Doctoral Thesis

Optical and Mechanical Properties of Static and Tunable Color Coatings Based on Ultrathin Semiconductors

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Optical and Mechanical Properties of Static and Tunable Color Coatings Based on Ultrathin Semiconductors

A thesis submitted to attain the degree of

DOCTOR OF SCIENCES of ETH ZURICH

(Dr. sc. ETH Zurich)

presented by

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Summary

Color coatings based on ultrathin semiconductors (< 30 nm) on top of reflective metals are attractive because of their considerably smaller film thickness compared to conventional optical coatings based on transparent layers. The large absorption in the semiconductor and the wavelength-dependent phase-shift at the semiconductor interfaces yield an absorption resonance in the reflectance spectrum and thus the color appearance of the coating. The spectral position of this absorption resonance depends on the thickness of the semiconductor and a change of only a few nanometers results in a completely different color appearance. These coatings therefore are promising candidates for ultrathin solar cells or as decorative coatings for arts and jewelry.

This dissertation shows that the underlying materials are not exclusively limited to metals. Instead, the metal can be replaced by any material if several layers are used such that the effective optical constant of a highly reflective metal is mimicked. As a proof of concept color coatings with metal, semiconductor, and insulator substrate materials are presented. Deep and narrow absorption resonances and hence bright colors are obtained for semiconductors and underlying materials whose absorption coefficients strongly depend on the wavelength.

The latter result is exploited for tunable color coatings as a small change in the imaginary part of the refractive index changes the shape and spectral position of the absorption resonance. Thus, by reversibly switching the semiconductor between the amorphous and crystalline phase the color of the coating can be tuned. Amorphization of the semiconductor is achieved by a single femtosecond laser pulse of high intensity and crystallization is obtained by several pulses of low intensity. Reversible color switching between blue and gray is presented for the phase-change material Ge$_2$Sb$_2$Te$_5$ (GST). An optical contrast as large as 92% at wavelengths around 572 nm is even demonstrated for the conventional semiconductor Si which does not show a large natural optical contrast between its amorphous and crystalline phase. The base color can be tuned by the thickness of the semiconductor, the choice of substrate material, and the thickness of a transparent capping layer.

Due to the bistable nature of the color coatings they are promising candidates for display applications with low power consumption and as they work in reflectance stable color appearance is even achieved in bright sunlight. However, the functionality of static and tunable color coatings is based on the ultrathin brittle Si and GST films. A loss of integrity of these thin films might lead to failure of the entire device. Hence, it is of fundamental interest to characterize their cohesive and adhesive strength. In this work, failure of amorphous and crystalline Si and GST films on the commercially available polyimide substrate Kapton® E is studied.

III
In order to crystallize Si at temperatures below the maximum service temperature of the Kapton® E substrate, the aluminum-induced layer exchange mechanism is exploited. A parametric study reveal that the crystallization temperature can be reduced by choosing high sputter powers and low argon pressures during the fabrication process.

During uniaxial tensile tests of amorphous and crystalline Si and GST films various methods are employed to characterize the failure of the thin films. Reflectance anisotropy spectroscopy (RAS) is introduced as a new tool to evaluate the onset strain of fragmentation of thin brittle films. In comparison with other methods RAS is more sensitive to first cracks in ultrathin GST films.

Generally, thinner coatings exhibit better resistance against cracks due to smaller defect sizes. Moreover, a compressive residual stress of the coating helps to delay the onset strain of fragmentation while the opposite is the case for a tensile residual stress. The onset strains of fragmentation of Si and GST are similar but Si exhibits a larger fracture toughness due to the small Young’s modulus of GST. Crystalline Si delaminates at considerably lower strain values compared to GST, which might be caused by the aluminum-induced layer exchange mechanism.

Static and tunable color coatings based on amorphous Si as well as amorphous and crystalline GST show a lower resistance against cracks compared to single Si and GST films which might be due to a size effect.
Zusammenfassung


Das letztere Ergebnis kann für schaltbare Farbschichten ausgenutzt werden, da eine kleine Änderung des Imaginärteils des Brechungsindex die Form und spektrale Position der Absorptionsresonanz beeinflusst. Amorphe kristallise halbleiters ändert den Brechungsindex und damit die Farberscheinung. Dadurch lässt sich die Farbe der Beschichtung durch reversibles Schalten zwischen der kristallinen und der amorphen Struktur des Halbleiters einstellen. Reversibles Schalten zwischen blau und grau wird für das Phasenwechselmaterial Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} (GST) gezeigt. Der herkömmliche Halbleiter Si hat im Gegensatz zu GST keinen grossen natürlichen optischen Kontrast zwischen der amorphen und kristallinen Phase. Trotzdem kann ein optischer Kontrast von 92\% bei einer Wellenlänge von zirka 572 nm erzeugt werden. Die Basiskontrastfarbe und der Kontrast werden durch die Dicke der Halbleiterschicht, durch die Wahl des Substratmaterials und die Dicke der transparenten Deckschicht eingestellt.

Die Farbschichten sind bistabil und damit vielversprechend für Bildschirmanwendungen mit geringem Energieverbrauch. Zusätzlich beruht ihre Funktionsweise auf Reflexion, wodurch die Farberscheinung auch in hellem Sonnenlicht gegeben ist. Jedoch basieren sowohl die statischen als auch die einstellbaren Farbschichten auf den dünnen, spröden Si und GST Schichten. Das Versagen dieser Schichten

Der durch Aluminium-induzierte Schichttaustausch wird angewendet, um Si bei Temperaturen unterhalb der maximalen Betriebstemperatur von Kapton® E zu kristallisieren. Mit Hilfe einer Parameterstudie wird gezeigt, dass Schichten, bei denen während der Herstellung hohe Sputterleistungen und niedrige Argonflüsse genutzt werden, niedrige Kristallisationstemperaturen besitzen.

Es werden verschiedene Methoden angewendet, um das Versagen der amorphen und kristallinen Si und GST Dünnschichten zu untersuchen. Es wird gezeigt, dass erste auftretende Risse in GST Schichten mit Reflexionsanisotropie-Spektroskopie (RAS) bestimmt werden können. Im Gegensatz zu anderen angewendeten Methoden kann sie sogar für sehr dünne GST Schichten verwendet werden.


Statische und einstellbare Farbbeschichtungen mit amorphen Si, sowie amorphen und kristallinen GST Schichten weisen einen geringeren Bruchwiderstand auf als einzelne Si und GST Schichten, welches durch einen Grösseneffekt erklärt werden kann.
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List of symbols and abbreviations

1 eV = 1.602 · 10⁻¹⁹ J 1 electronvolt
\( e = 1.602 \cdot 10^{-19} \text{ As} \quad \text{Electron charge} \)
\( c = 299 458 792 \text{ m/s} \quad \text{Speed of light} \)
\( h = 6.626068 \cdot 10^{-34} \text{ m}^2 \text{kg/s} \quad \text{PLANCK’s constant} \)
\( \epsilon_0 = 8.854 \cdot 10^{-12} \text{ F/s} \quad \text{Vacuum permittivity} \)

AFM  Atomic force microscopy
Ag  Silver
Al  Aluminum
AILE  Aluminum-induced layer exchange
Al₂O₃  Aluminum oxide
Ar  Argon
Au  Gold
CdTe  Cadmium telluride
CB  Conduction band
Cr  Chromium
dc  Direct current
DBR  Distributed Bragg reflector
\( E \)  Young’s modulus
\( \epsilon \)  Strain
\( f \)  Frequency
fcc  Face-centered cubic
Fe  Iron
\( G_0 \)  Energy release rate
GaSb  Gallium antimonide
Ge  Germanium
GST  Germanium antimony telluride (Ge₂Sb₂Te₅)
hcp  Hexagonal close-packed
HgTe  Mercury telluride
InAs  Indium arsenide
InSb  Indium antimonide
\( k \)  Imaginary part of the refractive index
\( K_{IC} \)  Fracture toughness
List of symbols and abbreviations

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<td>$\bar{L}$</td>
<td>Mean crack distance</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Light wavelength</td>
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<tr>
<td>MEMS</td>
<td>Microelectromechanical system</td>
</tr>
<tr>
<td>MIC</td>
<td>Metal-induced crystallization</td>
</tr>
<tr>
<td>MILC</td>
<td>Metal-induced lateral crystallization</td>
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<tr>
<td>$n$</td>
<td>Refractive index</td>
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<td>$\nu$</td>
<td>Poisson’s ratio</td>
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<td>Numerical aperture</td>
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<td>$\xi$</td>
<td>Stress transfer length</td>
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<td>$O_2$</td>
<td>Molecular oxygen</td>
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<td>PCM</td>
<td>Phase-change material</td>
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<tr>
<td>$R$</td>
<td>Resistance</td>
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<td>rf</td>
<td>Radio frequency</td>
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<td>Rh</td>
<td>Rhodium</td>
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<td>SEM</td>
<td>Scanning electron microscopy</td>
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<td>Si</td>
<td>Silicon</td>
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<td>$\sigma_f$</td>
<td>Fracture strength</td>
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<td>$\sigma_{res}$</td>
<td>Residual stress</td>
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<td>SiN</td>
<td>Silicon nitride</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>Silicon dioxide</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
</tr>
<tr>
<td>TEM</td>
<td>Transverse Electromagnetic</td>
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<tr>
<td>Ti</td>
<td>Titanium</td>
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<td>TiN</td>
<td>Titanium nitride</td>
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<td>TiO$_2$</td>
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<td>Ti:sapphire</td>
<td>Titanium-sapphire (laser)</td>
</tr>
<tr>
<td>VB</td>
<td>Valence band</td>
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<td>XRD</td>
<td>X-ray diffraction</td>
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1. Introduction

In this chapter the motivation, structure, and theoretical background of the thesis are introduced. It gives an overview about color coatings based on thin-film interference and describes the relevant theory about uniaxial tensile tests.

1.1. Motivation

Colors are an integral part of this world and have a large effect on our daily life: Signal colors are used to warn of a danger for instance in road traffic. We are attracted by vivid colors in nature such as the colorful wings of butterflies, and the color of our food often tells us if it is flavorful.

Humans and animals detect color when the receptors in the eyes interact with the photons of various wavelengths of visible light. Light interferes with matter and the material properties define which portion of the visible light enters our eye. Geometrical optic is one origin of color appearance and is exploited in structural colors where scattering, diffraction, refraction, or interference are involved. Thin-film interference causes one of the simplest structural colors such as the color appearance of soap bubbles or thin oil films. Light that is incident on a thin film is partially reflected at the two interfaces of the film. These reflected beams interfere and, depending on the thickness and the refractive index of the film, the spectrum of the reflected light can be strongly modulated. Stacking two alternating quarter-wave-thickness layers of transparent thin films with different refractive indices results in antireflection coatings or distributed Bragg reflectors (DBRs) depending on the sequence of the layer stack. The former is applied to glasses, windows, or in telescopes for instance while the latter is heavily employed in optical resonators or waveguides. Generally, only transparent films are considered for thin-film interference and absorption in the film does not need to be taken into account. The thickness of the films is on the order of the wavelength of the light.

Recently, a new concept of color coatings was introduced by Kats et al. [1]. They showed that capping a highly reflective metal (Au) with an ultrathin lossy dielectric (Ge) causes an absorption resonance in the visible wavelength range, and consequently a color appearance of the coating. This effect was called strong interference because absorption plays a major role in contrast to common thin-film interference coatings. The spectral position of the absorption resonance depends on the thickness of the dielectric. Changing the thickness of the top layer by only a few nanometers spectrally shifts the absorption resonance by tens of nanometers. The authors demonstrated color appearance from yellow, orange, pink, blue to green for Ge film thicknesses between 0 nm and 25 nm.
These coatings are attractive because of the considerable reduction in layer thickness. Numerous applications are conceivable and partly also demonstrated by today: These coatings are excellent candidates for solar cells [2, 3] because reducing the thickness of the material ensures less purity defects in the films [4]. Consequently, the lifetime of the photo-excited charge carriers is sufficient to reach the electrical junctions. Moreover, the approach of strong interference is promising for new types of photodetectors with improved quantum efficiency, for monitoring the thickness of the deposition of nanometer-sized semiconductors, or for coloring metals for arts or jewelry.

The aim of this thesis is to lay the materials foundations for static and tunable color coatings based on strong interference and to investigate their optical and mechanical properties:

Chapter 1 introduces the theoretical background of color appearance and failure of thin films due to strain.

Chapter 2 describes the development of static color coatings based on strong interference. Here, it is demonstrated that optical coatings with ultrathin Si capping layers are not exclusively limited to metals as underlying materials. We explain which optical properties of substrate material and dielectric are required to obtain deep and narrow absorption resonances.

Chapter 3 explores that the strong interference effect can be enlarged to tunable color coatings by switching the dielectric between the amorphous and crystalline phase. Color switching is demonstrated for the phase-change material Ge$_2$Sb$_2$Te$_2$ (GST) and the semiconductor Si.

Our main findings on the aluminum-induced layer exchange (AILE) mechanism to crystallize ultrathin Si films on polyimides substrates are presented in Chapter 4.

The cohesive and adhesive properties of ultrathin amorphous and crystalline Si on polyimide are presented in Chapter 5. Moreover, the mechanical properties of a static color coating is investigated.

Chapter 6 introduces the onset strain of fragmentation, the fracture strength, and fracture toughness as well as the onset strain of delamination of thin amorphous and crystalline GST films on polyimide substrates. The cohesive properties of the tunable color coating based on GST are determined.

Chapter 7 discusses possible applications of the developed static and optical color coatings and compares their properties to existing display applications.

Finally, the main conclusions are summarized in Chapter 8.
1.2. Concept of color appearance

1.2.1. Color description

The portion of the electromagnetic spectrum in the wavelength range from 380 nm to 750 nm is called visible light spectrum [5]. This spectrum includes all colors: Violet has the shortest wavelength and red has the longest. Monochromatic light, which is composed of a single wavelength and mixtures of different wavelengths are detected by the eye as color. Sir Isaac Newton was the first to demonstrate that a natural white light beam consists of a superposition of all different colors. He experimented with prisms, and showed that violet light is refracted the most by a prism and red light the least. This can be explained by Snell’s law:

\[ n_1 \sin(\phi_1) = n_2 \sin(\phi_2) \]  

(1.1)

Here \( n_1 = 1 \) is the refractive index of air and \( n_2 \) is the refractive index of the prism. The incident and refracted angles of light are described by \( \phi_1 \) and \( \phi_2 \). The refractive index is linked to the density of a material and describes the ratio of the wave velocity in vacuum, \( c \), and the wave velocity in a medium \( v \). Material shows chromatic dispersion which means that \( n \) depends on the wavelength \( \lambda \). Consequently, the refractive angles of different wavelengths differ from each other which explains Newton’s observation.

