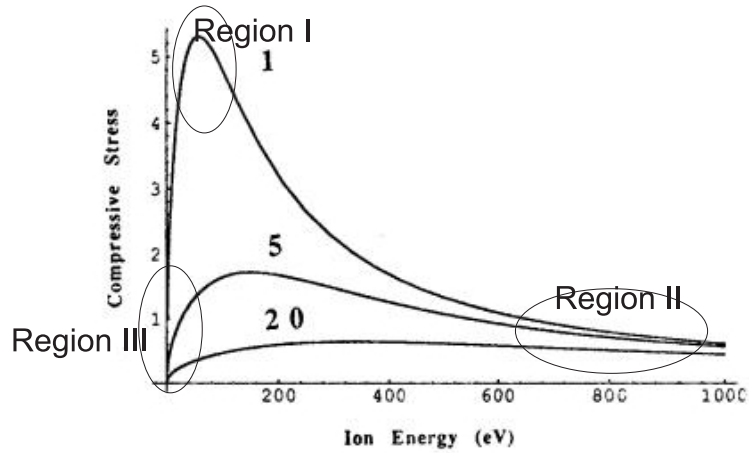


FIGURE 5.13: The build-up of compressive stress as a function of the kinetic energy of the impinging particles as predicted by the Davis model. The three curves correspond to different values of R/j . (See text for explanation of Region I, II and III). After ref. [19].

Means of reducing the compressive stress

From equation 5.17 two special cases can be identified:

- 1) When R/j is large compared to $kE^{5/3}$, the compressive stress (5.17) can be expressed as:

$$\sigma(E) = Y_f \cdot \frac{jE^{1/2}}{R} \quad (5.19)$$

- 2) When R/j is small compared to $kE^{5/3}$ i.e in the case of a large flux of highly energetic particles, the expression (5.17) reduces to:

$$\sigma(E) = Y_f \cdot \frac{1}{kE^{7/6}} \quad (5.20)$$

From equations (5.19) and (5.20) two ways of reducing the mechanical stress upon sputtering become obvious:

- For a reduced flux j , the compressive stress is approximated by (5.19). Hence the stress is determined by the magnitude of the kinetic energy of the incident particles i.e low compressive stress is found for small ion energies E (Region III in fig. 5.13).
- By use of a large flux j , equation (5.20) shows that the mechanical stress can be reduced when the energy of the ions E is increased (Region II in figure 5.13).

Large stresses can on the other hand be produced in a situation where both R/j is small and $kE^{5/3}$ is not too large i.e. in a situation where a large flux of particles of rather low energy is incident on

the film (region I in figure 5.13). In this case atoms are displaced into positions below the surface of the film, and compressive stress arises by knock-on implantation. However, for this to occur $kE^{5/3}$ must be low enough for the stress not to be relieved by thermal spikes.

In the case of crystalline materials the movement of atoms from inside the film to the surface is not as easy as in the case of amorphous films. Hence E_{is} is much larger for crystalline films than for amorphous ones. This means that the bombardment by energetic particles leads to a build-up of compressive stress that increases with increasing ion energy. The mechanism by which this takes place is called atomic peening and describes the situation where atoms during the bombardment are moved from the surface into volumes of the film that are smaller than the normal volume per atom. As the energy required for moving these atoms to the surface is large, little stress relaxation takes place for crystalline materials. In the case of amorphous films, stress relaxation can however take place as E_{is} is much lower than for crystalline materials.

5.5 Results

The results of the measurements of mechanical stresses as a function of the oxygen flow during deposition are summarized in figure 5.14. In the figures, the metallic mode, the transition region and the oxidic mode can be identified by the vertical dividing lines.

When looking at the data, several features become evident. First of all, it is obvious that for all samples produced in the oxidic mode i.e. for the fully stoichiometric oxides, the deposition stress is compressive. Second, the metallic sputtering is associated with large compressive stresses except for the case of vanadium. Third, it is evident that sputtering in the changing oxygen flow conditions within the transition region in most cases leads to abrupt changes to the deposition stress.

In the following sections possible explanations of the features of these deposition stress measurements are presented one by one.

5.5.1 General trends

As briefly mentioned in the preceding section, a few general trends can be identified. It is the objective of this section to give explanations for these features.

Metallic samples

The 8 metals deposited are crystalline. However the deposition stresses found differ quite dramatically. In table 5.2, the deposition stresses found for the metals are listed.

The general features include an increase of compressive stress when going vertically down within one column of elements. In the case of vanadium even a tensile stress is found.

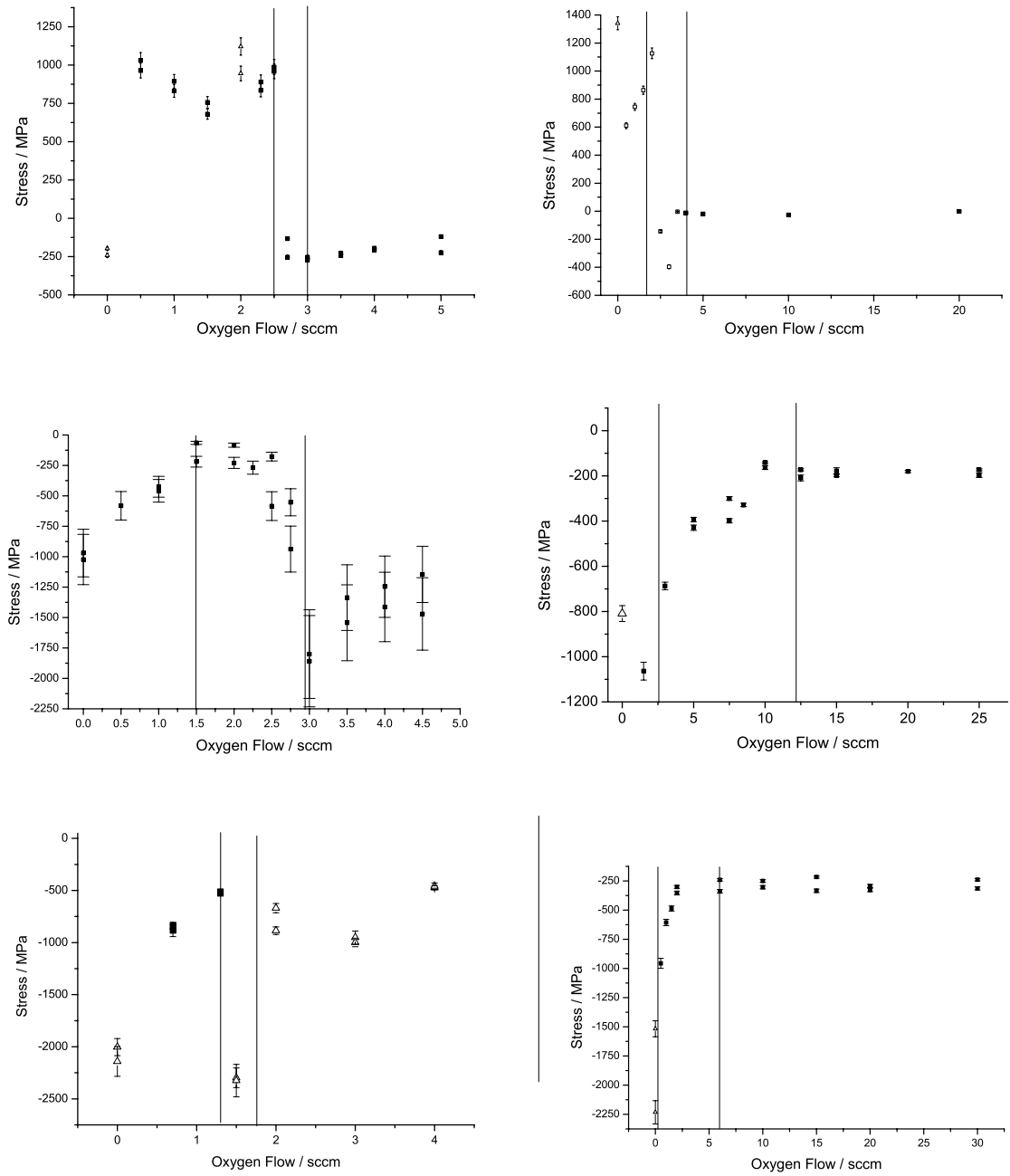


FIGURE 5.14: Deposition stresses in transition metal oxides as a function of oxygen flow. Top: TiO_x, VO_x. Middle: ZrO_x, NbO_x. Bottom: HfO_x, TaO_x.

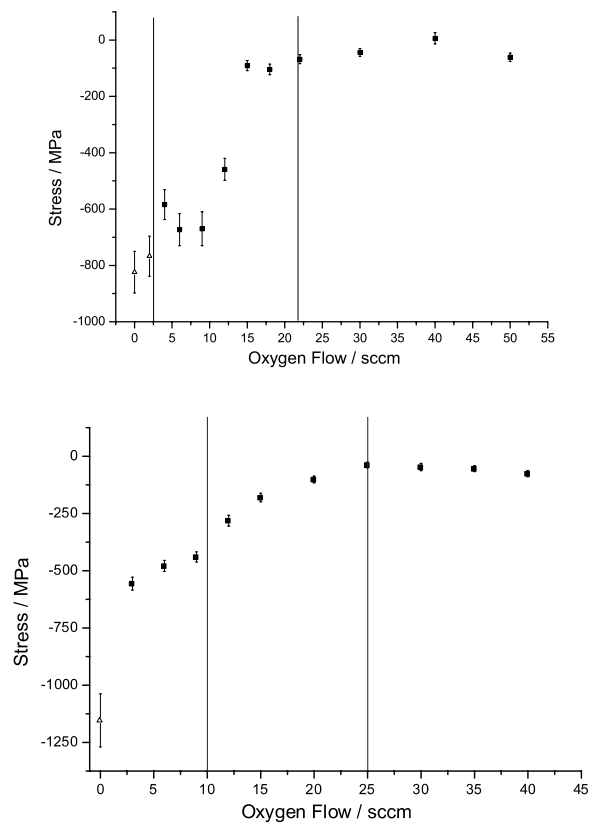


FIGURE 5.15: Deposition stresses in transition metal oxides as a function of oxygen flow. Middle: MoO_x. Bottom: WO_x.

Ti -250 MPa	V 1200 MPa	Cr —
Zr -1000 MPa	Nb -800 MPa	Mo -850 MPa
Hf -2000 MPa	Ta -2200 MPa	W -1200 MPa

TABLE 5.2: Deposition stresses for the transition metals.

TiO ₂ -200 MPa	V ₂ O ₅ -10 MPa	Cr -
ZrO ₂ -1500 MPa	Nb ₂ O ₅ -200 MPa	MoO ₃ -75 MPa
HfO ₂ -1000 MPa	Ta ₂ O ₅ -300 MPa	WO ₃ -100 MPa

TABLE 5.3: Deposition stresses for the stoichiometric oxides.

An explanation for this general trend can be found in the energy balance of the sputter process. Accelerated argon ions hit the target surface and transfer parts of their energy to metal particles that are detached from the target and directed onto the substrate (or the walls of the chamber). The energy transferred to a metal atom depends directly on its atomic mass. More important though, the energy of the reflected Ar neutrals as well as their flux is described by the equations (5.4) and (5.5). This means that the argon ions are recoiled away from the target and hit the growing film. As they possess a higher energy when reflected by heavier target materials, their impact is the biggest in the case of heavy target materials. When these energetic argon neutrals bombard the growing film, they move film atoms from the surface into non-lattice sites (like an interstitial site) in the film. The concentration of atoms in non-lattice point positions leads to the build-up of compressive stress by atomic peening as described in section 5.4.4. As the energy of the Ar neutrals is the highest for the heavy target masses, the highest stresses are also found for these elements as seen from table 5.2.

The process of atomic peening is associated with the incorporation of argon atoms themselves, but as mentioned in section 5.4.3, this incorporation does not lead to compressive stress build-up.

Fully stoichiometric oxides

The oxides produced in oxidic mode sputtering i.e. TiO₂, ZrO₂, HfO₂, V₂O₅, Nb₂O₅, Ta₂O₅, MoO₃ and WO₃ all possess compressive stresses upon deposition. In table 5.3, these deposition stresses are summarized.

A general trend is difficult to identify in these results. However, for ZrO₂ and HfO₂ the compressive stresses are far larger than the those found for the remaining oxides.

The Davis model states that high compressive stresses arise in situations where a low flux of energetic ions is incident on the film during deposition. It also states that low compressive stresses

are expected in situations where a large flux of particles of relatively low energy bombard the film.

Hence, a search for an explanation for the high stresses found in ZrO_2 and HfO_2 and the low stresses found in the other oxides begins with a comparison of their properties. In the context of varying the number of incident particles, the difference between the ionization potential of the metals and the oxygen electron affinity, $M_{IP}-EA_O$, can be regarded as an energy barrier for ionization of metal and oxygen. In table 5.4, values for $M_{IP}-EA_O$ are listed. It can be seen that $M_{IP}-EA_O$ is lowest for ZrO_2 and HfO_2 . Furthermore, when comparing the voltage for oxide sputtering V_O in the oxidic mode, it is evident that the voltages for these two oxides are also lower than for the other oxides.

This means that the energy of the produced oxygen ions is different among the oxides, as the voltage V_O will accelerate negative oxygen ions onto the substrate.

Based on these informations, the following statements based on the Davis model can be made:

- The large stresses found in the case of ZrO_2 and HfO_2 can be explained by the fact that the sputter voltage is the lowest in these two cases. This means that the ions, which also are created more easily for these two materials, possess the lowest energy when they arrive at the film surface. Hence a situation is found, where both of the terms R/j and $kE^{5/3}$ are relatively small. In this case a large flux of particles of relatively low energy is incident on the film. This corresponds to region I in the Davis model (figure 5.13) where large compressive stresses are produced.
- In the case of TiO_2 , V_2O_5 , Nb_2O_5 , Ta_2O_5 , MoO_3 and WO_3 high voltages are observed during sputtering. For these materials $M_{IP}-EA_O$ is larger than for ZrO_2 and HfO_2 . This indicates that for the former oxides, ions are not as easily created as in the case of ZrO_2 and HfO_2 . Hence a situation is found, where fewer ions are accelerated by a larger potential i.e R/j is large and the kinetic energy of the ions is also large. By comparison with eq. 5.17, it is evident, that this situation also corresponds to region III in the Davis model (figure 5.13), where low compressive stresses are found.

5.5.2 Behavior of NbO_x , TaO_x , MoO_x and WO_x

Looking at the dependence of the mechanical stress as a function of oxygen flow for the oxide sputtering of NbO_x , TaO_x , MoO_x and WO_x reveals a common characteristic behavior: With increasing O_2 flow, the compressive stress is gradually reduced across the transition region until an almost constant value is achieved in the oxidic mode. The arguments used in the preceding section can be applied again in these cases.

Characteristic for these four materials is a large increase of the sputter voltage $\Delta V/V_M$ when going from metallic (V_M) to oxidic mode (Table 5.4). This means, that the ions present during sputtering are accelerated by a growing potential as the oxygen flow is increased. Hence the conditions of sputtering are dramatically changed. The metallic mode can be identified as a situation,

TiO ₂ 41.79 eV 400 V 0.33	V ₂ O ₅ 63.75 eV 470 V 0.65	Cr 89.09 eV - -
ZrO ₂ 32.86 eV 290 V 0.12	Nb ₂ O ₅ 49.06 eV 550 V 0.77	MoO ₃ 66.52 eV 485 V 0.90
HfO ₂ 31.82 eV 285 V 0.02	Ta ₂ O ₅ - 350 V 0.76	WO ₃ - 485 V 0.91

TABLE 5.4: M_{IP} - EA_O for the stoichiometric oxides, the voltage for oxidic mode sputtering, V_0 , and the voltage increase $\Delta V/V_M$ upon the transition from metallic to oxidic mode.

where the argon neutrals create compressive stresses through the argon peening mechanism described in section 5.5.1. However as the potential increases, so does the kinetic energy of the ions present in the process. Additionally, the films are no longer crystalline, because only little oxygen is offered, and no stoichiometries are available in which a crystalline film can be produced. Hence a gradual transition is made to a situation where ions of larger energies reach the film where they initiate thermal spikes. Stress relaxation can then take place as E_{is} is lower for the non-crystalline films. Hence low compressive stresses is found corresponding to region III in the Davis model (figure 5.13). As the sputter voltage stabilizes when the oxidic mode is reached, the compressive stress also stabilizes at a constant value.

5.5.3 Behavior of ZrO_x, HfO_x

The dependence of the mechanical stress on the oxygen flow during deposition for ZrO_x and HfO_x, is very different to the dependence seen in the preceding section. In figure 5.14 different effects are identified:

- A reduction of compressive stress is observed in the metallic mode sputtering, even though no change of sputter voltage or sputter rate is observed (figure 5.4 and 5.7).
- In the transition region, a large increase of compressive stress is observed.

The explanation for the decrease of the compressive stress in the region of metallic mode sputtering comes from the threshold energy E_{is} needed to move an atom from the interior of the film to its surface. In the case of crystalline film, this process takes place by diffusion, and hence E_{is} is rather large. This is also the reason why the atomic peening mechanism works, as atoms placed in non-lattice point sites cannot easily move to the surface. However in amorphous films, the threshold energy E_{is} is lower, and it is easier for the film atoms to move from inside the film to the surface. As the films found in this region are all amorphous, these films will relieve stress

upon ion bombardment, while the pure metals will not. The slow reduction of compressive stress is observed with increasing oxygen flow as a result of the increasing loss of long range order in the film structure. This leads to a decrease of E_{is} and hence to a slow reduction of the compressive stress.

In the transition region, a large rather sudden increase of compressive stress is observed. Its explanation lies in the oxidation of the target occurring in this mode. This oxidation increases the number of oxygen ions present. Hence the flux j of ions incident on the growing film increases, and R/j decreases. This means that the compressive stress increases as seen in region I in the Davis model (figure 5.13).

5.5.4 Behavior of TiO_x , VO_x

The mechanical stresses found in the sputtering of titanium oxide and vanadium oxide differ from the stresses found for all other investigated materials. When produced in the metallic mode and in the transition region these materials can possess tensile stresses.

Different models for the build up of tensile stresses have been suggested as mentioned in section 5.4.2. However all are based on the presence of voids in the structure of the film. Hence it may be suggested that the structures found in the metallic and transition region for TiO_x and VO_x contain considerable amounts of voids, giving rise to the observed tensile stresses.

The change from tensile to compressive stresses within the transition region, can however be attributed to the increase in sputter voltage (figure 5.6) associated with this region. That this change of voltage leads to changes to the stress can be explained: In their modelling of the tensile to compressive stress transition, Knuyt et al. suggested that the total stress in the film could be described by equation 5.9.

This means that in the case of TiO_x and VO_x , the increase of the sputter voltage that is seen in the transition region will be associated with an increase of n_V , which will ultimately lead to an increase of the compressive stress term. Additionally, the oxidation of the target will lead to an increase of oxygen ions, i.e to an increase of the ion flux j . This will according to the model also lead to an increase of the compressive stress term. To complete the picture, the deposition rate R also decreases in the transition region (figures 5.6 and 5.8). From (5.9) it can be seen that this will also serve to increase the compressive stress term. That a transition from tensile to compressive stress is observed in the transition region can hence be explained.

5.5.5 Structure formation

During the study of the transition metal oxides and their deposition, it was discovered that a number of films were crystalline. In figures (5.14) and (5.15), these crystalline film are marked with an open up-triangle label, while the amorphous film carry a filled square label. As can be seen, the metallic films are crystalline. Apart from this, only a few films have been found to be crystalline. In titanium oxide a crystalline film of stoichiometry $(TiO_{1.2})_{0.787}$ is found at an O_2 flow of 2 sccm.

For HfO_x crystalline films is found at oxygen flows above 1.5 sccm. Similarly crystalline samples are found for ZrO_x at flows larger than 2.6 sccm.

The formation of crystalline stoichiometric oxides in oxidic mode sputtering can also be correlated with the ionization barrier $M_{IP}\text{-EA}_O$. In a model proposed by Ngaruiya *et al.* [92], it was suggested that crystalline stoichiometric transition metal oxide films were produced for low values of $M_{IP}\text{-EA}_O$. Comparing with table 5.4, the lowest values are found for ZrO_2 , HfO_2 and TiO_2 . The explanation given is that the low barriers for ionization result in a situation where a high flux of oxygen ions - presumably O^- - is sputtered from the target and is incident on the growing film. Additionally, the potential that accelerates these ions is lower in the case of ZrO_2 , HfO_2 (and partly TiO_2). That the potential does not increase as much for these oxides as for the other ones means, that for these oxides the emission of secondary electrons is not reduced as much as for the remaining transition metal oxides. As a result, the fewer oxygen ions that are incident on the growing film for these oxides only possess moderate energies compared the other oxides.

This combination of many ions having an energy lower than a certain threshold energy for required for the formation of amorphous films leads to crystalline films in the case of ZrO_2 , HfO_2 and for some cases of TiO_2 sputtering.

In contrast, in the case of the other transition metal oxides, the high energy barrier for ionization means that less oxygen ions are produced. Additionally, the coefficient of secondary electron emission is lower for these oxides, resulting in a large increase of the accelerating potential when going from the metallic mode to the oxidic mode. This in turn means that the fewer oxygen ions are accelerated by a higher potential.. Hence their energy upon arrival at the growing film is too high for the formation of a crystalline film. Instead an amorphous film is the result.

5.6 Summary

As described in section 5.1, transition metal oxide films have many interesting applications. However, it is crucial to control the mechanical stresses in the films, as high stresses could lead to failure, cracking or delamination of the films. In this study, the stresses of the group of transition metal oxides consisting of TiO_2 , ZrO_2 , HfO_2 , V_2O_5 , Nb_2O_5 , Ta_2O_5 , CrO_3 , MoO_3 and WO_3 were studied with the omission of CrO_3 which is hazardous. The reactive sputtering applied offered a way to study the change of stress in the single oxides when changing from metallic mode to oxidic mode sputtering. Additionally, the closely related materials allow a comparative study of deposition stresses of the oxides.

It was found that the stress correlates with the structure of the films. For crystalline films high stresses were found as seen for ZrO_2 and HfO_2 . For amorphous films lower stresses were found. The structural formation was related to the number and energy of the ions incident on the film, while the magnitudes of the stresses were related to E_{is} i.e the energy required for an atom to move from inside the film to the surface. This energy is large for crystalline films and lower for amorphous ones. The gradual transition from crystalline to amorphous and the related gradual reduction of compressive stress was monitored in the metallic mode of ZrO_x and HfO_x sputtering.

The transition from tensile to compressive stress as seen for TiO_x and VO_x was also predicted by application of the model of Knuyt *et al.* in combination with the sputter parameters for these materials (section 5.4.3).

Finally, the evolution of the deposition stress beginning at a metal and ending at its oxide, induced by increasing the oxygen flow during deposition was explained in detail. The number of oxygen ions formed in the transition region and their energies, which are largely determined by the sputter voltage, were found to allow an explanation for the gradual changes observed for the deposition stress.

Chapter 6

Switchable Coatings

Switchable coatings are certain to fascinate almost anyone. The sight of a metallic surface turning transparent and vice versa, or a transparent window coloring deep blue has prompted excited reactions by audiences at more than one public demonstration I've attended. Scientifically such materials have received considerable attention especially in recent years since the discovery of Lanthanide based switchable windows [50]. Other switchable coatings include metal oxides and metals like magnesium and palladium. The characterization and understanding of the processes involved in the switching is quite well established, and several applications, such as windows with switchable optical properties, rear view mirrors and displays, can be imagined. Apart from the interesting visual effect which has prompted interest from architects, the switchable windows offer a way to improve the energy balance of houses and buildings by allowing the control of the transmission of the solar radiation. Rear-view mirrors that automatically reduce the intensity of the reflected light as well as improved contrast ratios in displays are also possible applications. Yet there are still several challenges to be solved for applications based on switchable coatings to be commercially successful. In this work the effect of mechanical stresses on the lifetime and cyclability of switchable coatings were studied in detail in measurements employing the gas chamber described in section 3.3.2. Additionally, switchable coatings based on tungsten oxide, which are already employed in industrially available switchable windows [52] were subject to extensive studies. In the following sections (6.1)-(6.8) the principle of switchable coating operation, the theory of the switching in several known materials as well as a characterization of the materials investigated in this work, is presented. These materials are tungsten oxide, gadolinium, magnesium, platinum and palladium. Then in sections (6.9) - (6.12) the experimental results are found.

6.1 Suitable materials for switchable coatings

The group of materials that allow a reversible transition from an optically transparent state to an absorbing or reflecting state as a function of changes to an external parameter, such as an electric field, a change of the surrounding atmosphere, irradiation variations or a temperature change, is quite large. It carries the name "Chromogenics" [8] and includes oxides of transition metals, rare earth metals and organic materials.

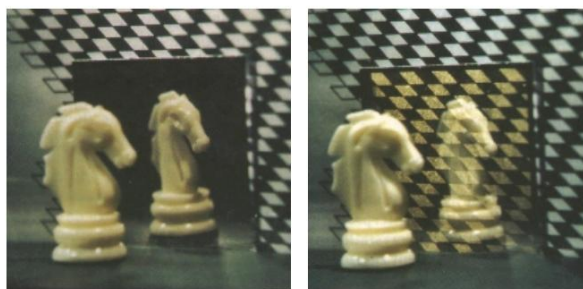


FIGURE 6.1: The switching of an yttrium based switchable window. Left) in the opaque state the chess board cannot be seen through the window. Right) in the transparent state, the chess board can be seen. From ref. [46].

In the case of oxides of transition metals, several compounds have been studied and are reviewed in the work of Granqvist [45]. The most promising of these oxides is tungsten oxide, whose switchable characteristics were discovered in 1973 [20]. It allows the reversible transition between a state which is absorbing in a wide range in the red and near-infrared (NIR) regions and hence has blue color, and a state which is transparent in the entire spectral range between the infrared (IR) and the beginning of the ultraviolet (UV) regions.

The switchable optical properties of rare earth metals were discovered in 1996 for yttrium and lanthanum [50]. Since then, it has turned out that all rare earth metals show a transition between the metallic state and a transparent semiconducting state when exposed to hydrogen as seen for yttrium in figure 6.1.

Organic polymer films have also been discovered to allow optical switching. Details on this material class can be found for instance in the work of Bange [8].

6.2 Principle of operation of switchable coatings

The variety of approaches that can be utilized in order to exploit the features of chromogenic materials is impressive. In this section, the technical realization of these switching mechanisms is described. For studies of mechanical stresses, the gasochromic switching (see section 6.2.1) is preferred, as this method involves a very simple configuration of the samples: A substrate coated with the active film and a catalyst film. Hence the change of the curvature, which is detected during the switching process can be assigned to the active film without complications. All chromogenic films considered in this work were switched by the gasochromic approach.

6.2.1 Gasochromic switching

In the gasochromic approach, the coating is exposed to a hydrogen containing gas to induce the optical transition and to an oxygen containing gas to force the reversible reaction back to the ini-

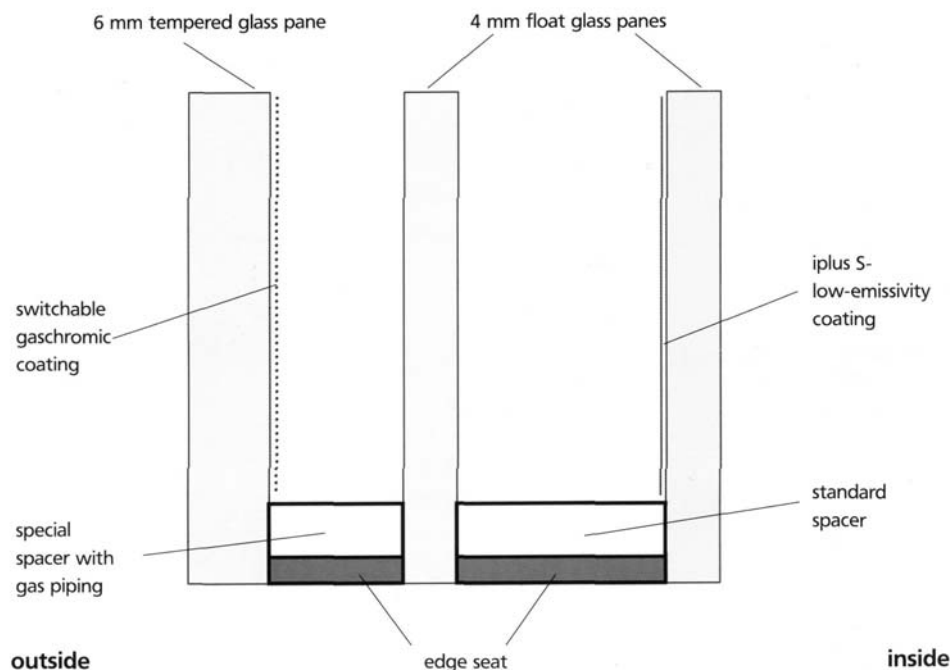


FIGURE 6.2: The principle of gasochromic windows. From ref. [52].

tial state. The kinetics of the switching can be improved by use of catalysts such as palladium or platinum. As described in section 6.6, the catalyst dissociate the H_2 molecules, and the resulting atoms are built into the film. The kinetics and the optical contrast of the switching can be controlled by the partial pressure of the active gases as can be deduced from simple thermodynamic considerations (see section 6.8). In industrially realized "smart windows" [52], a coated and a normal glass window form a cavity in which the film can be exposed to the gas (figure 6.2). In such an application, the hydrogen containing gas is normally a 2% H_2 in Ar mixture for obvious safety reasons.

6.2.2 Electrochromic switching

In the electrochromic approach, the ability of the film to reversibly change its optical properties in response to an applied electric potential or current is exploited. The basic setup includes two transparent electrodes, an electrolyte and an active electrochromic layer (figure 6.3). In solid state devices, which are preferred for applications, the electrolyte is replaced by the combination of an ion storage medium and an ion conducting layer. In the typical reaction, a potential is applied and the optical properties of the active film change. As an example, the coloration reaction in an active tungsten oxide film would look like:



where M represents atoms like H, Li, Na, etc. In this process, which is called the double-intercalation model [32], cations are built into the film and their charge is compensated by electrons from the electrode.

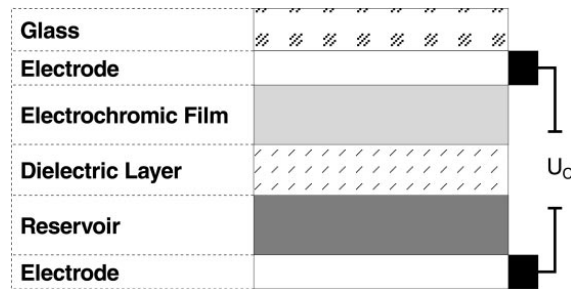


FIGURE 6.3: The principle of electrochromic windows. From ref. [8].

6.2.3 Thermochromic switching

In thermochromic switching the optical properties of the film change as a function of the temperature. Materials showing thermochromic behavior include metal oxides like for instance vanadium oxide. These materials are transformed from a transparent semiconducting state to an opaque metallic state, when heated above a certain temperature, while the initial optical properties are restored upon cooling to room temperature.