To define colors, a precise standard needs to be defined which was done by the Comission internationale de l’éclairage in 1931. This system is called CIE(1931) XYZ and has the advantage of an absolute color definition and it is able to encompass all colors distinguishable by the human eye. Thereby, a triplet representation of the colors is used in analogy to the human eye with its three distinct families of photosensitive cells. The process of determining colors is described by ASTM E 308-06 [6]. Firstly, an observer is defined by the CIE 1931 standard observer which corresponds to a field of view subtending a 2° angle of the retina (2° standard observer). Three dimensionless color matching functions \( \mathcal{X}(\lambda) \), \( \mathcal{Y}(\lambda) \), and \( \mathcal{Z}(\lambda) \) (see Figure 1.1 (a)) mimic the three main families of photosensitive cells in the human retina. As the curves strongly overlap and the blue color dominates, a clear edge reflector type reflectance curve is necessary to produce a red appearance. The CIE standard illuminant \( D_{65} \) (see Figure 1.1 (b)) is used to mimic sunlight. The following equations are obtained from [6]. The tristimulus values are calculated with the help of a reflectance curve \( R(\lambda) \) and the relative spectral power \( S(\lambda) \) (see Figure 1.1 (b)) of the 2° standard observer:

\[ X = k \int_{\lambda} R(\lambda)S(\lambda)\mathcal{X}(\lambda)d\lambda, \]

\[ Y = k \int_{\lambda} R(\lambda)S(\lambda)\mathcal{Y}(\lambda)d\lambda, \]  

(1.2)

\[ Z = k \int_{\lambda} R(\lambda)S(\lambda)\mathcal{Z}(\lambda)d\lambda. \]
The integration is carried out over the visible wavelength range and the normalization factor $k$ is defined as:

$$k = 100 / \int_{\lambda} S(\lambda) \overline{y}(\lambda) d\lambda.$$  \hfill (1.3)

In all practical calculations, the integrations are approximated by summations:

$$X = k \sum_{\lambda} R(\lambda) S(\lambda) \overline{x}(\lambda) \Delta \lambda,$$
$$Y = k \sum_{\lambda} R(\lambda) S(\lambda) \overline{y}(\lambda) \Delta \lambda,$$
$$Z = k \sum_{\lambda} R(\lambda) S(\lambda) \overline{z}(\lambda) \Delta \lambda.$$  \hfill (1.4)

with $k = 100 \left/ \sum_{\lambda} S(\lambda) \overline{y}(\lambda) \Delta \lambda \right.$.

These tristimulus values can be converted to Lab values, which are described with a three-dimensional coordinate system. The $a$-axis goes from green ($< 0$) to red ($> 0$), the $b$-axis from blue ($< 0$) to yellow ($> 0$), and the $L$-axis is a measurement of brightness ($L=0$ is black and $L=100$ is white) as can be seen in Figure 1.2.

$$L = 116 f(Y/Y_n) - 16,$$
$$a = 500 [f(X/X_n) - f(Y/Y_n)],$$
$$b = 200 [f(Y/Y_n) - f(Z/Z_n)],$$  \hfill (1.5)

with

$$f(Q) = \begin{cases} Q^{1/3}, & \text{if } Q > (6/29)^3, \\ \frac{4}{29} Q + \frac{4}{29}, & \text{if } Q \leq (6/29)^3. \end{cases}$$  \hfill (1.6)

$X_n$, $Y_n$, and $Z_n$ are defined for each illuminant (e.g. D$_{65}$: $X_n=95.047$, $Y_n=100$ and $Z_n=108.883$) and describe a white reference point. The difference between two
colors can be determined by the geometrical distance in the three-dimensional color space:

$$\Delta E = \sqrt{(L_2 - L_1)^2 + (a_2 - a_1)^2 + (b_2 - b_1)^2}.$$  

(1.7)

Here, $E$ represents the German word ”Empfindung” and means sensation. Human eyes start to distinguish two colors if the $\Delta E$-value is larger than 1. However, the human sensitivity to color differences depends also on the color. In the saturated yellow region for instance, a color difference of $\Delta E=3$ is sometimes harder to distinguish than a $\Delta E=0.5$ in midtone neutrals [7].

In computer technology the RGB system is more common and can be calculated from Equation (1.4). RGB values are given in the interval of $[0,255]$ and are obtained as follows [8]:

$$\begin{pmatrix} \tilde{R} \\ \tilde{G} \\ \tilde{B} \end{pmatrix} = \begin{pmatrix} 0.0324 & -0.0154 & -0.00499 \\ -0.00969 & 0.0188 & 0.000416 \\ 0.000556 & -0.00204 & 0.0106 \end{pmatrix} \begin{pmatrix} X \\ Y \\ Z \end{pmatrix}.$$  

(1.8)

with $R = 255f(\tilde{R})$, $G = 255f(\tilde{G})$, and $B = 255f(\tilde{B})$ and

$$f(Q) = \begin{cases} 1.055Q^{1/2.4} - 0.055, & \text{if } Q > 0.0031308 \\ 12.92Q, & \text{otherwise.} \end{cases}$$  

(1.9)

In this work the $Lab$ values of all simulated reflectance curves were determined by this calculation and usually the obtained color of the sample corresponds to the color of the graph.

### 1.2.2. Light interaction with material

The origin of colors in nature are described by Nassau [9]. He lists 15 different mechanisms, which include besides geometrical optics, also excitations and transitions between energy bands or molecular orbitals and transitions involving ligand-field effects. Here, we focus on two of them, namely the reflectance of metals and thin-film interference.
Introduction

Reflectance of metals

In contrast to semiconductors or insulators, metals exhibit a shiny appearance. The interaction of light with metals can be explained by electron band theory. The bonding of two atoms leads to two molecular orbitals, those of four atoms results in four molecular orbitals. Extrapolating this approach for a metal yields to countless energy levels which therefore, can be assumed to be continuous. The shape of these energy bands depends not only on the atomic orbitals but also on the spacing of the atoms. The valence bands include all electrons which are available for bonding. The highest filled electron energy level is called Fermi energy. In metals the valence bands are only partially filled up. There are three relevant optical excitations in a metal [10]:

(i) Intraband transition: These transitions involve the excitation of an electron from around the Fermi energy to an empty state within the same band. The absorbed light induces an alternating current on the metal surface which immediately re-emits the light out of the metal. Thus, if the absorption and re-emission of the light is equal for all wavelengths in the visible spectrum the metal appears silvery-white.

(ii) Interband transition: Excitation of an electron from a valence band close to the Fermi level to a conduction band above the Fermi energy requires light energies which at least correspond to the energy difference of the two involved bands. Light that excites the electrons is absorbed and thus missing in the reflectance spectrum. The onset of interband transitions is easily recognized in the reflectance spectrum of the metal. Gold for instance absorbs photons below 550 nm wavelength and therefore, blue and green light is missing in the reflectance spectrum which gives gold the typical yellow color appearance.

(iii) Plasma frequencies: A metal becomes transparent if the frequency of incoming light exceeds the plasma frequency of the metal. The high density of electrons in a metal leads to a collective oscillation of electrons (plasma) at the plasma frequency due to the Coulomb interaction. This motion produces fluctuations in the electron density. For most metals the plasma frequency lies in the ultraviolet spectral region.

Thin-film interference

Reflected and transmitted light from thin-film interference can be calculated from the so-called transfer matrix method. The analysis is carried out in terms of the quantities defined in Figure 1.3 and in analogy to [11, 12]. The boundary conditions state that the tangential components of the electric field \( \mathbf{E} \) and the magnetic field \( \mathbf{B} \) are continuous across the interfaces I and II (see Figure 1.3). Consequently, their magnitudes on either sides are equal. The electric field \( \mathbf{E} \) is chosen perpendicular to the normal vector of the plane of incidence.
Table 1.1.: Boundary conditions

<table>
<thead>
<tr>
<th></th>
<th>First interface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electric</td>
<td>$E_0 + E_{r1} = E_{t1} + E_{i1}$</td>
</tr>
<tr>
<td>Magnetic</td>
<td>$B_0\cos(\theta_0) - B_{r1}\cos(\theta_0) = B_{t1}\cos(\theta_{i1}) - B_{i1}\cos(\theta_{i1})$</td>
</tr>
<tr>
<td></td>
<td>$n_0 E_0\cos(\theta_0) - n_0 E_{r1}\cos(\theta_0) = n_1 E_{t1}\cos(\theta_{i1}) - n_1 E_{i1}\cos(\theta_{i1})$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Second interface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electric</td>
<td>$E_{t1}\exp(-i\delta) + E_{i1}\exp(i\delta) = E_{t2}$</td>
</tr>
<tr>
<td>Magnetic</td>
<td>$B_{t1}\cos(\theta_{i1})\exp(-i\delta) - B_{i1}\cos(\theta_{i1})\exp(i\delta) = B_{t2}\cos(\theta_{t2})$</td>
</tr>
<tr>
<td></td>
<td>$n_1 E_{t1}\cos(\theta_{i1})\exp(-i\delta) - n_1 E_{i1}\cos(\theta_{i1})\exp(i\delta) = n_s E_{t2}\cos(\theta_{t2})$</td>
</tr>
</tbody>
</table>

The phase factors $\exp(i\delta)$ and $\exp(-i\delta)$ with the phase difference $\delta = (2\pi/\lambda)n_1 d \cos(\theta_{i1})$ at the second interface result from the fact that the light travels through the film with thickness $d$. Moreover, it is taken into account that the magnitude of the electric field is the product of the wave speed ($v = c/n$) times the magnitude of the magnetic field. In the following, $E_{i1}$ and $E_{t1}$ are eliminated from the equations in Table 1.1:

$$1 + \frac{E_{r1}}{E_0} = \frac{E_{t2}}{E_0} \left[ \cos(\delta) - \frac{\gamma_s}{\gamma_1} i \sin(\delta) \right], \quad (1.10)$$

$$\gamma_0 - \gamma_0 \frac{E_{r1}}{E_0} = \frac{E_{t2}}{E_0} \left[ -i \gamma_1 \sin(\delta) + \gamma_s \cos(\delta) \right], \quad (1.11)$$

with $\gamma_0 \equiv n_0 \cos(\theta_0)$, $\gamma_1 \equiv n_1 \cos(\theta_{i1})$, and $\gamma_s \equiv n_s \cos(\theta_{t2})$. Equation (1.10) and

![Figure 1.3: Illustration of thin-film interference. The labeling corresponds to the derivation of the transfer matrix method in the text. The figure was motivated by [11].](image-url)
(1.11) written in matrix form yields:

\[
\begin{bmatrix} 1 \\ \gamma_0 \end{bmatrix} + \begin{bmatrix} 1 \\ -\gamma_0 \end{bmatrix} \frac{E_{r1}}{E_0} = \begin{bmatrix} \cos(\delta) & -i\frac{\sin(\delta)}{\gamma_1} \\ -i\gamma_1\sin(\delta) & \cos(\delta) \end{bmatrix} \begin{bmatrix} 1 \\ \gamma_s \end{bmatrix} \frac{E_{r2}}{E_0},
\]

which can be written as:

\[
\begin{bmatrix} 1 \\ \gamma_0 \end{bmatrix} + \begin{bmatrix} 1 \\ -\gamma_0 \end{bmatrix} r = M \begin{bmatrix} 1 \\ \gamma_s \end{bmatrix} t.
\]

\(M\) is known as transfer matrix, \(r\) is the reflection coefficient, and \(t\) the transmission coefficient. Equation (1.13) can be generalized for \(N\) layers with refractive indices \(n_1, n_2, n_3, \ldots, n_N\):

\[
\begin{bmatrix} 1 \\ \gamma_0 \end{bmatrix} + \begin{bmatrix} 1 \\ -\gamma_0 \end{bmatrix} r = M_1M_2M_3\ldots M_N \begin{bmatrix} 1 \\ \gamma_s \end{bmatrix} t,
\]

where the transfer matrices of the various layers are denoted with \(M_1, M_2, M_3, \ldots, M_N\). If the elements of the overall transfer matrix \(M\) are \(A, B, C,\) and \(D\),

\[
M = \begin{bmatrix} A & B \\ C & D \end{bmatrix},
\]

Equation (1.13) can be solved for \(r\) and \(t\) as follows:

\[
r = \frac{\gamma_0A + \gamma_s\gamma_0B - C - \gamma_sD}{\gamma_0A + \gamma_s\gamma_0B + C + \gamma_sD},
\]

\[
t = \frac{2\gamma_0}{\gamma_0A + \gamma_s\gamma_0B + C + \gamma_sD}.
\]

The reflectance \(R\) and the transmittance \(T\) are given by \(R = |r|^2\) and \(T = |t|^2\).

### 1.3. Si and Ge\(_2\)Sb\(_2\)Te\(_5\) properties

This work focuses on the semiconductors Si and Ge\(_2\)Sb\(_2\)Te\(_5\) (GST) applied to optical coatings based on strong interference. Hence, the most important properties and applications of Si and GST are shortly introduced.

**Si:**

The semiconductor Si is one of the most abundant materials on earth and can be found as compound in nature such as oxide or nitride. Elemental silicon is fabricated by reducing silica (SiO\(_2\)) in a high temperature furnace with coke as reducing agent [13]. Besides wafer applications, silicon is heavily employed in electronics and solar cells. It has a diamond crystalline structure which consists of two interpenetrated face-centered cubic (fcc) lattices overlapped with an offset of an unit cell vector of (1/4, 1/4, 1/4). Silicon is a semiconductor with an indirect band gap in which the valence band (VB) maximum is at another wave vector in k-space then the conduction band (CB) minimum. Therefore, recombination of an electron in the VB with a hole in the CB requires an interaction with a phonon to conserve momentum. This phonon interaction leads to heating of the crystal. The intrinsic
Table 1.2.: Crystal structure, band gap, and crystallization temperature $T_C$ of Si and Ge$_2$Sb$_2$Te$_5$.

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>Ge$_2$Sb$_2$Te$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>crystal structure</td>
<td>amorphous</td>
<td>metastable</td>
</tr>
<tr>
<td>band gap</td>
<td>1.12 eV [15]</td>
<td>0.7 eV [16]</td>
</tr>
<tr>
<td>$T_C$</td>
<td>$\approx 800^\circ$C [17]</td>
<td>$\approx 170^\circ$C [18]</td>
</tr>
</tbody>
</table>

The crystallization temperature of silicon is relatively high (see Table 1.2) and can be reduced by the presence of a metal: (i) The formation of compounds (silicide) helps to decrease the crystallization temperature. This is the case for Si in contact with a metal such as Ni, Pd, or Cu. (ii) Metals such as Al, Au, or Ag result in an eutectic metal-silicon system. Here, the silicon bonds are weakened and silicon nucleation is promoted [14]. This metal-induced crystallization is a promising approach for fabricating polycrystalline Si (poly-Si) films on cheap substrates such as glass or plastic and is employed in this work to investigate the mechanical properties of poly-Si on polyimide substrates (see Chapter 4 and 5).

Ge$_2$Sb$_2$Te$_5$: Ge$_2$Sb$_2$Te$_5$ (GST) belongs to the rare class of phase-change materials (PCMs). They can be rapidly and reversibly cycled between the amorphous and crystalline state. The reflectivity contrast between the two phases is up to 30 \% [20] and is exploited in rewritable optical data storage. The electrical resistivity changes up to several orders of magnitude.

Figure 1.4.: Illustration of a thermal cycle. The amorphous phase-change material is crystallized by a heating pulse above the crystallization temperature. Reamorphization occurs by melting the phase-change material and subsequently, rapid cooling of the liquid phase. This figure was motivated by [19].
orders of magnitude upon the phase transition [21] and offers great potential as non-volatile electronic memory. The principle of a thermal cycle is demonstrated in Figure 1.4. Crystallization of the PCM is realized by a low intensity heating pulse either by a laser pulse in optical data storage application or by an electrical current pulse in electronic memory devices. Heating the material above the glass transition temperature enables the atoms to arrange in the energetically favorable periodic structure. The crystallization time is the limiting factor for the switching speed [22]. Amorphous GST crystallizes in the meta-stable face-centered cubic NaCl structure where the Ge and Sb atoms and the vacancies randomly distribute the "Na" sites (4(b)) and the Te atoms are located at the "Cl" sites (4(a)) [23]. However, Kolobov et al. suggest a displacement of the Sb and Ge atoms such that the Ge atoms switch from tetrahedral to octahedral positions upon phase-change [24]. For GST the crystallization is nucleation-dominated in contrast to the PCM AgInSbTe which is growth-dominated [25]. The crystallization temperature and time strongly depends on the GST film thickness but also on the capping layer [26]. Reamorphization of the crystalline bit is obtained by a short laser or current pulse of high intensity to melt the material. A cooling rate higher than \(10^9\) K/s quenches the melt into the amorphous phase [22].

Although, the first phase-changing electrical characteristic was already discovered in 1917 by Waterman and since then numberless researchers have investigated and improved the properties of phase-change materials, still some open questions and challenges remain. For instance the large thickness decrease (GST: 6.5% [27]) upon crystallization yields to void formation over the bottom electrode [28]. Hence, the device can no longer be switched to the low resistance state and the cycling number is reduced.

Comparing the properties of GST to those of Si raises the question why a semiconductor such as Si is unfavorable as phase-change material. The atoms in crystalline Si form tight covalent bonds with each surrounding atom which yields a high melting temperature. Hence, a large energy needs to be applied to amorphize Si. Moreover, the high viscosity of amorphous Si results in slow atomic diffusion and therefore long crystallization times.

1.4. Concept of thin film failure

Stress in a thin film has three main origins which might lead to failure of the thin film: Thermal, intrinsic, and mechanical [29]. Thermal and intrinsic stress are summarized as residual stress and result from fabrication processes. For instance, during sputter deposition different parameters such as grain growth, phase transitions, or ion bombardment of the film may generate stress in the film. Moreover, differences in thermal expansion coefficients of film and substrate yield stress due to temperature changes. Here, the focus is on mechanical stress which arises from mechanical loads.

The tensile stress in a thin film on a compliant substrate increases during uniaxial loading. As soon as the stress exceeds the fracture strength of the largest defect, a crack is formed and grows perpendicular to the loading direction. The strain value at which the first crack occurs is called onset strain of fragmentation \(\epsilon_{on}\) and de-
Figure 1.5.: Example of mean crack distance as a function of strain. The first crack in the film appears at the onset strain of fragmentation \( \epsilon_{on} \). At the transition from the first to the second regime at \( \epsilon_c \), the stress relaxation zones start to overlap. In the third regime at \( \epsilon_{sat} \) no more cracks occur and the mean crack distance \( L_{sat} \) saturates.

The lateral contraction mismatch of substrate and coating leads to the formation of compressive stress in the coating perpendicular to the loading direction. During straining this compressive stress increases and induces delamination of the coating. Generally, delamination of the film start at the fragmentation boundaries at the location of maximal compressive stress.
2. Static color coatings based on ultrathin semiconductors

This chapter presents that optical coatings based on ultrathin highly absorbing dielectrics are not limited exclusively to metals as underlying material as assumed previously. We demonstrate that the underlying metal can be replaced by any material if several layers are used such that the effective optical constant resembles that of a highly reflective metal. Consequently, the optical properties are tunable by the choice of material, the number of layers, and the layer thickness and are hence more adaptable to the potential application.

The main findings presented in this chapter are published in Applied Physics Letters [31].

2.1. Introduction

Light interacting with nano- or microstructures results in intense and bright colors because of diffraction, scattering, or thin-film interference [9]. For instance, there have been numerous demonstrations of colors caused by interference in periodic multilayers [32–35]. The optical thicknesses of those transparent films are usually on the order of the wavelength [11]. Recently, Kats et al. [1] presented a new technique based on thin-film interference in ultrathin (5 - 25 nm) highly absorbing dielectrics on metals. The considerable reduction of the film thickness in comparison to transparent layers is enabled by a combination of the large absorption in the dielectric and the non-trivial phase-shift at the interface between metal and dielectric. A non-trivial phase-shift is not only limited to 0 or π as for transparent materials or perfect electric conductors but is wavelength-dependent. The resulting strong absorption resonance depends on the thickness such that various but not all bright colors are tunable.

In this work we show that thin-film interference in ultrathin dielectrics does not only appear on metals, but also on insulator layers and semiconductor structures. The required non-trivial phase-shift at the interface between the dielectric and the underlying material, as well as the high reflectance of the latter, are tunable by the number and thickness of the layers. In our devices, only one (two) bilayer(s) of insulators (semiconductors) are necessary for color appearance because of the low reflectance of the Si substrate. In contrast, it has been simulated [2] that anti-reflection resonances based on ultrathin dielectrics in solar cells require four to six bilayers. For color coatings based on ultrathin dielectrics, metals can be replaced by stacks of layers of various materials, provided their effective optical constants resemble those of a highly reflective metal. The effective optical constant is the optical
constant of an equivalent semi-infinite medium which can replace the multilayers and has the same optical properties.

### 2.2. Materials and Methods

Schematics of the three different studied structures are presented in Figure 2.1. The insulator and semiconductor structure were designed with the help of simulations. In a first step quarter-wave-thickness layers (at $\lambda = 550$ nm) with the high index material on top of the low index material were chosen as starting parameters to increase the reflectance of the multilayers (in analogy to a distributed Bragg reflector). In a second step the thickness of the layers were optimized for bright color appearance. We used amorphous Si with thicknesses between 0 and 30 nm as dielectric. For the metal structure 86 nm thick Au was utilized. The insulator structure comprises amorphous SiO$_2$ and amorphous TiO$_2$ while the semiconductor structure consists of a double layer of amorphous Ge and amorphous Si. All films were prepared by sputter deposition.

The Au and TiO$_2$ films were deposited by direct current (dc) and the Si, SiO$_2$, and Ge films by alternating current (ac) sputter deposition on (100) oriented Si wafers. The substrate was rotated during deposition in order to achieve uniform film thicknesses and the base pressure in the sputter chamber was lower than $10^{-4}$ Pa. For each structure the layers were deposited on the polished (smooth) surface and on the unpolished (rough) surface of a Si wafer to specify the sensitivity of the color to the angle of incidence of the light. The reflectances of the different structures were determined with a fiber spectrometer. The measurements were performed at an incidence angle of 0° and at wavelengths ranging from 300 to 800 nm. The refractive indices of SiO$_2$ and TiO$_2$ were measured by ellipsometry at an incidence angle of 70° and the ellipsometric parameters $\Psi$ and $\Delta$ were fitted with the Cauchy equation [36]. The refractive indices of Au [37], amorphous and crystalline Si [38], and amorphous [39] and crystalline [40] Ge were obtained from literature. The reflectance for s-polarized light was simulated with the transfer matrix method which can be found in optics textbooks [11, 41]. The colors of the samples were calculated from the simulated reflectance curves in analogy to [6] by using the standard illuminant D$_{65}$ [42].

![Figure 2.1](image_url)

**Figure 2.1.** Schematics of the different samples comprising ultrathin Si with thicknesses between 0 and 30 nm are presented. The underlying materials are (a) Au (metal structure), (b) TiO$_2$ and SiO$_2$ (insulator structure), and (c) a double layer of Ge and Si (semiconductor structure).
and the color matching functions [42] of the 1931 2° standard observer as described in Chapter 1. A Raman measurement was performed with a green laser (532.24 nm) and at low laser power of 0.5 mW to avoid a crystallization of the semiconductors [43].

2.3. Results

Figure 2.2 shows photographs of the various sample structures with variable Si thicknesses deposited as top layer. The photographs demonstrate bright color appearance for the metal and insulator structures. The colors of the metal structure on the smooth surface are in good agreement with those on the rough surface. However, this is not the case for the two other structures which indicates that the reflectances of the insulator and semiconductor structure vary more strongly with the angle of incidence of the light as compared to the metal structure. To support these findings theoretically, the incident angle-dependent reflectance was simulated for each structure coated with 15 nm Si (see Figure 2.3).

![Figure 2.2:](image)

**Figure 2.2:** I-IX: 0, 3, 5, 7, 10, 15, 20, 25, and 30 nm of Si deposited on the different sample structures on the polished side (smooth surface) and on the unpolished side (rough surface) of a Si wafer. The metal and insulator structures create a spectrum of bright colors from yellow, red, pink to blue while the semiconductor structure changes from gray to blue.

The absorption resonance of the metal structure remains prominent for angles of incidence from 0° to approximately 80°. However, the reflectance of the insulator structure is constant between 0° and 60° and the semiconductor structure only between 0° and 30°. Consequently, especially the reflectance of the semiconductor structure is strongly dependent on the angle of incidence of the light.

Figure 2.4 presents the experimental and calculated reflectance spectra of the metal, insulator, and semiconductor structures. The reflectance spectra were measured and calculated for the structures without Si and with Si in the thickness range between 5 nm and 30 nm. The colors of the graphs correspond to the measured or
Static color coatings based on ultrathin semiconductors

Figure 2.3.: Simulated reflectance spectra with s-polarized light for a 15 nm Si layer on (a) the metal structure, (b) the insulator structure, and (c) the semiconductor structure. The optical properties of the metal structure are more robust with respect to the incident angle than those of the two other structures. Nevertheless, the reflectances of all structures remain at least prominent between 0° and 30°.

Simulated colors of the sample. While the simulated and measured reflectance spectra and sample colors given in Figure 2.4 (a)-(f) are in excellent agreement with each other, small deviations between measurements and simulations can be explained by differences between the refractive indices of the sputtered films and those taken from literature caused by, e.g., different densities [44]. Both, the reflectance of the metal and the insulator structure show distinct absorption resonances which shift to longer wavelengths with increasing Si thickness. These distinct absorption resonances result in bright colors including yellow, orange, red, purple, and blue. Also the reflectance spectra of the semiconductor structure exhibit absorption resonances. However, they are not as deep and narrow as those of the other two structures. Consequently, the color appearance only changes from gray to blue as a function of Si film thickness.
The weak absorption resonances and hence also slightly pronounced colors of the semiconductor structure indicate that bright colors of the samples are obtained on the following three conditions:

- **Non-trivial phase-shift**: As already stated by Kats *et al.* [1], a non-trivial phase-shift at the interface between the dielectric and the underlying structure is required for an absorption resonance. This is fulfilled by using metal or semiconductor materials or several layers of insulator material as substrate.

- **Minimal reflectance**: A minimal reflectance of the underlying material guarantees the possibility of a deep absorption resonance and consequently a bright
Figure 2.5.: Simulated reflectance spectra and colors with the corresponding refractive indices of different semiconductors on Au and Fe. The refractive indices of InAs, HgTe, and Fe were taken from literature [37–39]. The positions of the absorption resonances are highlighted in gray. Narrow absorption resonances are observed if $|\frac{dk}{d\lambda}|$ of the metal and the dielectric are large. While in (a) only $|\frac{dk}{d\lambda}|$ of the dielectric is large, in (b) only the absorption of the metal is strongly dependent on the wavelength at wavelengths between 520 and 580 nm. In (c) an ideal combination of metal and dielectric is presented: $|\frac{dk}{d\lambda}|$ of both materials is pronounced in the same wavelength range and consequently bright colors are obtained.

color. The required reflectance of above 60% is given for most metals and is tunable by several layers for all other materials.

- **Dispersion:** Narrow absorption resonances occur at wavelengths $\lambda$ where $|\frac{dk}{d\lambda}|$ of the underlying material and the dielectric are large (in the following dispersion). Here, $k$ is the imaginary part of the refractive index. The gray highlighting in Figure 2.5 indicates that absorption resonances indeed appear as well when only $|\frac{dk}{d\lambda}|$ of the dielectric is large (see Figure 2.5 (a)). However, bright colors and distinct absorption resonances are only obtained if the absorption of both materials are strongly varying with the wavelength as presented in Figure 2.5 (c). Figure 2.5 (b) shows that a large $|\frac{dk}{d\lambda}|$ of the metal is not sufficient for an absorption resonance (see particularly in the wavelength range between 520 nm and 580 nm). In the following, the dependence of the absorption resonance on the material dispersion is derived in a simulation. Therefore, the reflection coefficient is calculated with light incident at an angle of 0° [41]:

$$r = \frac{r_{12} + r_{23}e^{2i\beta}}{1 + r_{12}r_{23}e^{2i\beta}},$$

(2.1)

with the Fresnel formulæ $r_{mn} = (\tilde{n}_m - \tilde{n}_n)/(\tilde{n}_m + \tilde{n}_n)$ and $\beta = (2\pi/\lambda)\tilde{n}_2h_2$. Here, $\tilde{n}$ is the complex refractive index $\tilde{n} = n + ik$, $h$ the film thickness, and $\lambda$ is the wavelength. Layer 1 is air, layer 2 is the semiconductor and layer 3 the metal. An absorption resonance ($r \approx 0$) only occurs for some combinations of the refractive indices of both materials. A large $|\frac{dk}{d\lambda}|$ causes strongly wavelength-dependent refractive indices. Therefore, the ideal combinations of
the refractive indices for \( r \approx 0 \) are given at a small (large) wavelength range if \(|dk/d\lambda|\) is large (small). Consequently, large \(|dk/d\lambda|\) lead to narrow absorption resonances and bright colors. To demonstrate this, the reflectance of a \( h_2=15 \) nm thin InAs film on Au is simulated for different \(|dk/d\lambda|\). Therefore, all parameters in Equation 2.1 are kept constant and only \( k(\lambda) \) is approximated linearly in small intervals of \( \lambda - \lambda_0=1 \) nm. \(|dk/d\lambda|\) can then be tuned locally with the help of the factor \( m \):

\[
k(\lambda) = k(\lambda_0) + m \frac{dk(\lambda_0)}{d\lambda} (\lambda - \lambda_0).
\]  

(2.2)

Figure 2.6 presents the simulated reflectances for three different \(|dk/d\lambda|\). If \(|dk/d\lambda|\) of both materials is increased (\( m=1.3 \)) the width of the absorption resonance is focused to a smaller wavelength range than for the original \(|dk/d\lambda|\) (\( m=1 \)) and consequently, a brighter color is expected. A smaller \(|dk/d\lambda|\) (\( m=0.7 \)) leads to a broader absorption resonance. Consequently, absorption resonances in materials with large \(|dk/d\lambda|\) are expected to generate bright colors. However, it could be argued that not \(|dk/d\lambda|\) but the different value of \( k \) origins the change of the shape of the absorption resonance. This can be ruled out, since an offset of \( k \) has the same effect as a different thickness of the semiconductor structure (optical path \( d = h \cdot n \)). Another approach to understand the dispersion dependence of the absorption resonance is in analogy to the work by Zhang et al. [2]. They tried to expand the phase of \( r_{23}(r_{23}) \) in the wavelength range from 550 nm to 650 nm to achieve anti-reflection resonance in this range with ultrathin semiconductors. As the following conditions are usually fulfilled, a large \(|dk/d\lambda|\) of both materials causes an increasing difference between \( k_2 \) and \( k_3 \) with respect to the wavelength. Above the band gap energy \(|dk/d\lambda|\) of a semiconductor is mostly negative. The absorption of a semiconductor decreases with increasing wavelength (decreasing energies) because the energy of the photons must be larger than the band gap. For metals, \(|dk/d\lambda|\) is larger or equal to zero. In the latter case, the efficiency of absorption and re-emission of light is equal at all optical energies and \(|dk/d\lambda|\) is greater than zero if the efficiency depends on selection rules.

\[
\phi(r_{23}) = \tan^{-1}\left( \frac{\text{Im}(r_{23})}{\text{Re}(r_{23})} \right)
\]

(2.3)

\[
\phi(r_{23}) = \tan^{-1}\left( \frac{2n_2(k_3 - k_2) + 2k_2(n_2 - n_3)}{(k_3 - k_2)^2 + 2k_2(k_3 - k_2) + n_3^2 - n_2^2} \right). 
\]

(2.4)

Consequently, a large \(|dk/d\lambda|\) of both materials (i.e. \( k_3 - k_2 \) is strongly wavelength-dependent) leads to a larger expansion of the phase (see Equation 2.4) and has the same effect as tuning the phase. However, our approach has the advantage that the refractive indices of the materials are in most cases given in literature and therefore, it is not necessary to calculate the phase.