6.2.4 Photochromic switching

In photochromic switching the optical properties of the film change as a result of UV irradiation, while they can be restored in darkness. The materials that show photochromic behavior include many organic materials that change their optical properties by processes such as tautomerization and isomerization [8]. In inorganic materials such as metal oxides, the photochromic behavior involves imperfections such as impurities and lattice defects in the films, which can induce the formation of electron-hole pairs and the trapping of charge carriers which lead to the formation of color centers (see section 6.3).

6.3 Tungsten oxide

Tungsten oxide (WO_x) is an indirect semiconductor. It has a band gap of 2.6 to 3.5 eV depending on its degree of crystallinity, and a refractive index in the range of $n=1.8$ to 2.3, depending on its exact composition [45]. While it is transparent in its stoichiometric form WO_3 down to $\text{WO}_{2.55}$ [40], it has a slightly blue color in the region of $2.55 > x > 2.45$ [40],[57]. All compositions can be switched to an intense blue appearance. However, the processes are not reversible for the latter group of compositions. Tungsten oxide with an oxygen content $x < 2.45$ is metallic. For sputtered films the desired composition can easily be controlled through the partial pressure of oxygen during the deposition (see Chapter 5.2).

The structure of crystalline tungsten oxide is similar to a Perovskite structure as seen in fig. 6.4. The central atom (C) is missing. The octahedron of WO_6 , where the distance W-O is of order 1.9

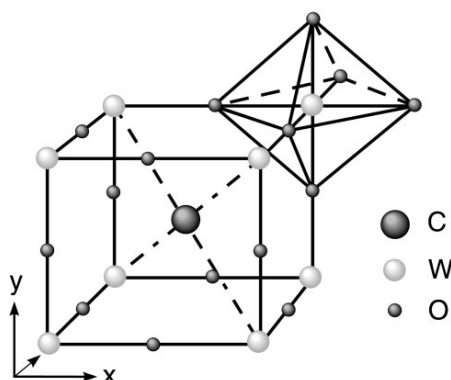


FIGURE 6.4: The principal structure of tungsten oxide. The central cite (C) is not occupied. From ref. [8].

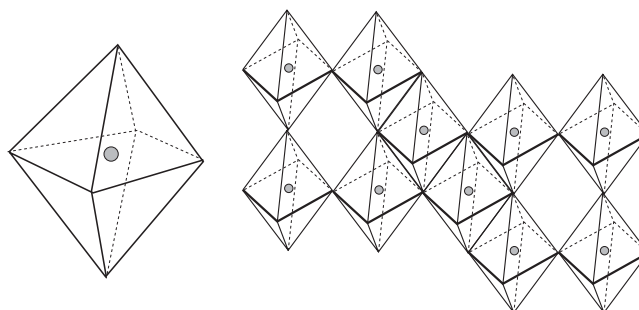


FIGURE 6.5: Left) The octahedron of WO_6 , where the tungsten atom is situated at the center. Right) In tungsten oxide the octahedra are joined at the corners, but in substoichiometric films (WO_{3-z}) the octahedra are connected along their edges to compensate for the missing oxygen atoms. This trend increases with increasing z . From ref. [45].

$\text{\AA}$ [86] is shown in fig. 6.5. These octahedra are joined at the corners, hence forming the structure displayed in fig. 6.5. In substoichiometric film WO_{3-z} the octahedra are increasingly connected along the edges with increasing z .

Thin films produced by sputtering at temperatures comparable to room temperature are not crystalline. X-ray experiments have shown that the films are amorphous and show little degree of order. Electron microscopy measurements have shown that crystallites of sizes up to 10 nm exist in the amorphous matrix [48]. Additionally, the films are very porous and possess a columnar structure [42],[116]. The features of such a structure can be intuitively comprehended when considering the results of simulations of tungsten oxide structures of a vapor deposited film as shown in figure 6.6. At low temperatures, which are characteristic for the sputtering process, the extent of vacant spaces in the film is quite pronounced.

6.3.1 The coloration mechanism of tungsten oxide

The mechanism of the switching of tungsten oxide is not unambiguously agreed upon in the literature. Two models have been suggested, each of which has its own group of advocates. One

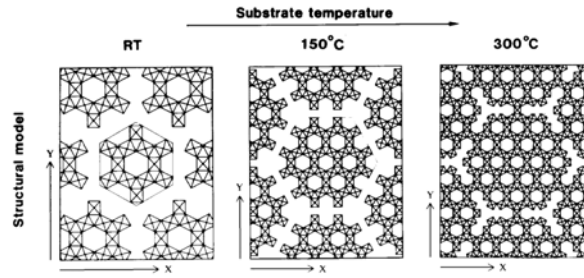


FIGURE 6.6: The porosity of tungsten oxide at different temperatures, as simulated by use of radial distribution functions. The arrows in x and y direction are 2 nm. From ref. [86].

model is known as the double-intercalation model. It suggests that hydrogen ions and electrons are simultaneously built into the film during coloring. The second model, which suggests the desorption of oxygen from the film through the formation of oxygen molecules, has been put forward by Khoobiar [55] and later by Georg [37]. Below, the two models are presented in detail.

The double intercalation model

The double intercalation model is widely accepted in the literature. It describes the coloration of tungsten oxide through the simultaneous absorption of (hydrogen) ions and electrons into the film by the reaction:



From electrochromic experiments one can correlate the flow of charge during coloration with the absorption of ions. Additionally, the model relies on knowledge of coloration mechanisms in crystalline metal-bronzes M_yWO_x [45]. The model is supported by measurements of diffusion constants for Li^+ and H^+ ions in WO_x coatings that yield values of 10^{-13} to 10^{-8} cm^2/s , which are typical values for diffusion constants in amorphous oxides [45],[139],[153].

Even though the double intercalation model is widely accepted, there are several experimental results that cannot be explained by it. Measurements of the hydrogen content in initially transparent films of zero hydrogen content show increases of the hydrogen concentration to $y=1.5 \pm 0.05$ (H_yWO_x) upon coloration. However, during subsequent bleaching no change of hydrogen contents is found: The hydrogen content of the transparent state is also $y=1.5 \pm 0.05$ [40] even though simultaneous measurements of the flow of charge related to the bleaching would predict a decrease Δy of 0.3 [32]. Hence it is suggested that the hydrogen occupies "active" sites in the colored state and "inactive" sites in the transparent state. Other measurements also showed little difference in the hydrogen contents of the colored and transparent states, but also found a significant increase of y in the transparent state from $y=0.75$ to $y=0.82$ upon cycling, also suggesting that hydrogen is absorbed into the film without affecting the absorption [106]. Investigations of the kinetics of the coloration as a function of the partial hydrogen pressure of the surrounding gas as performed by Georg *et al.* [37],[38] yield results that can not be understood using the double intercalation model. This model would imply, that the velocity of formation of color centers would be proportional to the partial pressure of hydrogen through $v(p_{H_2}) \sim p_{H_2}^n$, where $n = -1/2, 0$ or $1/2$. Instead a dependence $v(p_{H_2}) \sim p_{H_2}$ was found.

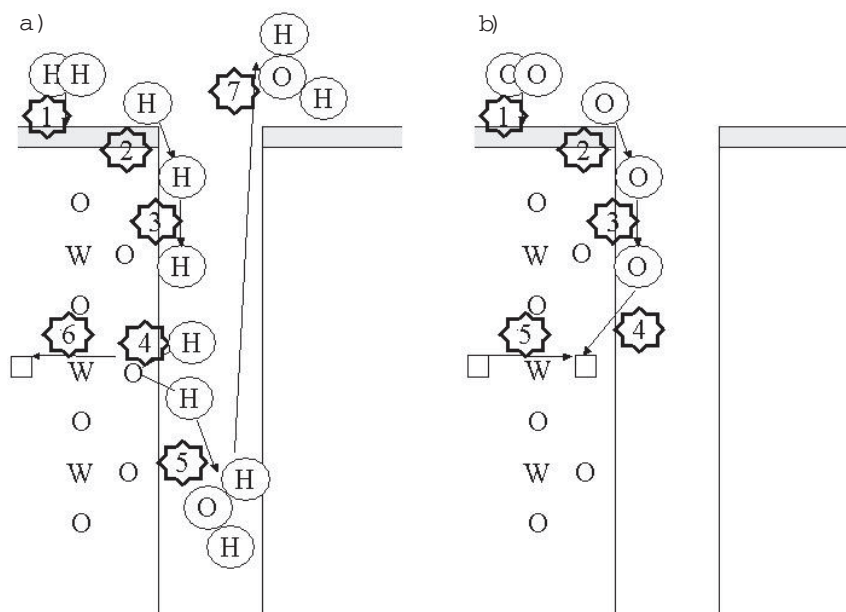


FIGURE 6.7: Schematic mechanism of a) the coloration of tungsten oxide. b) The bleaching of tungsten oxide. After ref. [37].

The desorption of oxygen upon coloration model

To explain that the velocity at which color centers are formed was found to be proportional to the partial pressure of hydrogen, a model suggesting that the coloration process is associated with the desorption of oxygen from the film has been put forward. This leads to the formation of water molecules in its pores. From there the water is slowly removed into the surrounding gas atmosphere [37],[38]. Such a model has also been suggested by Zhang and co-workers [153] to explain the constant hydrogen content in transparent and colored WO_3 , as found by Rutherford backscattering (RBS) experiments [7].

As mentioned in section 6.3, the model is based on the assumption, that the tungsten oxide films have a porous columnar structure. Hence the single steps of the coloration can be described as shown in figure 6.7.a:

1. Dissociation of H_2 at the catalyst.
2. Chemisorption of the hydrogen atoms at the WO_x .
3. The hydrogen atoms enter the pore.
4. Formation of a W-O-H_2 intermediate structure.
5. Formation of a H_2O molecule and an oxygen vacancy, which acts as a color center.
6. Diffusion of the oxygen vacancy into the WO_x .

7. Desorption of the water molecule from the pore.

Similarly, the steps of the bleaching are (figure 6.7.b):

1. Dissociation of O_2 at the catalyst.
2. Chemisorption of the oxygen atoms at the WO_x .
3. The oxygen atoms enter the pores.
4. Occupation of a vacancy at the surface of the pores by an oxygen atom.
5. Diffusion of vacancies to the surface of the pores, i.e. annihilation of the vacancy acting as a color center.

Using this model Georg and co-workers succeeded in describing several results of their studies of the coloration kinetics. The model also allows an explanation of the different coloration velocities found for films that are treated differently before the experiments. Hence the films are classified as either "films of quick diffusion" where the steps 4) to 6) determine the kinetics, or "films of slow diffusion" [39],[38] where step 3) is decisive for the kinetics. In these cases, the formation of color centers has an exponential dependence on time in the former case, while it is proportional to $t^{1/2}$ in the latter. The principle of formation of water in the pores of the WO_x films also allows an explanation of the observation of the deeper and slower coloration of films, that were dried before the coloration experiments; the water in the pores allows a quicker diffusion of the hydrogen atoms in the pores, hence resulting in the quickest switching in cases of wet films. On the other hand, the desorption of oxygen from the film becomes very slow once the pores are saturated with water molecules. At this stage further switching is only possible when water molecules escape from the pores. Hence the contrast achieved in a wet film in which water is already present, is not as high as that achieved in initially dry films.

6.3.2 The absorption in tungsten oxide

The absorption of tungsten oxide ranges across a wide part of the spectral range. Crucial for the possible applications of tungsten oxide is its absorption in the infrared having its maximum between 0.7 and 1.4 eV [45]. As the absorption stretches into the visual spectral range, it produces the characteristic blue color of the absorbing state. The explanation for the absorption is independent of the mechanisms described above: During coloration electrons are built into the film. These electrons occupy states in the band gap or in the conduction band [83] and induce the reduction of the oxidation state of the tungsten atoms to a W^{V+} state [100]. The reason is that the electron induces a lattice displacement in the near neighborhood of a tungsten atom "A" (figure 6.8). This creates a potential well at this atom inside which the electron itself gets trapped in a process known as "self-trapping". As a result, the wavefunction of the electron becomes localized and the electron is called a "small polaron" [113]. These polarons are responsible for the absorption. The absorption of a photon allows the polaron to jump across the potential barrier (figure 6.9) to

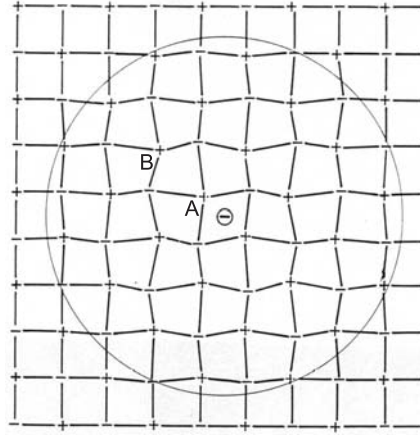


FIGURE 6.8: The lattice displacement arising in the tungsten oxide lattice as a result of localized electrons.

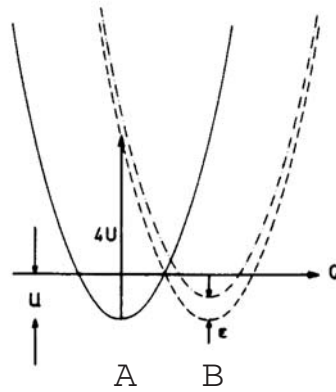
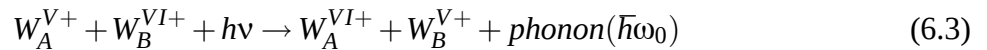


FIGURE 6.9: The absorption of a photon allow the polaron to jump across the potential barriers from atom A to atom B. From ref [113].

a neighboring tungsten atom. This process can be considered a Franck-Condon transition (see ref. [113] for details). Hence the lattice displacement is moved to the neighboring atom "B" under the emission of a phonon of energy $\hbar\omega_0$ [113], [45]. Consequently the absorption process can be described as:



This expression is not a complete description of the absorption in tungsten oxide. The experimental findings are quite confusing, but all indicate a more complex process. Gerard *et al.* found that in substoichiometric WO_{3-z} , the states W^{VI+} and W^{V+} are already present in the transparent state [41]. This doesn't conform with the picture given above. It has also been found that the contrast ratio between the colored and the transparent state depends on the stoichiometry of the WO_{3-z} [153]. Hence it has been suggested that the W^{IV+} state, which has been shown to be present in the colored state, is involved in the absorption process [153],[41]. From Raman spectroscopy measurements the W^{V+} state was not observed at all in the transparent state; only W^{VI+} and W^{IV+} were observed, while all states W^{VI+} , W^{V+} and W^{IV+} were found in the colored state

[66],[67],[68]. These findings supports a model suggesting that the transparent state of WO_{3-z} has a composition [153]

$$WO_{3-z} = (1-z)W^{VI+}O_3 \cdot zW^{IV+}O_2 \quad (6.4)$$

without any W^{V+} states. The W^{VI+} and W^{IV+} states don't produce any polarons. Thus the state is transparent. Only the electrons supplied to the film during coloration induce the conversion to W^{V+} states. By application of the double intercalation model, the absorption process can now be described as

$$(1-z)W^{VI+}O_3 \cdot zW^{IV+}O_2 + \frac{y}{2}H_2 \rightleftharpoons (1-z-y)W^{VI+}O_3 \cdot yHW^{V+}O_3 \cdot zHW^{IV+}O_2 \quad (6.5)$$

The polaron hopping responsible for the absorption is assumed to take place between both the W^{V+} and the W^{VI+} states and the W^{IV+} and the W^{V+} states [67],[68],[69]. Hence, the absorption mechanism in tungsten oxide can be expressed as

$$W_A^{V+} + W_B^{VI+} + h\nu \rightarrow W_A^{VI+} + W_B^{V+} + \text{phonon} \quad (6.6)$$

$$W_A^{V+} + W_B^{IV+} + h\nu \rightarrow W_A^{IV+} + W_B^{V+} + \text{phonon} \quad (6.7)$$

The absorption band shape expected from such a process is given by [114],[113]:

$$\alpha(\hbar\omega) \propto \hbar\omega \cdot \exp\left(\frac{-\hbar\omega - \varepsilon - 4U^2}{8U \cdot \hbar\omega_0}\right) \quad (6.8)$$

where $4U$ is the height of the potential barrier, ε denotes the possible shift of the potential energy because of inequivalent lattice sites, while $\hbar\omega_0$ is the energy of the phonon.

The strength of the absorption depends on several factors. Crucial is however the concentration of polarons or color centers N , which is often approximated using Smakula's equation [21], [32]:

$$N = 8.7 \cdot 10^{16} \text{cm}^{-3} \frac{1}{f} \frac{n}{(n^2 + 2)^2} \alpha_{\max} W \quad (6.9)$$

where f is the oscillator strength reported to be of the order of 0.1 [32], n is the refractive index, $\alpha_{\max}$ is the maximum value of α , and W is the full width at half maximum of the optical absorption band. The effect of color centers on the absorption can be approximated through [37]:

$$\alpha(\hbar\omega) \sim N \quad (6.10)$$

Hence the absorption of the film which can be determined by spectroscopy can be regarded as a measure of the concentration of color centers.

6.4 Gadolinium and rare earths

The group of rare earths to which gadolinium belongs consist of 15 Lanthanides, as well as scandium and yttrium. All elements are trivalent (except for Ce, Pr and Tb which can be tetravalent and Eu and Yb which are divalent) [15]. Related to this common structure of the outer electronic

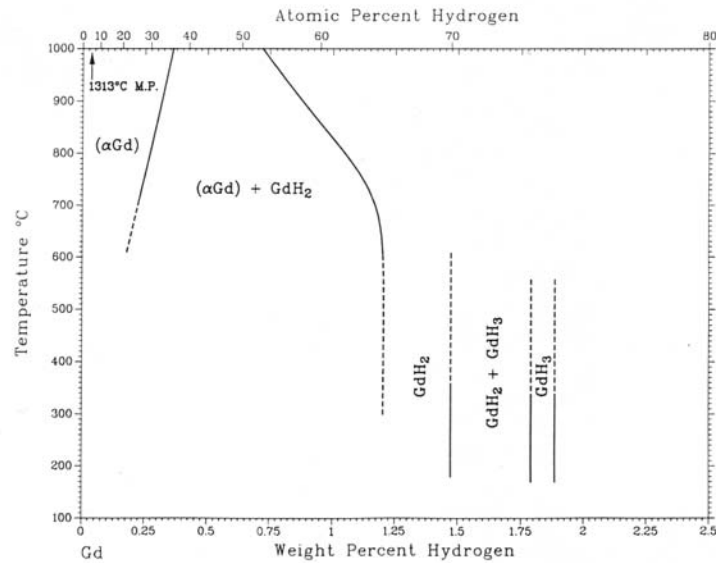


FIGURE 6.10: The phase diagram of Gd. α -Gd is found at low atomic percentages of hydrogen, while a phase co-existence of α -Gd and β -Gd is found at an atomic hydrogen percentage of 66 % or less. At this stage β -Gd is found. At even higher hydrogen content, a co-existence of β -Gd and γ -Gd is found until the γ -phase is isolated at an atomic hydrogen percentage of about 75 %. These limits depend slightly on the temperature especially the transition into an out of the α -Gd and β -Gd co-existence zone. From ref. [74].

shell, these elements possess similar structural and chemical properties. Their switchable properties have been known and studied since the discovery of this property in yttrium and lanthanum in 1996 [50]. This section summarizes the relevant information found for Gd. As Gd is very similar to yttrium, many features of yttrium will be included, as this material has been subject to the most extensive studies in the literature.

Gd as well as yttrium have hcp crystal structures. During their absorption of hydrogen these materials generally exist in three phases (figure 6.10). They are characterized as:

- The metallic alpha phase:

At low hydrogen concentrations $x < 0.25$ [74], the hydrogen atoms occupy the energetically favorable tetrahedral interstitial sites in the Gd lattice. The resulting system remains metallic. Hence the optical properties of the alpha phase are similar to those of a metal, namely a high reflectivity and a low transmission.

- The metallic beta phase:

When all tetrahedral interstitial sites are occupied, the hcp lattice is reconstructed to an fcc lattice structure (CaF_2) as the ABABAB... stacking is transformed into an ABCABC... stacking. In the fcc lattice the eight tetrahedral interstitial sites are occupied by hydrogen, resulting in a GdH₂ composition with a structure as shown in figure 6.13. The optical properties of the GdH_x phase begin to become transparent at a hydrogen concentration of $x \sim 1.7$. At this point a transmission window at energies between 1.6 and 2.0 eV opens. This is seen

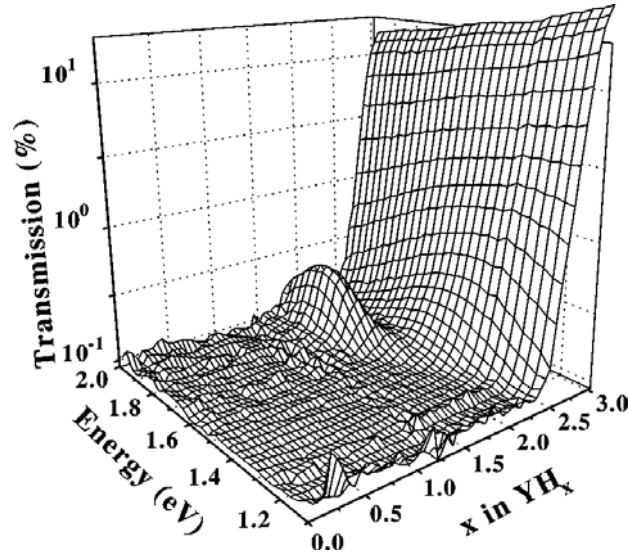


FIGURE 6.11: Transmission window in YH_x . From ref. [61].

for yttrium in figure 6.11. The reason for the formation of this window has not been fully understood, but it is believed that it arises as a result of interband and intraband transitions [61]. At $x \leq 1.5$ there is no transmission as expected from a metallic film. In the region of the stable dihydride $1.7 \leq x \leq 2.1$ the window arises between 1.6 and 2.0 eV. Below 1.6 eV all light is reflected from free-electrons - a typical Drude-like free electron plasma scenario, while above 2.0 eV absorption is dominant, resulting in no transmission. However, in the region of 1.6 to 2.0 eV neither absorption nor reflection is dominant. For YH_2 the observed transmission window was simulated using the dielectric function and the refractive index (fig. 6.12) [61]. At higher hydrogen concentration, the transmittance is decreased due to the filling of the octahedral sites [140] resulting in an enhanced screening.

- The dielectric gamma phase:

When the hydrogen concentration is increased even further, the hydrogen atoms at first begin to occupy the octahedral interstitial sites in the bcc lattice. Eventually, this structure is transformed back into an hcp structure in which the tetrahedral and octahedral interstitial sites are occupied. A lattice expansion of 15 % along the c-axis has been observed for yttrium [107]. The increase of the hydrogen concentration leads to the formation of a transparent semiconducting state with a band gap of around 2.0 eV [118]. This transition is believed to arise as a result of an energy band created by the formation of a super lattice formed by the hydrogen atoms on the octahedral sites [70].

The structural properties of GdH_x are summarized in Table 6.1.

The reaction of gadolinium with hydrogen can be summarized in the following reaction steps:



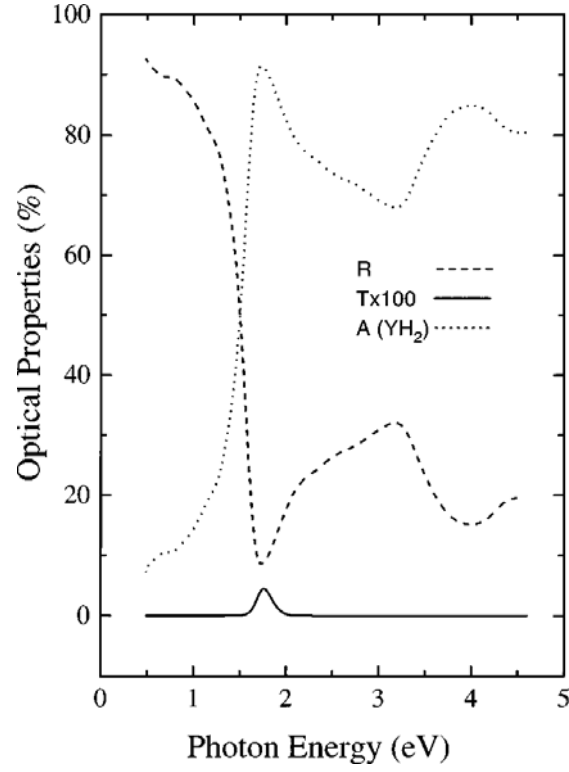


FIGURE 6.12: Simulation of the transmittance, T , the reflectance, R and the absorption A for YH_2 . In the transmission, a window of transparency is found at 1.6 to 2.0 eV. From ref. [61].

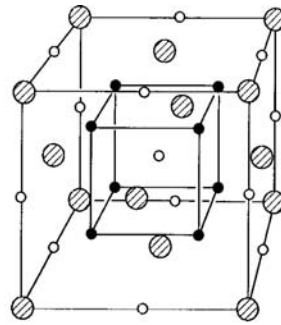


FIGURE 6.13: The structure of GdH_x . The open circles denote octahedral hydrogen sites, the filled circles denote tetragonal hydrogen sites, while the shaded circles are the Gd atoms. In the formation of GdH_2 , the hcp lattice is transformed to an fcc lattice in which the tetragonal sites are filled. From ref. [91].

	Structure	a [Å]	c [Å]	V/Gd [Å ³]	$\Delta V/V_{Gd}$ [%]
Gd	hcp	3.636	5.7836	33.1	-
GdH ₂	fcc	5.30	-	37.3	12.7
GdH ₃	hcp	6.4662	6.7173	40.6	22.7

TABLE 6.1: Structural properties of GdH_x structures. From the lattice constants, the volume of the unit cell can be calculated. From this a mean volume per Gd atom can be computed. The volume change per atom of GdH₂ and GdH₃ with respect to the volume per Gd atom is denoted $\Delta V/V$.

As indicated, the transition from the alpha to the beta phase (6.11) is irreversible, while the transition of the beta to the gamma phase (6.12) is reversible. The reason for this can be comprehended from simple thermodynamic considerations (see section 6.8). It is the reversible nature of the second reaction step that is responsible for the switchable properties of the material.

6.5 Magnesium

Magnesium is known as the metal with the highest solubility of hydrogen. Therefore it has been the subject of numerous investigations with the objective of hydrogen storage in mind [107], [11], [34], [63], [62]. Additionally, magnesium possesses optically switchable properties. This section summarizes these properties.

Mg is a metal with hcp structure. When exposed to hydrogen it absorbs the hydrogen atoms in either of the following two phases:

- The metallic alpha phase:

At low hydrogen concentrations $x < 0.03$ [70], the hydrogen atoms occupy the energetically favorable tetrahedral interstitial sites in the Mg lattice. The resulting system remains metallic, and hence the optical properties show a high reflectance and a low transmission.

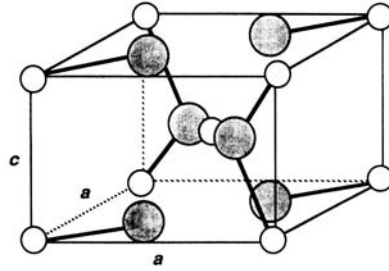
- The insulating beta phase:

At higher concentrations of hydrogen, the lattice structure remains hcp [74] or changes to a tetragonal structure in which two tetrahedral and two octahedral interstitial sites are occupied resulting in a MgH₂ structure [70] (figure 6.14). Additionally an orthorhombic structure is possible. Resistance measurements have shown that this structure is insulating and transparent [63]. The structural information is summarized in Table 6.2.

Hence the reaction of magnesium with hydrogen can be summarized in the following reaction:



As it was the case for GdH_x, thermodynamic considerations yield information on the reversibility of the process (see section 6.8).

FIGURE 6.14: The structure of MgH_2 . From ref. [152].

	Structure	a [Å]	b [Å]	c [Å]	V / Mg [Å ³]	$\Delta V/V$
Mg	hcp	3.2094	-	5.2108	23.5	-
MgH ₂	hcp	4.54	-	10.99	28.3	0.20
MgH ₂	tetragonal	4.517	-	3.0205	30.8	0.31
MgH ₂	orthorhombic	4.53	4.93	5.44	30.4	0.29

TABLE 6.2: Structural properties of MgH_x structures. Using the lattice parameters, the volume of the unit cell can be determined, and a mean volume V per Mg atom can be estimated. $\Delta V/V$ denotes the volume change per Mg atom with respect to the volume per Mg atom in pure magnesium.

6.6 Palladium and platinum

To improve the kinetics of switchable coatings based on the absorption of hydrogen, it is beneficial to coat them with a catalyst film of palladium or platinum. These coatings also protect films like Gd and Mg that oxidize extremely easily. The understanding and knowledge of the properties of the catalyst materials is crucial for the measurements considered in this work, as it allows the separation of the changes in the active gasochromic coating from the total changes of the layer stack.

The catalyst properties of these metals arise from their dissociative absorption of hydrogen. In this process the bonds of the H_2 molecules are broken once they arrive at the metal surface, and hydrogen atoms are absorbed individually and dissociate into the metal. As the diffusion constants of hydrogen in catalyst metals are very large ($D_{\text{Pd}} = 1.6 \cdot 10^{-7} \text{ cm}^2/\text{s}$ [71]), the concentration of hydrogen in a thin film can be considered to be constant on the timescale of seconds that is involved in measurements of the kinetics and mechanical stresses of switchable coatings: The mean distance that a hydrogen atom travels within a time t is:

$$\bar{x} = 2\sqrt{\frac{Dt}{\pi}} \quad (6.14)$$

Using $t = 0.01 \text{ s}$ a mean distance of $\bar{x} = 451 \text{ nm}$ is found.

Both Pd and Pt belong to the so-called "Platinum group" of elements with the remaining members being ruthenium, osmium, rhodium and iridium. Within this group, palladium (and to a lesser extent platinum) sets itself apart by its property of being able to absorb hydrogen. As the unique combination of the properties of high diffusivity and solubility of hydrogen stretching over a wide

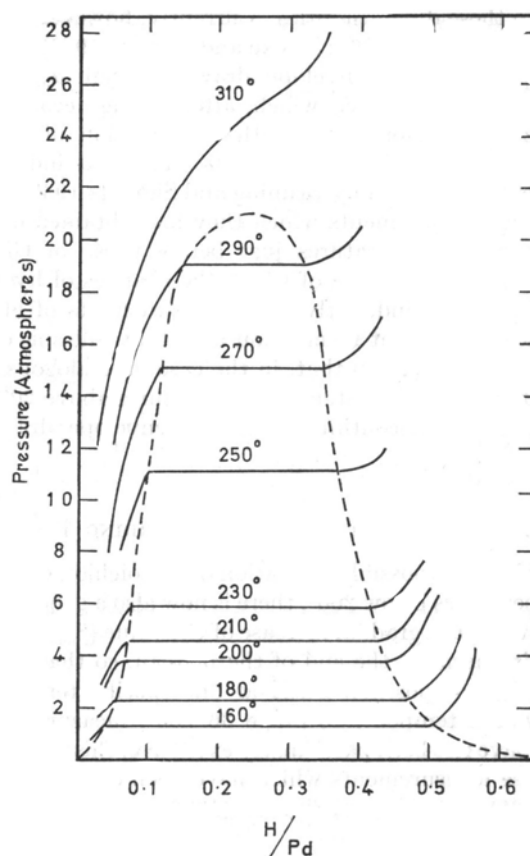


FIGURE 6.15: The p-c (pressure-concentration) diagram for PdH_2 . From ref. [71].

temperature range is of interest to both physicist and chemists, these properties have been studied extensively for Pd. In the case of Pt, the studies are not very extensive, because of the superior properties of palladium.

6.7 General properties of the Pd-H and Pt-H systems

To characterize a system like Pd-H or Pt-H, a pressure vs. hydrogen concentration diagram (p-c diagram) is crucial. It relates the hydrogen concentration in the metal to the equilibrium pressure of the hydrogen gas at a fixed temperature. In the case of palladium (figure 6.15) it is found that:

- At low hydrogen pressures, the hydrogen concentrations in the Pd increases continuously. The hydrogen can be considered to be dissolved in the palladium lattice. This phase carries the label "alpha phase".
- At a certain value for the hydrogen pressure, the hydrogen concentration increases without a simultaneous increase in the pressure. This point represents the maximum solubility of hydrogen in the alpha phase. Above it, the hydride "beta phase" can be formed.

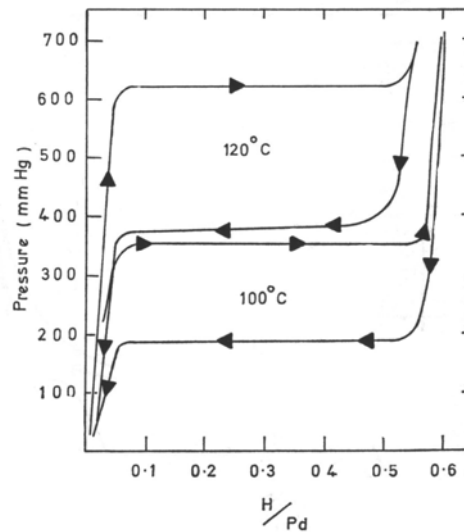


FIGURE 6.16: The hysteresis behavior in the p-c diagram of palladium. From ref. [71].

- In the plateau of constant equilibrium pressure, there is a co-existence of the alpha and the beta phases. As the hydrogen concentration rises, the balance is shifted towards the beta phase.
- After completion of the phase transformation, the equilibrium pressure begins to increase again as the hydrogen concentration in the beta phase increases.
- There exists a critical temperature above which the co-existence of the two phases is impossible.
- Closer inspection of the transformation from the alpha to the beta phase and vice versa, shows that the path in the p-c diagram depends on the direction of the transformation i.e. whether the hydrogen concentration increases or decreases (figure 6.16). This violation of "Gibb's phase rule" has been explained by mechanical stresses in the palladium, which adds an additional degree of freedom. Hence the equilibrium pressure is not unequivocally defined in the transition area [115].

For platinum, the solubility of hydrogen is far lower than it is in palladium (fig. 6.17). At room temperature the solubility is $H/Pt \simeq 10^{-7}$ in the case of Pt, while it is about 0.7 H/Pd atoms in the case of Pd (at 1 atm H_2) [70]. Thus, the difference in solubility between the two materials is 6 to 7 orders of magnitude at room temperature. On the basis of this difference, the dramatic changes to the equilibrium pressure for a given hydrogen concentration as seen when alloying Pd and Pt (fig. 6.18) can be intuitively understood.

6.7.1 Structural properties of the Pd-H and Pt-H systems

Both palladium and platinum crystallize in an fcc structure. The lattice constants are 3.8829 Å and 3.9152 Å respectively [70], while the Young's moduli and the Poisson's ratios are 121 GPa and

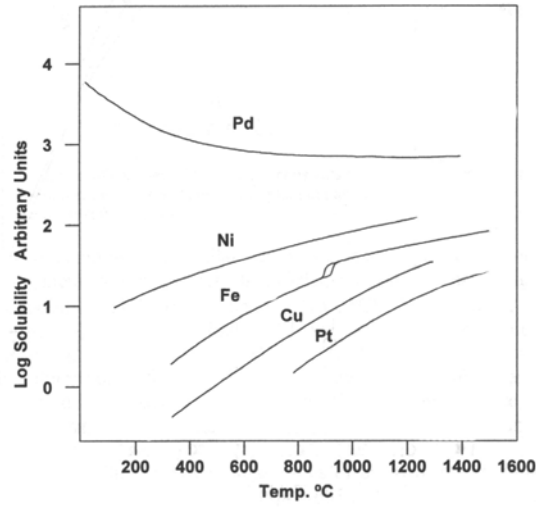


FIGURE 6.17: The difference in solubility of hydrogen in Pd and Pt is marked. At room temperature the solubility in Pt is 6 to 7 orders of magnitude smaller than for Pd. From ref. [70].

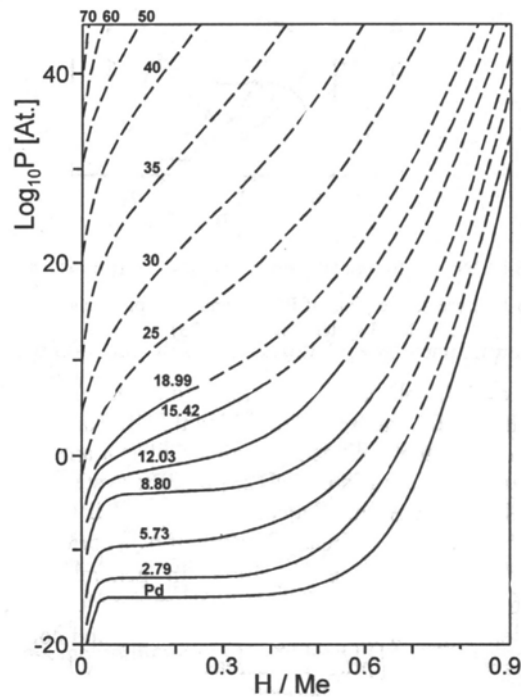


FIGURE 6.18: The dependence of the hydrogen concentration on the equilibrium pressure in PdPt alloys. The curves are labelled corresponding to the Pt alloy percentage. The dotted lines represent estimated relations. From ref. [70].

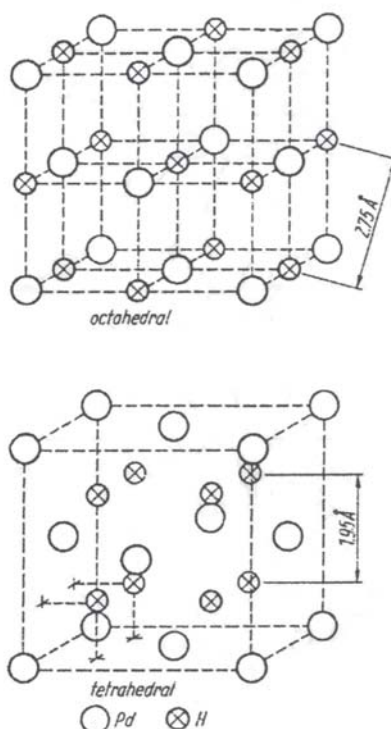


FIGURE 6.19: In palladium hydrogen has a preference for occupying the octahedral interstitial sites (top) as opposed to the tetrahedral sites (bottom) From ref. [70].

0.39 for Pd and 168 GPa and 0.38 for Pt. The diffusion constants for hydrogen in the materials are about $3 \cdot 10^{-7} \text{ cm}^{-2} / \text{s}$ for Pd and $2 \cdot 10^{-9} \text{ cm}^{-2} / \text{s}$ for Pt.

The effect of absorption of hydrogen is thoroughly investigated for Pd. On the other hand little information can be found for Pt. In the case of palladium, the hydrogen atoms have been found to have a preference for occupying the octahedral interstitial sites as seen in figure 6.19. In the α -phase no periodical order is found in the occupation of the interstitial sites. The hydrogen must be imagined jumping around between the interstitial sites with a frequency, that for Nb is of the order of 10^{-11} s^{-1} [2]. In the β -phase however, where the hydrogen concentration increases dramatically, the mobility of the hydrogen atoms is decreased, and a long-range periodical order emerges.

Associated with the phase transformation from the alpha to the beta phase is an increase in the lattice parameters of the fcc unit cell. In table 6.3 the lattice parameters found by use of X-ray diffraction [71] are listed. As can be seen from figure 6.20, pure Pd has a lattice constant of 3.8829 Å. This lattice constant increases to 3.895 Å in the alpha phase. In the equilibrium pressure plateau, where the alpha and beta phases are both present, diffraction peaks for both phases are observed. At the end of the plateau, the lattice constant for the beta phase is found to be 4.016 Å, and further increase of the hydrogen concentration results in an almost linear increase of the lattice constant. At a pressure of 1 bar, a value of 4.04 Å is found. Comparing to the volume of the Pd unit cell, a volume change of 0.9 % is expected within the alpha phase while the transformation to the beta

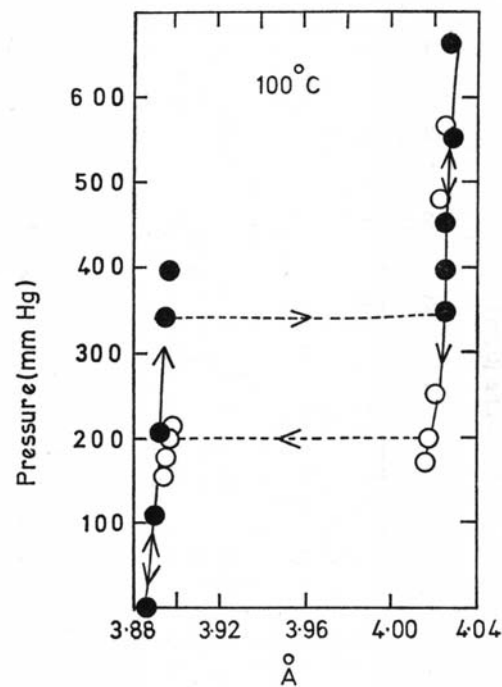


FIGURE 6.20: The lattice constant of palladium-hydride as a function of the hydrogen pressure. From ref. [71].

	Pd	α -Pd	β -Pd	β -Pd (1 bar H ₂)
d [Å]	3.8829	3.895	4.016	4.04
$\Delta V/V_{Pd}$ [%]	-	0.9	10.6	12.6

TABLE 6.3: The lattice parameter d of the different Pd phases. From the lattice parameter, the unit cell volume can be calculated, and hence a mean volume per Pd atom. $\Delta V/V_{Pd}$ is the change of volume of the considered phase with respect to the initial Pd phase.

phase is associated with a volume increase of 10.6 %. In nanocrystalline samples slightly lower increases of the lattice constant upon transition to the beta phase of 2.7 to 3.1 % were found [25]. This increase translates to a volume change of about 9.5 % compared to the Pd unit cell.

6.7.2 Optical properties of the Pd-H and Pt-H systems

The knowledge of the optical properties of palladium upon exposure to hydrogen is crucial, when it comes to isolating the contribution of the active film from the total change of the optical properties of the sample. In the case of palladium, a change of the optical properties is directly associated to the absorption of hydrogen. Hence an application as a hydrogen sensor has been suggested for palladium. Transmission experiments on a thin film of 26 nm thickness showed an increase of the transmission of palladium from 7.8 to 9.2 % when exposed to a gas of 3 % hydrogen at a total pressure of 1 bar [73].

Although this increase is very low, it cannot be overlooked when considering and analyzing the total transmission of a primary switchable coating such as tungsten oxide, gadolinium or magnesium, coated with a palladium catalyst film, which must be considered as a switchable coating itself.

For the Pt-H system no data were found.

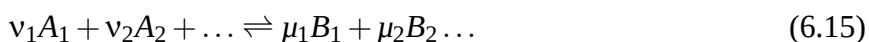
6.8 Thermodynamic considerations

Thermodynamic considerations yield an explanation for the reversible switching behavior explained above. It should be stressed though, that such considerations only yield information on whether a certain reaction is energetically possible or not. There is no information on the kinetics of the processes to be found by this approach.

In this section a brief resume of the standard approach of thermodynamic considerations will be given. A thorough treatment of this theory is given in standard chemistry textbooks such as [1].

6.8.1 Basic definitions

To describe the reaction



where ν_i and μ_i are the number of species of the reactants A_i and the products B_i , it is necessary to consider a number of thermodynamic state functions. The advantage of these thermodynamic coordinates is that they are independent of the history of the system and only depend on the state of the components, which is defined by state variables like pressure, temperature, volume etc. In describing the reaction (6.15), the relevant state functions are the entropy S , the enthalpy H and the Gibbs free energy G , which are related through:

$$G = H - TS \quad (6.16)$$

where T is the temperature. The change in Gibbs free energy at fixed temperature and pressure for a given reaction (hence the subscript "r") is then calculated using:

$$\Delta_r G = \Delta_r H - T \Delta_r S \quad (6.17)$$

The calculation of the change in Gibbs free energy is facilitated by tabulated values for the standard enthalpy of formation $\Delta_f H_i^o$ and standard entropy S_i^o , which are known for most chemical species i . Using these numbers the standard reaction enthalpy, $\Delta_r H^o$ and standard reaction entropy $\Delta_r S^o$ can be calculated using:

$$\Delta_r H^o = \sum_i \mu_i \cdot \Delta_f H_{(B_i)}^o - \sum_j \nu_j \cdot \Delta_f H_{(A_j)}^o \quad (6.18)$$

and

$$\Delta_r S^o = \sum_i \mu_i \cdot S_{(B_i)}^o - \sum_j \nu_j \cdot S_{(A_j)}^o \quad (6.19)$$

Hence $\Delta_r G^o$ can be calculated at the standard conditions $p^o=1013$ hPa and $T^o=298.15$ K, which are symbolized by the superscript ^{o} .

6.8.2 Gibbs's free energy at arbitrary temperatures

At temperatures that do not deviate too much from T^o , one can assume that the reaction enthalpies and entropies are constant. Hence the change in Gibbs's free energy is linearly dependent on temperature:

$$\Delta_r G(T) = \Delta_r H^o - T \Delta_r S^o \quad (6.20)$$

This approach is not an accurate one though. Finding the correct method begins at the expression of the molar heat capacity at constant pressure:

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p \quad (6.21)$$

which can be integrated to yield the following temperature dependence of $\Delta_r H$:

$$\Delta_r H(T) = \Delta_r H^o + \int_{298K}^T dT' \cdot \Delta C_p^o(T'). \quad (6.22)$$

Similarly the expression

$$\Delta_r S(T) = \Delta_r S^o + \int_{298K}^T dT' \cdot \frac{\Delta C_p^o(T')}{T'}. \quad (6.23)$$

can be deduced for the entropy. Hence the change in Gibbs's free energy at a given temperature can be calculated using:

$$\Delta_r G(T) = \Delta_r H(T) - T \Delta_r S(T) \quad (6.24)$$

6.8.3 Gibbs's free energy at arbitrary pressures

For reactions at pressures different from p^o , a similar approach must be taken. Beginning at the fundamental equation:

$$dG = -SdT + Vdp \quad (6.25)$$

one can deduce the following expression at a constant temperature:

$$\left(\frac{\partial G}{\partial p} \right)_T = V. \quad (6.26)$$

A straightforward integration now yields:

$$\int_{G_1}^{G_2} dG = \int_{p_1}^{p_2} V dp \quad (6.27)$$

For an ideal gas, where $V = nRT/p$, the following expression for Gibbs's free energy is now found:

$$G(p, T) = G^o(T) + nRT \ln \frac{p}{p^o}. \quad (6.28)$$

where $R=8.314 \text{ J/(K}\cdot\text{mol)}$, and n is the amount of gas in moles.

6.8.4 Chemical equilibrium

When considering a reaction like (6.15), one cannot assume that the reaction will begin with the species on the left hand side and end with the species on the right hand side. Instead a state of chemical equilibrium is reached. This state is found when the rate of the reaction towards the right hand side and the rate towards the left hand side are opposite and equal in size. The equilibrium state is characterized by the equilibrium constant K , defined as:

$$K = \frac{\prod_i a_{B_i}^{\mu_i}}{\prod_j a_{A_j}^{\nu_j}}. \quad (6.29)$$

where a_k is the activity of species k . The activity is generally defined as the fugacity related to the standard fugacity. For a solid the activity is always 1, while ideal gases have activities given as $a_i = p_i/p^0$.

The relation between the equilibrium constant and the Gibb's free energy is:

$$\Delta_r G(T) = -RT \ln K. \quad (6.30)$$

Hence the Gibb's free energy also can be used to find the equilibrium state of a certain reaction.

At standard conditions equation 6.30 can be rearranged to:

$$\ln K = -\frac{\Delta_r H^0}{RT} + \frac{\Delta_r S^0}{R} \quad (6.31)$$

which is known as the Van't Hoff equation.

6.8.5 Thermodynamic approach to the switching of WO_x , Gd and Mg

In this section, the concepts of thermodynamics summarized above is applied to the optically switchable systems, that are investigated in this work. As all experiments were carried out at room temperature, the calculations are performed at $T=T^0$. Using thermodynamics, the equilibrium pressure for the reactions of the different switchable coatings can be deduced.

The gasochromic reactions considered here are all of the form:



As mentioned in section 6.8.4, the activity of solids is 1. Hence the equilibrium constant given by equation 6.29, for these reactions reduces to:

$$K = \frac{a_{\text{Solid}2}}{a_{\text{Solid}} \cdot a_{H_2}} = \frac{1}{\frac{p_{H_2}}{p^0}} \quad (6.33)$$

Using (6.30) the following expression for the equilibrium hydrogen pressure of a given reaction is found:

$$p_{H_2} = p^0 \exp \left[\frac{\Delta_r G(T^0)}{RT} \right] \quad (6.34)$$

	$\Delta_r H$ / kJ/mol	$\Delta_r S$ / J/mol·K	p_{eq} /Pa
GdH ₂	-190.4	-	$3 \cdot 10^{-27}$
GdH ₃	-	-	-
MgH ₂	-76.2	-132.32	$4 \cdot 10^{-7}$

TABLE 6.4: Thermodynamic properties of the investigated hydrides [89],[17].

where the change in Gibb's free energy is given by the equation:

$$\Delta_r G^o = \Delta_r H^o - T^o \Delta_r S^o \quad (6.35)$$

Expression 6.34 allows a statement on whether the gasochromic reactions considered in this work, from a thermodynamic perspective, can actually take place at a given pressure, if the process is controlled by energetics. Using tabulated values of enthalpy of formation and entropy of formation as given in Table 6.4, equilibrium pressures of $4 \cdot 10^{-7}$ Pa for MgH₂ and $3 \cdot 10^{-27}$ Pa for GdH₂ (where the reaction entropy was assumed to arise only from the H₂ gas: $S_{H_2}^o = 130.8$ J/mol) are found for the coatings considered here. For tungsten oxide no data were found.

This means that hydrogen is absorbed into the systems considered here, when the partial pressure of hydrogen is above the equilibrium pressure of the system. Otherwise the hydrogen is desorbed.

6.9 Results of mechanical stress measurements

The results of the studies of mechanical stresses in optically switchable coatings are presented in this chapter. As mentioned in chapter 2, it is important to understand the mechanical stresses in the thin film constituting the active coating in order to ensure that no irreversible, inelastic stress relief processes take place during the switching as these could reduce the cyclability of the films.

The description of the findings of these studies commence with the surprising findings of the initial experiments (fig. 6.21). Here a sample consisting of a 200 nm tungsten oxide deposited on 150 μ m glass with a 10 nm palladium catalyst film on top was exposed to a hydrogen gas at a partial pressure of 20 mbar. Surprisingly the transmission was found to show an initial abrupt increase before its expected decrease. Similarly, when the fully colored sample was exposed to an oxygen containing atmosphere, an initial abrupt reduction of transmission was observed, before it slowly increased to its initial value. These sudden quick jumps in transmission were first thought to be related to sample movement resulting from a less than perfect clamping of sample in the gas chamber, but as several measurement showed that the features seen in figure 6.21 could be reproduced, the catalyst film was identified as a candidate for optical switching itself. Hence a detailed investigation of the optical and mechanical stress changes upon switching for the palladium catalyst film itself was carried out (section 6.10).

After the discussion of the properties of the catalyst film, an effort to compare the properties of these material classes of switchable coatings was carried out. This study focused on a representative from each class, namely tungsten oxide, Gd and Mg (section 6.11). As a result of the findings

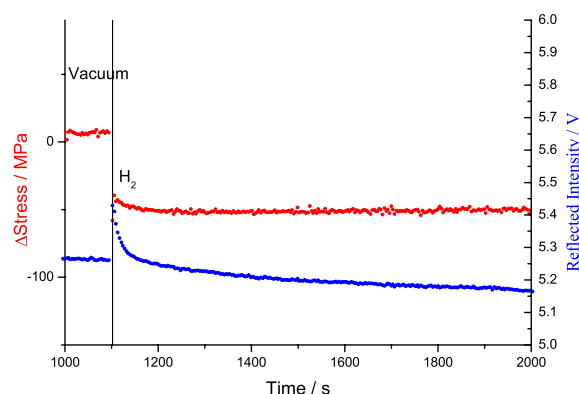


FIGURE 6.21: The first experiments measuring mechanical stresses (top) and transmission (bottom) in a 10 nm Pd / 200 nm WO_x / 150 μ m glass switchable system yielded unexpected results. The sudden increase of transmission upon exposure to hydrogen and decrease in oxygen (not shown) were puzzling. After eliminating the possibility of any deficiencies and anomalies induced by the gas chamber, the catalyst Pd film was identified as a candidate for optical switching itself.

of this study, the most promising candidate for application in switchable window technology was subject to further studies (section 6.12).

6.10 Mechanical properties of catalyst films

After identifying the catalyst film as a possible candidate for optical switching, and hence also as a possible origin for the unexpected features of the switching seen in figure 6.21, a series of measurements monitoring optical transmittance and mechanical stresses in both palladium and platinum films were carried out. In section 6.10.1 the results for palladium are shown, while platinum is the topic of section 6.10.2.

6.10.1 Palladium

The sample used for the study of the mechanical behavior of palladium, was a 150 μ m glass substrate coated with a Pd-film with a thickness of 10 nm. The thickness of the Pd film was chosen to be identical to the thickness which is typically used for catalyst films. In a comprehensive series of loading and unloading cycles, this film was exposed to Ar/H₂ gas atmospheres containing different concentrations of hydrogen (Fig. 6.22). The hydrogen partial pressure was varied in steps ranging from 0.05 mbar up to 1000 mbar in the order (mbar): 25, 1, 0.5, 0.075, 0.75, 0.25, 0.1, 0.05, 1, 10, 5, 7.5, 2.5, 25, 50, 50, 75, 100, 250, 500 and 1000. Each hydrogen phase was retained for 15 minutes, after which the gas cell was evacuated for 5 s to a pressure of approximately 0.3 mbar. In the following step, this vacuum state was replaced by an atmosphere of pure O₂ at a pressure of 1000 mbar. This phase also lasted 15 minutes. This use of oxygen accelerates the

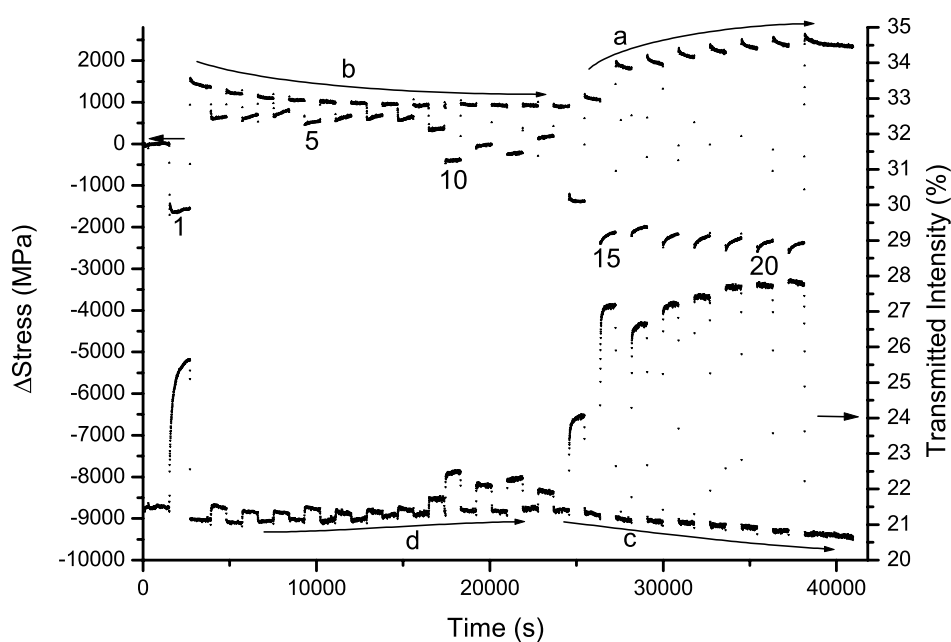


FIGURE 6.22: Change of mechanical stress (top) and transmittance (bottom) as a function of loading with hydrogen and unloading in oxygen of a 10 nm thick palladium film deposited on a 150 μm thick glass substrate. The switching was carried out in the following order: Ambient air, vacuum, (hydrogen, vacuum, oxygen, vacuum,) hydrogen, and so on. The oxygen pressure was 1000 mbar, while the sequence of the hydrogen partial pressures was (mbar): 25, 1, 0.5, 0.075, 0.75, 0.25, 0.1, 0.05, 1, 10, 5, 7.5, 2.5, 25, 50, 50, 75, 100, 250, 500 and 1000 (Every 5th phase is labelled). It can be seen that the hydrogen loading is associated with a compressive stress of several hundreds up to thousands of MPa and an increase in transmittance. Additionally, the stress state of the unloaded phase is shifted towards larger tensile stresses with increasing hydrogen pressure in the preceding phase. Presumably this is a result of the removal of a thin oxide layer. This is supported by the behavior of the transmittance. The level of the unloaded phase decreases once the hydrogen pressure is large at the end of the measurement and also in the very first loading.

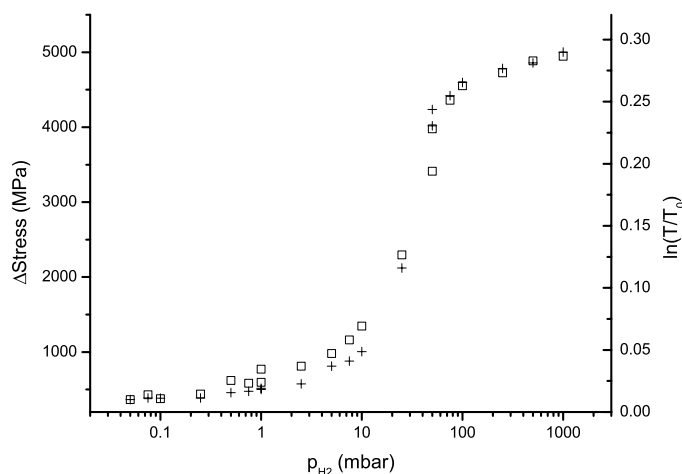


FIGURE 6.23: Change of stress (boxes) and transmittance (crosses) upon loading as a function of the hydrogen partial pressure. The characteristic steep increase indicating the transition from the α - to the β -phase is seen at about 30 mbar, which is slightly higher than found in bulk palladium and clusters (24 mbar).

kinetics of the hydrogen desorption without changing the overall behavior of the Pd-films. After evacuation for 5 s, the next hydrogen phase followed and so forth.

As expected, contact to hydrogen, even in the lowest concentrations, leads to an increase in optical transmittance of the Pd-film and to a build-up of compressive stress in the film. Both effects become more pronounced with increasing hydrogen concentration. This comes as no surprise, because the chemical potential of hydrogen in a gas atmosphere increases with its partial pressure. Therefore the amount of hydrogen absorbed in the Pd-film also increases with increasing pressure. Because of the α - to β -phase transition of the palladium-hydrogen system, the relationship between the gas pressure and the amount of absorbed hydrogen is not linear, as can be seen in Fig. 6.23.

At 1000 mbar partial pressure of hydrogen an increase in transmittance from 20 % to 28% was observed, when compared to a hydrogen-free atmosphere. Correlated with this change in optical transmittance is a compressive stress in the film of approximately 5 GPa, which arises due to the interstitially placed hydrogen atoms.

The most intriguing result of this series of measurements is the fact that the levels of both mechanical stress and optical transmittance observed in the oxygen phases, directly preceding and following any hydrogen phase, whose pressure does not deviate substantially from the pressure of preceding hydrogen phases, are virtually the same (Fig. 6.22). Hence it seems that the changes to the lattice constant of palladium induced by the absorption of hydrogen atoms are reversible even at relatively high hydrogen concentrations.

However, while the oxygen-induced changes of stress and transmittance hardly vary from step to step, they change substantially during the whole duration of the measurement. The most pronounced shift occurs with the first contact of the Pd film to hydrogen: Here the optical transmittance and the measured stresses in the vacuum phase following the hydrogen absorption are very

different from their initial values. A similar effect can be seen later on in the measurement, when the hydrogen partial pressures increase above the level of the first loading (Fig. 6.22).

A possible explanation for these irreversible changes in the mechanical stress is, that the samples were not in a stress free state at the beginning of the measurements. It is possible that they were in a state of compressive stress due to an oxide layer on top of the pure Pd sample: Other experiments on microscopic Pd samples showed their tendency to form oxide layers at the surface if kept in air for a prolonged period of time [112]. The same experiments showed, that it is possible to completely remove those oxide layers by bringing the sample in contact with hydrogen for 24 h at 1000 mbar.

In the period between preparing the Pd samples and performing the measurements, the samples were kept in ambient air for several days. This probably allowed them to oxidize on the surface. During the first contact to hydrogen, this layer is partially removed, resulting in a shift of the stress state of the Pd as seen from the difference between the initial stress and the stress in the first oxygen phase.

At the higher hydrogen concentrations used towards the end of the measuring series the oxide layer is removed completely (indicated by arrow (a) in Fig. 6.22), leaving behind a pure Pd film. On the other hand, the relatively short oxygen phases used in between the hydrogen phases are too short to form substantial amounts of new palladium oxide, as can be seen from the rather small shift of the stress change in the unloaded state (indicated by arrow (b) in Fig. 6.22). Hence the mechanical stress as shown in Fig. 6.22 can be considered a superposition of reversible loading and unloading with hydrogen and an irreversible removal of the oxide. This is supported by the behavior of the optical transmission. Upon loading with higher hydrogen pressures, the transmission is reduced, which is consistent with a removal of a thin oxide layer (arrow (c) in Fig. 6.22). Additionally, alternating cycles of low hydrogen pressure phases and oxygen phases result in a small increase of transmission (arrow (d) in Fig. 6.22), indicating the formation of a very thin oxide layer.

Under the assumption, that the changes in mechanical stress for the Pd films are elastic and reversible in the whole range of applied hydrogen pressures, it makes sense to plot these changes as a function of the hydrogen pressure. The resulting plot can be seen in Fig. 6.23. In the same graph the changes in the optical densities ($\ln(T/T_0)$) as calculated from the transmittance measurements were plotted. Both sets of points show a similar behavior: At low hydrogen pressures the changes in stress and transmittance are small. As the stress change can be interpreted as a measure for the concentration of hydrogen atoms absorbed into the palladium lattice, this implies that a low concentration of hydrogen atoms is found in the Pd film. However, at a hydrogen partial pressure of about 30 mbar, a sharp increase in both the optical transmittance and the mechanical stress is observed, indicating a pronounced increase of the hydrogen concentration in the palladium film. At hydrogen pressures above 100 mbar, the transmittance and the stress increase only slightly with a further increase of the hydrogen pressure.