In summary, a large \(|dk/d\lambda|\) leads to narrow absorption resonances since the ideal refractive indices for a reflectivity \( r \approx 0 \) are limited to small wavelength ranges. This condition is in agreement with the observation of [1], where
The imaginary part of the refractive index of InAs (a) and Au (b) is shown. A change of the slope \( m \) of the refractive indices of InAs and Au causes a change of the absorption resonance (c). An increase of \( |dk/d\lambda| \) \((m=1.3)\) leads to a sharper reflectance minimum and consequently, a brighter color is expected. If \( |dk/d\lambda| \) is decreased \((m=0.7)\) the absorption resonance is expanded.

Bright colors for ultrathin Ge films on Au (large \( |dk/d\lambda| \) of Ge and Au) and only pastel colors for Ge on Ag were obtained. Remarkably, bright colors can be observed for thin amorphous Si layers on Ag, because the absorption of amorphous Si varies stronger with the wavelength than that of Ge. This allows for the tuning of the semiconductor properties to the optical properties of the conducting materials. A material leading to bright interference colors on top of Ag, for instance, would be CdTe.

The Raman measurement (see Figure 2.7 (a)) of the semiconductor structure indicates that the sputtered Si and Ge layers are amorphous as the peak positions are

The peak positions of the Raman spectrum of the semiconductor structure (a) are in good agreement with amorphous Ge-Ge modes and amorphous Si-Si modes [45]. To show that bright colors can be achieved with a semiconductor structure, simulations of the colors and reflectance spectra (b) of a crystalline semiconductor structure (analogous to those in Figure 2.1(c) but with four instead of two bilayers) coated with 0 to 30 nm Si are shown.
in good agreement with amorphous Si-Si modes at 475 cm$^{-1}$ and with amorphous Ge-Ge modes at 275 cm$^{-1}$ (marked with gray lines in the figure) [45]. To demonstrate distinctive absorption resonances for a semiconductor structure, a simulation of a structure analogous of that in Figure 2.1 (c) but with crystalline Si and Ge and with four instead of two bilayers is presented in Figure 2.7 (b). The resulting colors are intensive and can compete with those of the metal and insulator structures.

It should be mentioned that a reduction in interference layer thickness in contrast to conventional optical coatings poses additional demands on the layer thickness accuracy to obtain a predefined color. However, strong interference in ultrathin semiconducting layers does not influence the periodicity of higher-order interference. Our approach has the advantage that a lot more parameters (e.g. thickness, number of layers, or material type) are adjustable for an effective optical constant which resembles that of a metal and is consequently more adaptable to the corresponding application. Moreover, not only a larger number of colors, but also other characteristic features such as electrical, thermal, mechanical, or chemical properties or even material costs are tunable by choosing the corresponding material class. For instance, coating a Bragg reflector consisting of transparent material with ultrathin dielectrics allows different bright colors to appear not only in reflectance but also in transmittance depending on the thickness of the dielectric as can be seen in the simulations in Figure 2.8.

**Figure 2.8.**: Simulation of the (a) reflectance and (b) transmittance of 2 bilayers of SiO$_2$-TiO$_2$ coated with amorphous Si with varying thickness on a glass substrate (layer thicknesses are in analogy to Figure 2.1 (b)). Completely different colors are obtained for the transmittance measurement in comparison to the reflectance measurement.
A possible application for this approach is coloring glass to produce color appearance depending on the position of the light source. Furthermore, other material classes like polymers are also potential candidates as underlying material for these color coatings.

2.5. Conclusion

In conclusion we propose color coatings with ultrathin Si layers on a variety of substrate materials. The effective optical constant of the substrate material must resemble that of a highly reflective metal. Furthermore, the absorption coefficients of the dielectric and the underlying materials need to depend strongly on the wavelength to achieve deep and narrow absorption resonances and therefore bright colors. This study confirms that various material systems can be chosen to improve the optical appearance and decrease the material costs.
3. Tunable color coatings based on ultrathin Si and Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5}

This chapter demonstrates that optical coatings based on strong interference are attractive for tunable color coatings by reversibly switching ultrathin phase-change materials on Au between two colors with femtosecond laser pulses. The optical contrast is enhanced compared to conventional thick phase-change materials, and its spectral maximum is tunable via the thickness of the phase-change material. Color switching is even feasible if the phase-change material is replaced by a conventional group IV semiconductor, whose amorphous and crystalline phases are optically less distinct. These structures hold significant promise for optical data storage and for display applications. The content of this chapter was published in similar form in ACS Photonics [46].

3.1. Introduction

Phase-change materials can be switched rapidly and reversibly between the amorphous and the crystalline state associated with a large optical and electrical property contrast [20]. They are applied in optical data storage devices and offer great potential as non-volatile electronic memories [24, 47]. Recently, Hosseini et al. [48] have combined the optical and electronic property modulation of PCMs. They demonstrated electrically induced color changes in phase-change materials (Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5}) with transparent electrodes. The device works analogous to an optical cavity where the thickness of the transparent electrode acts as cavity length. Consequently, the color appearance can be tuned via the thickness of the transparent film. These devices are promising candidates for applications such as ultrafast displays or artificial retina devices.

Here, we present that recently established static color devices [31, 49] can be rapidly cycled between two colors. Ultrathin semiconductors (5-30 nm) on appropriately chosen [31] highly reflective metals lead to bright color appearances. Here, the strong interference effect is applied to dynamically tunable color devices. The shape of the absorption resonance is strongly dependent on the slope of the imaginary part of the refractive index of the semiconductor. Consequently, only a small change in refractive index results in a large change in reflectance. We demonstrate that ultrathin phase-change materials and even conventional semiconductors on appropriately chosen metal substrates change color upon a phase transformation. The phase transitions are induced either thermally in a furnace or by femtosecond optical excitation. Conventional semiconductors such as Si typically do not exhibit
a strong phase-induced optical contrast compared to phase-change materials [50]. Here, it is shown that the optical contrast of 12 nm thick Si on Ag is comparable to that of PCMs. These findings could lead to a paradigm shift in optical data storage applications. Replacing PCMs by conventional semiconductors reduces the costs of production and prevents both the need for toxic materials and the contamination of the processing equipment. Moreover, these layer structures are interesting for non-volatile, ultrafast display applications.

3.2. Materials and Methods

The Cr, Au, Ag, Ti, TiN, and GST layers were deposited by direct current, and the Si and SiO\textsubscript{2} films by alternating current sputter deposition on a (100)-oriented Si substrate with 50 nm SiO\textsubscript{2} and 50 nm SiN\textsubscript{x} diffusion barriers. The substrate was rotated at 30 rpm during deposition to achieve uniform film thicknesses, and the base pressure in the chamber was lower than 10\textsuperscript{−4} Pa. To crystallize the layers, the GST sample was annealed at 175 °C for 5 min and the Si sample was annealed at 800 °C for 10 s in a rapid thermal anneal oven. The reflectance of the different samples was measured with a fiber spectrometer at an incident angle of 0° and in the wavelength range between 300 nm and 800 nm. Photographs were taken with a Nikon D7100 camera with a Nikon 200 mm f/4 AF-D macro lens. The samples were illuminated with RB 218N HF lighting units from Kaiser with a color temperature of 5400 K. The microscope images were taken with a Nikon Eclipse L200D optical microscope. The built-in light source was a 12 V/100 W halogen lamp.

The reflectance for s-polarized light was simulated with the transfer matrix method described in Section 1.2.2. The refractive indices were taken from literature [37, 38, 51–53]. The colors of the samples were calculated from the simulated reflectance curves by using the standard illuminant D\textsubscript{65} and the color matching functions of the 1931 2° standard observer [6].

The Raman measurements were performed with a green laser at 532 nm. The laser intensity was reduced to 0.25 mW \textmu m\textsuperscript{−2} for the Si sample and to 0.16 mW \textmu m\textsuperscript{−2} for the GST sample to avoid crystallization of the sample.

A Ti:sapphire laser illuminated the material with 60 fs laser pulses at 800 nm wavelength. The incident angle was 0°, and the fluence was adjusted with a polarizing beam splitter for amorphization and crystallization. A HeNe laser at 633 nm wavelength was used to determine the reflectance contrast at the spots. The laser spot diameter of the HeNe laser was 60 \textmu m. The incident angle was 6°, and the reflectivity change was recorded with a photodiode with a temporal resolution of 1 ns. The temporal resolution of the setup is limited by the sampling rate of the oscilloscope in combination with a low-pass filter, which limited the frequency range to 10 MHz and was employed to reduce the impact of high-frequency noise coming from the fast photodiode. The laser spot diameter of the Ti:sapphire laser was 270 \textmu m for the GST sample and 120 \textmu m for the Si sample.
3.3. Results

In Figure 3.1 (a), a cross-sectional transmission electron micrograph shows the layer structure of the tunable color device based on GST, as fabricated by magnetron sputter deposition. Au is chosen because its imaginary part of the refractive index $k$ is strongly dependent on the wavelength. The SiO$_2$ capping layer prevents oxidation and evaporation of the phase-change material, and Ti and TiN act as diffusion barrier between Au and GST. The position of the absorption resonance can be controlled via the thickness ($h_{GST}$) of GST.

To experimentally verify that only a small change in the refractive index is sufficient for color changes, a sample device with ultrathin Si on Ag was sputter deposited (see Figure 3.1 (b)). The optical contrast at 633 nm wavelength between amorphous and crystalline Si is increased if the underlying metal Au is replaced by Ag. Narrow absorption resonances and, therefore, bright colors are expected for Si on a metal because the absorption coefficient of Si strongly depends on the wavelength [31].

Figure 3.2 shows photographs of amorphous and crystalline thin films of GST with different thicknesses embedded in a layer structure analogous to that in Figure 3.1 (a). The color of the amorphous GST structure changes from purple to blue to gray-blue and the absorption resonance shifts to longer wavelengths with increasing film thickness (see Figure 3.3). The absorption resonance is broad because the absorption coefficient of amorphous GST is only slightly dependent on the wavelength. The crystalline samples are grayish for all film thicknesses and the reflectance spectra are almost unchanged for thicknesses above 12 nm. Consequently, the maximal optical contrast between the amorphous and the crystalline samples shifts to longer wavelengths with increasing GST thickness.

Figure 3.4 presents photographs and measured reflectance curves of layer stacks based on Si. The absorption resonances are deep and narrow for amorphous and crystalline Si. An increase of only 2-3 nm in Si thickness shifts the position of the ab-
Tunable color coatings based on ultrathin Si and Ge$_2$Sb$_2$Te$_5$

Figure 3.2.: Photographs of amorphous and crystalline films of GST with different thicknesses are shown. The sample structure is in analogy to that in Figure 3.1 (a).

Absorption resonance about 50 nm to longer wavelengths. Consequently, samples with Si of varying thickness are clearly distinguishable by their different color appearance. The absorption coefficient of crystalline Si decreases stronger with increasing wavelength than that of amorphous Si. Therefore, the absorption resonances of crystalline Si structures are not as deep as those of amorphous layer structures for longer wavelengths. This difference in absorption coefficient at longer wavelengths results in a large optical contrast.

Figure 3.3.: Reflectance spectra of amorphous and crystalline GST samples with (a) 8 nm, (b) 12 nm, (c) 15 nm, (d) 18 nm, and (e) 20 nm thick GST. The colors of the curves correspond to the measured colors of the sample. Here, the crystalline samples were annealed at 200°C for 5 min.
Figure 3.4.: Photographs and reflectance spectra of amorphous and crystalline Si samples are presented. The colors of the curves correspond to the measured colors of the samples.

3.4. Discussion

In simulations the thickness of GST $h_{GST}$ is optimized to maximize the reflectance contrast $(R_c - R_a)/R_c \cdot 100$ between amorphous and crystalline GST (see Figure 3.5). $R_c$ and $R_a$ denote the reflectance of the crystalline and amorphous phase, respectively. The design goal is to optimize the optical contrast at 633 nm wavelength because the reflectance change upon phase-change is probed for reversible color-switching with a continuous laser beam at this wavelength. The maximal optical contrast at 633 nm wavelength $\Delta R/R_c = 74\%$ is achieved for 18 nm thick GST. This optical contrast exceeds the typically required value for optical data storage of 60% [54]. Figure 3.6 (a) shows the measured and simulated reflectance spectra of an as-deposited amorphous sample and a crystalline sample annealed at $175^\circ$C for 5 min in a furnace.

In the amorphous phase GST exhibits semiconducting behavior, while its crystalline cubic phase is a degenerate semiconductor with orders of magnitude higher carrier concentration [55]. Consequently, an amorphous PCM on top of a metal leads to the strong interference effect and, therefore, a color appearance, while it is metallic-gray in the crystalline phase. The measured and simulated reflectance curves of the amorphous and crystalline layer stacks are in good agreement.

To prove that the color change is associated with a phase-change, i.e., crystallization, we performed Raman spectroscopy on both samples (see Figure 3.6 (b)). The Raman peaks of the as-deposited sample at 129 cm$^{-1}$ and 152 cm$^{-1}$ are in good agreement with those corresponding to amorphous GST [24, 56]. Also the
Figure 3.5.: The thickness of GST is optimized in a simulation to maximize the optical contrast between amorphous and crystalline GST at 633 nm wavelength. The white line indicates the maximum optical contrast for each wavelength.

Raman peak of the annealed sample and that of cubic GST in literature are in good agreement and confirm the phase transition to the cubic phase upon oven-annealing [24]. The measured optical contrast at 633 nm wavelength is $\Delta R/R_c=76\%$ and slightly exceeds the simulated one.

For display or data storage applications, fast and reversible color switching is crucial. We demonstrate this by illumination of the sample with femtosecond laser pulses for six switching cycles (see Figure 3.7 (a)). The reflectance is measured at 633 nm wavelength. Femtosecond laser pulses were chosen because of two advantages compared to nanosecond pulses: The fluence values are lower due to the absence of thermal loss during the heating process, and the amorphization time is shorter [57]. To amorphize GST, a single pulse of 60 fs at 800 nm is applied with a fluence of $14.3\pm0.8 \text{ mJ cm}^{-2}$. The crystalline phase is obtained after repetitive excitation.

Figure 3.6.: Measured and simulated reflectance curves of amorphous and crystalline samples are shown (a). The colors of the curves correspond to the measured and simulated colors of the samples. (b) A comparison with a Raman spectroscopy measurement in literature [24] indicates that the annealed sample is crystalline.
at a lower fluence of 4.0 ± 0.3 mJ cm⁻². To induce crystallization in the as-deposited amorphous layer, the sample is exposed to 60 fs long pulses for 32 s at a repetition rate of 40 Hz. The phase transformation of as-deposited amorphous GST is limited by nucleation, but recrystallization of a melt-quenched amorphous spot is found to occur faster possibly because of the presence of subcritical crystalline nuclei [58]. Here, the melt-quenched amorphous spot was recrystallized by repetitive illumination for 16 s. Increasing the repetition rate of the laser to 960 Hz (see Figure 3.7(b)) reduces the crystallization time to 500 ms. Consequently, in the present case this switching time is limited by the repetition rate of the laser, but it is well-known from literature that crystallization can be completed within tens of nanosecond [59] after optical excitation. Figure 3.7(c) shows the reflectance change during amorphization. The configuration of the setup limited the determination of the amorphization time to a 100 ns time resolution. The dashed lines in Figure 3.7(a) indicate the reflectivity of the as-deposited amorphous and oven-annealed crystalline samples. The reflectance of the laser amorphized GST is higher than that of the as-deposited sample. This is also visible in Figure 3.7(e). The region that was reamorphized by laser is slightly brighter than the as-deposited amorphous surrounding.