The general behavior of the stress and the transmittance curves as a function of the hydrogen pressure can be interpreted in terms of the palladium-hydrogen phase diagram. Bulk palladium samples show a phase change between an α -phase with low hydrogen concentration and a β -phase with higher hydrogen concentration. This transition takes place at a hydrogen pressure of

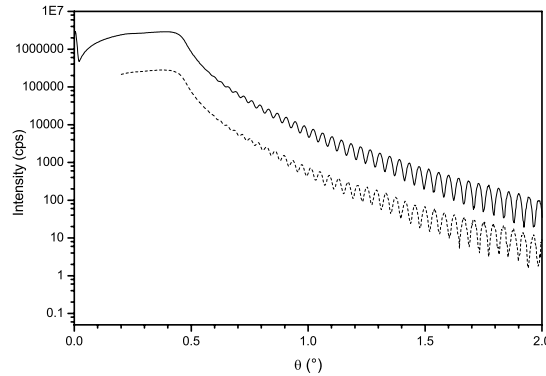


FIGURE 6.24: XRR scan of a roughly 100 nm thick palladium film in ambient air, and placed in a H_2/Ar atmosphere at a total pressure of 1 bar (dashed curve). The shift of the oscillations at higher angles indicates a thickness change upon loading. The analysis yields a thickness of 99.4 nm in the unloaded phase and 100.75 nm in the loaded phase. The vertical shift between the curves arise as a result of the use of the Ar/H_2 gas for loading.

approximately 24 mbar [73]. Our measurements on thin Pd films also show this phase transition, but the equilibrium pressure is shifted to a slightly higher value of 30 mbar, and the transition is not as abrupt when compared to the results found in bulk [73] and clusters [112].

The absolute value of compressive stress measured at the highest hydrogen concentration was about $\sigma_1 = 5000$ MPa. This corresponds to a strain ϵ of the lattice constant of 2.8 % as calculated using Hooke's law (eq. 2.3):

$$\epsilon = \frac{1 - \nu_{Pd}}{E_{Pd}} \sigma_1 \quad (6.36)$$

where it was assumed that the elastic modulus $E_{Pd} = 110$ GPa and the Poisson's ratio $\nu_{Pd} = 0.39$ are independent of the hydrogen content in the film [96]. This result is in agreement with the increase in the lattice constant of between 2.7 % and 3.1 % reported by Eastman *et al.* [25]. Further support for the elastic behavior of the palladium comes from in-situ XRR measurements, in which the thickness of an approximately 100 nm thick palladium film was measured in the loaded state (Fig. 6.24). From the shift of the oscillations between the unloaded and the loaded state, a thickness increase from 99.4 nm to 100.75 nm at a hydrogen pressure of 20 mbar was found. Because of the constraint of the substrate, this thickness change is related to a biaxial mechanical stress σ_2 , which in the case of elastic processes is given by (2.93):

$$\sigma_2 = -\frac{E_{Pd}}{1 + \nu_{Pd}} \epsilon \quad (6.37)$$

Hence the total thickness change of $\epsilon_{zz} = 0.014$ corresponds to a compressive stress of 1100 MPa. Even though the hydrogen pressure of 20 mbar falls directly in the transition region, it can be seen from Fig. 6.24, that we find a stress of the same order (about 1400 MPa) at 20 mbar hydrogen pressure. This also indicates a reversible volume change upon switching.

Additionally, no delamination or blistering of the films was observed in these studies, which is remarkable given the large stresses of 5000 MPa measured. However, as seen from equation

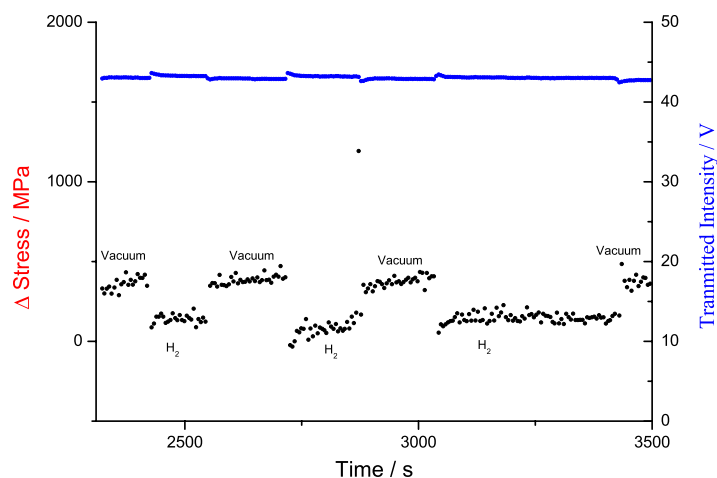


FIGURE 6.25: The optical and mechanical properties of an 8 nm platinum catalyst film on a 150 μm glass substrate as a function of the hydrogen loading and unloading. The transmission change (top) is of the order of 1 %, while the stress change (bottom) is about 200 MPa at a hydrogen partial pressure of 4.0 bar. The switching is observed to be reversible.

2.102, delamination and cracking is closely related to the thickness of the film. The very thin films studied here (10 nm) are hence not as prone to crack as thicker films. Other explanations for the delamination that was been observed by others [95] could be related to the adhesion of the films and the cleaning of the substrates.

6.10.2 Platinum

As an alternative to Pd as a catalyst, platinum is a candidate. As mentioned in chapter 6, little information is available on the properties of the Pt-H system. Hence the criteria important for a catalyst film for the application in stress measurements were investigated directly. An 8 nm thick Pt film on a 150 μm glass substrate was produced at the facilities of Interpane E&B [52]. It allowed a preliminary and at the same time conclusive study of the optical and mechanical properties of Pt when exposed to hydrogen.

In fig. 6.25 the results of the study are shown. After evacuation of the gas chamber to a pressure of approximately 0.3 mbar, the Pt film was exposed to a hydrogen partial pressure of 4.0 bar for a period of 3 min. Subsequently, the chamber was again evacuated before being flooded with hydrogen again. It is seen that the transmittance change associated with the exposure to hydrogen is of the order of 1 %. Simultaneously a change of mechanical stress of 200 MPa is found. During the following evacuation, the transmittance returns to its initial value as does the mechanical stress. The subsequent switching cycles show similar reversible behavior.

It is important to notice that the direction of the transmittance shift in the Pt film upon loading with hydrogen is the same as the one expected for tungsten oxide. Hence the platinum film work

with the tungsten oxide film, in contrast to the example of the palladium film where the change of transmission works in opposite direction of the transmittance change of the tungsten oxide film. The use of platinum will thus help increase the contrast ratio that can be achieved in switchable window systems.

For the application in mechanical stress measurements, it is however even more important, that the stress change induced by the hydrogen loading is only 200 MPa at a hydrogen partial pressure of 4.0 bar as opposed to the 5000 MPa found for Pd at a similar hydrogen partial pressure. The contribution of the catalyst layer is in fact super-positioned in relation to its thickness onto the contribution of the real active tungsten oxide film (or other optically switchable coatings), when the mechanical stress is measured. The reduction of stress in the catalyst film that is achieved by using Pt instead of Pd, means that when the ratio of film thickness to catalyst film thickness is 20:1, the stress contribution of the catalyst layer is only a mere 10 MPa in the case of platinum at the hydrogen partial pressure of 4 bar. In contrast, for palladium the contribution depends dramatically on the hydrogen partial pressure as seen in section 6.10.1. However at a similar hydrogen pressure of 4.0 bar, the contribution the total stress is about 250 MPa.

It should be noted though, that in a situation where the partial pressures is kept so low that Pd remains in its α -phase, the stress contribution would be just 50 MPa for a 20:1 thickness relation between the active film and the catalyst film. However, as an additional complication, the precise value of the contribution from the Pd film, depends on the kinetics of switching for the catalyst film. Hence, it is extremely hard to calculate the exact change of stress in the active film by subtracting the catalyst contribution. As a consequence it is extremely helpful, that the contribution to the total stress from the Pt film can be neglected, once the ratio of film thickness to catalyst film thickness is above 20.

6.11 Comparison of different switchable films

In this section, the results of a study of the mechanical properties of optically switchable coatings from three material classes are found. WO_x , Gd and Mg were subjected to hydrogen loading and unloading.

6.11.1 Tungsten oxide

In Fig. 6.26 the mechanical stress (top portion) and transmittance (lower portion) of a 100 nm WO_x film covered by a 10 nm Pd catalyst film deposited on $150\text{ }\mu\text{m}$ are shown. During the first coloration, which is done by exposing the sample to a gas atmosphere consisting of 2% H_2 in argon at a total pressure of 0.6 bar, the transmittance is reduced from 36% to 30% within a few minutes. Simultaneously, the stress change reaches a minimum value of -65 MPa, which remains constant once the transmission reaches its constant value. During the following first bleaching performed under the exposure to ambient air, both the transmittance and the stress change return to their initial values. Subsequent switching cycles show the same behavior suggesting that the processes involved in the switching of WO_x are reversible and elastic.

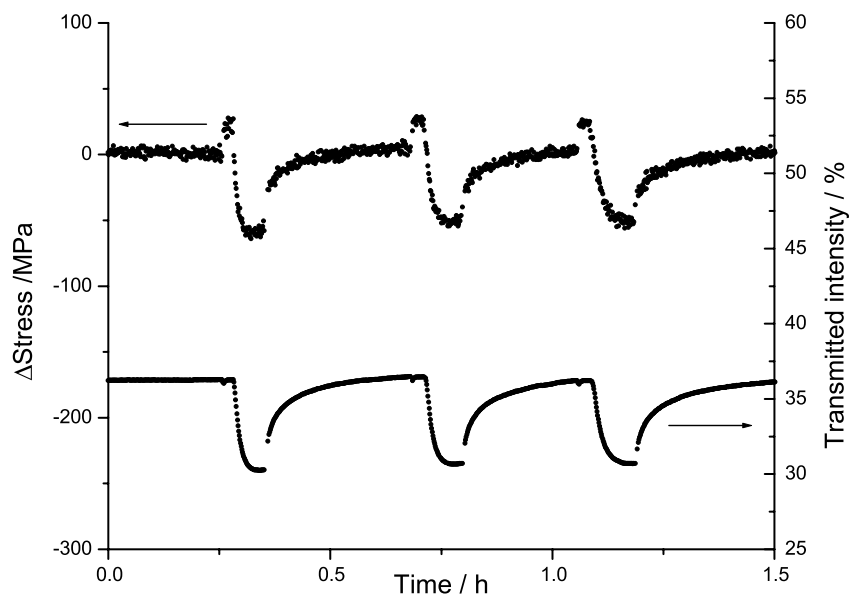


FIGURE 6.26: Stress and transmitted intensity for a 100 nm WO_x film covered by a 10 nm Pd film on a 150 μm glass substrate. The switching order was air, vacuum, hydrogen, vacuum, air... and so on. A reversible and elastic switching between two optically distinguishable states is observed.

6.11.2 Gadolinium

In Fig. 6.27 the transmittance and the corresponding stress changes of a switching experiment for a 50 nm Gd film covered by 10 nm Pd are shown. During the first loading in a gas mixture of 2 % H_2 in argon at a total pressure of 0.6 bar, the transmission increases rapidly from 4 % to 14 % as the film begins to form the $\text{GdH}_{3-\gamma}$ phase. Simultaneously the stress changes and reaches a maximum value of -2100 MPa, from which the stress relaxes to a constant value of -1750 MPa. The subsequent coloration in an oxygen containing atmosphere into the GdH_2 state is combined with a change of transmission to 11 % and a stress change to -1000 MPa. Subsequent bleaching and coloration steps involve a reversible switching between the two states GdH_2 and $\text{GdH}_{3-\gamma}$. The former is characterized by a stress of -1000 MPa and a transmittance of 11 %, while the latter is associated with a stress of -1750 MPa and a transmittance of 14 %. The optical switching between these two states involves a distinct local minimum in transmission with increasing hydrogen incorporation. This phenomenon has already been observed in the switching behavior of other rare-earth hydrides [50], [44], [60]. The reversible behavior involved in the switching between the dihydride and the trihydride phases is not affected by the irreversible stress relief in the initial formation of the GdH_2 phase, which is indicated by the decrease in the stress change found only during the initial switching.

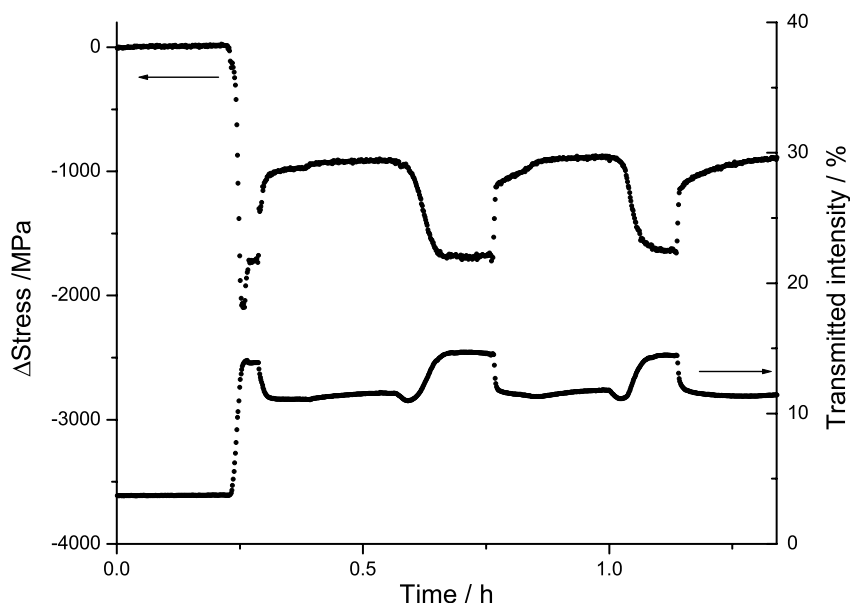


FIGURE 6.27: Stress and transmitted intensity for 50 nm gadolinium covered by a coating of 10 nm Pd on a 150 μm glass substrate. An irreversible stress change is visible during the first exposure to H_2 , but is followed by a reversible and elastic switching between two optically distinguishable states.

6.11.3 Magnesium

Fig. 6.28 displays the mechanical stress (top portion) and transmittance (lower portion) of a 150 nm thin Mg film covered with a 10 nm Pd catalyst film, which was subjected to gasochromic switching. Upon the first bleaching, which is done by exposing the sample to a gas atmosphere consisting of 2 % H_2 in argon at a total pressure of 1.5 bar, the transmittance is increased from 0.3 % to 18 % during a period of 4 hours. Simultaneously, the stress changes linearly to a minimum value of -650 MPa after 40 min, from where it is reduced to a value of -600 MPa, which remains constant for the remainder of the experiment. As the absorption coefficient of magnesium is higher than the absorption coefficient of MgH_2 , the change in transmitted intensity can be taken as a measure for the incorporation of hydrogen through the Lambert - Beer law. Thereby several interesting features become obvious. First, the transmission only starts to increase rapidly once the stress change has reached its maximum value of -650 MPa. Subsequently, the stress remains constant at -600 MPa, even though the increase of the transmission clearly shows that the hydrogen incorporation continues throughout the entire duration of the measurement. Hence we propose the following model to explain the features of the switching behavior of magnesium: During the first 40 min hydrogen is incorporated in the film, which responds elastically as the stress increases. When the stress reaches a value of -650 MPa, the stress is relieved by an irreversible mechanism. As shown in Fig. 6.29, magnesium films were found to crack and even delaminate. Hence we believe that cracks or defects start to form at this stage. The formation of defects also offer an entrance path for the hydrogen atoms into the magnesium, and hence the transmission changes more rapidly after

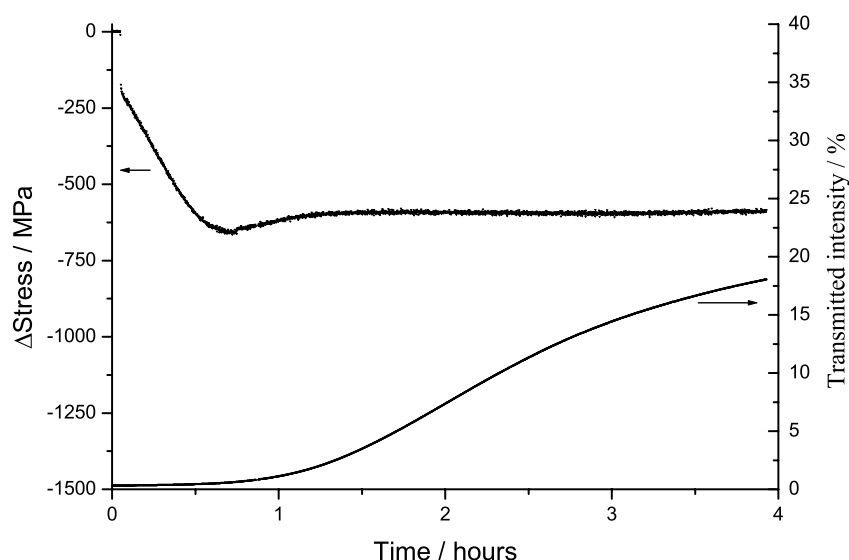


FIGURE 6.28: Stress and transmitted intensity for a 150 nm magnesium film covered with 10 nm Pd on a 150 μm glass substrate, which is exposed to a gas of 2 % in argon at a total pressure of 1.5 bar . An irreversible stress change is visible during this first exposure to H_2 .

the defects have been formed. The constant level of the stress change at -600 MPa during hydrogen incorporation indicates that the stress continues to be relieved, as the volume change induced by the continuing incorporation of hydrogen atoms from the elastic theory would induce a substantial stress change.

Another experiment supports the scenario of defect formation. In Fig. 6.30, a sample of 50 nm magnesium covered by 10 nm Pd is subjected to three bleaching and coloration cycles. During the first bleaching performed using a pure H_2 gas at a total pressure of 1.1 bar, similar features as those found in Fig. 6.28 can be seen. A maximum stress change of -650 MPa is reached, from which the stress relaxes to -500 MPa. During the loading the transmitted intensity increases to 28 %. Upon changing the ambient atmosphere to normal air, the transmittance is reduced to 0.5 % over several hours, while the stress change reverts to close to 0 MPa. Hence the initial values of mechanical stress and transmittance are reached. The second and third bleaching processes in H_2 gas are carried out after 3 hours and 6 hours respectively. In both cases the transmitted intensity increases, but only to 25 % and 23 % respectively, while the stress change in both cases continues to reach -500 MPa. From the spacing between the data points, whose time spacing (5 s) is constant, it can additionally be seen that the second bleaching step is slower than the first one, and the third bleaching process is even slower than the second one. Similar features hold for the second and third coloration steps. During the first coloration in air, the transmittance reaches a value of 5 %, during the second coloration a 9 % transmittance is achieved, while the third coloration yields a transmitted intensity of 12 %. Hence the contrast deteriorates upon switching. As for the bleaching processes, the coloration steps also become increasingly slow, as can be seen from

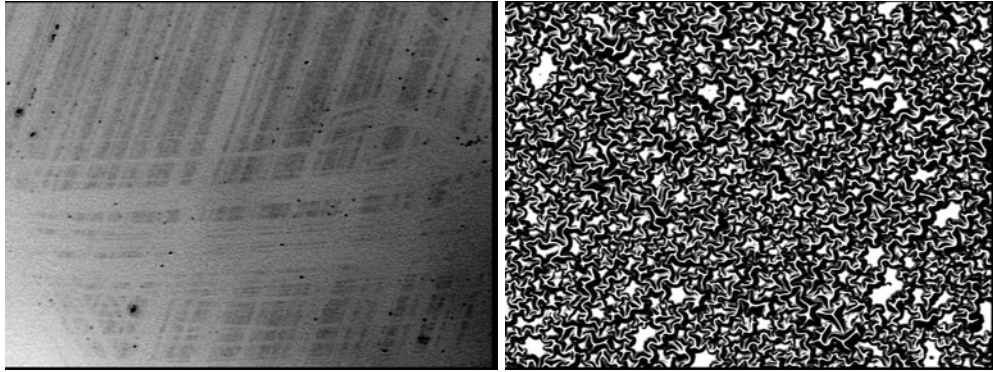


FIGURE 6.29: Microscope picture ($800\ \mu\text{m} \times 600\ \mu\text{m}$) of a Mg film after deposition (left), the cracks seen in a 150 nm magnesium film coated with 10 nm Pd on a $150\ \mu\text{m}$ glass substrate after two switching cycles (right). The cracks are presumably formed to relieve mechanical stress in the film during the bleaching in a hydrogen containing gas.

the distance between the data points. This experiment supports the scenario of crack formation. While cracks in the magnesium film stretching through the covering Pd film offer a favorable path for the hydrogen atoms into magnesium, they also allow reactive oxygen atoms generated at the surface of the catalyst to access the magnesium film, leading to increasing oxidation of it. The magnesium oxide formed is stable against hydrogen exposure and therefore leaves the oxidized Mg atoms in an optically transparent, non-metallic state, which is inactive to the optical switching process ($\Delta_f H(\text{MgO}) = -601.6\ \text{kJ/mol}$ and $\Delta_f H(\text{MgH}_2) = -75.34\ \text{kJ/mol}$). This scenario leads to a deterioration of the switching properties of the film, as seen in the experiment.

6.11.4 Comparison with elastic theory

A comparison between the observed mechanical stresses and the stresses that one would expect assuming elastic volume changes, gives another indication that the plastic stress relaxation observed in the transition from the metallic Gd to the GdH_2 beta-phase does in fact take place. The volume per Gd atom can be calculated based on the lattice parameters of the three phases [30], [29]. The resulting volume changes can now be used to calculate the expected value for the change in mechanical stress upon the transition by use of Hooke's law (eq. 2.3):

$$\Delta\sigma = \frac{E_f}{1 - \nu_f} \epsilon = \frac{E_f}{1 - \nu_f} \frac{\Delta V}{3V_0} \quad (6.38)$$

where it was assumed that the elastic modulus $E_f = 55\ \text{GPa}$ and the Poisson's ratio $\nu_f = 0.26$ are independent of the hydrogen content in the gadolinium film. The results are summarized in Table 6.5. It can be seen that the stress change in Gd when loaded into the GdH_2 phase is smaller in the experiment: It is $-2100\ \text{MPa}$ compared to an expected stress of $-3100\ \text{MPa}$. Similarly, the stress observed upon further loading into the $\text{GdH}_{3-\gamma}$ phase is lower than expected. This is in fact to be expected as the loading from the gas atmosphere leaves a ratio γ of GdH_2 in the film. In the case of magnesium, the expected stress exceeds the experimentally observed stress by far: $-6200\ \text{MPa}$

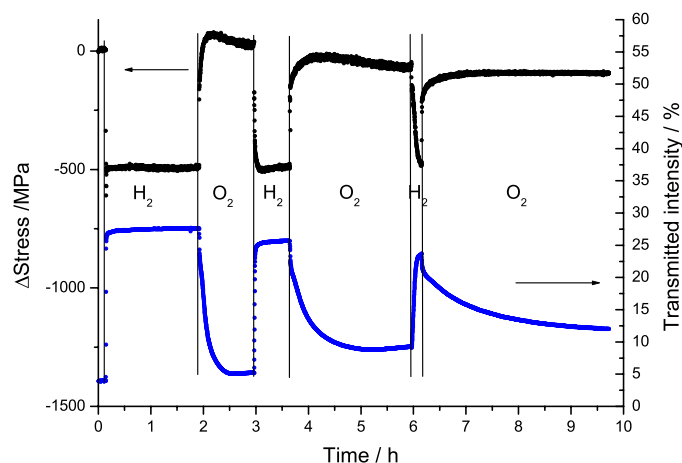


FIGURE 6.30: Stress and transmitted intensity from a 50 nm magnesium film coated with 10 nm Pd on a 150 μm glass substrate. The performance of the magnesium film deteriorates after the first exposure to oxygen, as the cracks formed during the first H_2 phase reduce the protective function of the Pd coating. Subsequent hydrogen and oxygen cycles lead to further deterioration of the switchable properties of the film.

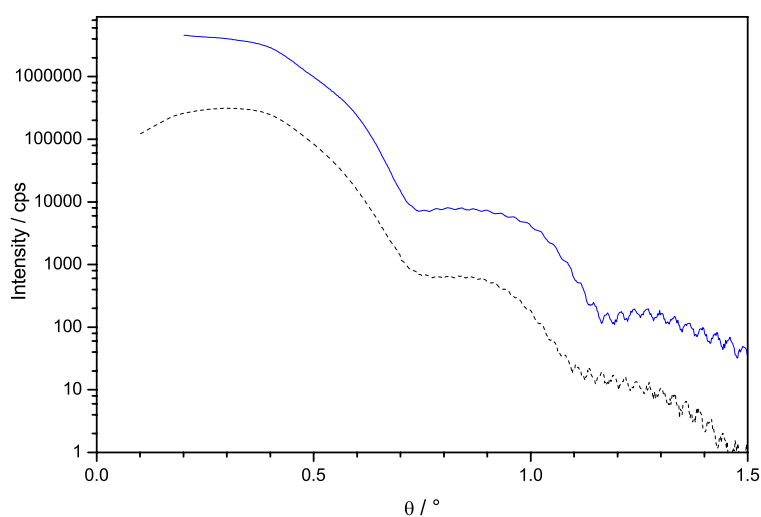


FIGURE 6.31: XRR scan of a 127 nm thick gadolinium film coated with a 10 nm palladium film in ambient air, and placed in a hydrogen partial pressure of 20 mbar (dashed curve). The decrease of the intensity upon loading with hydrogen arises from the Ar content in the 2% H_2/Ar gas used for the experiment. The shift of the oscillations at higher angles indicate a thickness change upon loading. Detailed analysis yields a thickness of 142 nm in the loaded phase. This corresponds to a thickness increase $\Delta d/d = 11.8\%$.

	$\Delta V/V[\%]$	$\Delta\sigma_{Exp}[MPa]$	$\Delta\sigma_{Meas}[MPa]$
$Gd \rightarrow GdH_2$	12.7	-3100	-2100 ⁱ
$GdH_2 \rightleftharpoons GdH_3$	22.6	-2200	-750 ⁱⁱ
$Mg \rightarrow MgH_2$	29.3	-6200	-650

TABLE 6.5: Change of volume per metal atom between the different gadolinium and the different magnesium phases, respectively. Using the volume change, the expected mechanical stress upon loading with hydrogen can be calculated using Hooke's law (eq. 2.3). ⁱ The maximum stress change observed before the stress relaxation. ⁱⁱ The observed change of stress between $GdH_2 \rightarrow GdH_{3-\delta}$.

	$\Delta\sigma_{Meas}[MPa]$	Nature of switching
Gd	-2100	1. Inelastic 2. Plastic
WO _x	-85	Elastic
Mg	-650	Plastic

TABLE 6.6: Comparison of the magnitude of the mechanical stresses as well as the nature of the stress changes associated with the optical switching for Gd, Mg and WO_x studied here. See text for explanation.

compared to -650 MPa. These findings support the scenario of stress relaxation upon loading in both gadolinium and magnesium as described above. Additional confirmation comes from in-situ XRR experiments. Here, the thickness change upon loading a 127 nm thick Gd film coated with a 10 nm Pd film with hydrogen at a partial pressure of 20 mbar was measured (Fig. 6.31). From the shift of the oscillations, a thickness increase of 15 nm was found. Assuming an elastic behavior of the film, the expected biaxial stress can be calculated using the relation 2.93:

$$\sigma = \frac{E_f}{1 + \nu_f} \epsilon_{z,total} \quad (6.39)$$

Hence the observed total strain $\epsilon_{z,total} = 0.12$ is expected to be associated with a biaxial stress of -5150 MPa. As seen in the measurements of mechanical stress, we only observe stresses of the order of -2100 MPa. This also indicates that stress is in fact relieved during the loading of gadolinium.

6.11.5 Comparison of the materials studied

The comparative results of the studies of Mg, Gd and WO_x above are summarized in Table 6.6. Based on these findings, it is evident that tungsten oxide shows a mechanical behavior which is very much suited to an application in the field of switchable coatings. The mechanical stresses that arise during switching are relatively low and the processes are reversible.

Gadolinium also shows reversible behavior in the switching between the dihydride and the trihydride states, but this switching is preceded by an initial inelastic and irreversible process. Additionally, the stress change associated with the switching in Gd is an order of magnitude larger than the stress change for tungsten oxide.

For Mg irreversible inelastic processes is found to occur during initial switching. This was shown to lead to cracking and deterioration of the switchable properties of the film.

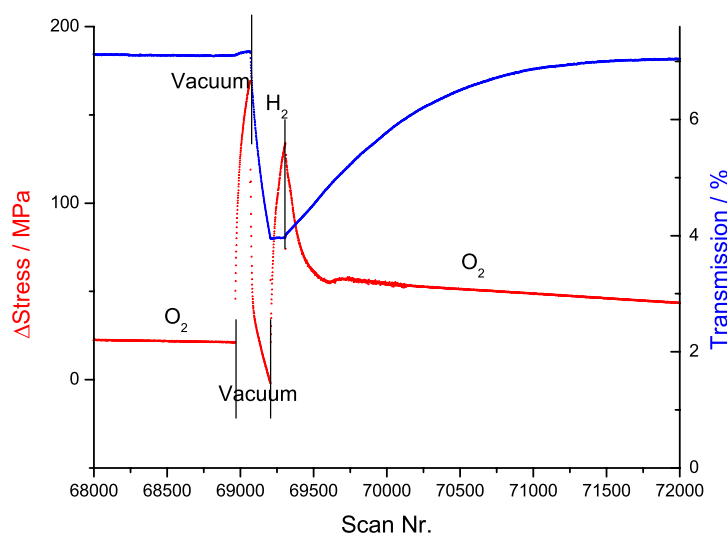


FIGURE 6.32: The change of transmission (top) and stress (bottom) upon switching in of a 8 nm Pt / 692 nm WO_x / 150 μm glass sample. The evacuation of the gas cell is associated with a large stress change even though no change of transmission is observed.

6.12 Detailed study of tungsten oxide

In the previous section it was shown, that when considering the applicability of the studied materials in smart window technology from a perspective of mechanical stresses, WO_x is the material most suited. Therefore further studies into the topic of stress in tungsten oxide were carried out. The results of these studies are presented in this section.

After the conclusive studies above, both regarding the choice of catalyst film and the choice of the active switchable film, a sample was produced courtesy of Interpane [52] consisting of 8 nm Pt / 692 nm WO_x / 150 μm glass.

This sample was subjected to switching cycles as presented above i.e. coloration in H₂ and bleaching in O₂ (fig. 6.32), which were made possible by the use of the purpose-built gas system described in section 3.3.2. An example of the results of initial experiments on this sample is shown in figure 6.32.

Interestingly, during the first phase of the measurement, significant stress changes are found in the initial evacuation or vacuum phase. Starting from a value of 25 MPa in the preceding oxygen phase, a tensile change of stress of about 170 MPa in fact arises during the brief evacuation of the gas cell. The first coloration in hydrogen is associated with the expected change of stress to a value of -10 MPa. However, it is vastly unexpected that the subsequent vacuum phase again is associated with a change of stress to 150 MPa, especially considering that the transmitted intensity does not change simultaneously. Indeed further cycles of hydrogen phases followed by vacuum phases show that this behavior is reversible (figure 6.33): In vacuum a stress change towards a value of about 200 MPa is reached, while the hydrogen phases are associated with changes of

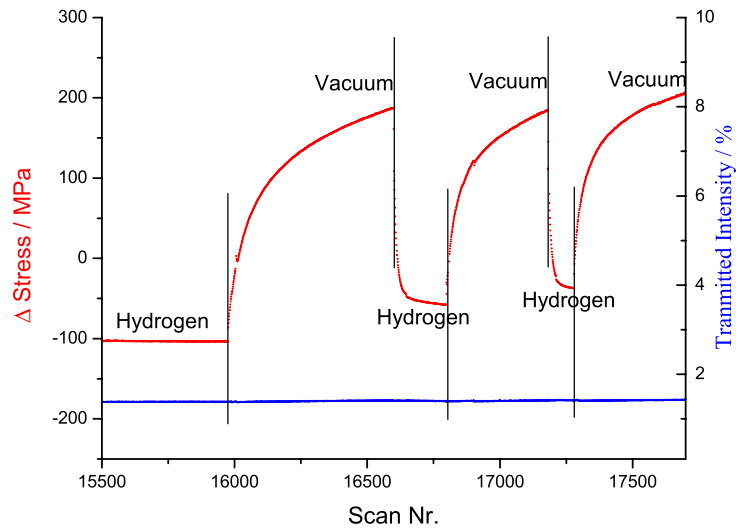


FIGURE 6.33: The change of stress (top) and transmission (bottom) upon switching of a 8 nm Pt / 692 nm WO_x / 150 μm glass sample. At the beginning of the measurement, the film is in its fully colored state. The shown vacuum and hydrogen cycles show large stress changes. However, these stress changes are not associated with any change in the transmission.

stress towards the compressive region. The most interesting feature of these cycles is however, that these stress changes are not associated with any simultaneous transmission changes.

On the basis of this measurement, the following idea was considered: Is the porous structure responsible for the stress changes in tungsten oxide?

If this theory was to be verified, a direct coupling between the density and the change of stress upon coloration should be found. Additionally, such investigations could possibly show that the coloration velocity depends on the density, as in contrast to a massive film a porous structure would allow easier penetration of the hydrogen atoms into the film.

In the following section, the results of a detailed study on the relation between density and stress in tungsten oxide films will be presented.

6.12.1 Stresses as a function of the density in WO_x films

The detailed characterization of the sputter properties of tungsten oxide carried out by C. Salanga [111] and H. Weis [141] shows, that the density of sputtered tungsten oxide films depends dramatically on the total pressure used during deposition. In fact, films with densities in the range of 5.5 g/cm^3 to 6.65 g/cm^3 can be produced. The exact dependence of the density of tungsten film on the total sputter pressure is shown in figure 6.34. It can be seen that the lowest densities are achieved for pressures below 0.8 Pa and for pressures above 3 Pa, while the highest density is found in film sputtered at total pressures ranging from 0.8 - 3 Pa.

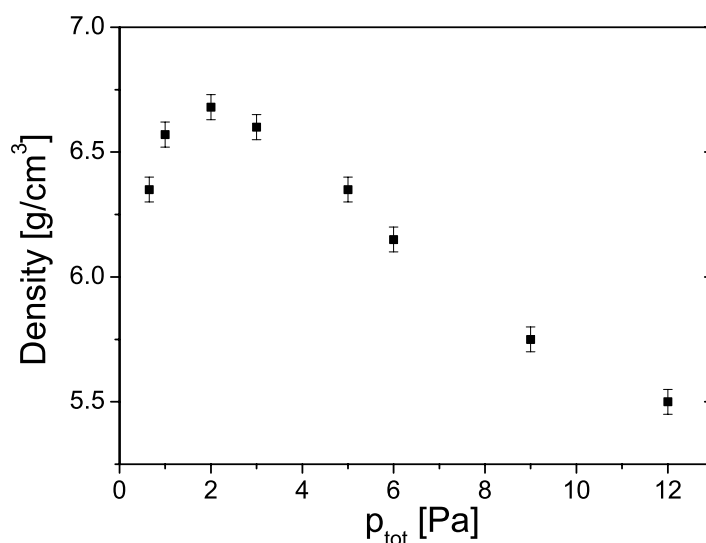


FIGURE 6.34: The density of WO_x changes as a function of the total sputter pressure during deposition. High density films are produced for total pressures ranging from 0.8 to 3 Pa. Films of lower density are produced at the lowest and in particular at the highest total pressures.

For the purpose of studying the dependence of mechanical stresses on the density of the tungsten oxide films, a series of samples were produced. The total sputter pressures used were: 0.7, 1, 2, 3, 5, 6, 12 Pa. Each of these tungsten oxide film were deposited with a thickness of 200 nm on 150 μm glass substrates, and subsequently coated with a 1 nm thin Pt film.

All samples were subjected to a sequence of pressures consisting of 60 s evacuation followed by a longer phase in H_2 at a pressure of 2 bar. This phase was allowed to continue until constant stress and transmittance levels were achieved. Then after another 30 s of evacuation, 1 bar of O_2 entered the gas cell to bleach the films. The results of these measurements are shown in figure 6.35.

When studying these results, several features become evident. First, the mechanical stress associated with the loading in hydrogen is not constant. It varies substantially with the film density. Second, the time needed for the stress and the transmission to reach a constant value depend dramatically on the film density, as does the relative change of transmittance associated with the coloration.

These general trends become obvious in the figures 6.36 and 6.38, which capture the general results of these measurements. It can be seen that films of high density show the lowest stress changes and also the lowest change in transmittance, while the films of lowest densities show much larger stresses associated with the coloration and also show the largest change of transmission.

On other hand, the coloration in films of high density proceeds very slowly indeed, while the process happens a lot quicker in the films of lowest density (fig. 6.38).

This means that it can be concluded, that the mechanical stress change upon loading in hydro-

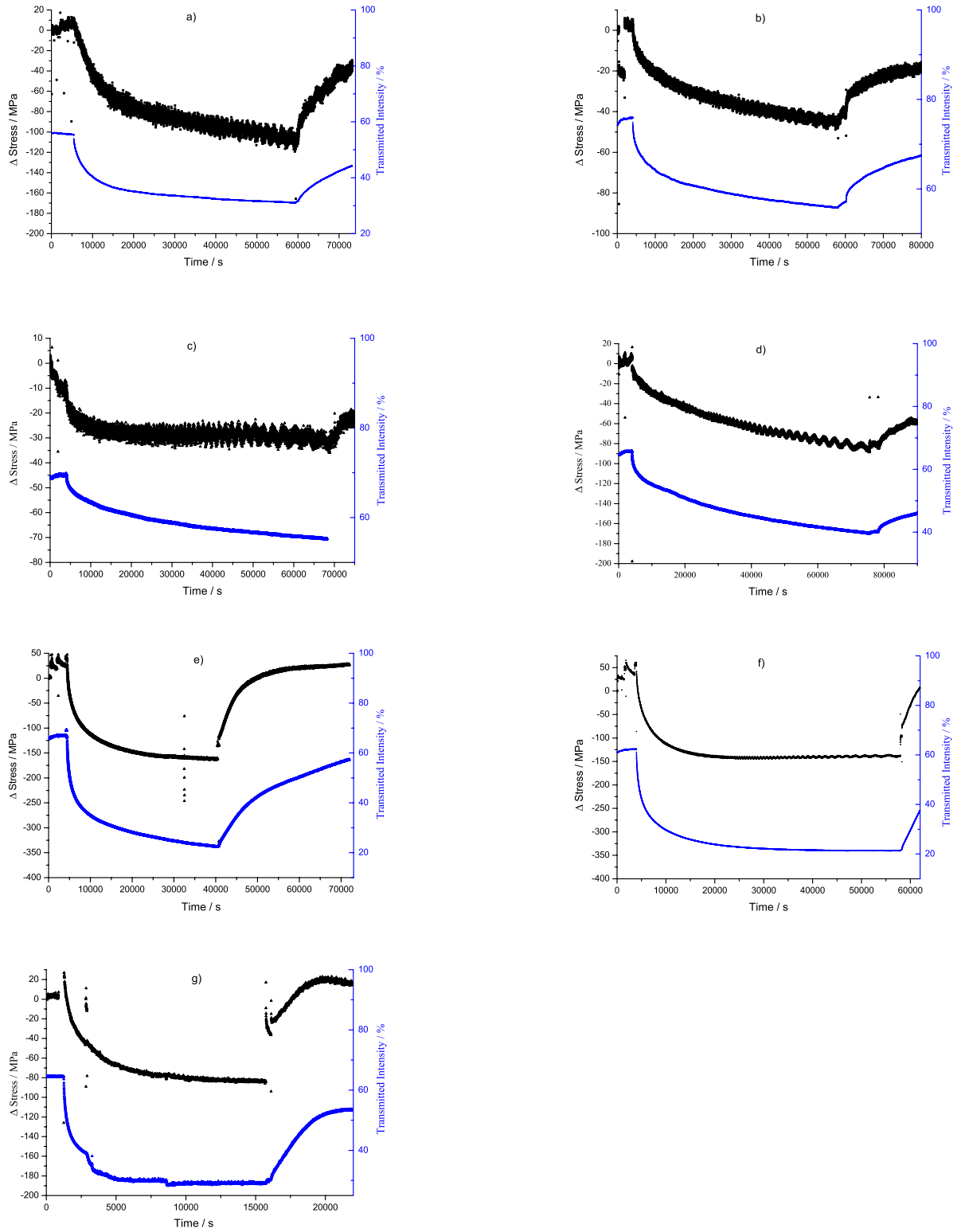


FIGURE 6.35: The change of stress (top) and transmittance (bottom) upon exposure to an atmosphere of 2 bar H_2 for WO_x films of varying density. a) 0.7 Pa, b) 1 Pa, c) 2 Pa, d) 3 Pa, e) 5 Pa, f) 6 Pa and g) 12 Pa.

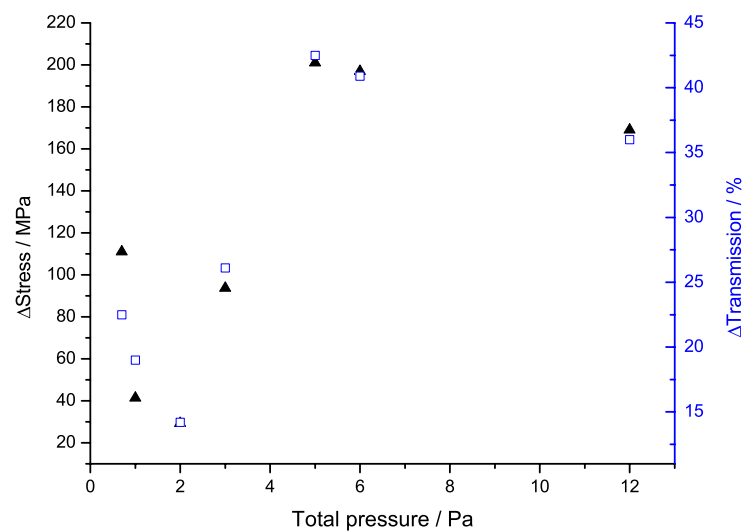


FIGURE 6.36: The change of stress (up triangles) and transmittance (open squares) upon exposure to 2 bar H_2 as a function of the sputter pressure for the WO_x films.

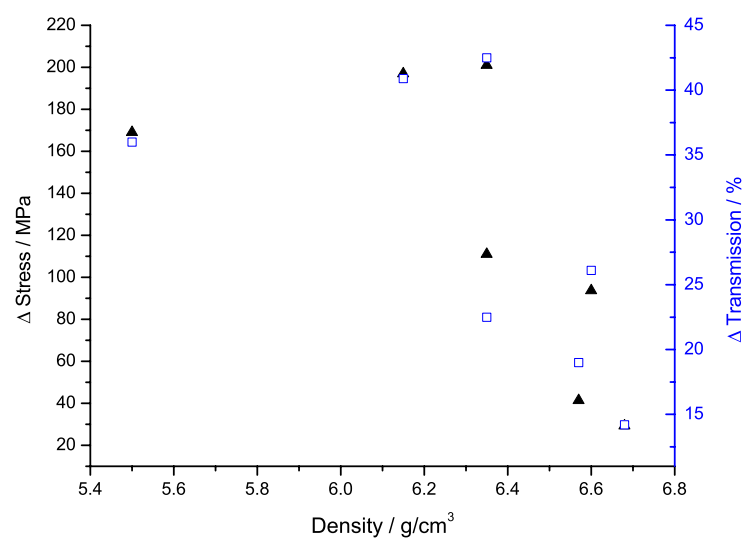


FIGURE 6.37: The change of stress (up triangles) and transmittance (open squares) upon exposure to 2 bar H_2 as a function of the density of the WO_x films.

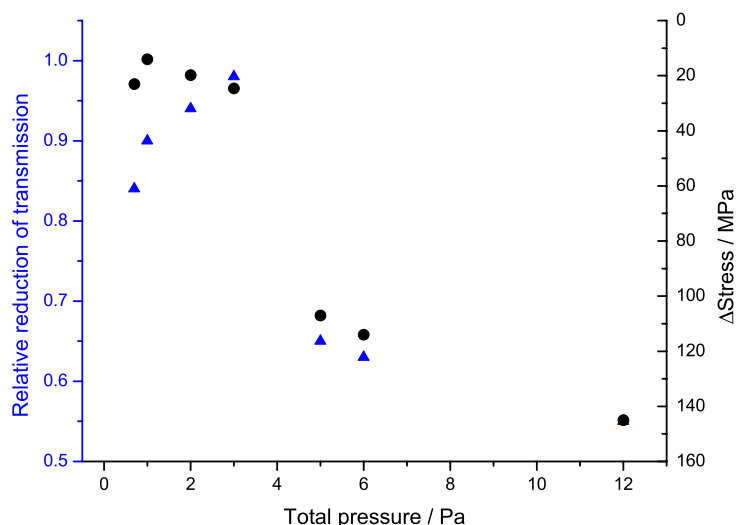


FIGURE 6.38: The coloration velocity (up triangles) and stress change (closed circles) as a function of the total sputter pressure of the WO_x films when exposed to 2 bar H_2 . The changes shown were taken after 30 min.

gen depends on the density of the tungsten oxide films. WO_x of high density shows the lowest compressive stress change at 30 MPa, while films of low density show the highest stress changes at 200 MPa. However the correlation is not completely unambiguous. Samples of similar density sputtered at different total pressures show somewhat different properties. However, the theory put forward in the preceding section is supported by the findings of this study. This means, that the build up of stress in tungsten oxide films is accounted for by gas atoms entering the pores of the film thereby introducing compressive stresses.

That the coloration velocity increases in films of lower density can be understood on the basis of the coloration model shown in chapter 6.3.1. The increased porosity allows the hydrogen atoms to penetrate into the film, and hence allow the coloration steps to take place at a higher velocity.

6.12.2 Stress changes and the models for coloration.

Each of the models for coloration i.e. the hydrogen-intercalation model and the model based on the desorption of oxygen upon coloration, predict a certain order of the processes responsible for the coloration and bleaching of WO_x . In this section the stress changes observed will be associated with the processes in each of the models.

The hydrogen-intercalation model.

Beginning with the stress change cycle shown in figure 6.32, each of the steps of the cycle can be interpreted based on the hydrogen-intercalation model (figure 6.39):

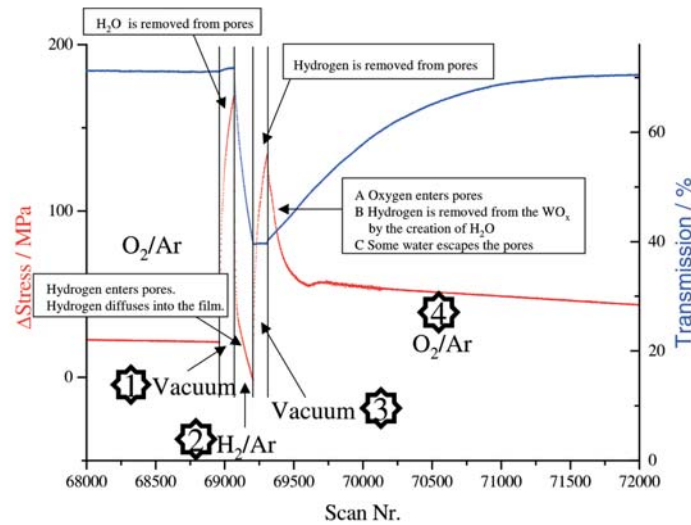


FIGURE 6.39: The stress changes upon optical switching in WO_x can be explained by the hydrogen-intercalation model, as indicated in the figure (see text for details).

- In the bleached state the pores are filled with H_2O molecules.
- When exposing the sample to "vacuum" conditions, the water molecules will be removed from the pores. This leads to a stress change towards tensile stresses.
- A subsequent exposure to a hydrogen gas leads to the filling of the pores with hydrogen, from where hydrogen atoms diffuse into the tungsten oxide film, where they form color centers. Both the filling of the pores and the diffusion of hydrogen into the film lead to a stress change towards the compressive region.
- The next vacuum phase leads to the an evacuation of the pores. This results in a stress change towards the tensile region. Associated with this evacuation no change of transmission change is observed, meaning that the concentration of color centers remains constant in this phase i.e. no hydrogen is removed from the film, only from its pores.
- During the bleaching carried out in an oxygen atmosphere, oxygen atoms enter the pores. This leads to a stress change towards the compressive region. Additionally the hydrogen atoms from the films interior are removed into the pores to form water molecules which can slowly leave the pores. The removal of hydrogen atoms from the film is associated with a change of stress towards the tensile region; however this change might be balanced by the stress change towards the compressive region associated with the formation of water molecules. Any water molecules which might leave the pores would induce a change of stress towards the tensile region. However, as the bleaching is associated with the filling of the pores, a change of stress towards the compressive region, as it is observed, is readily expected.

Hence the direction of the stress changes observed in every step of the switching cycle can be explained by the hydrogen intercalation model.

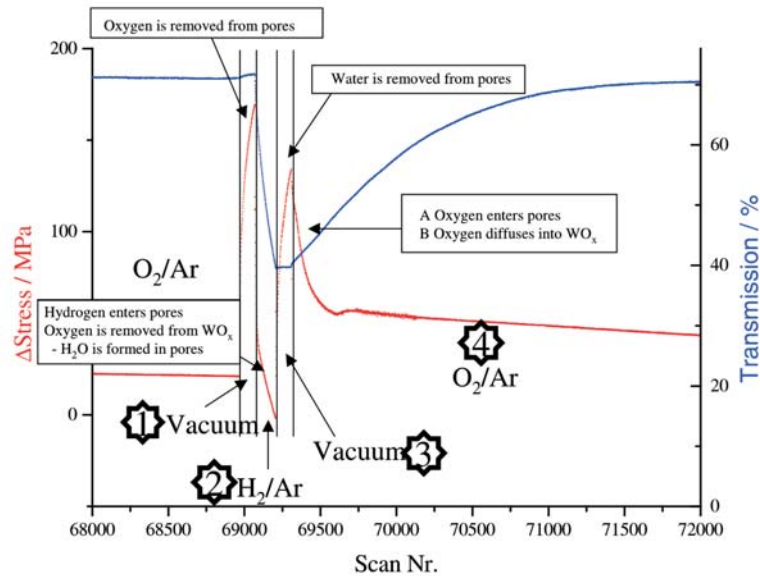


FIGURE 6.40: The stress changes upon optical switching in WO_x can be explained by the model based on the desorption of oxygen upon coloration (see text for details).

The desorption of oxygen upon coloration model

The model based on the desorption of oxygen upon coloration can however also be used to explain the stress changes observed during switching (figure 6.40):

- In the bleached state, the pores are filled with oxygen atoms.
- During evacuation, the oxygen atoms will be removed from the pores. This leads to a stress change towards tensile stresses.
- The following exposure to hydrogen leads to a filling of the pores with hydrogen. From there, two hydrogen atoms form a water molecule with an oxygen atom from inside the film. The filling of the pores leads to a stress change towards the compressive region, while the removal of oxygen from inside the film will induce a stress change towards the tensile region. This change will however be opposed by a stress change towards the compressive region induced by the presence of the oxygen in the pores. Hence a total stress change towards the compressive region is expected, as it is also observed.
- The subsequent vacuum phase leads to the a removal of the water molecules from the pores. This results in a stress change towards the tensile region. Associated with this evacuation no change of transmission change is observed, meaning that the concentration of color centers remains constant in this phase.
- By exposing the film to an oxygen gas, it is bleached. The associated filling of the pores with oxygen atoms induce a stress change towards the compressive region. From there oxygen atoms diffuse into the film to fill vacancy sites. This also leads to a stress change towards the compressive region.

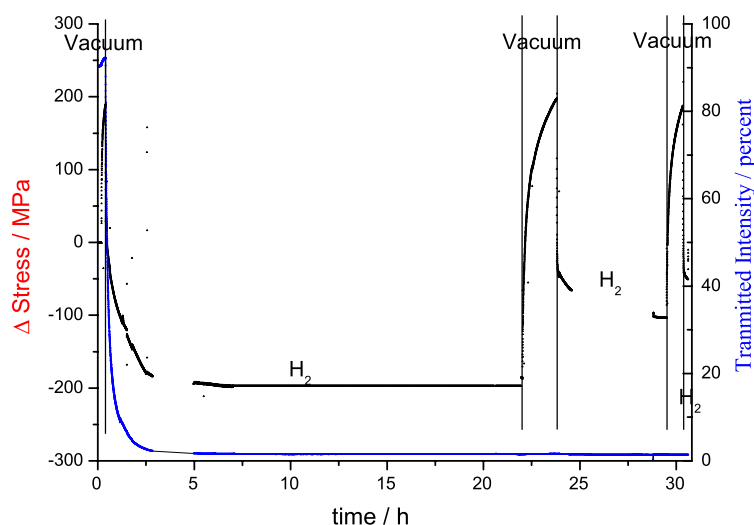


FIGURE 6.41: A stress cycling in colored state. After the first coloration, the film is exposed to alternating vacuum and hydrogen phases. The shift of the stress level (top) indicates that the model based on desorption of hydrogen upon coloration is credible(see text for details).

Hence this model can also be used to explain the stress changes observed during a switching cycle.

Stress cycling in the colored state

Further information on the processes taking place in the film can be gathered from a "stress cycling" in the colored state as shown in figure 6.41.

After the first evacuation cycle, a stress change towards the tensile at 195 MPa is observed. Then during coloration in hydrogen at a partial pressure of 4 bar, the stress changes to a value of -190 MPa, while the film is fully colored to a transmitted intensity of about 1%. In the subsequent vacuum phase, the stress change returns to a value of 195 MPa. However, the second hydrogen phase at a partial pressure of 4 bar is only associated with a stress change to -90 MPa. This trend is reproduced in the third cycle: A stress level of 195 MPa is associated with the vacuum phase, while the hydrogen phase leads to a stress change to -90 MPa. Hence a large difference between the first hydrogen phase and the subsequent ones is found.

This finding cannot be explained by the hydrogen intercalation model. In this model, the difference between the phases would only be, that during the first hydrogen phase hydrogen enters the pores and diffuses into the film, while the subsequent hydrogen phases only fill the pores with hydrogen. However as these cycles are carried out in the fully colored state, no change of the transmission is observed. This means that the concentration of color centers i.e. the hydrogen concentration, can be regarded as constant. Therefore the contribution to the stress from the hydrogen inside the film is expected to be constant in the three hydrogen cycles. As the hydrogen pressure

applied is also constant, equal compressive stresses would have been expected, as opposed to the shift in stress between the first and the subsequent hydrogen phases observed.

On the other hand, the model based on desorption of oxygen upon coloration offers a possible explanation. In the first hydrogen phase i.e. upon coloration, oxygen is removed from inside the film to the pores where H_2O molecules are formed. This creates a stress change towards the compressive region in the pores, while the removal of oxygen from inside the film induces a change of the stress towards the tensile region. As the pores are evacuated in the subsequent vacuum phase a slight change of stress should hence be observed, as it is the case. Then in the second hydrogen phase the pores are filled with hydrogen. This time there is no removal of oxygen, as the transmission is observed to be constant. Hence the stress change towards the compressive region is only induced by the hydrogen atoms in the pores and not by oxygen atoms from the film. Thus a smaller compressive stress change is expected as it is observed. The third hydrogen cycle only reproduces this finding.

Based on these results, it is evident that the model based on the desorption of hydrogen is more credible than the hydrogen intercalation model.

In-situ thickness measurements

Further evidence supporting the validity of the model based on desorption of oxygen upon coloration comes from in-situ thickness measurements during switching as they were carried out using ellipsometry [79]. As seen in figure 6.42, a tungsten oxide film of 548 nm thickness was subjected to a switching cycle. Upon coloration in 2 % H_2 in argon at a total pressure of 1 bar, the film thickness is found to decrease to 545 nm. During subsequent bleaching in an oxygen atmosphere at 1 bar, the original film thickness of 548 nm is reproduced. The associated spectroscopic transmittance measurement, which is also simulated along with the ellipsometry data shows a similar thickness decrease from 541 nm in the initial state to 534 nm in the colored state. This means that a thickness decrease in the range of 0.5 - 1.3 % is observed upon loading with hydrogen.

The significance of this finding is evident, when one considers possible explanations by the two models for coloration.

In the hydrogen intercalation model, hydrogen diffuses into the film. Hence one should expect a thickness increase as the volume of the film is increased. On the other hand the volume of the film is expected to decrease in the model based on desorption of oxygen upon coloration. Hence one would associate a thickness decrease with this model. As a thickness decrease is in fact found from *in-situ* ellipsometry, this can be regarded as another indication of the validity and credibility of the model based on oxygen desorption upon coloration.

6.13 Summary

Switchable coatings are of considerable technological interest because of their interesting applications. However, the volume change associated with the incorporation of gas atoms in the solid

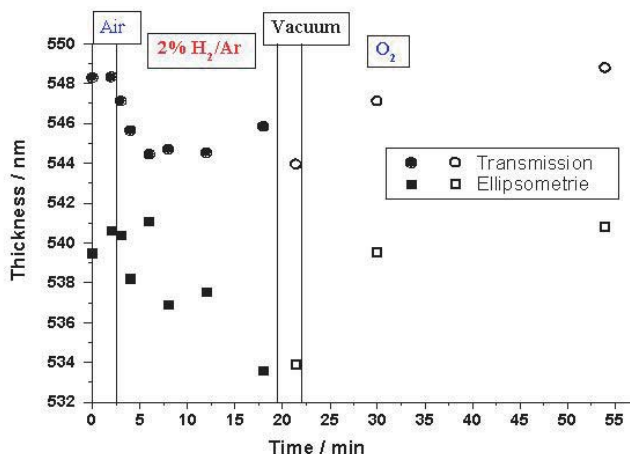


FIGURE 6.42: Using *in-situ* ellipsometry the thickness of a tungsten oxide film was measured during coloration and switching. It can be seen that the thickness decreases upon coloration and increases during bleaching. This supports the validity of the model based on desorption of oxygen upon coloration.

film induces significant mechanical stresses in such films. As described in chapter 2, mechanical stresses can lead to failure of the film through cracking or delamination. For this reason, it is important to understand the mechanical stresses in these films.

In this work, a comparative study of the mechanical stresses in switchable materials belonging to three different material classes i.e. tungsten oxide, gadolinium and magnesium, were studied. Additionally, the switchable properties of the catalyst and protective coatings of Pd and Pt were studied. It was found that the stresses in Pt are a factor of 25 lower than those found in the beta-phase of Pd. Additionally, Pt shows almost no change of optical properties upon loading with hydrogen. For this reason the films used for mechanical stress measurements should preferably be coated with Pt rather than Pd catalyst films.

The comparative study of GdH_x , MgH_x and WO_x showed that the switching of Mg is associated with stresses of the order of -600 MPa upon loading. Additionally, inelastic stress relief processes were observed leading to film cracking. This film cracking was shown to allow the formation of inactive magnesium oxide upon bleaching, and hence to a deterioration of the switching properties of the film. For Gd large stresses of the order of -2100 MPa were observed. The stress changes were however found to be much lower than the stress expected for elastic behavior. During the initial switching to GdH_2 , inelastic stress relaxation was observed. However the subsequent switching between the GdH_2 and the GdH_3 states was found to behave elastically and reversibly. For tungsten oxide stress changes of the order of -85 MPa were found. The switching between the colored and the bleached state was found to be reversible and elastic, as no stress relaxation was observed. Hence it was concluded that WO_x from a perspective of mechanical stress is the material most suited for application, as it combines low mechanical stresses with elastic processes.

As tungsten oxide was found to be very promising for application, it was subjected to extensive studies. It was found that a correlation between the mechanical stress and the density of the tungsten oxide films exists. Hence it was concluded that the majority of the mechanical stress observed in WO_x arises from gas atoms present in the pores of the tungsten oxide structure. Additionally, a correlation between the density of films and the kinetics of switching was found. In films of low density the coloration and bleaching steps take place at a higher velocity than for films of high density.

In section 6.3.1 two models for the switching of tungsten oxide were presented. Based on stress measurements in the fully colored state, it was found that the stress changes upon repeated switching between vacuum and a hydrogen atmosphere could only be explained by the model based on oxygen desorption upon coloration. This finding was supported by the thickness decrease upon coloration that was found using *in-situ* ellipsometry.

Chapter 7

Phase change materials

One only has to look at the size of the market for data storage to realize how interesting the associated technologies and their research are to humans focused on economic success. This market has a net annual revenue of \$114 billion in 2002 [128]. Hence companies across the world invest huge amounts of money and manpower to make them competitive in this market. For this reason amongst others, the modern computer which nowadays can be found in almost every office and every home in the modern world, has a performance that is very impressive considering the capabilities of the initial personal computers from the early eighties. Graphics resolution and -capacity, processor speed and sound quality are among the aspects that have been improved considerably. Even with this in mind, the progress that has been made in field of data storage is amazing. The initial PC's were only equipped with a magnetic 5.25" floppy disk of 360 kB capacity, while systems having multiple storage options totalling hundreds of GB are common today. Although magnetic storage devices remain the primary media for storage, a significant amount of data is today stored using optical storage devices. This optical data storage technology has the huge advantage compared to magnetic systems, that it allows easy back-up of information compared to early magnetic tapes, and also allows the easy physical transfer of large amount of data from location to location by means of the compact disc (CD) and the digital versatile disc (DVD), which have storage capacities that are several hundred times as large as that of a normal 3,5" floppy disk. While the CD and DVD were initially write-once media, the recent development of the now also commercially available rewritable DVD allows the optical technology to compete with magnetic media.

The principle of optical storage systems is called "phase change optical recording". It exploits the significant difference in optical properties of two different physical states of the active material; the amorphous and the crystalline state. Ingenious methods of heating microscopic volumes of the material by irradiation enable a phase transition between these two states, hence creating areas with a reflection that differs from that of the surrounding matrix and thus allowing the storage of information. Today, materials that allow a reversible phase transition between the two states are used. This means that the data storage media such as CD-RW and DVD-RW work as rewritable media.