In Figure 3.8(a), the measured and simulated reflectance spectra of the as-deposited and annealed crystallized Si samples are presented. The absorption resonance around 570 nm shifts to shorter wavelengths upon phase transformation, and consequently, the optical contrast is largely enhanced. Measurements and simulations are in good agreement, and the small differences could be explained by differences in the refractive indices of the sputtered samples and reference data from

**Figure 3.7.:** Reversible switching between amorphous and crystalline GST is presented (a). Initialization of the crystallization was performed on a different spot with the same setup parameters and was added to the reversible switching cycles. Crystallization with a 960 Hz repetition rate is shown (b). The time scale of the edge is limited by the experimental resolution (c). The microscope images show crystallized (d) and reamorphized areas (e) of an as-deposited amorphous sample (scale bar: 20 µm).
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literature. The phases are identified by Raman spectroscopy (see Figure 3.8 (b)). The amorphous sample has a wide peak at 480 cm$^{-1}$, and the crystalline phase is characterized by a sharp peak at 520 cm$^{-1}$ which is in good agreement with literature [60]. The peaks at 150 cm$^{-1}$ and 300 cm$^{-1}$ are caused by overtones [61, 62].

Reversible switching between amorphous and crystalline Si by laser pulses was already demonstrated in literature [63]. As a proof of principle, Figure 3.9 (a) and (b) demonstrate that laser pulses can induce amorphization and crystallization associated with a color change. The color of the initial crystalline state in image (a) is in good agreement with the laser-induced crystalline spot in image (b). Color deviations between the microscope images and the photographs can be explained based on differences between the light sources. The material was partly crystallized with 60 fs laser pulses at 800 nm for 1 s at a 960 Hz repetition rate and with a fluence of 18.7 ± 0.7 mJ cm$^{-2}$. Crystallization of the illuminated spot is verified by Raman measurements, which show a small crystalline peak at 520 cm$^{-1}$ in Figure 3.9 (c). A single 60 fs laser pulse with a fluence of 63.8 ± 2.5 mJ cm$^{-2}$ is sufficient to fully amorphize the material, as indicated by the Raman spectrum. Reversible color switching of Si was not feasible, as diffusivities and vapor pressures are high at the melting temperature of Si. For reversible color switching of a standard semiconductor three different approaches are possible:

- Si could be replaced by a semiconductor with lower crystallization and melting temperature, e.g., InSb, GaSb, or Ge.

- A thermal barrier between Si and Ag could be deposited to confine the heat affected zone to the semiconductor. Here, Al$_2$O$_3$, which has a low thermal conductivity, is a possible choice of material.

- Ag could be replaced by a bright metal with high melting temperature such as Cr or Rh.

Replacing Si by InSb is the most promising approach, as the laser power can be strongly reduced for the amorphization cycle, as the melting temperature of InSb is

![Figure 3.8](image)

**Figure 3.8:** The reflectance curves (a) of as-deposited amorphous and annealed crystalline samples were measured and simulated. The colors of the curves correspond to the measured and simulated colors of the samples. The phases of the as-deposited and annealed sample are confirmed by Raman spectroscopy (b).
Tunable color coatings based on ultrathin Si and Ge$_2$Sb$_2$Te$_5$

![Diagram](image.png)

**Figure 3.9.** As a proof of principle the samples were amorphized (a), and crystallized (b) with 60 fs laser pulses. Scale bar: 20 µm. The laser pulse fully amorphized the oven-annealed crystalline Si layer (a) but crystallization of the as-deposited amorphous Si (b) by laser was only partly possible, as indicated by Raman spectroscopy measurements (c).

below 630 °C [64] in comparison to Si which has a melting temperature of 1412 °C [65]. Therefore, ablation and diffusion are less likely when switching InSb.

In the following the color device introduced by Hosseini *et al.* [48] is compared to the tunable color device based on strong interference. Therefore, the color appearances of GST and Si embedded in both systems are simulated (see Figure 3.10). Figure 3.10 (a) and (d) present the two different sample structures. Hosseini *et al.* modified the color appearance by changing the thickness of the transparent buffer layer while the color of the device based on strong interference is varied by changing the thickness of the GST/ Si layer. Note that the thickness variation of GST/ Si is only some nanometers while the ITO layer thickness needs to be tuned several tens of nanometer to achieve a significant color change. Hosseini’s approach leads to a situation in which the color of the system also changes when the GST layer is crystallized (see Figure 3.10 (b)) while our system is gray for crystalline GST (see Figure 3.10 (e)). However, the additional buffer layer increases the number of layers and the film thickness and therefore, also increases the probability of ablation during laser application.

Moreover, the approach by Hosseini *et al.* results in a large optical contrast for PCMs but not for semiconductors. Replacing the GST layer by Si results in very similar colors for both phases (see Figure 3.10 (c)). An ITO thickness of 150 nm results e.g. in pink color appearance for both, amorphous and crystalline Si. In contrast, the color device based on strong interference clearly changes color upon phase-change (see Figure 3.10 (f)). Upon crystallization 6 nm Si changes from pink to orange.

The system by Hosseini *et al.* is not as sensitive to changes in the refractive indices of the semiconductor as the system based on strong interference (see Figure 3.10 (f)). Consequently, the strength of the color device based on strong interference lies in its flexibility in choice of materials. This system is not only limited to materials with a naturally large optical contrast. For the current choice of materials the design by Hosseini *et al.* is better suited for display applications, whereas this current one has its advantages in data storage.
3.5. Conclusion

In conclusion, we introduced a new application for the strong interference effect. Ultrathin phase-change materials and semiconductors on metals can be switched between the amorphous and crystalline phase, associated with a large color change. The reflectance spectra are robust with respect to the angle of incidence of the light [31, 49]. This is important for color consistency on flexible substrates or for display applications (see Chapter 7). The optical contrast of GST integrated in this structure is enhanced, and reversible color switching between blue and gray with femtosecond laser pulses is demonstrated. Besides display applications without power consumption in the static mode, these layer structures are also interesting for applications in optical data storage devices. Pure GST, for example, does not exhibit the required optical contrast for wavelengths around 405 nm and has been replaced by Ge-rich PCMs for third-generation storage media such as Blu-ray disks. In Figure 3.11, we demonstrate that optimizing the thickness of GST and SiO₂ on
Al results in a sufficiently large optical contrast of more than 87% around 405 nm. Here, Al was chosen as underlying metal, as it results in the largest optical contrast at 405 nm wavelength compared to other highly reflective metals. Consequently, Ge$_2$Sb$_2$Te$_5$ can be integrated in a current Blu-ray disk if this layer structure is used. This indicates that a lack of optical contrast, which makes new or sometimes established materials unfavorable for novel optical data storage, may be overcome by exploiting the strong interference effect demonstrated in this chapter.

We show that even Si, which is not known for a large optical contrast, can switch between two colors if it is deposited on a metal. Ultrathin Si layers on Ag change from blue to pink upon crystallization with an optical contrast as large as 92% at wavelengths around 572 nm. To embed these layer structures in optical data storage devices, the crystallization time should be minimized with either longer laser pulses or higher repetition rates. Weidenhof et al. [66], for example, demonstrated crystallization with laser pulses as short as 10 ns, and Cotton et al. [67] showed that employing a femtosecond laser double pulse with an interpulse delay time shorter than 100 ps could trigger partial crystallization of GST.

For future reversible color switching, semiconductors with lower melting points and lower diffusion coefficients may prove to be very useful to save energy and simplify the layer architecture.

**Figure 3.11.** Using a sample structure (a) with ultrathin GST on top of Al and optimizing the thickness of GST and SiO$_2$ in a simulation (b) can enhance the optical contrast to about 87% at 405 nm wavelength.
4. **Aluminum-induced crystallization of ultrathin Si films**

This chapter focuses on the synthesis of ultrathin polycrystalline Si films on polyimide substrates. The challenge lies in the considerably lower service temperature of Kapton® E compared to the crystallization temperature of bulk Si. The aluminum-induced layer exchange mechanism is well-known to reduce the crystallization temperature of Si. Here, a parametric study is conducted to determine the deposition parameters of Si and Al that lead to a reduction of the crystallization temperature of Si below 400°C. The results are of great interest for applications such as solar cells or thin-film transistors based on thin polycrystalline Si films on plastic substrates.

4.1. Introduction

Static color coatings based on the structures introduced in Chapter 2, or tunable color coatings based on ultrathin Si which were described in Chapter 3, are potential candidates as decorative coating. Moreover, ultrathin amorphous and polycrystalline Si (poly-Si) films are heavily employed in microelectromechanical systems (MEMS) [68], in solar cells [3, 69], or transistors [70–72]. The loss of integrity of a thin Si film might lead to failure of the entire device. Therefore, it is of great importance to determine the cohesive and adhesive properties of ultrathin amorphous and poly-Si films on flexible substrates. Generally, flexible substrates are made of plastic with a limited service temperature which, for e.g. Kapton® E polyimide substrates, lies between 360°C and 410°C [73]. However, Si crystallizes at 800°C [17]. Therefore, a method to crystallize Si at temperatures below 400°C is required. Laser crystallization of ultrathin Si films below 100 nm is difficult due to the large penetration depth of light in Si (see Figure 4.1). The light intensity at 532 nm wavelength decreases to 1/e at a penetration depth of e.g. 65 nm in amorphous, and 312 nm in poly-Si. Consequently, only a small part of the light is absorbed for Si films below 100 nm thickness. On the one hand, high light power is required to crystallize the Si films. On the other hand, this light power damages the underlying plastic substrate. Moreover, laser crystallization limits the crystalline Si film to a small area and results in an interface of amorphous and crystalline Si which induces stress concentrations. Therefore, here, laser-induced Si crystallization is dismissed. Other methods, such as substrate annealing below 400°C, and ion bombardment of Si films during sputter deposition, do not result in crystalline Si.

As an alternative approach metals in contact with amorphous Si can induce crystallization of the amorphous semiconductor at temperatures as low as 150°C [74].
Various metals have been found to promote crystallization at reduced temperatures as compared to bulk crystallization temperatures. Si in contact with transition metals such as Ni, Pd, Pt, or Cu forms multiple compounds and a so-called metal-induced lateral crystallization (MILC) process is often realized for such systems. Post-transition metals such as Al, In, Sn, Pb, Sb, or Bi constitute eutectic binary systems with Si and a metal-induced layer exchange (MILE) process can often be observed. Metal-induced crystallization (MIC) temperatures of Si in contact with post-transition metals are generally lower than that of Si in contact with transition metals [75]. Here, we use Al to induce crystallization of ultrathin Si films. The
mechanism is illustrated in Figure 4.2 and described as follows [75]: Amorphous Si wets high-angle Al grain boundaries (see Figure 4.2 (b)) and crystallizes exclusively there above a critical temperature of about 140°C (see Figure 4.2 (c)). The growth and crystallization of Si at the original grain boundaries leads to compressive stress in the Al layer and tensile stress in the amorphous Si film. Consequently, a diffusion potential gradient is formed for the Al atoms and they start to diffuse into the amorphous Si film which has a large free volume (see Figure 4.2 (c)). The resulting Al plums in amorphous Si move upwards and grow in size as more and more Al atoms diffuse into the Si film. Hence, during crystallization the Al and Si layers exchange their initial position (see Figure 4.2 (d)).

Small variations in the microstructure of the Al film might lead to different crystallization temperatures and crystallization behaviors [76, 77]. Moreover, the substrate material, the Al-Si interface, the layer sequence, and the layer ratio have a large influence on the crystallization behavior [76, 78, 79]. Researchers have investigated the influence of various fabrication methods such as electron beam evaporation, sputter deposition, or thermal evaporation [80]. Moreover, Chu et al. [81] have shown that the dc sputtering power during Al deposition influences the film stress, the surface roughness, and the crystal quality. However, to our knowledge, the influence of sputter parameters on the crystallization temperature of Si is unknown.

Here, we investigate the crystallization time and temperature of Si films in contact with Al films sputtered at different dc powers and different Ar pressures. Moreover, the influence of substrate bias during both, Si sputtering and Al sputtering is examined. The aim of this study is to determine the sputter parameters for which the crystallization temperature of Si on Kapton® E substrates is reduced below the maximum service temperature of the Kapton® E sheet.

### 4.2. Materials and Methods

Thin films were fabricated by magnetron sputter deposition (PVD Products) with a base pressure of less than 8·10⁻⁵ Pa. Polyimide sheets (Kapton® E from DuPont) with a thickness of 50 µm were used as substrates. Prior to deposition, the polyimide sheets were cleaned in acetone (at least 15 min) and isopropanol (at least 15 min) in an ultrasonic bath. Subsequently, they were pre-shrunk in a furnace at 200°C for at least 6 hours to remove trapped residual solvents. During sputter deposition, the substrate was rotated with 30 rpm in order to achieve a homogeneous film thickness. Various sputter parameters were used to deposit 150 nm Al on top of 150 nm Si films on a polyimide substrate. Note that the samples were not exposed to air in between Si and Al sputter deposition. For each sample only one parameter was changed at a time such that the influence on the crystallization temperature could be observed. Table 4.1 gives an overview of the deposition parameters. Thin films in the table are arranged according to the power they were deposited at.

Thermal annealing at various annealing temperatures (250°C, 300°C, and 350°C) and for various annealing durations (1 h, 4 h, 10 h, and 24 h) was employed to achieve crystallization of the Si films. Annealing was performed in a vacuum furnace at a pressure of 2 Pa.

The cross sections of the thin films were polished by a Hitachi IM4000 broad ion
Table 4.1: Al and Si thin film deposition parameters, with magnetron power $P$, Ar pressure $p$, rf substrate bias, and Ar flow.

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beam (BIB) miller. Firstly, the films on the Kapton® E substrates were attached to the polished side of a Si wafer piece by silver paste. Two or three films were sandwiched together such that they were polished in one run. The polished side of the wafer faced the films on the polyimide substrates. To minimize the polishing time in the BIB miller, all Kapton® E substrates were arranged parallel to each other and their edges were slightly higher than the edge of the Si wafer. Hence, only the polyimide substrates and the films, but not the Si wafer were polished. Secondly, the Si wafer piece was mounted to a modified SEM stub such that the cross-sectional area which was polished was arranged parallel to the stub surface. Finally, the samples were aligned in the BIB miller and the parameters during milling were 6 kV acceleration voltage and 0.1 sccm Ar flow.

Imaging of the prepared cross sections was performed utilizing a FEI Magellan 400 scanning electron microscope at 10 kV. Secondary electrons were detected as the image contrast of back-scattered electrons of Al and Si atoms is little because of the similar atomic number.

The surfaces of as-deposited and annealed films were investigated with a confocal light microscope (WITec CRM200). Raman spectra were obtained from measurements with a confocal Raman system (WITec CRM200) with 532 nm excitation, a 100x objective lens with numerical aperture NA=0.9, and a fiber-coupled grating spectrometer (2400 lines/mm). The laser intensity at the sample surface was reduced to 35.5 µW/µm² to minimize sample heating.

4.3. Results

Figure 4.3 presents surface optical micrographs of the samples prepared by various sputtering powers and sputtering pressures. The optical appearance of Al is much brighter than that of Si. Thus, the metal-induced layer exchange mechanism was completed as soon as the color of the optical micrographs changed from blue to light blue. For all samples, a higher annealing temperature and a longer annealing duration led to an increase of light blue colors of the optical micrographs.

However, a complete layer exchange mechanism was accomplished for only three of the eight samples sputtered at different deposition parameters. The AILE mechanism was achieved for an Ar pressure of 0.67 Pa, a dc sputter power of 100 W and 300 W, as well as an rf substrate bias during Al deposition. Still, small dark dots in the micrographs of these three samples indicate that some Si did not exchange the layer position.