Even though these optical storage devices have been extremely successful in the past, there are still several improvements to be made in various fields. Other technologies allow higher storage

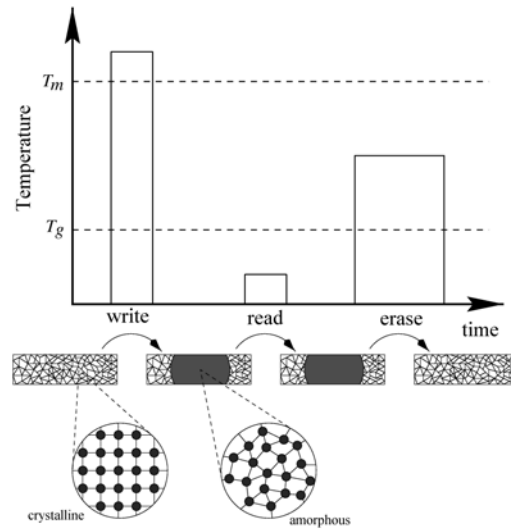


FIGURE 7.1: Principle of phase change recording. By an intense pulse the area in the crystalline film is heated above the melting temperature T_m . Because of the rapid cooling, the region is stabilized in the amorphous phase. The reading takes place by monitoring the reflection of a laser pulse that does not heat the sample above the glass transition temperature T_g . The amorphous mark is erased by a pulse that heats the mark above T_g and has a longer duration. From ref. [143].

densities and data transfer rates and hence represent areas where phase change optical recording must improve to make the technology even more competitive.

The objective of this work is to investigate the mechanical stress associated with the phase transition. This is important in relation to the cyclability of the phase change film i.e. the number of reversible phase transitions possible without deterioration of its physical properties. As the cyclability is related to the elastic or inelastic properties of the stress change upon the phase transition as seen from chapter 2, these stress measurements have a direct impact on the comprehension of the cyclability of phase change materials. The importance of understanding this topic arises as a limited cyclability could be a major concern, if phase change media were to replace hard disk drives in demanding applications such as file servers etc. It has been found that the cyclability is affected by various properties of the phase change media, including the temperature profile in the layer stack [98], [72], the dielectric layers surrounding the phase change film [26], [150] and even its composition [110], [12]. The stress changes associated with the phase transitions have however not been studied in detail. In this work it was carried using the furnace described in section 3.4.

In the following section, the principle of phase change optical recording, and the theory of the phase transition including an in-depth look at the theory of glass transitions will be presented (sections 7.2 to 7.5). Then in section 7.6 a group of suited phase change materials are presented, while the stress measurements on these materials are found in sections 7.7 to 7.9.

7.1 Principle of phase change recording

Phase change recording is based on the reversible transformation between an amorphous and a crystalline state of microscopic volumes of the phase change film. The transformation is induced by heating of the volume by irradiation of a laser pulse. The principle of operation is shown in figure 7.1. Starting from the crystalline state, a tiny area (bit) of the film is irradiated by a focused laser beam. This results in a local temperature increase above the melting temperature, T_m . After the irradiation the volume cools down rapidly with a rate of 10^9 - 10^{10} K/s. Cooling rates of this magnitude means that the temperature of the bit reaches the glass transition temperature, T_g , before the crystalline state is formed. Hence the disorder of the molten phase is frozen, and the resulting bit is amorphous. From this state, the crystalline state can be reproduced by heating the volume to a temperature above T_g but below T_m . Since the optical properties of the amorphous and the crystalline states differ quite dramatically - the contrast ratio is of the order of up to 70%, the state of the bit can be determined by observing the reflection or transmission of a laser beam of such low intensity, that it does not modify its structure.

7.2 Theoretical description of structural phase transitions

In this section the transition from crystalline to amorphous and vice versa will be described from a thermodynamical point of view allowing an understanding of the material properties required for a successful application in phase change technology.

When the solid material is heated above its melting temperature T_m , it becomes a liquid. Depending on the cooling rate as well as the properties of the material itself, it can enter two different configurations of atomic arrangement. For low cooling rates it can crystallize by nucleation and growth of crystalline nuclei. This discontinuous process leads to a crystalline state. Another process is also possible, though. At high cooling rates, the liquid can enter an undercooled state in which it is continuously hardened as the dynamics of the liquid is slowed down. In the undercooled state, the liquid remains in internal equilibrium, meaning that the size of the molecular mobility still allows a sampling of all thermodynamically accessible molecular configurations. This state of internal equilibrium is lost at the glass transition temperature T_g . The reason is that the timescale of atomic rearrangement becomes larger than the time window available. Hence the undercooled liquid is configurationally frozen at this temperature. Its atomic arrangement represents the statistical structure of a liquid at a given time, and hence it has no long range translational symmetry. This structure is labelled "amorphous" and the frozen solid state is called a "glass". The minimal cooling rate necessary for glass formation depends on the material itself. For easy glass forming materials such as SiO_2 , cooling rates larger than 10^{-2} K/s are necessary, while marginal glass forming materials such as Fe_9B_5 requires cooling rates larger than 10^{12} K/s [122].

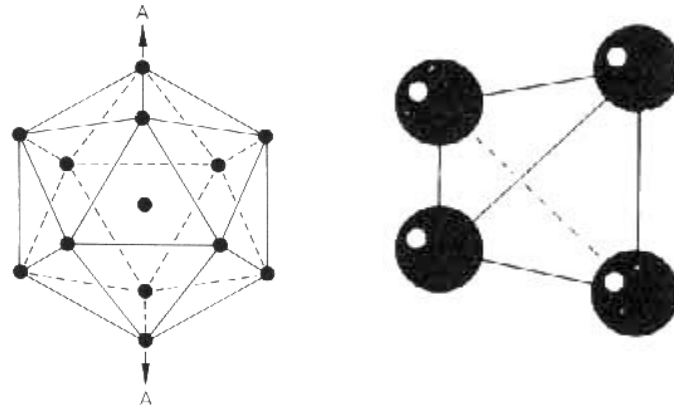


FIGURE 7.2: The structure of glasses. The icosahedron structure (left) consists of 20 tetrahedrons (right), that are arranged in to share a common vertex. This means that they are slightly distorted. From ref. [51].

7.3 Atomic configuration of glasses

In a description of the structure of glasses there are two scales to consider. Most important is the fact that glasses do not possess a periodic long range order. This even applies to the case of infinitively slow cooling, where the structure is determined by short range rules for atomic arrangements that only allow one unambiguous way of constructing the entire structure. The result is a state of zero entropy. As the case of infinitively slow cooling cannot be obtained experimentally, all glasses possess a residual entropy at low temperatures as a result of their abandoning of internal equilibrium. On a short range scale, metallic glasses on the other hand do possess a degree of order. The atoms are ordered in a structure that resembles that of icosahedral quasicrystals. The icosahedron which is characteristic for this structure can be seen in fig. 7.2.a. It consists of 20 tetrahedrons (fig. 7.2.b), which are slightly distorted allowing them to share a common vertex in the icosahedral structure. As mentioned above, the icosahedrons in a glass are not arranged with a long range order.

7.4 A thermodynamic approach to the formation of glasses

Thermodynamics offer a straightforward framework for considerations regarding the stability of glasses. As described in section 7.2, the glass is not in internal equilibrium as this property is lost at the glass transition temperature. A simple law of thermodynamics states, that a system at constant temperature and pressure is in a state of equilibrium at the global minimum value of the Gibb's free energy. Hence glasses will tend to lower their Gibb's free energy in order to reach their equilibrium atomic configuration. The Gibb's free energy is given as (6.16):

$$G = H - TS \quad (7.1)$$

Hence the difference in Gibb's free energy between the liquid and the crystal, ΔG_{lc} , can be expressed as:

$$\Delta G_{lc}(T) = \Delta H_{lc}(T) - T\Delta S_{lc}(T). \quad (7.2)$$

Expressions for the enthalpy and the entropy differences can be found by considering the basic thermodynamic relations:

$$dH = C_p dT \quad (7.3)$$

and

$$dH = TdS + VdP \quad (7.4)$$

Assuming a constant pressure, the following expressions can now be deduced:

$$\Delta H_{lc}(T) = H_l(T) - H_c(T) = \Delta H_f + \int_{T_m}^T \Delta C_{p,lc}(T') dT' \quad (7.5)$$

and

$$\Delta S_{lc}(T) = S_l(T) - S_c(T) = \Delta S_f + \int_{T_m}^T \frac{\Delta C_{p,lc}(T')}{T'} dT' \quad (7.6)$$

where $\Delta H_f = H_l(T_m) - H_c(T_m)$ is the heat of fusion, which represents the heat that is used to break the bonds upon melting of the crystal, and $\Delta S_f = S_l(T_m) - S_c(T_m)$ is the entropy of fusion.

An important relation appears when one considers that the change in Gibbs free energy at the melting temperature for a single component system is:

$$\Delta G_{lc}(T_m) = 0 \quad (7.7)$$

Hence the following relation between the heat of fusion and entropy of fusion can be found:

$$\Delta S_f = \frac{\Delta H_f}{T_m} \quad (7.8)$$

The thermodynamic features of liquid-crystal systems can now be appreciated from plots of C_p , ΔG_{lc} , ΔH_{lc} and ΔS_{lc} versus the temperature (Figure 7.3).

From figure 7.3.a it is seen that the heat capacity of the undercooled liquid is larger than that of the crystal, because of the additional configurational degrees of freedom of the liquid. Additionally, it can be appreciated, that the transition from an undercooled liquid to a glass is associated with a dramatic decrease of the heat capacity. The exact temperature at which the transition occurs is dependent on the cooling rate. The reason is that the time window for atomic rearrangements in the liquid decreases with higher heating rates. Hence a quick cooling results in a glass transition at a higher temperature as indicated by path a) in the figure. A slow cooling result in a glass transition at a lower temperature as represented by path b). As the structure of the glass mirrors the configuration of the undercooled liquid at the time of the glass transition, the undercooled liquid is said to be configurationally frozen, and the different paths a) and b) are called isoconfigurational states. After the transition, at temperatures below T_g , the heat capacities of the crystal and the glass are roughly equal.

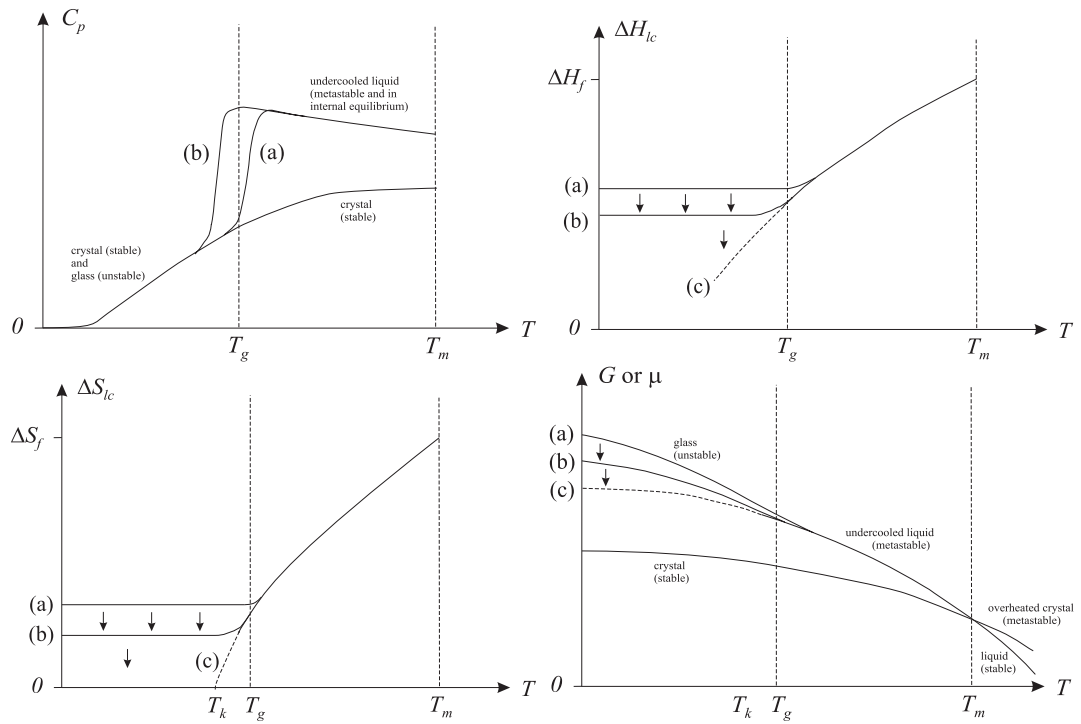


FIGURE 7.3: Top left) Heat Capacity C_p upon cooling below T_m of a glass former in various stability regimes . (a) Fast cooling. (b) Slow cooling. Top right) Difference in enthalpy H between liquid and crystal in two stability regimes: metastable equilibrium between T_g and T_m ; unstable isoconfigurational states below T_g . Bottom left) Difference in entropy S between liquid and crystal in two stability regimes: metastable equilibrium between T_g and T_m ; unstable isoconfigurational states below T_g . Bottom right) Gibbs free energy G or chemical potential $\mu = \frac{G}{N}$ (N = number of particles) in various stability regimes. From ref. [53]

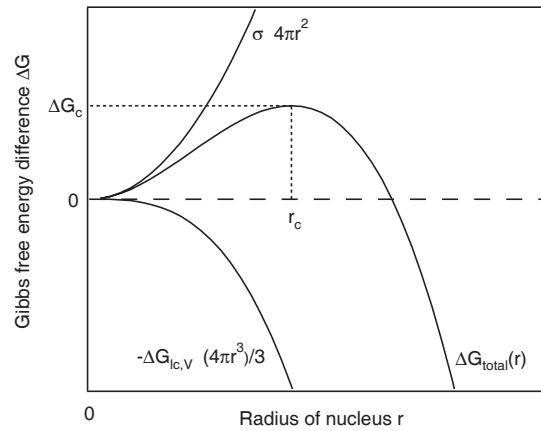


FIGURE 7.4: The terms of the Gibb's free energy change upon formation of a crystalline nucleus of radius r . At radii above r_c the nuclei becomes stable.

In case of the enthalpy and the entropy, it can be seen from figure 7.3.b and 7.3.c, respectively, that slow cooling (paths b) results in a lower ΔH_{lc} and ΔS_{lc} at temperatures below T_g than fast cooling (paths a). The dotted lines (path c) represents the case of infinitively slow cooling, in which case the undercooled liquid does not transform into a glass, but remains in a state of internal equilibrium. This scenario is obviously a theoretical case and not obtainable experimentally. For the entropy this extrapolation leads to a temperature T_k , at which ΔS_{lc} is zero. T_k is called the Kauzmann temperature and represents the temperature below which the undercooled liquid becomes completely ordered [54]. The Gibb's free energy, which is plotted in figure 7.3.d shows the stable physical state at all temperatures. The path of fast cooling results in a state of higher ΔG_{lc} than the slow cooling. The glass will tend to relax towards the equilibrium structure represented by path c), which is the configuration of lowest Gibb's free energy. As a result of this, physical properties which depend on the atomic arrangement of the glass depend dramatically on its history [134]. This constitutes a major problem in studies of amorphous materials as variations of 10 in Young's modulus, 0.5 in mass density and changes of several orders of magnitude for the diffusivity and the shear viscosity have been found [129],[108],[13],[109].

7.5 Crystallization

Eventually the glass will tend towards the crystalline structure, which is the overall state of lowest Gibb's free energy (fig. 7.3.d). However, in doing this the system does not only gain the energy difference between the two states, but also has to spend an energy to create an interface between the liquid and the crystalline nucleus. This energy is called the interfacial energy ΔG_σ . As elastic energy terms do not change the general description and can be ignored, the total change in Gibb's free energy for a homogeneous nucleation where the crystalline nucleus is completely surrounded

by the liquid is [120]:

$$\begin{aligned}\Delta G_{total} &= -\Delta G_{lc} + \Delta G_{\sigma} \\ &= -\Delta G_{lc,V} \cdot V + \sigma \cdot A,\end{aligned}\quad (7.9)$$

where A and V denote the area and the surface of the nucleus, $\Delta G_{lc,V}$ is the difference in Gibb's free energy per volume between the liquid and the crystal, and σ is the interface tension of the crystal melt. For a spherical nucleus with radius r , the expression can be rewritten as:

$$\Delta G_{total}(r) = \Delta G_{lc,V} \cdot \frac{4}{3}\pi r^3 + \sigma \cdot 4\pi r^2. \quad (7.10)$$

When plotting ΔG_{total} versus r (figure 7.4), it can be seen that the Gibb's free energy difference increases at small radii, while it obtains a maximum value at a radius of r_c . Hence at $r < r_c$, the growth of a nucleus is accompanied by an increase in ΔG_{total} . As this is not thermodynamically favorable, the nucleus is not stable and will tend to decay. On the other hand nuclei with $r > r_c$ are stable and continue to grow as further growth is associated with a decrease of ΔG_{total} and hence is thermodynamically favorable. The formation of a stable nucleus is called crystal nucleation. Because of this, r_c is called the critical radius, which by solving $\frac{d(\Delta G_{total})}{dr} = 0$ can be expressed by:

$$r_c = \frac{2\sigma}{\Delta G_{lc,V}} \quad (7.11)$$

Associated with the critical radius is the critical change in Gibb's free energy, ΔG_c . This can be considered as a barrier for nucleation and can by use of (7.10) be expressed as:

$$\Delta G_c = \frac{16\pi}{3} \frac{\sigma^3}{(\Delta G_{lc,V})^2}, \quad (7.12)$$

Another case of crystallization is the heterogeneous crystallization, where foreign materials such as a substrate are involved. The energy barrier for nucleation can in this case be expressed as [120]:

$$\Delta G_c^{(*)} = \frac{16\pi}{3} \frac{\sigma^3}{(\Delta G_{lc,V})^2} \cdot f(\theta), \quad (7.13)$$

where $f(\theta)$ is a geometrical factor [$0 \leq f(\theta) \leq 1$] which reduces to 1 in the case of homogenous crystallization [120].

The nuclei are formed and decay continuously because of thermal fluctuations. By use of Maxwell-Boltzmann statistics, the number of nuclei of radius r that are present once equilibrium is attained after a duration called the incubation time, can be expressed as:

$$n(r) = n_0 \cdot \exp\left(-\frac{\Delta G_{total}(r)}{k_B T}\right) \quad (7.14)$$

where n_0 is a constant describing the total number of nucleation sites. Hence the total number of critical nuclei in equilibrium is:

$$n_c = n_0 \cdot \exp\left(-\frac{\Delta G_c}{k_B T}\right) \quad (7.15)$$

Correspondingly, the crystal nucleation frequency in steady state can be expressed by [10],[133]:

$$I_{ss} = I_0 \cdot k_j \cdot \exp\left(-\frac{\Delta G_c}{k_B T}\right) \quad (7.16)$$

where k_j is the jump frequency per atom across the liquid-crystal interface and I_0 is a constant.

Once stable nuclei have been formed they continue to grow, as atoms move across the liquid-crystal interface. The crystal growth velocity associated with this process is defined as [120]:

$$u_{cg} = u_0 \cdot k_j \cdot \left[\exp\left(\frac{\Delta G_{lc, atom}}{k_B T}\right) - 1 \right] \quad (7.17)$$

where $\Delta G_{lc, atom}$ is the difference in Gibb's free energy per atom between the liquid and the crystal phases, and u_0 is a constant.

For pure liquids consisting of just one element the crystallization is collision-limited as neighboring atoms are identical. Hence k_j in this case can be expressed by:

$$k_j = \frac{u_{sound}}{\lambda} \quad (7.18)$$

where λ is the interatomic distance, and u_{sound} the sound velocity of the liquid. For alloys where neighboring atoms are not necessarily alike, the crystallization is diffusion limited, as the atoms must interchange their occupation of specific sites. In this case, the jump frequency per atom is:

$$k_j = \frac{6D}{\lambda^2} \quad (7.19)$$

Here D is the diffusivity of the liquid, which is related to the viscosity of the liquid through the Stokes-Einstein relation:

$$\eta D = \frac{k_B T}{3\pi a_0} \quad (7.20)$$

where a_0 is of the order of a molecular diameter [121],[120].

Through a combination of the expressions (7.16), (7.17), (7.19) and (7.20), the steady state crystal nucleation frequency in the diffusion limited case can be expressed as:

$$I_{ss}^{(dl)} = 2I_0 \frac{k_B T}{\pi \lambda^2 a_0} \frac{1}{\eta} \cdot \exp\left(-\frac{\Delta G_c}{k_B T}\right) \quad (7.21)$$

and the crystal growth velocity in steady state can be written as:

$$u_{cg}^{(dl)} = 2u_0 \frac{k_B T}{\pi \lambda^2 a_0} \frac{1}{\eta} \cdot \left[\exp\left(\frac{\Delta G_{lc, atom}}{k_B T}\right) - 1 \right] \quad (7.22)$$

The functions (7.22) and (7.21) are qualitatively plotted in fig. 7.5 as a function of the reduced temperature $T_r = T/T_l$, where T_l is the melting point of liquidus temperature. The three curves correspond to different values of the reduced glass transition temperature $T_{rg} = T_g/T_l$ namely $T_{rg} = 2/3$, $T_{rg} = 1/2$ and $T_{rg} = 1/3$.

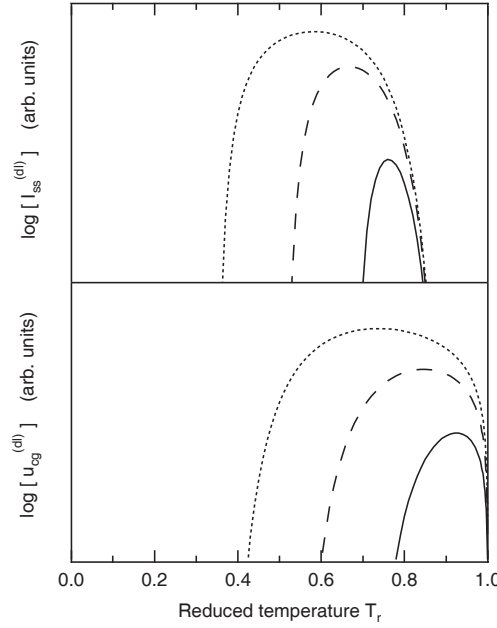


FIGURE 7.5: Nucleation frequency $I_{ss}^{(dl)}$ and crystal growth velocity $u_{cg}^{(dl)}$ for three values of the reduced glass transition temperature: $T_{rg} = \frac{2}{3}$ (solid), $T_{rg} = \frac{1}{2}$ (dashed), and $T_{rg} = \frac{1}{3}$ (dotted). From [53].

The curves are based on the following assumptions: The viscosity, can be estimated by the Fulcher-Vogel equation. There is a unique melting temperature T_g equal to T_0 (the temperature below which the viscosity is divergent as defined in (2.116)). The tension σ between the crystal and the melt is proportional to T_r , and ΔG_{lc} is proportional to the undercooling $(1-T_r)$.

The factor that by far has the biggest influence on the shape of the curves is the viscosity i.e. the Fulcher-Vogel behavior. Interestingly, the maxima of the curves for $u_{cg}^{(dl)}$ and $I_{ss}^{(dl)}$ is found at different temperatures, as can be explained by the different temperature dependence of (7.21) and (7.22).

The reduced glass transition temperature used for plotting has the physical implication, that it serves as a criterion for the glass forming ability of a material [131]. As found by Turnbull, at values of $T_{rg} > 2/3$, glass formation upon quenching is almost guaranteed, as $I_{ss}^{(dl)}$ is almost negligibly small.

A particular case of interest when considering crystallization is the case of isothermal homogeneous crystallization. In this case, the so-called Johnson-Mehl-Avrami equation [133], [5], [64] gives a measure of the crystallized volume fraction of space f_c , as a function of time:

$$f_c(t) = 1 - \exp \left(-\frac{4}{3} \pi u_{cg}^3 \cdot \int_0^t I(t') \cdot (t - t')^3 dt' \right) \quad (7.23)$$

where $I(t)$ is the time-dependent crystal nucleation frequency. Considering the steady state scenario as described above, where $I(t)$ is described by (7.16), equation 7.23 reduces to:

$$f_c(t) = 1 - \exp \left[-(k_{mt})^4 \right] \quad (7.24)$$

where it was applied that $\int_0^t (t - t')^3 dt' = \frac{t^4}{4}$. Here

$$k_m = \left(\frac{1}{3} \pi u_{cg}^3 I_{ss} \right)^{\frac{1}{4}} \quad (7.25)$$

is called the rate constant. Its temperature dependence is described by equations 7.16 and 7.17, but it can be approximated by a simple Arrhenius behavior:

$$k_m(T) \propto \exp \left(-\frac{E_A}{k_B T} \right) \quad (7.26)$$

where E_A can be seen as the effective activation energy for crystallization.

7.6 Materials suited for phase change application

Only a small group of materials have been found to be suited for application as phase change materials. Many candidates have been deemed unsuitable, as short recrystallization times are a difficult requirement to fulfil. Materials found suitable for application include the alloy families of GeTe, GeSbTe, GeTeSnO, AgInSbTe, InSbTe, SnTeSe and InSe [154]. Currently the most popular and applied materials are the ternary GeSbTe and the quaternary AgInSbTe alloy families. Depending on its exact composition, an alloy of the former group can be found in the ternary-diagram of these materials (fig. 7.6). Incidentally the compositions which have been found most suited for a phase change application until now are all situated on the so-called pseudo-binary line [97], that has its name from the fact that the two components of the supposedly binary alloy are GeTe and Sb₂Te₃. These compositions include Ge₂Sb₂Te₅, Ge₁Sb₂Te₄ and Ge₁Sb₄Te₇. This work is limited to the study of the following three alloys:

- Ge₂Sb₂Te₅
($T_M=620.5^\circ\text{C}$)
- Ge₄Sb₁Te₅
($T_M=685.0^\circ\text{C}$)
- AgInSbTe
($T_M=536.8^\circ\text{C}$)
(Ag 5.5%, In 6.5%, Sb 59%, Te 29% as determined by inductively coupled plasma emission spectroscopy and energy dispersive X-ray analysis)

but systematic efforts searching for other suitable compositions are currently being carried out [149], [22].

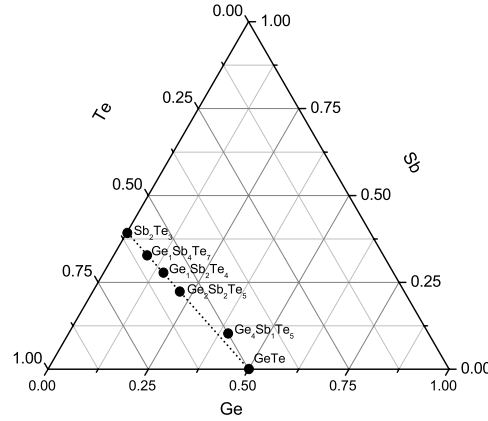


FIGURE 7.6: Phase diagram of the GeSbTe alloy system. The alloys which have been found suitable for phase change applications are marked. The pseudo-binary line (see text for details) is shown in the lower left part.

7.7 Results of stress measurements

In this chapter the findings of the investigation of mechanical stresses in phase-change materials will be presented. The objective is to measure the stress change upon crystallization of different phase change materials. The knowledge of the stress change associated with the phase transition is important, as the cyclability of the phase change materials is related to the elastic or inelastic nature of this stress change, as seen in chapter 2. Hence these measurements have a direct impact on the understanding of the cyclability of the phase change process.

The phase transformation between the amorphous and crystalline state is accompanied by a considerable volume change. This is demonstrated in fig. 7.7 for three different phase change alloys, where the relative film thickness is shown after annealing for 10 min at different temperatures.

The films, which had thicknesses between 35 and 60 nm were sputter deposited onto Si wafers. To facilitate the comparison of the data, the thickness, which has been measured by X-ray reflectometry to better than 1 Å (0.2 - 0.3%) is normalized with respect to the thickness of the as-deposited film. For the three different alloys studied here, crystallization proceeds at around 155°C for AgInSbTe, 130°C for Ge₂Sb₂Te₅ and 170°C for Ge₄Sb₁Te₅. In all cases the crystallization is accompanied by a considerable reduction in film thickness. The smallest thickness decrease of 5.5 % is observed for AgInSbTe, while Ge₂Sb₂Te₅ shows a 6.5 % thickness decrease upon crystallization. Ge₄Sb₁Te₅ is even characterized by a 9.0 % thickness reduction. These changes in film thickness will lead to pronounced mechanical stresses in the films (chapter 2.4) and could even cause severe limitations for the cyclability of the material, if these stresses are relieved by viscous flow. Indeed it has been shown that the cyclability of phase change media can be improved if oxygen or nitrogen atoms, which are argued to suppress the flow of the active layer, are added to the phase change film [27].

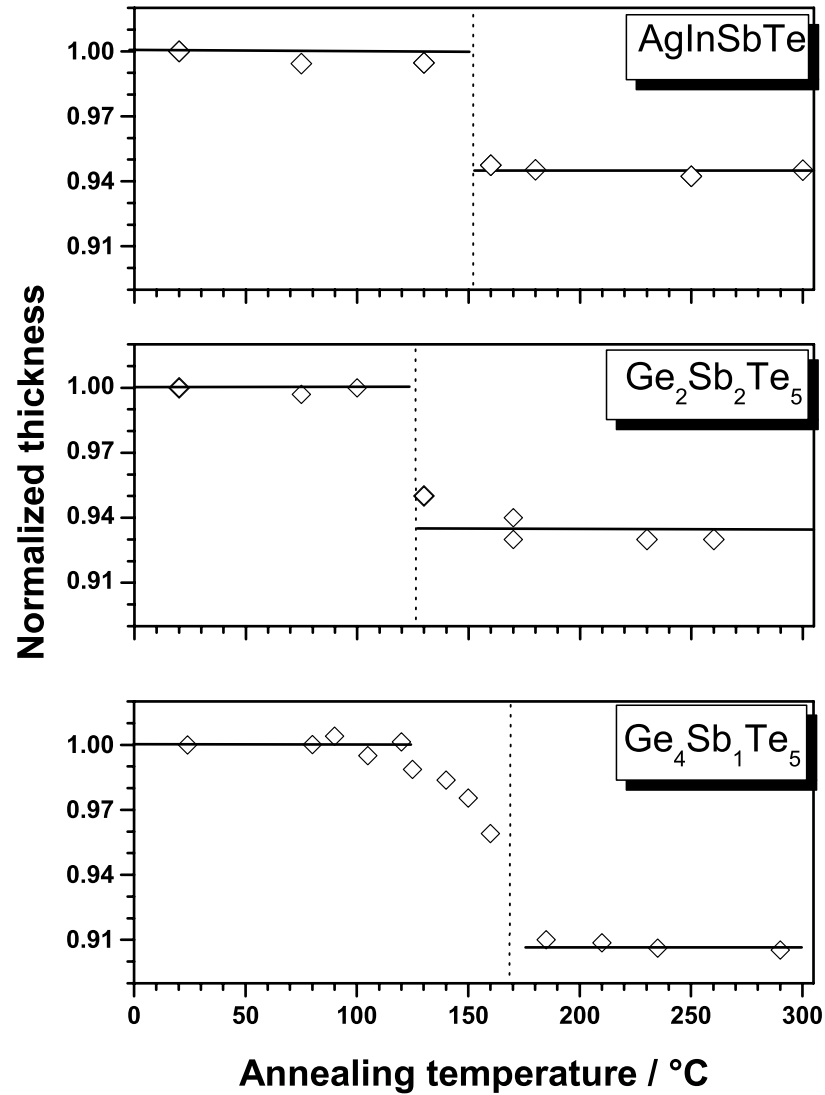


FIGURE 7.7: Film thickness of AgInSbTe, Ge₂Sb₂Te₅ and Ge₄Sb₁Te₅ films as a function of increasing annealing temperature as measured by X-ray reflectometry. Crystallization, which leads to a sudden decrease in film thickness, is observed at 155°C for AgInSbTe, 130°C for Ge₂Sb₂Te₅ and 170°C for Ge₄Sb₁Te₅. The more gradual thickness change upon annealing for Ge₄Sb₁Te₅ is partly due to the formation of a thin oxide film. To facilitate a comparison of different data sets, all thicknesses are normalized with respect to the thickness of the as-deposited film. Crystallization leads to a 5.5 % thickness decrease for AgInSbTe, a 6.5 % thickness decrease for Ge₂Sb₂Te₅ and a 9 % thickness reduction for Ge₄Sb₁Te₅.

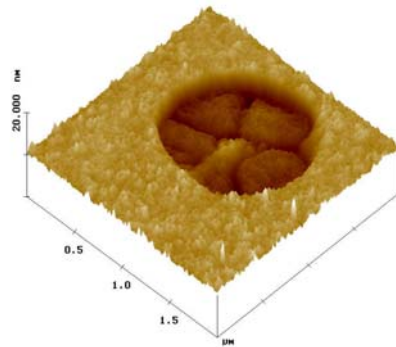


FIGURE 7.8: AFM picture of a crystalline area in an amorphous matrix. Inside the crystalline region cracks are observed. From ref. [142].

We have observed such stress induced effects also in atomic force microscopy (AFM) images of crystalline bits, that were produced by a pulse of a focussed laser (fig. 7.8) [142]. While the AFM image shows that upon laser irradiation a well-defined circular area is crystallized, it also reveals that nanometer sized cracks are formed in the crystalline film. These are presumably formed to relieve the film stress (chapter 2). Unfortunately from such rather qualitative observations no quantitative information on the local film stress can be obtained. Therefore the detailed investigation of the stress associated with the phase transformation was carried out using the wafer curvature system described in chapter 3.

As a direct descendant of these investigations, a detailed study of the stress relief properties of the phase change materials were carried out. Special care was taken in investigating the viscous flow behavior of the amorphous phase (section 7.9).

7.8 Stress upon crystallization

The investigations of the change of stress when the materials change structure from amorphous to crystalline were carried out using the furnace of the stress measurement system (section 3.4). The films were deposited on glass or Si substrates and heated at constant heating rates of 1-10 K/min. For the comparison of the different alloys (section 7.8.1), a constant heating rate of 3 K/min was used. The deposition stress was not measured for these specific samples; hence the graphs below do not show absolute stress values but only the changes of stress induced by the thermal cycling.

7.8.1 Comparison of phase change materials

Fig. 7.9.a shows the reflectance (top portion) and the mechanical stress (lower portion) for a 150 μm thick glass substrate covered by 85 nm AgInSbTe. Upon heating above 160°C (heating rate 3 K/min), a pronounced change in reflectance is observed. Once the reflectance has increased by 35% after heating above 170°C, it remains virtually constant even after subsequent cooling down to

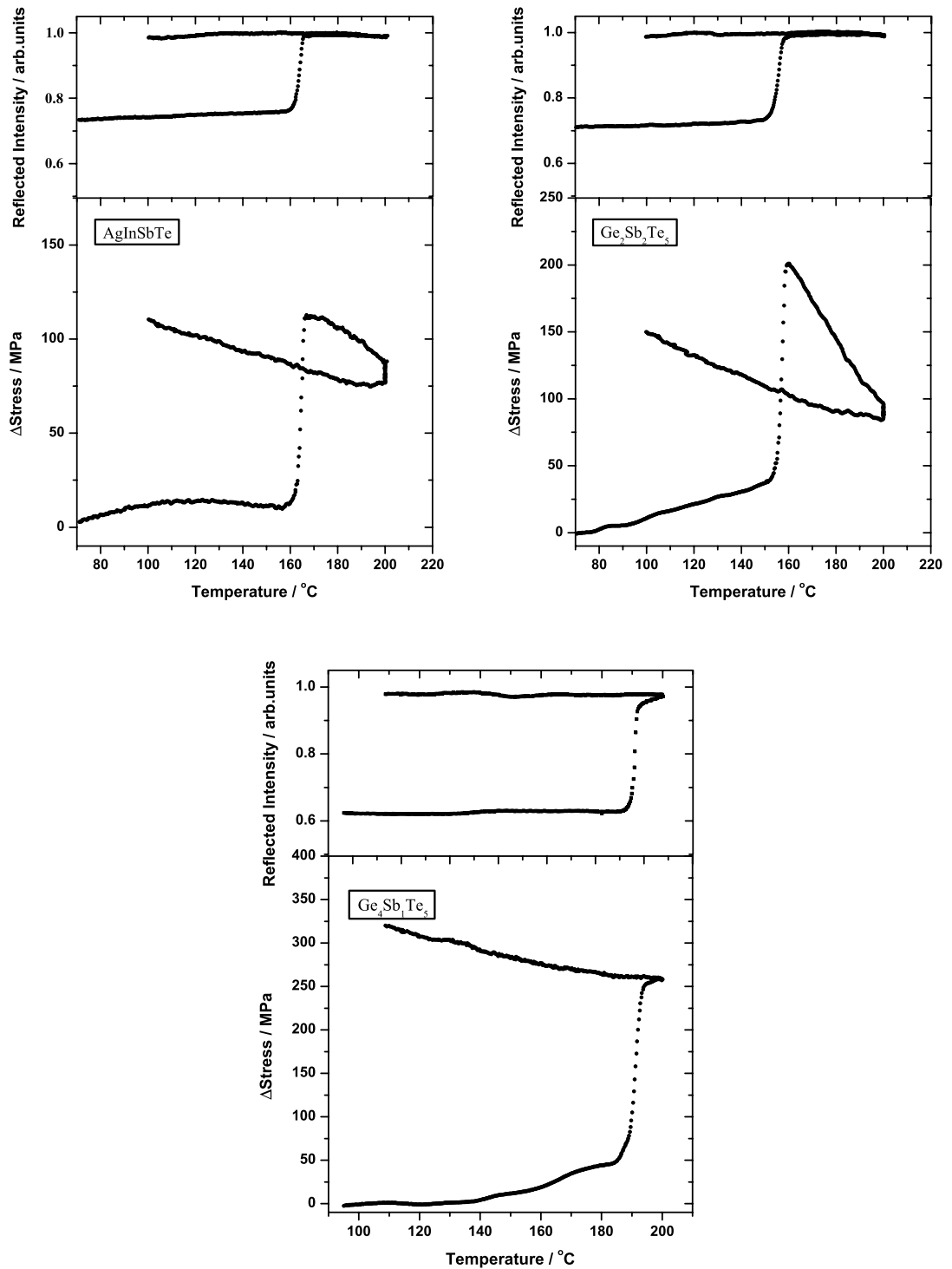


FIGURE 7.9: Stress and reflected intensity from a 85 nm AgInSbTe on a 150 μm glass substrate, a 85 nm Ge₂Sb₂Te₅ on a 200 μm Si wafer and a 61 nm Ge₄Sb₁Te₅ on a 200 μm Si wafer. For all materials studied here the reflectance change upon crystallization is accompanied by an irreversible stress change. Irreversible stress changes are also observed for the data in the two top graphs, where a considerable stress reduction is observed upon annealing for 5 minutes at 200 $^{\circ}\text{C}$. From the stress change upon subsequent cooling down to room temperature, the coefficient of thermal expansion and the biaxial modulus have been determined.

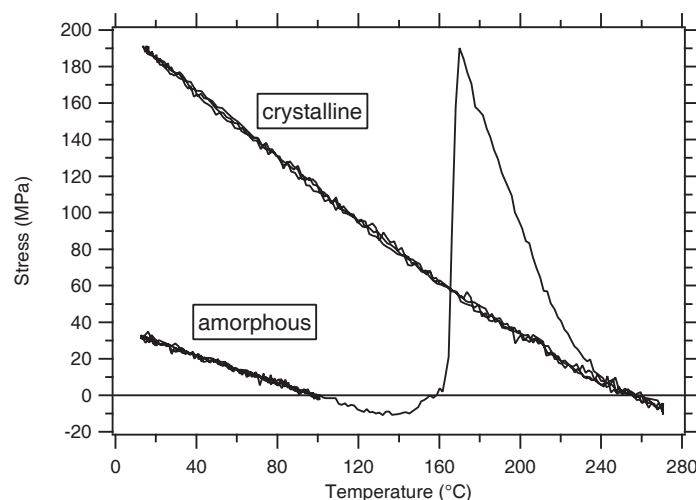


FIGURE 7.10: Reversible thermal cycling of a 965 nm $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film on a 200 μm Si substrate. Thermal cycling was carried out in both the amorphous and the crystalline state. The large stress increase at 167°C arises as a result of the crystallization and the associated volume change of the film.

room temperature. This reflectance change is characteristic for crystallization as confirmed by X-ray diffraction measurements. Correlated with the phase transition is a stress change of 105 MPa. Further heating of the sample leads to a reduction in film stress. Neither the rapid stress build-up upon heating above 160°C nor the subsequent stress decrease upon further heating are reversible. This can be seen from the stress data upon cooling down to room temperature. Subsequent heating back to 200°C leads to a reversible change of the film stress, which is attributed to the different coefficients of thermal expansion of the film and the substrate, as explained in section 2.5. By comparing the reversible stress change upon heating or cooling for films deposited onto different substrates, we have determined the coefficient of thermal expansion and the biaxial elastic modulus for the different phase change materials shown (section 7.8.2).

Similar behavior upon heating is observed for $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (Fig.7.9.b) and $\text{Ge}_4\text{Sb}_1\text{Te}_5$ (figure 7.9.c). At temperatures of 159°C for $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and 191°C for $\text{Ge}_4\text{Sb}_1\text{Te}_5$, the films crystallize. The crystallization is associated with changes of stress of 165 MPa and 215 MPa, respectively. The associated reflection changes are in the range of 40-60 % for all alloys. In neither of the experiments, the sudden stress change upon crystallization nor the stress decrease seen upon further heating to 200 °C is recovered during the subsequent cooling. After the first heating and cooling steps, the samples were subjected to additional heating and cooling cycles, that in all cases resulted in a reversible linear behavior. This linear behavior is expected from the thermal stress associated with the difference between the coefficients of thermal expansion of the film and the substrate (chapter 2.5).

7.8.2 Determination of the elastic constant for phase change materials

To determine the elastic constants of the phase change alloys, identical films were deposited on the two thermally stable substrates, (100) Si and (0001) sapphire (Al_2O_3). The biaxial moduli of these

	Structure	$\left(\frac{\Delta\sigma_{f, Si}}{\Delta T_{Si}}\right)$ [MPa/K]	$\left(\frac{\Delta\sigma_{f, Sapp}}{\Delta T_{Sapp}}\right)$ [MPa/K]	Y_f [GPa]	α_f [$10^{-6}/K$]
AgInSbTe ₂	amorphous	-0.332 ± 0.001	-0.303 ± 0.011	10.5 ± 2.2	34.4 ± 12.9
AgInSbTe ₂	crystalline	-0.676 ± 0.001	-0.609 ± 0.012	22.6 ± 2.2	32.6 ± 7.5
Ge ₂ Sb ₂ Te ₅	amorphous	-0.385 ± 0.001	-0.307 ± 0.008	27.6 ± 4.7	16.8 ± 2.6
Ge ₂ Sb ₂ Te ₅	crystalline	-0.971 ± 0.001	-0.846 ± 0.009	45.2 ± 8.2	24.4 ± 3.8
Ge ₄ Sb ₁ Te ₅	amorphous	-0.375 ± 0.001	-0.281 ± 0.008	33.9 ± 5.8	14.0 ± 1.9
Ge ₄ Sb ₁ Te ₅	crystalline	-0.895 ± 0.001	-0.723 ± 0.010	62.4 ± 10.8	17.2 ± 2.3

TABLE 7.1: The data for the determination of the biaxial moduli and the coefficients of thermal expansion of the phase change alloys

substrates are $Y_{Si} = 180.50$ GPa and $Y_{Sapphire} = 609.0$ GPa.

To allow a measurement of the elastic constants of the amorphous phase, the slope $\frac{\Delta\sigma}{\Delta T}$ was measured at temperatures below 100°C after an annealing phase of 48 hours at 100°C. During this annealing phase the film stress completely relaxed. Hence viscous flow during the measurements of thermal stresses was minimized. The results of the thermal cycling of a 965 nm Ge₂Sb₂Te₅ film on a 200 μ m Si substrate is seen in fig 7.10. As expected from theory, the thermal stress was found to be independent of the heating rates used, ranging from 0.5-3 K/min. Linear fitting was applied over the temperature range from 20-100°C, and the slopes of the thermal stress were thus determined. The results found from averaging over the slopes for several samples and different cooling rates are shown in Table 7.1.

After completion of the thermal cycling of the amorphous phase, the samples were heated above the crystallization temperature to between 240-280°C. Subsequently, thermal cycling was carried out between 20 and 200°C. From averaging over several cycles and several samples, $\frac{\Delta\sigma}{\Delta T}$ was determined by use of linear fitting (Table 7.1). The temperature ranges chosen for the fitting for Si substrates were: 20-140°C, 20-120°C and 20-160°C for AgInSbTe, Ge₂Sb₂Te₅ and Ge₄Sb₁Te₅, respectively. For the films on sapphire substrates fitting intervals of 40-100°C were used. Additionally the decrease of the film thickness upon crystallization of 9.0 % (Ge₄Sb₁Te₅), 6.5 % (Ge₂Sb₂Te₅) and 5.5 % (AgInSbTe) (see section 7.7) had to be considered to allow correct calculation of the stress changes of the crystalline phase.

From the determined slopes of thermal stress upon thermal cycling, the biaxial modulus and the coefficient of thermal expansion were determined using equation 2.100. For the substrate values of the coefficient of thermal expansion, the following values corresponding to a temperature of 70°C were used: $\alpha_{Si} = 2.90 \pm 0.30 \cdot 10^{-6}/K$ and $\alpha_{Sapphire} = 5.67 \pm 0.35 \cdot 10^{-6}/K$. The errors given here take into account, that the coefficients of thermal expansion have a minor temperature dependence within the fitting interval.

When comparing the biaxial moduli for the crystalline phase to those of the amorphous phase (Table 7.1), it can be seen that they are close to a factor of two higher. That higher values are found for the crystalline phases is expected, as it is easier to displace atoms in amorphous networks compared to rigid crystalline structures. The coefficients of thermal expansion are however similar in the two phases, which is expected for glass forming materials [54]. Comparing the alloys among each other, it is evident that Y_f increases with the melting temperature while α_f decreases.

	γ_{amorph}	$\gamma_{crystal}$
AgInSbTe	0.49 ± 0.34	0.96 ± 0.52
Ge ₂ Sb ₂ Te ₅	0.62 ± 0.27	1.38 ± 0.60
Ge ₄ Sb ₁ Te ₅	0.62 ± 0.25	1.29 ± 0.53

TABLE 7.2: The Grüneisen constant γ as calculated for the amorphous and crystalline phases by use of the elastic constants and coefficients of thermal expansion found in this section.

This finding agrees nicely with the general rule of thumb that the elastic modulus increases and the coefficient of thermal expansion decreases with increasing melting temperature. Additionally, the Grüneisen constant γ is normally found in the range of 1 to 3. It is given by [4]:

$$\gamma = \frac{3\alpha \cdot B}{C_V} \quad (7.27)$$

where B is the bulk modulus, which can be expressed by the biaxial modulus and the Poisson's ratio:

$$B = \frac{1}{3} \cdot \frac{1 - \nu}{1 - 2\nu} \cdot Y_f \quad (7.28)$$

and C_V is the heat capacity at constant volume of the film. It can be estimated by the Dulong-Petit value [4]:

$$C_V = \frac{3 \cdot k_B \cdot N}{V} \quad (7.29)$$

where N/V is the number of atoms per volume. For Ge₄Sb₁Te₅, C_V can be calculated to:

$$C_V = \frac{3 \cdot k_B \cdot \rho \cdot (4 + 1 + 5)}{4 \cdot M_{Ge} + 1 \cdot M_{Sb} + 5 \cdot M_{Te}} \quad (7.30)$$

Using the values for Y_f and α_f found in this section, the values for γ shown in table 7.2 are found for the different alloys in the amorphous and crystalline phases, respectively. For C_V an error of 10% was assumed. It can be seen that the values of the Grüneisen constant are in agreement with the Grüneisen's law. The values found for the crystalline phase fall in the range normally found for γ i.e between 1 and 3. However the values for the amorphous phase are a little lower at close to 0.5, meaning that these values are rather low.

7.8.3 Comparison of the stress changes with elastic theory

As shown in chapter 7.7, the phase transition from amorphous to crystalline is associated with large thickness decreases of 5.5 % for AgInSbTe, 6.5 % for Ge₂Sb₂Te₅ and 9.0% for Ge₄Sb₁Te₅. By combining these thickness changes with the values for the biaxial moduli of the phase change materials, one can estimate the stress change upon crystallization under the assumption, that the process proceeds elastically. Under this condition the stress change is (2.93):

$$\Delta\sigma = -Y_f \cdot \frac{1 - \nu_f}{1 + \nu_f} \cdot \epsilon_{zz,total} \quad (7.31)$$

	$\varepsilon_{zz,total} / \%$	$\sigma_{elast}^a / \text{GPa}$	$\sigma_{elast}^c / \text{GPa}$	$\sigma_{exp} / \text{GPa}$	$\frac{\sigma_{exp}^a}{\sigma_{elast}^a} / \%$	$\frac{\sigma_{exp}^c}{\sigma_{elast}^c} / \%$
AgInSbTe	$-(5.5 \pm 0.2)$	0.3 ± 0.1	0.7 ± 0.2	0.105	33.9	15.6
Ge ₂ Sb ₂ Te ₅	$-(6.5 \pm 0.2)$	1.0 ± 0.3	1.6 ± 0.5	0.165	17.0	10.4
Ge ₄ Sb ₁ Te ₅	$-(9.0 \pm 0.3)$	1.6 ± 0.5	3.0 ± 1.0	0.215	13.1	7.1

TABLE 7.3: The stress change upon crystallization for phase change films on different substrates. $\varepsilon_{zz,total}$ describes the total change in film thickness upon crystallization, while σ_{elast} is the expected stress change upon crystallization assuming elastic behavior for ^a amorphous, and ^c crystalline samples. The observed stress change is denoted as σ_{exp} , and the fraction of observed stress to expected stress is $\frac{\sigma_{exp}}{\sigma_{elast}}$.

where $\varepsilon_{zz,total}$ is the total expansion in z-direction, and the biaxial modulus Y_f has been derived from the reversible stress change upon heating and cooling for different substrates as seen in section 7.8.2. ν_f is assumed to be 0.3, which is a value typical for many materials including chalcogenides. Hence the stress change for an elastic process is now determined to 0.3 or 0.7 GPa for AgInSbTe, 1.0 or 1.6 GPa for Ge₂Sb₂Te₅, and 1.6 GPa or 3.0 for Ge₄Sb₁Te₅, for the amorphous and crystalline cases, respectively (Table 7.3).

The measured stress changes are however much smaller. Values of 105 MPa for AgInSbTe, 165 MPa for Ge₂Sb₂Te₅ and 215 MPa for Ge₄Sb₁Te₅ are found. This means that only a fraction of the stress change calculated assuming elastic behavior is actually measured for the phase transition in the different films. The accurate fractions of the observed stress changes can be found in table 7.3 and range from 7.1 % to 33.9 %. This clearly demonstrates that a considerable fraction of the stress in the phase change film is relieved by inelastic processes in the material.

Upon further study of the experimental data in section 7.8.1, it becomes evident that the stress relief must occur in the amorphous phase. Indeed, a comparison of the rates of stress change in the amorphous and crystalline phases yields very different values. In Figure 7.9 it can be seen, that upon annealing of the crystalline phase of AgInSbTe for 5 min at 200°C, the stress relaxation rate of about 0.04 MPa/s is very small compared to the rate of stress relief of around 1.0 MPa/s, that is found within 100 s upon crystallization. This difference between the stress relaxation rates implies, that the inelastic stress change must be accommodated in the amorphous phase by viscous flow mechanisms and not by stress relief mechanisms in the crystalline phase.

7.8.4 Crystallization mechanism

Further information on the mechanism of stress formation comes from a comparison with data obtained for films with a thin dielectric layer on top of the phase change material. The influence of thin capping layers on phase change kinetics has already been addressed in several studies [97], [127], [49]. The simultaneous detection of mechanical stresses, however, has the tremendous advantage of enabling fast and unequivocal insight into the crystallization mechanism. This is displayed in fig. 7.11 (closed circles). A 61 nm thick Ge₄Sb₁Te₅ film, on top of which a thin (~ 1 nm) native oxide film is formed, was heated to 220°C. Hence the heating proceeded above the crystallization temperature of the film. When comparing with the data in fig. 7.9.c, two important differences are evident. The optical reflectance change already takes place at a considerably lower

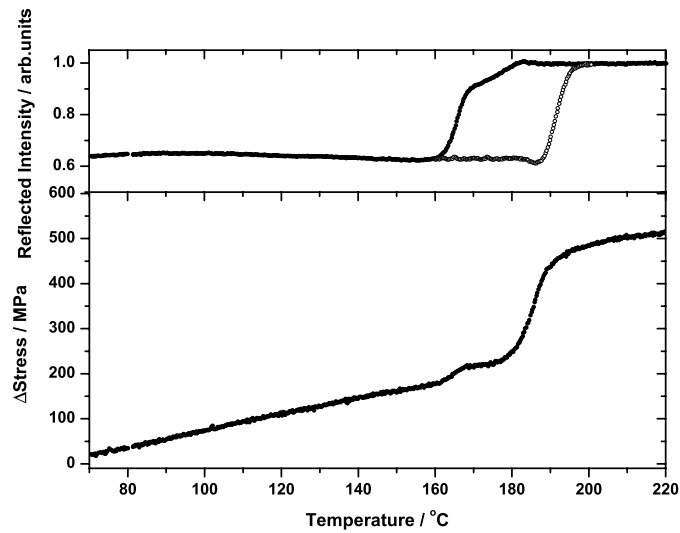


FIGURE 7.11: Stress and reflected intensity from a 61 nm $\text{Ge}_4\text{Sb}_1\text{Te}_5$ film on a $150\text{ }\mu\text{m}$ glass substrate. The phase change film is covered by a 1 nm thin oxide film. This leads to a pronounced shift of the transition temperature in the reflection but not in the stress measurement. Measurements from the sample backside, i.e. through the glass substrate on the interface between the phase change film and the substrate show a delayed change in reflectance (open circles) but the same stress measurement (not shown). This shows that the oxide layer leads to heterogeneous crystallization at the film surface, which then grows towards to substrate.

temperature i.e. 162°C as compared with 182°C for the non-oxidized film. This is evidence that the crystallization proceeds via heterogeneous nucleation at the interface between the oxide and the phase change film. The onset of crystallization is accompanied by a small stress change, but the major stress change is only observed after the reflectance change is almost complete. This implies that a large fraction of the stress is only formed when different grains start to form a continuous crystalline film. Such a scenario is indicative for a high viscous flow rate of the amorphous phase, which reduces the maximum film stress that can be observed. The scenario of interface driven heterogeneous crystallization can be confirmed by a straightforward experiment. Turning the sample upside down, the laser beam passes through the glass substrate onto the phase change film. This geometry leaves the stress measurement unaffected, but leads to a rather different reflectance change (open circles): Since the laser beam now has to first pass through the amorphous $\text{Ge}_4\text{Sb}_1\text{Te}_5$ film, the onset of crystallization at the interface is not visible. This directly confirms the heterogeneous crystallization process at the oxide/phase change interface presented above.

7.9 Viscosity measurements

From the studies of the stress change upon crystallization, it was found the the stress relief presumably takes place by viscous flow in the amorphous phase of the phase change materials. Hence in an effort to understand the mechanism of viscous flow, which is predominant in these materials, careful studies of viscous flow in these materials was carried out.

The experiments were carried out in a fashion that exploits the build up of thermal stress in thin films. Phase change films deposited on Si substrates were heated rapidly to a temperature well below the crystallization temperature. Thereby thermal stress was induced in the films by equation 2.97. Subsequently, the temperature was kept constant until the introduced stress had relaxed. In a next step, the temperature was rapidly increased to another temperature below the crystallization temperature. Again the relaxation of the thermal stress introduced was monitored at a constant temperature. Hence as an example the films were subjected to a temperature cycle which when plotted as a function of time looks like shown in figure 7.12.

The temperatures used for these studies were chosen from the criterion, that they had to introduce a sufficient thermal stress in the film in order to get sufficient signal during the measurement. It was also desirable to have at least two phases of viscous flow per sample. Additionally the temperatures were chosen to be as low as possible to minimize the risk of crystallization.

7.9.1 Results of viscosity measurements

In figures (7.14), (7.13) and (7.15) examples of the results of the studies of viscous flow are shown for each of the three alloys. Similarities between the behavior of the alloys are evident:

First of all, a compressive stress is induced in the film during the initial heating. This stress arises as a result of the coefficient of thermal expansion for all alloys being larger than that of the silicon substrates used. Because AgInSbTe has the lowest biaxial elastic modulus, the thermal stress induced is lowest for that alloy.

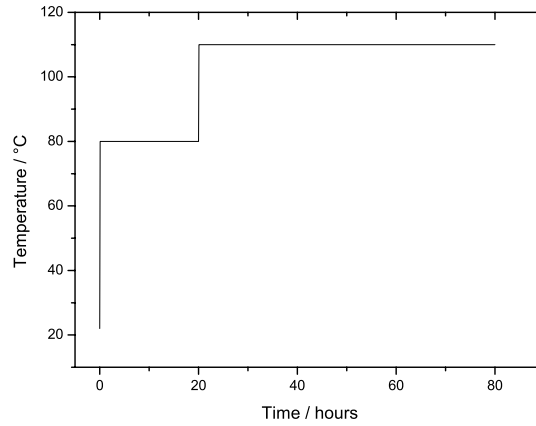


FIGURE 7.12: Example of the temperature cycle used for studies of stress relaxation by viscous flow in the amorphous phase of phase change materials. Thermal stress is introduced in the film through rapid heating to 80°C and later to 110°C. Simultaneously, the stress relaxation is monitored as a function of time.

Secondly, the stress was monitored for longer times at the highest temperature. This procedure was carried out in an effort to determine the initial curvature of the sample. The values determined using this method proved to be much more consistent with stress relaxation data, compared to the alternative approach of measuring R_0 after removal of the film using nitric acid. That this is in fact the case is no surprise. The irregular shape and curvature of silicon substrates that was often found, led to rather large errors in deposition stress measurements performed using films deposited on Si substrates (see chapter 5).

As the viscosity depends drastically on the determination of R_0 through (2.115):

$$\eta(t) = -\frac{Y_f}{6} \frac{\kappa(t) - \kappa(0)}{\dot{\kappa}(t)} \quad (7.32)$$

it was found that the only approach leading to meaningful results for the viscosity, was to determine $\kappa_0 = 1/R_0$ as a fitting parameter at the highest annealing temperature.

That the annealing temperatures used to monitor the viscosity subsequently increase can be understood from figure 7.16. If one assumes that no structural relaxation takes place when the temperature is rapidly changed, the viscosity will change along the dotted lines corresponding to isoconfigurational states. However, upon annealing at a fixed temperature, the viscosity increases due to structural relaxation. It must be stressed though, that when the annealing temperature is reduced from T_3 to T_4 , the viscosity is already so high, that no stress relaxation can be observed within normal experimental time frames - not even within the time frames of several tens of hours applied here. Hence the samples were considered to be used up after annealing at the highest temperature.

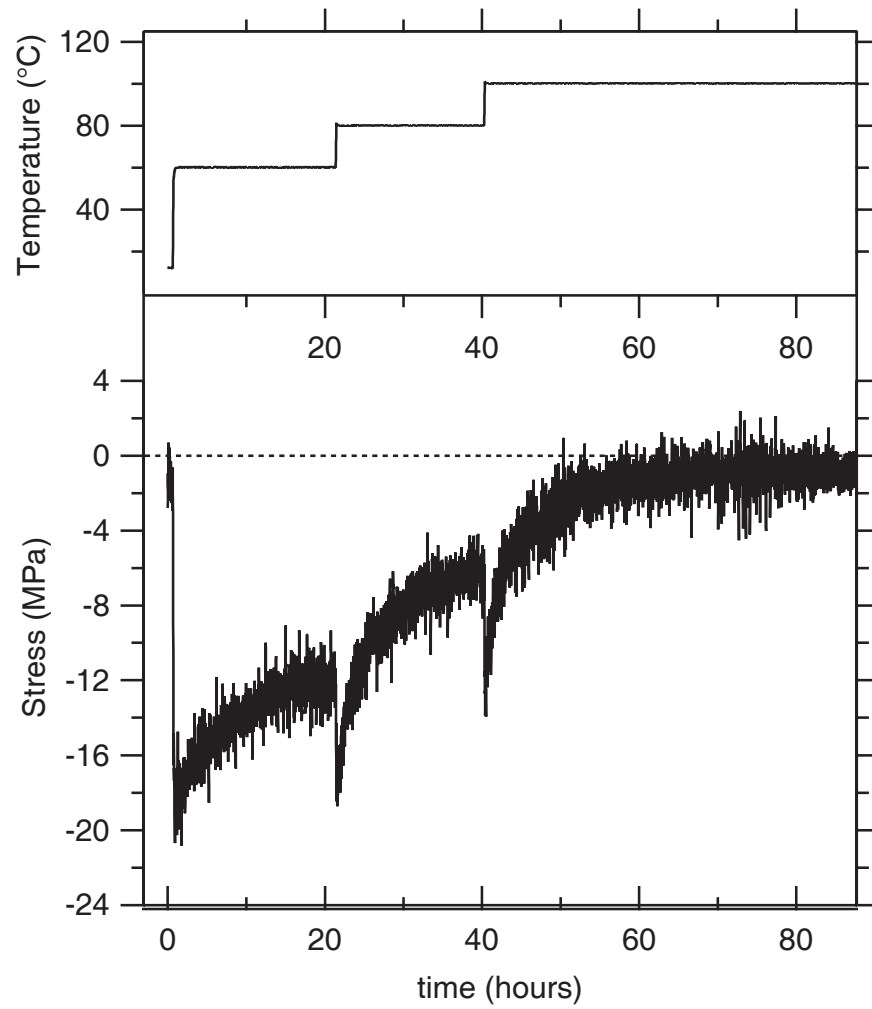


FIGURE 7.13: The relaxation of thermal stress in a 965 nm thick $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film deposited on a $180\text{ }\mu\text{m}$ Si substrate.