Rf substrate biasing during Al deposition resulted in a completed AILE mechanism at the lowest annealing temperature and the shortest annealing time. Here, only 4 h annealing at 250°C were sufficient to crystallize the Si film. However, applying an rf substrate bias during Si and Al sputtering was challenging. The plasma was not stable and hence, reproduction of the sample was difficult. To some extent the plasma existed at a limited part of the sample and rotated together with the substrate holder. Moreover, applying an rf substrate bias sometimes resulted in sparks at the substrate and black damaged Kapton® E sheets.
Figure 4.3.: Surface images of sputtered Al and Si films before and after various annealing durations and temperatures. Initially, the Si film was sputtered on top of the Al film. Al has a larger reflectance than Si and a bright blue color indicates a complete AILE mechanism. These images are marked with a green frame.
An Ar pressure of 0.67 Pa and a dc sputter power of 100 W and 300 W during sputter deposition of the Al film led to crystallization of Si after 10 h annealing at 300°C. Also, the other samples exhibit bright spots in the optical micrographs at this annealing temperature and duration which indicates that some Al atoms diffused into the Si top film. However, a complete layer exchange was not achieved. Exemplarily, Figure 4.4 depicts Raman spectra of the samples sputtered at 0.67 Pa Ar pressure and 300 W dc power annealed to different temperatures. The as-deposited sample (dark blue graph) exhibits a broad amorphous peak at 480 cm$^{-1}$. Annealing the sample to 250°C for 1 h and 4 h (bright blue and violet graphs) resulted in a small intensity Raman peak at 520 cm$^{-1}$ and the broad peak at 480 cm$^{-1}$ decreased compared to the peak of the as-deposited sample. This indicates that Si partly crystallized. Further annealing of the sample to 300°C for 10 h (rose graph) led to a decrease of the crystalline Si Raman peak at 520 cm$^{-1}$ and the amorphous Si Raman signal disappeared. Determining the Raman signal of the sample annealed to 350°C for 24 h yields two different spectra: (i) The Raman measurement of one of the dark dots visible in the micrograph in Figure 4.3 (red graph) exhibits a crystalline Si signal. As the AILE mechanism was completed no underlying Al could absorb the laser light and consequently, the observed background noise originated from the polyimide substrate. (ii) Raman spectrum of the top Al layer (orange graph) did not result in any signal.

![Figure 4.4](image-url) Figure 4.4.: Raman spectra of samples deposited at 300 W dc sputter power and 0.67 Pa Ar pressure at various annealing temperatures and durations are shown.
Figure 4.5.: Cross-sectional SEM micrographs of sputtered Al and Si films before and after various annealing times and temperatures. Different sputter parameters were used for the Al films. The last row of the table shows cross sections of Al and Si films where 30 W rf bias was applied during Si deposition.
Figure 4.5 presents cross-sectional SEM micrographs of the samples sputtered at different deposition parameters and annealed to various temperatures. Here, secondary electrons were detected as the Z-contrast of Al and Si is too low to distinguish between both elements with back-scattered electrons. Al is more conductive than Si and appears brighter in the SEM images.

4.4. Discussion

The sample annealed to 350°C for 24 h does not show any Raman signal (see Figure 4.4). At this temperature the AILE mechanism was already completed as shown in Figure 4.3. Al took the initial position of Si and most of the laser light was absorbed in the Al top film. The light intensity at 532 nm wavelength decreases to 1/e at 7 nm in Al which was calculated from the imaginary part of the refractive index of Al [52]. Hence, the Raman signal of the underlying Si cannot be measured and the low intensity Raman peak at 520 cm\(^{-1}\) resulted from small Si particles in the Al film. Generally, Al films sputtered at higher pressures are more porous than those sputtered at lower pressures as can be seen in the left column of Figure 4.5. This result is expected for sputter-deposited films and it is in good agreement with the structure zone model derived by Thornton [82]. The SEM images of these high pressure sputtered films indicate that the pores in the Al film cause a layer exchange of single grains and not the whole Al film. Hence, also after annealing the sample to 350°C Si grains were found in both, the initial Al and the initial Si layer.

It was demonstrated that an rf substrate bias during Al deposition results in porous Al films [83]. This is difficult to observe from the SEM image of the as-deposited film. However, for samples annealed to at least 250°C for 4 h small dark dots in the Al top layers are visible which may be pores or defects. Rf substrate bias during Si deposition leads to void formations in the Si layers and even pores in the underlying Al film which can be seen in the lower left SEM micrograph of Figure 4.5. These voids and pores remain even after annealing the sample. Generally, single grains in the Al film could neither be detected by a through the lens detector (used here) nor by a circular back-scatter detector. Therefore, the grain size as a function of sputter parameters could not be observed. However, it is known [84] that films deposited at high sputter powers and low pressures tend to form fibrous grains. The films are dense as a result of atomic peening and low levels of gas impurity incorporation into the film are ensured by the high deposition rate. Contrary to that, films deposited at low sputter powers and high gas pressures are less dense, exhibit large grain sizes, and incorporate gas impurities. As it is known that high-angle grain boundaries are preferred for diffusion of Si into the Al grain boundaries, it can be assumed that the samples which exhibit a complete layer exchange have at least some high-angle grain boundaries.

4.5. Conclusion

The influence of sputter parameters used during Si and Al deposition on the crystallization temperature of Si was investigated with the objective of finding ideal parameters to reduce the crystallization temperature below the maximum service
Aluminum-induced crystallization of ultrathin Si films

Several sputter parameters are advantageous to complete a layer exchange mechanism at low temperatures:

- Low Ar pressure during Al sputtering is preferred. The films are denser and the diffusion of Si into the grain boundaries occurs at lower temperatures.

- High Al sputter powers lead to Si crystallization at lower annealing temperatures compared to Si on Al films sputtered at low power.

- Rf substrate bias during Si deposition is not recommended because it leads to void formation in the Si film and pores in the underlying Al film. Moreover, the layer exchange is not feasible for annealing temperatures up to 350°C.

- Rf substrate bias during Al deposition results in a complete layer exchange of Si and Al films at the lowest annealing temperature (4 h at 250°C). However, the plasma at the substrate is not stable during sputtering and in some extent sparks at the substrate are built which might damage the Kapton® E substrates.

In conclusion, Al should be sputtered at low Ar pressures (0.67 Pa) and at high dc powers (300 W). Substrate bias causes reduced crystallization temperatures but is not recommended for the PVD sputter tool used here, as the plasma is unstable.
5. Mechanical properties of amorphous and crystalline Si films

In this chapter, fragmentation and buckling of 8-103 nm thin amorphous and polycrystalline (poly-) Si films on polyimide substrates have been studied by in situ light microscopy, Raman spectroscopy, and resistance measurements. Generally, a smaller film thickness and a compressive residual stress delays the fracture of the film. The fracture strength of poly-Si films is larger compared to that of amorphous Si films while the adhesion to the substrate is better for amorphous Si compared to poly-Si. The onset delamination as a function of film thickness differs for the two phases and is described by two different models. Thin-film models for fracture toughness (amorphous Si: $K_{IC} = 1.4 \pm 0.22$ MPa m$^{0.5}$, poly-Si: $K_{IC} = 3.36 \pm 1.37$ MPa m$^{0.5}$) are applied, discussed, and found to be consistent with literature values. Moreover, the mechanical properties of the insulator structure introduced in Chapter 2 based on ultrathin Si top layers of different thicknesses are investigated. The content of this chapter is based on the work published in Acta Materialia [85].

5.1. Introduction

Ultrathin Si films in the nanometer-range are, amongst others, implemented in solar cells [3, 69], microelectromechanical systems (MEMS) [68], transistors [70–72], or interference coatings [31, 86]. The functionality of the devices relies on their mechanical integrity during service life. Strain due to bending or torsion of devices on flexible substrates or thermal stress could lead to failure. Fracture toughness, which corresponds to the resistance to the propagation of cracks is a relevant factor when it comes to brittle materials such as Si. Many researchers have evaluated the fracture toughness of Si samples with different crystallographic phases and geometries. Poly-Si films in the micrometer range thickness were studied extensively and fracture toughness values between 1.1 MPa m$^{0.5}$ and 4.5 MPa m$^{0.5}$ were reported [87–89]. The fracture toughness of single crystalline specimens lies around 0.8 MPa m$^{0.5}$ and 1.3 MPa m$^{0.5}$ [90, 91]. Ballarini et al. investigated the fracture toughness of micrometer-thick amorphous Si. They determined a value of 1.0 MPa m$^{0.5}$ [92]. However, they assumed that the Young’s modulus of amorphous Si is the same as that of poly-Si, which is unlikely [93, 94]. Waller et al. determined an energy release rate of 16 J/m$^2$ for a 230 nm amorphous Si film (aSi:H) which corresponds to a fracture toughness of 1.2 MPa m$^{0.5}$ [95].

To our knowledge there is a lack of information on the mechanical properties of
nanometer-sized Si films. It can be expected that they have much better cohesive and adhesive properties compared to micrometer thick films because of a size-effect. It was shown that nanometer-sized Si layers on various substrate materials exhibit bright color appearance and can be used as static color coatings (see Chapter 2). Moreover, ultrathin Si films deposited on metals switch their color upon amorphization and crystallization, respectively [46]. Consequently, it is of interest to compare the mechanical properties of amorphous and crystalline Si films of various thicknesses for the application as tunable color coating. In this study, both gaps are filled by investigating the fracture behavior of 8-103 nm thick amorphous and poly-Si films on polyimide substrates. The onset strain of fragmentation and buckling, the fracture strength, and the fracture toughness are obtained from uniaxial tensile tests and, these values are compared to literature values where available.

5.2. Materials and Methods

Sample fabrication
Thin Si films were fabricated by magnetron sputter deposition (PVD Products) with a base pressure of less than $8 \cdot 10^{-5}$ Pa. Polyimide sheets (Kapton® E from DuPont) with a thickness of 50 µm were used as substrates. Prior to deposition the polyimide sheets were cleaned in acetone (at least 15 min) and isopropanol (at least 15 min) in an ultrasonic bath and subsequently annealed in a furnace at 200 °C for at least 6 hours. During sputter deposition the substrate was rotated with 30 rpm in order to achieve a homogeneous film thickness. Amorphous Si films were fabricated by alternating current sputter deposition using a power of 300 W, a pressure of 0.67 Pa and an argon flow of 50 sccm. This resulted in 8 nm, 18 nm, 25 nm, 43 nm, and 96 nm thick amorphous Si films on Kapton® E. For in situ resistance measurements during straining amorphous Si films with a thin conductive Pt capping layer were sputtered without breaking the vacuum in between. A direct current power of 100 W, a pressure of 0.67 Pa, and an argon flow of 20 sccm were used for Pt.

Poly-Si was fabricated from amorphous Si by an aluminum-induced layer exchange (AILE) mechanism as described in Chapter 4. The crystallization temperature of Si on Kapton® E must be below 400 °C because the maximum service temperature of Kapton® E is between 360 °C and 410 °C [73]. Compared to the ideal sputter parameters of Al and Si derived in Chapter 4 we further improved some parameters to ensure a continuous poly-Si film which crystallizes at low temperatures.

In this study, the film thickness of Al was always slightly thinner than that of Si (ratio approx. 5:6) in order to ensure a continuous poly-Si film [78]. First, Al was sputtered onto Kapton® E with a power of 300 W at 0.67 Pa and with an Ar flow of 10 sccm. Second, the film was exposed to air for 5 min such that a thin Al oxide layer was formed [96]. Third, amorphous Si was sputtered onto the Al layer. The rf power was adjusted to 300 W, the pressure was set to 0.40 Pa, and the Ar gas flow was 50 sccm. After annealing the samples in a vacuum furnace (2 Pa) at 400 °C for 18 h the layer exchange was completed. This was confirmed by cross-sectional high resolution scanning electron microscope (SEM) images (FEI Magellan 400 FEG XHR-SEM). In a last step the Al was etched according to [97].
Mechanical properties of amorphous and crystalline Si films

Figure 5.1.: Cross section SEM images of sputtered Al and Si film on Kapton® E before (a) and after annealing ((b) and (c)). On top of the films silver particles can be seen which are due to the cross section preparation process. After wet-chemical etching of the Al film (c), small Si crystallites remain on top of the continuous poly-Si layer.

with 16 H₃PO₄:1 HNO₃:1 HAc:2 H₂O at 50 °C. Finally, the poly-Si films on polyimide had a thickness of 32 nm, 40 nm, 45 nm, 100 nm, and 103 nm. Typical SEM cross-sectional micrographs during the AILE mechanism are depicted exemplarily for 103 nm Si in Figure 5.1 (a)-(c). The as-deposited Al and amorphous Si films on Kapton® E are shown in Figure 5.1 (a). In Figure 5.1 (b), the AILE mechanism was completed and the Si was crystalline after annealing. The film thickness of the as-deposited Si film was slightly larger than the Al film thickness such that some crystalline Si particles stayed in the Al film (see Figure 5.1 (b)). After etching the Al film a continuous poly-Si film remains covered with some Si crystallites (see Figure 5.1 (c)).

Characterization

The residual stress of the Si films was determined by two different methods. For amorphous Si the curvature of the polyimide substrates with the Si films was measured by optical microscopy and the residual stress was calculated using the Stoney equation [98]. For poly-Si films this method was not reliable because the long exposure to 400 °C results in a plastic deformation of the polyimide substrate. Consequently, the curvature did not originate only from the film but also from the substrate. Here, the stress was calculated from Raman spectra obtained from measurements with a confocal Raman system (WITec CRM200) with 441 nm excitation, a 100x objective lens with numerical aperture NA=0.9, and a fiber-coupled grating spectrometer (2400 lines/mm). The laser intensity at the sample surface was reduced to 35.5 µW/µm² to minimize sample heating. The peak positions of the Si spectra were fitted with a MATLAB routine employing Lorentzian curves. For each film, 4 line scans with 20 spectra each were measured and the Si peak
positions were averaged. For uniaxial tensile tests, the samples were mounted into a tensile machine (Kammrath & Weiss GmbH) equipped with a 200 N load cell. Each sample was 5 mm wide and the gage length \( l \) was 14 mm (resistance measurement) or 30 mm (optical microscopy and Raman spectroscopy measurement). The corresponding strain rates were \( 10^{-4} \text{sec}^{-1} \) and \( 4.7 \cdot 10^{-5} \text{sec}^{-1} \), respectively. Crack patterns and crack distances of the films were investigated with a confocal light microscope (WITec CRM200) and simultaneous stepwise loading of the sample. The mean crack distance \( \overline{L} \) was determined with a MATLAB routine [99] based on optical micrographs. In situ resistance measurements of amorphous Si with a thin Pt capping layer were performed with an electrical resistance module. During uniaxial loading the current was minimized (100 mA) to prevent heating of the sample and the change of voltage was recorded. Platinum has the advantage that it can be deposited as a continuous thin film so that the film thickness is small enough that the cracking behavior of Si is not influenced. Cracks in the Si film leads to instantaneous fracture of the platinum top layer due to strain localization [100]. Typically resistance measurements are compared to the ideal plastic deformation curve [101, 102]. As Si does not exhibit plastic deformation, here the change of resistance is calculated as a function of uniaxial strain in the elastic regime. For this ideal resistance change \( R/R_0 = (1 + \epsilon)(1 + 2\nu_f \epsilon) \) the Poisson’s ratio of the film \( \nu_f \) and the applied uniaxial strain \( \epsilon \) need to be considered. The change of the normalized electrical resistance \( R/R_0 \) with the initial resistance \( R_0 \) of the film before loading was measured for different film thicknesses. This method could not be applied for poly-Si because the Si crystallites on top of the poly-Si film prevent a smooth substrate surface for the Pt top layer. Hence, Raman spectroscopy was applied to spots where no Si crystallites cover the poly-Si film. The adjustments of the Raman spectroscope were identical to those for measuring the residual stress. Line scans were performed for various strains always at the same spot to record the change of the peak position as a function of strain. Each line scan included 40 spectra which were fitted with Lorentzian curves. The resulting peak positions were averaged for each line scan.

5.3. Results

5.3.1. Residual stress

The determined residual stresses \( \sigma_{res} \) of the amorphous and poly-Si films are summarized in Table 5.1. The residual stress is compressive for all films and varies as a function of film thickness. The errors of the residual stress of amorphous Si result from error estimations on the determined curvature. Note, that the Pt capping layer may slightly influence the residual stress although the Pt films are very thin. Nevertheless, these films with the Pt capping layer are only used to determine the onset strain of fragmentation by resistance measurements to compare the results with the onset strain of fragmentation obtained from optical microscopy.

For poly-Si, the residual stress was calculated from Raman measurements. The Raman peak of unstrained Si at \( x_r = 520 \text{cm}^{-1} \) was used as a reference for all measurements. The AILE mechanism results in an Al doping of the poly-Si films. Energy-
dispersive X-ray (EDX) spectroscopy measurements showed that the poly-Si films contain 5.2 wt. % Al which is homogeneously distributed in the film as confirmed by an EDX mapping. The phase-diagram of Al and Si indicates that this small amount of Al is insoluble in Si. Consequently, the Al content neither influence the Raman peak position nor the cohesive and adhesive properties of poly-Si [92]. The residual stress $\sigma_{res}$ is given by [103]: $\sigma_{res} = -250 \text{ MPa cm}^{-1} \cdot \Delta \omega$ with $\Delta \omega = x_p - x_r$, where $x_p$ is the average peak position of poly-Si. The specified errors result from averaging at least 4 line scans with 20 Raman measurements each. These errors are large compared to those of amorphous Si. Figure 5.2 shows a stress map of a poly-Si film obtained by Raman spectroscopy. The position of the stress map is sketched in an optical micrograph.

Raman spectra were obtained in an area of $10.0 \times 5.4 \, \mu \text{m}^2$ spaced at intervals of 200 nm. Figure 5.2 exhibits the inhomogeneous stress distribution. The residual stress is largely compressive where no crystalline particles cover the film but is nearly completely relaxed where Si crystallites cover the poly-Si film. Consequently, the measured residual stress is strongly dependent on the position on the sample.

![Figure 5.2.](image-url)

**Figure 5.2.** Optical micrograph image of a 103 nm poly-Si layer with crystalline Si particles (darker features) on top. In the inset a stress map which was measured by Raman spectroscopy is shown. It indicates that the residual stress of the film is not homogeneously distributed. The residual stress is compressive where no crystalline particles can be found and it is relaxed where particles cover the poly-Si layer.
and the resulting errors of the residual stress are large. To minimize the effect of the Si crystallites on the poly-Si film only areas where no Si crystallites could be seen by optical microscope are taken into account for the analysis. However, the resolution of the optical microscope is limited and still small crystallites may influence the result.

5.3.2. Cohesive and adhesive failure of amorphous and poly-Si

Exemplarily, the fracture patterns of a uniaxially loaded 25 nm thick, amorphous Si film are displayed in Figure 5.3 (a). The crack density increases with increasing tensile load and the cracks are straight and perpendicular to the loading direction. Interestingly, the crack openings of all Si films are large enough to detect first cracks by optical microscopy. Crystallization of the amorphous Si samples at 400 °C caused a color change and a plastic deformation of the polyimide substrate. To ensure that the strain in the substrate is still homogeneous, a Kapton® E substrate was tested in the tensile machine after annealing. The local strain values were derived from monitoring the spacing between several markers on the surface. A comparison of the resulting local strain values exhibit a deviation of at most 10 % which needs to be considered in the following. The annealed polyimide substrates are stable until approximately 10 % strain which is sufficient for this study. Micrographs of crack patterns of a 32 nm poly-Si film are presented for various strains in Figure 5.3 (b). The dark spots are Si crystallites on top of the film. The cracks are perpendicular to the loading direction but they do not channel directly completely through the film.

![Figure 5.3](image_url)

**Figure 5.3:** (a) Exemplarily, light micrographs of crack patterns of 25 nm thick amorphous Si at different strains are shown. The cracks are perpendicular to the loading direction. At 12 % strain buckling is visible. (b) Optical micrographs of crack patterns of 32 nm poly-Si at various tensile strains are shown. The dark spots are Si crystallites on the films which result from the layer exchange mechanism. The cracks are perpendicular to the tensile direction. In contrast to the amorphous Si films, the cracks do not channel through the whole film after reaching the critical length but stop at obstacles like e.g. grain boundaries.
Mechanical properties of amorphous and crystalline Si films

Figure 5.4.: (a) Mean crack distance as a function of strain for all amorphous Si films are shown. The onset strain of fragmentation decreases with increasing film thickness and the mean crack distance in the saturation regime is linearly dependent on the film thickness of the film. For the error bars only positive deviations of the measured values are considered because the field of view of the optical microscope is limited. (b) Normalized resistance curves for all Si films with a Pt top layer are shown. A deviation from the ideal law (dashed lines) indicates the first cracks.

Figure 5.4 (a) shows the mean crack distance evolution of amorphous Si coatings for various thicknesses. The onset strain of fragmentation decreases as a function of film thickness. In Figure 5.4 (b), the normalized resistance curves of Pt top layers on the amorphous Si films are illustrated. The dashed lines represent the ideal resistance change $R/R_0 = (1 + \epsilon)(1 + 2\nu_f\epsilon)$ (black dashed line) and a deviation of 5% (red dashed line) from this ideal behavior. A deviation of more than 5% from the theoretical curve is attributed to cracking as defined by Lu et al. [102]. In Figure 5.5 (a) the mean crack distance as a function of strain is depicted for all material as it is the case for the amorphous Si films. Here, the cracks slightly deviate from straight paths because they have to propagate along the grain boundaries.
Mechanical properties of amorphous and crystalline Si films

Figure 5.5: (a) Mean crack distance of all strained poly-Si films as a function of applied strain. (b) The average Raman peak position against applied strain is plotted. For a better overview the data set of each film thickness is shifted in ordinate direction. For each data point 40 Raman spectra of a line scan are averaged. With increasing tensile strain the peak position shifts to smaller wavenumbers until the first crack appears. The onset strain of fragmentation is indicated by small dashed rectangles.

poly-Si films. Figure 5.5 (b) illustrates the average Raman peak position for various poly-Si film thicknesses as a function of strain. At low strains an increase in strain results in a shift of the peak position to smaller wavenumbers which corresponds to tensile stress. As soon as the first crack occurs, the film starts to relax and the peak position shifts to larger wavenumbers. This onset strain of fragmentation is indicated by dashed rectangles for each film thickness.

Upon onset strain of fragmentation, stress relaxation occurs in the loading direction. This relaxation induces an additional mismatch of lateral contraction between coating and substrate and leads to compressive stress perpendicular to the loading direction. This compressive stress results in delamination of the film. The mean delamination distance is the average spacing between adjacent buckles on individual
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fragments. For both, amorphous and poly-Si films the mean delamination distances as a function of strain are presented in Figure 5.6.

At low strains the mean delamination distance decreases rapidly as a function of applied strain and saturates at higher strains. Poly-Si films delaminate at lower strains compared to amorphous Si layers. Generally, the mean delamination distance increases as a function of film thickness at high strains. For 8 nm amorphous Si and 103 nm poly-Si only the onset strain of delamination but not the mean delamination distance was determined because the resolution of the optical microscope was not adequate.

5.3.3. Cohesive and adhesive failure of Si embedded in the insulator structure

Three different color coatings based on ultrathin amorphous Si were introduced in Chapter 2. These sample structures are potential candidates for decorative coatings on both, rigid and flexible substrates. For the latter application it is important to investigate the cohesive and adhesive properties of ultrathin Si embedded in these structures. Here, the onset strain of fragmentation and onset strain of delamination of the insulator structure with 5 nm, 15 nm, and 25 nm amorphous Si were determined. This structure was investigated because compared to the two other structures, the insulator structure exhibits bright color appearance not only in reflectance but also in transmittance. The same structure as that presented in Figure 2.1 (b) with TiO_2 and SiO_2 as underlying material is used. Note that the structure on Kapton® E does not lead to bright color appearance as it is the case for the structure on a silicon wafer. Some light is transmitted through the Kapton® E substrate. Consequently, deep absorption resonances on Kapton® E substrates would be obtained for two instead of one bilayer of SiO_2-TiO_2. This structure was used to color glass substrates in reflectance and transmittance (see Figure 2.8).

Figure 5.7 presents optical micrographs of 5 nm (a), 15 nm (b), and 25 nm (c)
amorphous Si deposited on the insulator structure. In the following, the insulator structure with the Si capping layers go by the name of the thickness of the ultrathin Si films. Fragmentation in all three samples is perpendicular to the loading direction and cracks do not appear straight through the layers. In contrast to 15 nm Si (b) and 25 nm (c) Si, first cracks in 5 nm Si (a) are short and do not channel through the whole film as soon as they occur which indicates that obstacles exist in the layer structure. Thicker Si top layers result in larger crack distances than thinner Si films which is e.g. visible at 10.4% strain. All three structures exhibit delamination at large tensile strains with an onset strain of delamination which depends on the thickness of the top Si layer (5 nm Si: 16.0% strain; 15 nm Si: 16.8% strain; 25 nm Si: 17.6% strain). The mean crack distance as a function of applied strain is plotted in Figure 5.8 for all film thicknesses. No film thickness-dependent trend of the onset strain of fragmentation is observable. The insulator structure with 5 nm amorphous Si top layer fractures at lower strains than the other two samples. The highest onset strain of fragmentation can be observed for 15 nm Si.

The saturated mean fragment lengths decrease with decreasing film thickness and range from 1 \( \mu \text{m} \) for 5 nm Si to 2 \( \mu \text{m} \) for 25 nm. The whole layer stack has a thickness between 175 nm and 195 nm. A thickness change of the Si layer of 10 nm...
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![Graph showing mean crack distance as a function of strain for 5 nm, 15 nm, and 25 nm amorphous Si films.](image)

**Figure 5.8.** Mean crack distance of 5 nm, 15 nm, and 25 nm amorphous Si as a function of strain. In the saturation regime the mean crack distance depends on the thickness of the Si top layer.

corresponds to only 6% change of the whole thickness. Consequently, a size-effect of the saturated mean fragmentation lengths is expected to be small.

## 5.4. Discussion

### 5.4.1. Residual stress

The Raman mapping in Figure 5.2 illustrates that the residual stress is zero where Si crystallites cover the poly-Si film. As can be seen in Figure 4.1 the penetration depth of the Raman laser ($\lambda=441$ nm) into poly-Si is 73 nm (intensity decays to 1/e). Consequently, most of the laser light is absorbed inside the Si crystallites and only the residual stress of the crystallites and not of the poly-Si film is measured. After etching the Al film these crystallites are free-standing which leads to a complete stress relaxation. The stress measurement of Si crystallites cannot be completely avoided because some crystallites are too small to detect them in the optical microscope. Consequently, the underestimation of the compressive residual stress of thicker poly-Si films is larger, whereas that of thinner films is smaller.

### 5.4.2. Onset strain of fragmentation and delamination

The onset strains of fragmentation of amorphous and poly-Si observed with different methods are summarized in Figure 5.9. The error bars result from stepwise loading and correspond to the strain applied between two measurement steps. The strain at onset fragmentation of amorphous Si films with and without Pt top layer is in good agreement. The onset strains of fragmentation observed by *in situ* resistance measurement are not influenced by the Pt top layer, as it does not prevent the detection of the first cracks. Provided, cracks are straight and span the entire width.
of the sample, the resistively determined onset strains of fragmentation are more precise. First cracks outside the field of view are not recorded optically but cause a significant increase of the resistance. Here, the intersection of the resistance curves with the 5\%, 10\%, and 20\% deviations from the ideal resistance change are plotted as onset strain of fragmentation. However, the magnitude of the deviation from the ideal behavior affects the onset strain of fragmentation only little. Amorphous Si is very brittle and as soon as a crack forms it channels through the whole film such that the resistance increases drastically. The surprisingly large onset strain of fragmentation of the 96 nm amorphous Si film observed by resistance measurement can be explained by a 16 nm thick Pt film instead of 6 nm as it was the case for all other amorphous Si films. First cracking in the Si film may not induce cracks in the 16 nm thick Pt top layer due to plastic deformation.

The onset strains of fragmentation of poly-Si measured by two different methods are in good agreement. However, both measurement methods are limited to small fields of view and cracks outside this view are not detected. Hence, the onset strain of fragmentation of poly-Si films might be slightly overestimated. Nevertheless, it can be concluded that poly-Si films crack at higher strain than amorphous Si layers. This has two reasons: (i) Materials property: It is generally accepted that annealing reduces the density of defects. The first crack is formed as soon as the local stress exceeds the lowest fracture strength of a defect. Consequently, fewer defects increase the probability of larger onset strains of fragmentation. (ii) System property: The residual stress of poly-Si films is more compressive than that of the amorphous Si layers. This large compressive stress helps to delay the onset strain of fragmentation of poly-Si. To calculate the onset strain of fragmentation $\epsilon_{onr}$ of a coating which does not exhibit residual stress from the measured onset strain of fragmentation $\epsilon_{on}$ the residual stress $\sigma_{res} = E_f \epsilon_{res}$ needs to be considered : $\epsilon_{onr} = \epsilon_{on} + \sigma_{res}/E_f$. The second reason is more significant as sputter defects may be reduced by annealing.
Mechanical properties of amorphous and crystalline Si films

Figure 5.10: (a) Strain at onset delamination for amorphous and poly-Si films. Amorphous Si adheres well to the polyimide film and the onset strain of delamination decreases as a function of film thickness. The data is modeled by the strain energy criterion and results $G_0=33 \text{ mJ/m}^2$ as fit parameter. Poly-Si films delaminate at lower strains and the data is fitted by buckle delamination. Here, the fit parameter is the buckle width $b=840 \text{ nm}$. For comparison, graphs with different $G_0$, respectively $b$, are plotted to show the sensitivity to the fit parameters. (b) Schematic drawing of the two delamination models. When the onset strain of strain energy delamination $\varepsilon_{sed}$ exceeds the onset strain of buckle delamination $\varepsilon_b$, buckling is expected.

but the AILE mechanism may lead to other defects such as small Al particles inside the poly-Si film.

In Figure 5.10 (a), the onset strains of delamination of amorphous and poly-Si films are depicted. Two different failure modes may induce delamination: Buckle-limited delamination and delamination that follows the strain energy criterion. Delamination that is evaluated by the strain energy criterion is called strain energy delam-
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ination in the following. Optically, the two different delamination modes are not distinguishable because both, strain energy and buckle delamination, start at the fragmentation boundaries at the location of maximal compressive stress. However, buckle delamination indicates a weak adhesion of the coating to the substrate and the onset strain of delamination as a function of film thickness differs for both models.