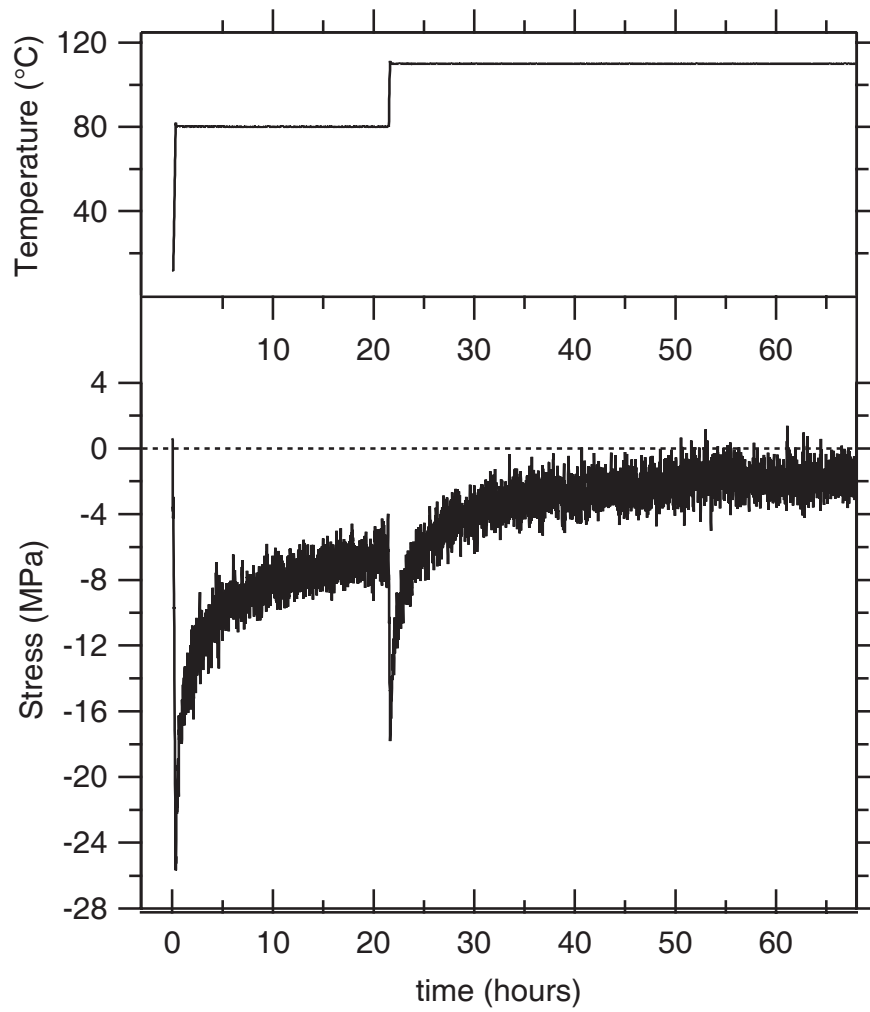


FIGURE 7.14: The relaxation of thermal stress in a 850 nm thick AgInSbTe film deposited on a 180 μm Si substrate.

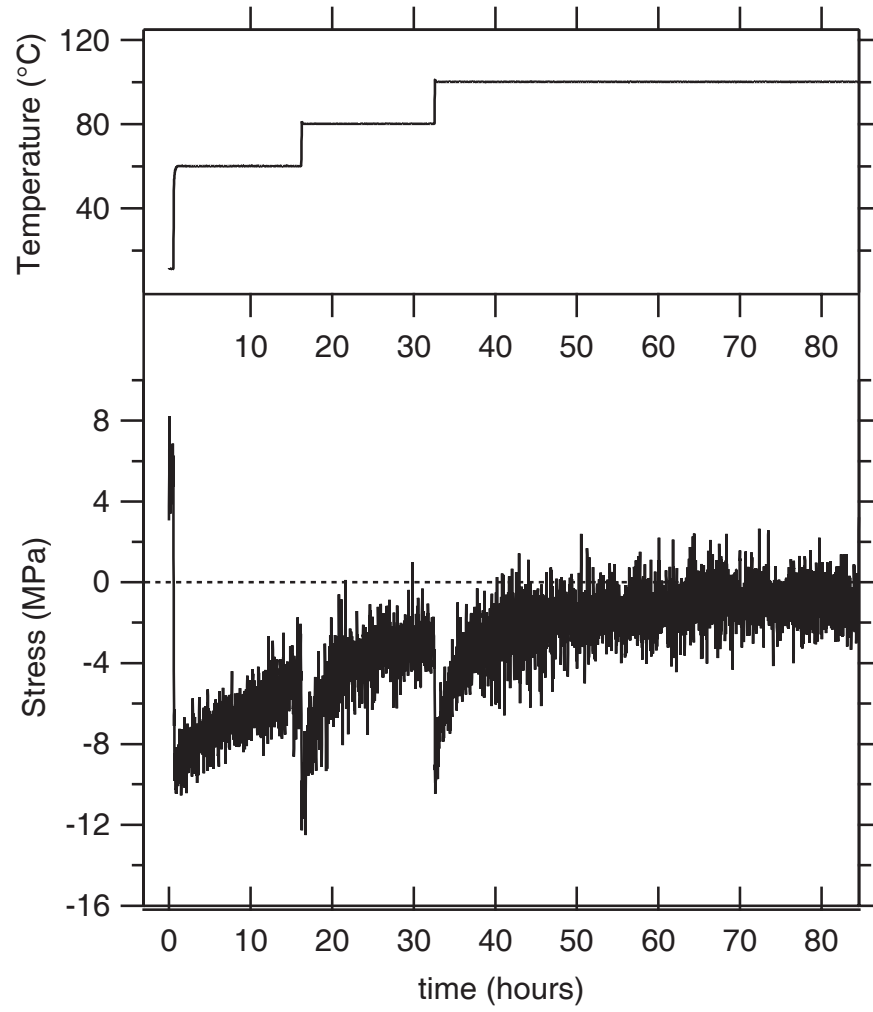


FIGURE 7.15: The relaxation of thermal stress in a 725 nm thick $\text{Ge}_4\text{Sb}_1\text{Te}_5$ film deposited on a $180\text{ }\mu\text{m}$ Si substrate.

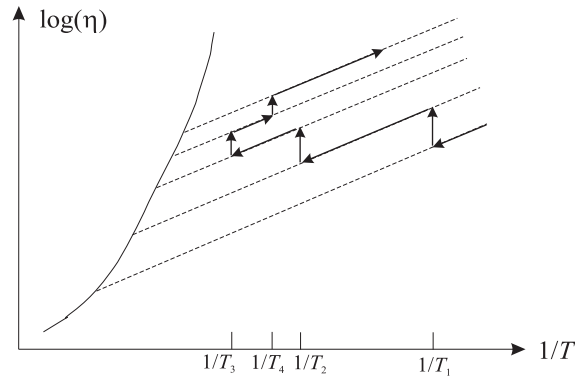


FIGURE 7.16: The viscosity evolution during a stress relaxation experiment as shown in figures 7.13 to 7.15 can be qualitatively tracked as seen here. During annealing at the temperatures T_1 , T_2 and T_3 the viscosity increases due to structural relaxation. Neglecting any structural relaxation during heating from temperature to temperature, the viscosity will change along the dotted lines corresponding to isoconfigurational states. Lowering the annealing temperature as seen from T_3 to T_4 results in a situation, where the viscosity is so high, that any stress relaxation cannot be observed within normal experimental time frames. From ref. [53].

7.9.2 Fitting the viscosity measurements

In chapter 2.8.4 three approaches applicable for modelling the time-dependence of the viscosity were shown. The models proposed either of the following assumptions:

- Constant viscosity
- Temperatures far below T_g i.e. far away from equilibrium
- Temperatures close to T_g i.e. close to from equilibrium

The first conclusion about the behavior of the viscosity can be made from plotting the $\ln\left(\frac{\sigma(t)}{\sigma_0}\right)$ versus time. In fig. 7.17 this was done for the stress evolution the $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (fig. 7.13) at 80°C . For other alloys and other temperatures, the plots looked qualitatively similar. It can easily be seen that $\Delta\ln\left(\frac{\sigma(t)}{\sigma_0}\right)/\Delta t$ decreases with time. Hence the simple approach of a time-independent viscosity does not apply here, as the decreasing slope implies, that the viscosity must increase with time. In addition, this means, that the annealing temperature is below the glass transition temperature (see fig. 2.21).

The stress relaxation data were now fitted using equations (2.136.a) - (2.137.c). The fitting parameters were η_0 , $\eta_{f,eq}$, k , the different k_r 's, and σ_0 . Additionally the original curvature, κ_0 was included in the fitting as the fitting parameter, $\sigma_{base} = \frac{Y_s d_s^2}{6d_f} \kappa_0$. However this parameter was only included in the fitting at the highest temperature used for each sample. The values found for σ_{base} at this temperature were fixed during fitting at lower temperatures.

Figure 7.17 shows the results of all fits. The dotted line corresponds to the results found using both equations (2.136.a) and (2.137.a) i.e the unimolecular relaxation model far away from and

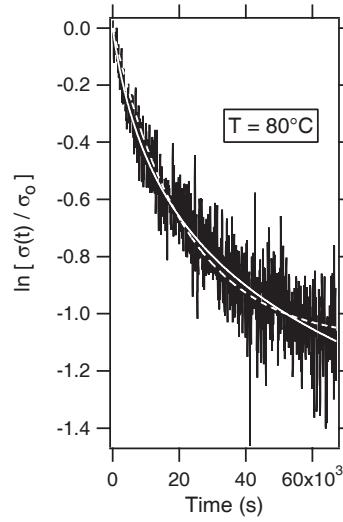


FIGURE 7.17: A logarithmic plot of the viscosity evolution of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ at 80°C during a stress relaxation experiment (fig. 7.13). The slope is found to decrease implying an increasing viscosity. The data are fitted using the unimolecular (dotted line) and the bimolecular (solid line) approaches. A least squares data analysis yielded that the bimolecular process fits the data slightly better.

close to equilibrium, respectively. This situation arises since their common fitting parameters were the same in the two cases, while $\eta_{f,eq}$ was extremely large. As can be seen from the equations, (2.137.a) trends towards (2.136.a) for $\eta_{f,eq} \rightarrow \infty$.

Similarly the solid line in Figure 7.17 corresponds to (2.136.b), (2.137.b) and (2.137.c) i.e the bimolecular relaxation model far away from and close to equilibrium and the intermediate relaxation model, respectively. Again identical fitting parameters η_0 , k and σ_0 were found, while $\eta_{f,eq}$ was found to be several orders of magnitude larger than η_0 . A look at the equations give the explanation of the identical fitting curves: For $\eta_{f,eq} \rightarrow \infty$, (2.137.b) and (2.137.c) trends towards (2.136.b).

For all alloys and all temperatures, similar results were found. In all cases, the fitting procedures assuming either unimolecular or bimolecular relaxation yielded identical results. Hence it can be concluded that the glasses are far away from equilibrium, and equations (2.136) must thus be applied.

As can be seen from figure 7.17, the two approaches fit the data only slightly different. The reason for this is that the viscosity only increases very slowly with time. However, when performing a least squares analysis on the data, it was found that even though the two fits differ only slightly as $\frac{\chi_b^2}{\chi_u^2} = 0.94$, for all alloys and all annealing temperatures the bimolecular model fitted the data better than the unimolecular model. Because of this consistency, it can be concluded that the structural relaxation taking place in these materials is bimolecular for all three alloys. This implies that the viscosity increases linearly with time.

Looking at the fitting parameters of the bimolecular approach, it is obvious, that k (see eq. (2.129b) and (2.130)) can be interpreted as a constant viscosity increase rate, $\dot{\eta}$. From (2.133) is it seen that $\dot{\eta}$ is expected to show a linear behavior with time when plotted in an Arrhenius

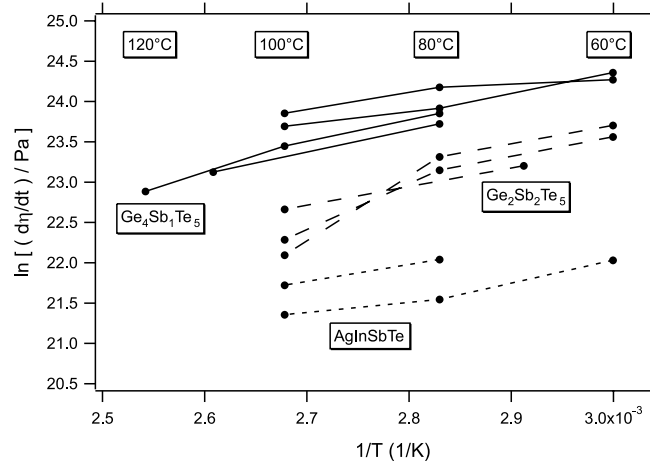


FIGURE 7.18: Arrhenius representation of the fitting parameter $\dot{\eta}$ as a function of temperature. Each group of connected points correspond to the same sample. The dotted lines represent AgInSbTe samples, the $\text{Ge}_2\text{Sb}_2\text{Te}_5$ samples are represented using dashed lines, while solid lines are $\text{Ge}_4\text{Sb}_1\text{Te}_5$ samples.

representation. Such a plot can be seen in figure 7.18. Each connected group of points represent data from the same sample. It can be seen that each sample yielded slightly different values for $\dot{\eta}$, but in general it is evident that the temperature dependence of $\dot{\eta}$ is roughly Arrhenius. Additionally, it can be seen that for all temperatures, the lowest values of $\dot{\eta}$ are found for AgInSbTe (dotted line). $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (dashed line) result in the second lowest values, while the $\text{Ge}_4\text{Sb}_1\text{Te}_5$ alloy has the highest viscosity increase rate.

From the slopes of the Arrhenius representation, average values Q_{rate} were determined to 0.21 ± 0.03 , 0.34 ± 0.08 and 0.18 ± 0.02 for $\text{Ge}_4\text{Sb}_1\text{Te}_5$, $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and AgInSbTe, respectively.

7.9.3 Determination of the isoconfigurational activation energy

In the situation where structural relaxation during heating can be neglected, the temperature dependence of the viscosity would be given by equation 2.123 i.e. in an Arrhenius representation like fig. 2.21, the slopes of the viscosities of the isoconfigurational states would be Q_{iso}/k_B .

In figure 7.19, the initial and final viscosities at the temperatures 60°C, 80°C and 100°C are plotted for all three alloys. The points corresponding to each alloy are connected by a dotted line (AgInSbTe), a dashed line ($\text{Ge}_2\text{Sb}_2\text{Te}_5$) or a solid line ($\text{Ge}_4\text{Sb}_1\text{Te}_5$). In a situation where structural relaxation during heating can be neglected, the slope of the lines connecting final viscosities at a lower temperature and initial viscosities at a higher temperature, is expected to be Q_{iso}/k_B .

However, structural relaxation must be considered. This correction to Q_{iso} was realized by use of a computer simulation, which takes into account both the isoconfigurational changes and the structural relaxation: During the heating from T_1 to T_2 the behavior of the viscosity is divided into small segments in which the isoconfigurational changes and the structural relaxation are considered

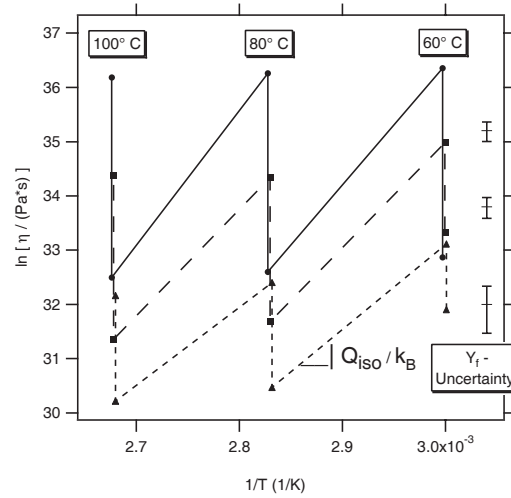


FIGURE 7.19: Arrhenius representation of the initial and final viscosities. Each group of connected points corresponds to the same sample. The dotted lines represent AgInSbTe samples, the $\text{Ge}_2\text{Sb}_2\text{Te}_5$ samples are represented using dashed lines, while solid lines describe $\text{Ge}_4\text{Sb}_1\text{Te}_5$ samples.

successively (figure 7.20). The measured viscosities at the beginning and at the end of the heating were used as boundary conditions. Further details on the fitting procedure can be found in ref. [53].

The simulation leads to a minor correction of about 0.1 eV to the values of Q_{iso} (Table 7.4). Coincidentally, Q_{iso} roughly scales with the melting temperature T_m i.e the ratio Q_{iso}/T_M is almost constant for all materials.

Using the values for $\dot{\eta}$, a simulation of the viscosity evolution and stress evolution upon heating was later carried out for heating rate of 5-80 K/min [53]. This simulation showed that the time needed for relaxing the stress to the values observed experimentally is much larger than the time

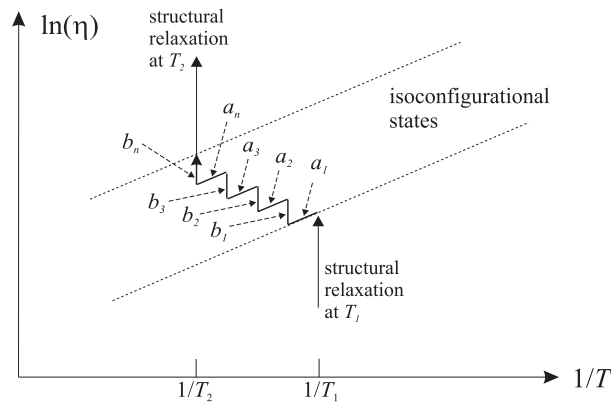


FIGURE 7.20: Principle of the computer simulation, which takes into account both the isoconfigurational change and the structural relaxation during heating. From ref. [53].

	Q_{iso} [eV]	T_m [°C]	Q_{iso}/T_m [eV/°C]
$Ge_4Sb_1Te_5$	1.94 ± 0.09	685.0	23.4 ± 1.3
$Ge_2Sb_2Te_5$	1.76 ± 0.05	620.5	22.9 ± 0.7
$AgInSbTe$	1.44 ± 0.07	536.8	20.6 ± 1.0

TABLE 7.4: Average values of the isoconfigurational activation energy Q_{iso} for the viscosity, melting temperatures T_m [53] and calculated ratio Q_{iso}/T_m .

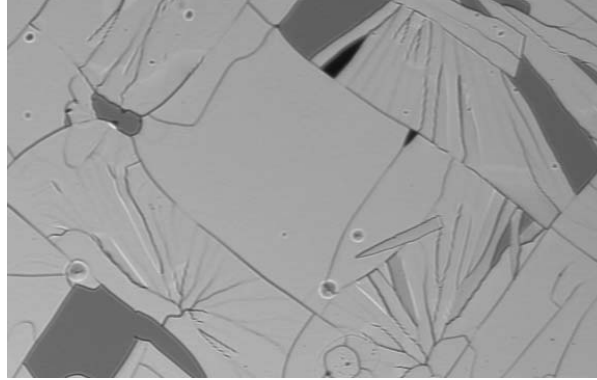


FIGURE 7.21: Microscope picture ($650 \mu m \times 410 \mu m$) of a $1 \mu m$ thick $Ge_4Sb_1Te_5$ film that was heated and crystallized. The corresponding stress measurement is shown in fig. 7.22.

window of about 100 s found in the experiments. Hence it was suggested that other mechanisms are involved in the relaxation of the stress. These mechanisms include viscous flow for inhomogeneous stress distributions in the film, as well as delamination. In fact delamination was observed for $Ge_4Sb_1Te_5$ films of $1 \mu m$ thickness as seen in figure 7.21.

In the associated stress measurement fig. 7.22, it is seen that upon crystallization the maximum stress level is 260 MPa. However when this value is also reached upon cooling at $100^\circ C$, the stress and reflectivity behavior below $100^\circ C$ indicate that film delamination takes place: The reflectivity drops, and the stress behavior differs substantially from the expected linear dependence on the temperature. These findings indicate that film delamination takes place, at it is observed in the corresponding microscope picture taken after the measurement (figure 7.21). However it cannot be excluded that this process begins to take place upon crystallization, hereby relieving the stress observed.

7.10 Summary

Phase materials are have interesting properties for applications as the active film in data storage media. The operation of such media is very simple as seen in section 7.1. Additionally, the description of the amorphous phase and the phase transition itself is well established as seen in sections 7.2 to 7.5. However, the cyclability of phase change media is affected by the elastic or inelastic nature of the phase transition. The studies of the stress change upon crystallization as presented in section 7.8 show that only a fraction of the stress that could be expected assuming an

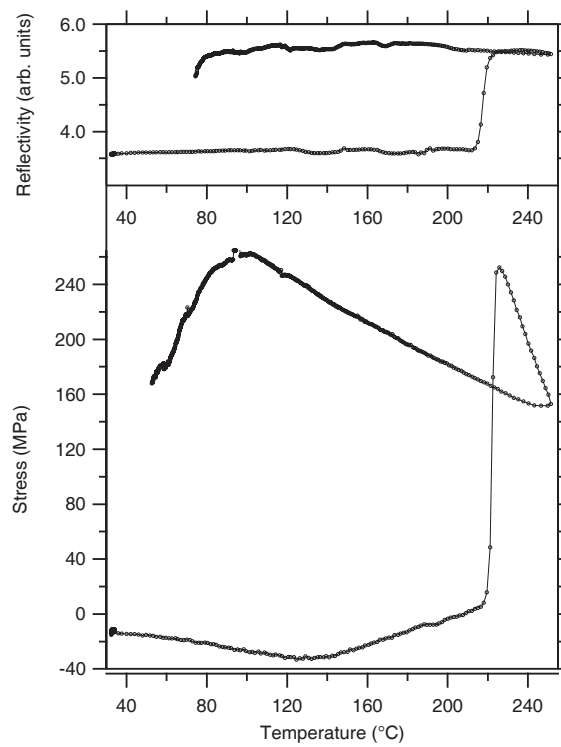


FIGURE 7.22: Stress measurement on a $1\ \mu\text{m}$ thick $\text{Ge}_4\text{Sb}_1\text{Te}_5$ film. The maximum stress observed is 260 MPa. This value is reached upon crystallization and upon cooling. During cooling the stress and reflectivity behavior below 100°C indicate that film delamination takes place.

elastic behavior is actually found in the measurements. In fact only between 7.1 % and 33.9 %, depending on the material and the choice of elastic modulus, of the expected elastic stress is found (section 7.8.3). Additionally, a comparison of the stress relaxation rates of the amorphous and the crystalline phases shows that this relaxation can only be accommodated in the amorphous phase. Studies of the viscous flow in the amorphous phase yielded that the stress relaxation can be simulated using a bimolecular model (section 7.9.2). Using this approach the viscosity increase rate $\dot{\eta}$ and isoconfigurational activation energy Q_{iso} characteristic of the studied alloys were determined. It was found that $\dot{\eta}$ and Q_{iso} were highest for $\text{Ge}_4\text{Sb}_1\text{Te}_5$, second highest for $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and lowest for AgInSbTe .

Chapter 8

Conclusion

Mechanical stress is an important parameter to control in the many functional coatings which have found their way into applications in recent years and led to exciting new technological inventions. The reason is that high stresses can lead to failure of the properties of the film through fatal processes like cracking or even delamination.

The topic of this work was to study and understand the nature of the stress behavior of materials within certain application fields. Thereby the focus was set on determining the deposition stresses, the magnitude of the stresses involved in certain processes like optical switching or phase changes, as well as studying the elastic or inelastic nature of the stress changes associated with these processes.

The basis for such a study is a well-functioning experimental setup. As described in chapter 3, such a system was custom-built and subsequently continuously improved until it showed satisfactory properties. Once this was realized, carefully selected topics could be studied.

The first of these topics is deposition stresses in transition metal oxides. These oxides have a large number of applications. They are used as functional coatings in many devices, yet their main field of application is as optical coatings. Used as coatings on window glass, such thin oxide films can help improve the energy balance of houses and buildings. Additionally, metal oxide films are used as transparent conductive oxides, hard coatings etc. Therefore the control of the deposition stresses in these films is extremely important as stress-induced processes can lead to a complete loss of the functionality in case of delamination. Hence the topic of deposition stresses in DC-sputtered films was studied systematically in the group of the transition metal oxides: TiO_2 , ZrO_2 , HfO_2 , V_2O_5 , Nb_2O_5 , Ta_2O_5 , MoO_3 and WO_3 .

The stress was found to correlate with the structure of the films. The formation of either crystalline or amorphous films was related to the number and the energy of the ions incident on the growing film. For amorphous films, lower compressive stresses were found, while higher compressive stresses were found in the case of crystalline films as seen for ZrO_2 and HfO_2 . This finding was explained by a combination of a lower value of the threshold energy E_{is} required for stress relaxation in amorphous films compared to crystalline films, and the the number and energy of the incident ions.

Furthermore, for each of the transition metal oxides, films were produced at different oxygen flows resulting in samples ranging from metallic to oxidic. For all oxygen flows deposition stresses were measured. These deposition stresses were all explained by use of the models given in chapter 5, including the transition from tensile to compressive stress as seen for TiO_x and VO_x . These findings showed how sensitive the deposition stress is to changes of sputter parameters such as the sputter voltage.

Similarly, in the field of phase change materials applied in optical data storage media, several materials suited for an application are available. Phase change materials exploit the difference in optical properties between the crystalline and the amorphous state of the materials. The phase change from crystalline to amorphous is carried out by heating the material to a temperature above its melting temperature. Through a very high cooling rate, the liquid can be stabilized in the amorphous structure. The reverse transition is then performed by heating the amorphous phase above its glass transition temperature. This leads to crystallization. In this study, the stress-wise behavior upon crystallization of the compounds $\text{Ge}_2\text{Sb}_2\text{Te}_5$, $\text{Ge}_4\text{Sb}_1\text{Te}_5$ and AgInSbTe was investigated.

The transition from amorphous to crystalline is associated with a volume decrease ranging from 5.5-9.0 % for the three alloys. This volume change will lead to mechanical stresses in the films because of the constraint condition induced on the film by the substrate. To determine the magnitude of the expected stress assuming an elastic behavior, the elastic properties of the films were measured. This was done by exploiting the different thermal stresses induced in equal films deposited on different substrates. In the amorphous phase values of 10.5 GPa, 27.6 GPa and 33.9 GPa were found for AgInSbTe , $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and $\text{Ge}_4\text{Sb}_1\text{Te}_5$, respectively. In the crystalline phase values of 22.6 GPa, 45.2 GPa and 62.4 GPa were found. Hence the stress change for an elastic process could be determined to be 0.3 or 0.7 GPa for AgInSbTe , 1.0 or 1.6 GPa for $\text{Ge}_2\text{Sb}_2\text{Te}_5$, and 1.6 or 3.0 GPa for $\text{Ge}_4\text{Sb}_1\text{Te}_5$, where the given values refer to use of the Young's moduli for the amorphous and the crystalline phase, respectively.

However, the measured stress changes upon crystallization are smaller than these predictions. Values of 105 MPa for AgInSbTe , 165 MPa for $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and 215 MPa for $\text{Ge}_4\text{Sb}_1\text{Te}_5$ were found. The precise fractions of the observed stress changes hence range from 7.1 % to 33.9 %. This means that only a fraction of the stress change calculated assuming elastic behavior is actually measured for the phase transition in the different films. It can thus be concluded that a considerable fraction of the stress in the phase change film is relieved by inelastic processes in the material.

A comparison of the stress relaxation rates in the amorphous and the crystalline phases showed that in the amorphous phase the rate is far larger than that found in the crystalline phase (1.0 MPa/s compared to 0.04 MPa/s). Hence it was concluded that the stress relaxation takes place in the amorphous phase. For this reason a detailed study of the viscous flow properties of the amorphous phase were carried out.

Finally, the exciting properties of optically switchable coatings were studied. These films exploit the optical contrast, that can be achieved in an active film either by an electrochromic, a thermochromic or a gasochromic approach. In this study only gasochromic films i.e. films that change their properties upon exposure to a certain gas, were studied. The films chosen for the study were tungsten oxide, gadolinium, magnesium. As these materials belong to three different material classes a comparative study was carried out.

Mg, Gd and WO_x all show a change of their optical properties upon exposure to a hydrogen gas. However it was found that the magnitude of stresses associated with this optical switching, as well as the nature of the stress changes, varied considerably between the materials. In Gd large stresses of the order of -2100 MPa were observed. Additionally, the stress changes were found to be much lower than the stress expected for elastic behavior (-3100 MPa). This finding agreed with a feature of the *in-situ* stress measurement, which showed that the initial switching to GdH_2 is associated with an inelastic stress relaxation. It must however be noted that the subsequent switching between the GdH_2 and the GdH_3 states was found to behave elastically and reversibly. This was however not the case for the switching of Mg. In that case, the optical switching was found to be associated with stresses of the order of -600 MPa upon loading. Additionally, inelastic stress relief processes were observed, which led to deterioration of the switching properties and also to film cracking. For WO_x stress changes of the order of -85 MPa were found. Furthermore, the switching between the colored and the bleached state was found to be elastic and reversible, as no stress relaxation was observed.

By considering these findings from a perspective of mechanical stresses, it was concluded that WO_x is the material best suited for application as it combines low mechanical stresses with elastic switching processes.

Therefore a detailed study of the switching of tungsten oxide was carried out. It was found that the magnitude of the stress change depends on the density of the film. Stress changes upon switching in a 2 bar H_2 atmosphere ranged from 30 MPa to 200 MPa. Based on this finding, as well as the discovery that significant stress changes could be induced in the film by placing it in vacuum conditions, without observing a simultaneous optical switching, it was concluded that the majority of the stress changes observed upon switching in WO_x film arises from gas atoms in the pores of the film structure.

This finding was exploited in an experiment where a fully colored film was exposed to a number of vacuum and hydrogen phases. It was found that the first coloration was associated with a different compressive stress than the subsequent hydrogen phases, which all showed a similar stress level. This difference could only be accounted for using the model based on the desorption of oxygen upon coloration. The hydrogen intercalation model did on the other hand not offer any possible explanation for this finding. Therefore it was concluded that the former model is more credible. *In-situ* ellipsometry measurements were subsequently found to yield a thickness decrease upon coloration, a finding that could also only be explained by use of the model based on desorption of oxygen upon coloration. Hence it was concluded that this model is credible.

Regarding the complete findings of these studies, it is evident that they show the immense importance of control of mechanical stresses in functional coatings. The dramatic failure of the film through cracking and delamination is fatal for any application relying on the properties of such coatings. Such failures were also encountered in this work, most notably in the case of optical switching of Mg, as well as in rather thick phase change films. Additionally, the power of mechanical stress measurements was exploited to gather interesting knowledge on the nature of the phase change materials via the viscosity measurements, and of the tungsten oxide films through the switching of films of different density. Stress measurements even allowed a statement on the credibility of the proposed models for switching.

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Lebenslauf

Persönliche Daten

Name, Vorname: Pedersen, Tom Peder Leervad
Geburtsdatum: 15.02.1974
Geburtsort: Aarhus, Dänemark
Familienstand: Ledig

Studium und Ausbildung

1980-1989 Bredagerskolen, Jelling, Dänemark
1989 9.klasse udvidet afgangseksamen (Grundschule)
1989-1992 Rødkilde amts gymnasium, Vejle, Dänemark
1992 Studentereksamen (Abitur)
1992-1998 Aarhus Universitet, Institut for Fysik og Astronomi,
Aarhus, Dänemark
1998 cand. scient. in Physik/Chemie
1999-2003 Wissenschaftlicher Mitarbeiter am I. Physikalisches
Institut der RWTH Aachen, Aachen, Deutschland.