The film thickness dependence on the tensile strain $\epsilon_{ten}$ for both cases can be calculated if the residual stress is considered and the transverse compressive strain $\epsilon_{com}$ is derived from the tensile strain $\epsilon_{ten}$ $\epsilon_{com}=(\nu_s-\nu_f)\cdot\epsilon_{ten}$. For the onset strain of strain energy delamination $\epsilon_{sed}$ the expression follows [104]:

$$\epsilon_{sed} = \sqrt{ \frac{2G_0 (1-\nu_f^2)}{E_f(\nu_s-\nu_f)^2} d^{0.5} - \frac{\sigma_{res} (1-\nu_f^2)}{E_f(\nu_s-\nu_f)}}$$

(5.1)

with $E_f$ and $\nu_f$ the Young’s modulus and the Poisson’s ratio of the film ($E_f=80$ GPa and $\nu_f=0.22$ for amorphous Si [93]; $E_f=170$ GPa and $\nu_f=0.22$ for poly-Si [16]), $\nu_s$ the Poisson’s ratio of the substrate which we assume to be the same as the one of Kapton® HN ($\nu_s=0.34$ [73]) and $G_0$ the energy release rate of the film.

For the case of buckle delamination [105] buckling occurs as soon as the onset strain of buckle delamination $\epsilon_b$ attains the value:

$$\epsilon_b = \frac{\pi^2}{12b^2(\nu_s-\nu_f)}d^2 - \frac{\sigma_{res} (1-\nu_f^2)}{E_f(\nu_s-\nu_f)}$$

(5.2)

where $b$ is half the buckle width. When the onset strain of strain energy delamination $\epsilon_{sed}$ exceeds the onset strain of buckle delamination $\epsilon_b$, buckling is expected (see Figure 5.10 (b)).

Generally, poly-Si starts to delaminate at lower strains than amorphous Si. This gives evidence that the adhesion to the substrate is worse which might be caused by the Al-induced layer exchange mechanism. Moreover, the strain at onset delamination increases as a function of film thickness for poly-Si, while it decreases for amorphous Si. This indicates that the delamination of amorphous Si films follows the strain energy criterion while thin poly-Si films are buckle-limited. In Figure 5.10 (a) both, buckle and energy strain delamination models are fitted to the data. Here, the residual stress is taken as fit parameter to compare it to the determined residual stress calculated from the curvature of substrate and amorphous Si and calculated from the Raman peak position of poly-Si. For amorphous Si, the fit of the strain energy delamination model yields an energy release rate $G_0=33$ mJ/m$^2$ and a compressive stress $\sigma_{res}=-400$ MPa. The compressive stress is slightly larger than that observed by measuring the substrate curvature. However, it has the same order of magnitude. The determined energy release rate is small and shows that the adhesion between amorphous Si and Kapton® E is weak. For comparison graphs for $G_0=100$ mJ/m$^2$ and $G_0=10$ mJ/m$^2$ are plotted in Figure 5.10 (a). Equation 5.2 is based on buckle delamination and was fitted to the onset strain of delamination of poly-Si films. Here, 100 nm and 103 nm thick poly-Si films were excluded from the fit as it can be assumed that for thicker poly-Si films the onset strain of buckle delamination exceeds the onset strain of strain energy delamination. Consequently, thicker poly-Si films follow the behavior of the strain energy criterion. The fit of the onset
delamination of poly-Si films yields a buckle width of $b=840\,\text{nm}$ and a compressive residual stress of $\sigma_{\text{res}}=-750\,\text{MPa}$. This compressive residual stress of poly-Si has the same order of magnitude as the experimentally determined values and confirms that poly-Si films are more compressively stressed than amorphous Si films. The buckle width is slightly larger than that measured by atomic force microscopy which yield a mean buckle width of $280 \pm 100\,\text{nm}$ for a 32 nm poly-Si film and $b=360 \pm 70\,\text{nm}$ for a 100 nm poly-Si after uniaxial loading to a strain of 7.3\% and 13.6\%, respectively. Note that the resulting fit parameters only yield an order of magnitude but not exact values of $b$, $G_0$, and $\sigma_{\text{res}}$. The residual stresses determined from the fit parameters e.g. are less reliable than those determined experimentally as the fit yields only one residual stress for all film thicknesses which is unlikely.

### 5.4.3. Stress transfer length

The stress transfer length $\xi$ was determined experimentally from the crossover fragment length $L_c$ at the transition between the first and the second regime of the fragmentation process. At this strain $\epsilon_c$ the stress transfer length is defined as $\xi = L_c/2$. In Figure 5.11, $\xi$ is plotted against film thickness $d$ for amorphous and poly-Si. The limited cases of constant shear stress transfer with $\xi \sim d$ and linear elastic shear stress transfer $\xi \sim d^{0.5}$ are included. The linear slopes $a$ of the log($d$) versus log($\xi$) curves were determined and are close to 0.5. This indicates that the mechanical interaction between substrate and film are represented by a linear elastic shear lag model [30]. Linear elastic means that the shear stress at the interface of coating and substrate is proportional to the difference of the displacements of coating and substrate. At the fragmentation boundaries the shear stress is zero and it is maximal in the middle of the fragment. It follows that the shear lag solutions in each

![Figure 5.11: Stress transfer length $\xi=L_c/2$ as a function of film thickness for amorphous and poly-Si. The slopes $a$ of the log($\xi$) versus log($d$)-curves are close to 0.5 which indicates that the stress transfers between substrates and coatings are linearly dependent.](image)
fragment is hyperbolically shaped [106]. A constant shear stress transfer is unlikely for polyimide substrates as it assumes perfectly plastic deformation of the substrate.

5.4.4. Fracture strength

The fracture strength of the coating is defined as the stress in the coating where the crossover between the first and second regime of the crack evolution is reached. A Weibull-type size-dependent probability of failure $F(\sigma)$ of the coating fragments is used to calculate the fracture strength [107]:

$$F(\sigma) = 1 - \exp \left[-\frac{L}{L_0} \left(\frac{\sigma}{\lambda}\right)^k\right]$$  \hspace{1cm} (5.3)

$L_0$ is a normalizing factor and equal to 1 µm, $\lambda$ is the Weibull scale factor and $k$ the Weibull modulus. The Weibull parameters can be obtained from the average

![Fracture strength graph](image)

**Figure 5.12.** Calculated fracture strengths of amorphous (a) and poly-Si (b) versus film thickness. The data have been fitted according to Griffith’s law ($\sigma_f \propto d^{-0.5}$). The shaded areas indicate the fit parameter $b$ which corresponds to the fracture strength of bulk amorphous and poly-Si.
Mechanical properties of amorphous and crystalline Si films

The crack distance $L$ at small strains \[108\]:

$$L = L_0 \left( \frac{\sigma}{\lambda} \right)^{-k} \approx L_0 \left( \frac{E_f \epsilon}{\lambda} \right)^{-k}$$  \hspace{1cm} (5.4)

The effective Young’s Modulus $E_f = E_f/(1 - \nu_f^2)$ is calculated from the Young’s modulus $E_f$ and the Poisson’s ratio $\nu_f$ of the film. The expected value of the probability distribution corresponds to the fracture strength in which the residual stress needs to be included:

$$\sigma_f = \lambda \left( \frac{L_c}{L_0} \right)^{-\frac{1}{k}} \Gamma(1 + 1/k) + \sigma_{res}$$  \hspace{1cm} (5.5)

In Figure 5.12, the fracture strength of the amorphous (a) and poly-Si (b) films are presented. It increases with decreasing film thickness and the values are larger for poly-Si compared to amorphous Si films. Only a few data points could be used to determine the Weibull parameters $\lambda$ and $k$ which results in large error bars of the fracture strength. Griffith’s law ($\sigma_f \propto d^{-0.5}$) is based on the assumption that the relevant factor determining the fracture strength is defect growths throughout the film thickness. Thicker films result in smaller $\sigma_f$ values because the larger film volume implicates more volume defects, and consequently also the probability of critical defects at a certain stress is larger. However, the fracture strength converges against a bulk fracture strength value. Fitting Griffith’s law $\sigma_f = a \cdot d^{-0.5} + b$ to the data gives the bulk strength $b$ as fit parameter ($b = 0.04 \pm 0.29$ GPa for amorphous Si and $b = 1.78 \pm 1.22$ GPa for poly-Si) which corresponds to the shaded areas in Figure 5.12. The order of magnitude of the determined bulk fracture strength can be confirmed by literature bulk fracture strengths of single crystalline Si which range from 0.2 GPa to 5.0 GPa \[109\]. The fit parameter $a$ includes the fracture toughness $K_{1C}$ and a geometry factor. However, the geometry factor is unknown and hence, the fracture toughness needs to be determined by a different method.

5.4.5. Fracture toughness

The fracture toughness $K_{1C}$ can be evaluated by numerous methods which are either stress-based or energy-based. For small-scale samples, the energy-based approach is preferred because the precise quantification of the geometry, which is required for the stress-based approach, is non-trivial \[110\]. Here, two energy-based models are applied to determine the fracture toughness of the amorphous and poly-Si films. Beuth \[111\] derived a model which relies on a linear elastic response of substrate and coating. The energy release rate of steady-state channeling cracks is given by

$$G_{\text{Beuth}} = \frac{\pi \sigma^2 d \left( 1 - \nu_f^2 \right)}{2E_f} g(\alpha, \beta).$$  \hspace{1cm} (5.6)

The function $g(\alpha, \beta)$ is a non-dimensionalized integral of the crack opening displacement and depends on the Dundurs’ parameters $\alpha$ and $\beta$ which can be calculated from the Young’s moduli, the Poisson’s ratios, and the shear moduli of substrate and
coating (amorphous Si: \( g(\alpha, \beta) \approx 7.67 \); poly-Si: \( g(\alpha, \beta) \approx 4.63 \)). The film stress \( \sigma \) corresponds to the fracture strength \( \sigma_f \) at the critical strain \( \epsilon_c \). The second energy-based model to determine \( K_{IC} \) was derived by Frank \textit{et al.} [112] and is based on a two-dimensional shear lag model. The energy release rate \( G_F \) depends on the mean crack distance \( L \), the dimensionless parameter \( \lambda = \xi / L \) and the stress in tensile direction \( \sigma_x = \frac{E_f \epsilon_1 - \nu_f \nu_s}{1 - \nu_f} + \sigma_{res} \):

\[
G_F = \frac{L}{E_f} \left( 1 - \nu_f^2 \right)^2 \sigma_x^2 \left[ \frac{3\lambda \sinh \left( \frac{1}{\lambda} \right) - 1}{2 \cosh^2 \left( \frac{1}{2\lambda} \right)} - \frac{3\lambda \sinh \left( \frac{2}{\lambda} \right) - 2}{4 \cosh^2 \left( \frac{1}{\lambda} \right)} \right]
\]

(5.7)

For all films, \( G_F \) is calculated in the strain regime \( \epsilon_c < \epsilon < \epsilon_b \) because the model is not representative if buckling occurs, and the mean crack distance \( L \) for strains \( \epsilon < \epsilon_c \) is probably underestimated because of the limited field of view of the optical microscope. The fracture toughness can be calculated from the energy release rate by \( K_{IC} = \sqrt{E_f \cdot G} \).

Figure 5.13 (a) depicts \( K_{IC} \) as a function of strain calculated by the model of Frank \textit{et al.} for all film thicknesses. For amorphous Si, it is constant and independent of the film thickness. This is because brittle fracture is the dominant failure mode for Si films and plasticity of the coating is not expected. The fracture toughness of poly-Si decreases with increasing strain which is counterintuitive. It is expected that the fracture toughness increases as a function of strain until it reaches a constant value at the crossover strain \( \epsilon_c \). The opposite behavior observed here could be explained as follows. The calculations are based on a model which was derived for Ta [30]. This material is a typical getter material [113] which results in a good adhesion between Ta and Kapton® E. However, the relatively low onset buckling values of poly-Si indicate that the adhesion between substrate and coating is very weak. If a crack results in reduced adhesion, this leads to larger relaxation zones and smaller energy release rates such that the fracture toughness decreases as a function of strain. In Figure 5.13 (b), the results of both models are compared. The averaged fracture toughness of amorphous Si calculated with the model of Frank \textit{et al.} is in excellent agreement with \( K_{IC} \) determined with the model of Beuth. For poly-Si, the fracture toughness is scattered and varies as a function of film thickness. These deviations could have different origins: (i) Annealing of the films caused a plastic deformation of the substrate which may influence the Young’s modulus and the Poisson’s ratio of the Kapton® E film. The resulting inaccuracies in \( E_s \) and \( \nu_s \) may have a large influence on \( g(\alpha, \beta) \) which would falsify \( K_{IC} \) determined with the model of Beuth. (ii) As already described, the annealing of the substrate yields local strain variations of 10% which affects the result. (iii) The large surface roughness of the poly-Si films may lead to stress concentrations during loading. Consequently, an exact value for \( K_{IC} \) of poly-Si cannot be given here. However, most of the determined \( K_{IC} \)-values are larger than those of amorphous Si and we can conclude that poly-Si is tougher than amorphous Si. This result is supported by the higher onset fracture and the larger fracture strength of poly-Si compared to amorphous Si. Possible explanations are defect reduction in the poly-Si films caused by annealing, the dangling bonds in amorphous Si which decrease the overall bonding strength, and the tortious crack path in poly-Si films.

The determined fracture toughness of amorphous and poly-Si thin films are in very
good agreement with $K_{1C}$ values of micrometer-sized Si films reported in literature. Fracture toughness values of nanometer-sized, brittle films are reported in literature for $\beta$-Ta, SiO$_2$, TiO$_2$, ZrO$_2$, ITO, or amorphous C amongst other [100, 112, 114, 115]. Here, $K_{1C}$-values between 1 and 5 MPa m$^{0.5}$ were measured. The comparison with our results shows that amorphous Si belongs to one of the more brittle films while the toughness of poly-Si is comparable to that of other thin brittle films.

**Figure 5.13.** (a) Fracture toughness $K_{1C}$ as a function of applied strain for amorphous and poly-Si films calculated by the model introduced by Frank et al. The $K_{1C}$-values of amorphous Si are constant for all applied strains and for all film thicknesses while the $K_{1C}$-values of the poly-Si films decrease with increasing strain. (b) The $K_{1C}$-values obtained by the models of Frank et al. and Beuth are plotted as a function of film thickness. For amorphous Si, the obtained values are independent of thickness and are in good agreement for both models. For poly-Si, the values are scattered and generally, larger than those of amorphous Si.
5.4.6. Onset strain of fragmentation and delamination of Si embedded in the insulator structure

In Figure 5.14 the onset strains of fragmentation and delamination as a function of film thickness are depicted for Si deposited onto the insulator structure and for single layers of ultrathin amorphous Si films, SiO₂, and TiO₂ films. Both, the onset strain of fragmentation and delamination values of SiO₂ and TiO₂ were taken from literature [100].

Generally, thicker films fracture at lower strains than thinner films. Hence, the onset strains of fragmentation of the insulator structures are smaller than those of ultrathin Si films. The values are similar to those of SiO₂ and TiO₂ with film thicknesses of the same order of magnitude. However, it is counterintuitive that the fracture resistance of the insulator structure with 5 nm Si is lower than those of the insulator structures with thicker capping layers. The SEM micrographs in Figure 5.15 reveal that the structures exhibit rough surfaces. This roughness might result in stress concentrations during tensile loading and consequently, crack formation. Moreover, the Si film thickness difference between the three samples is minor compared to the overall thickness of the structures. Hence, for the ultrathin Si films deposited on the insulator structure no size-effect is observed.

The onset strains of delamination of all films are depicted in Figure 5.14 (b). The onset strain of delamination increases with increasing film thickness with the exception of the ultrathin Si single films. As it was already the case for the onset strain of fragmentation also the onset strain of delamination of Si films deposited onto the insulator structures are in the same order of magnitude as those of SiO₂ and TiO₂ with similar film thicknesses.

The observed increasing onset strain of delamination as a function of film thickness indicates that the delamination of the layer structure is buckle-limited and that the

![Figure 5.14: Onset strain of fragmentation (a) and onset strain of delamination (b) as a function of film thickness. For comparison also the strains of onset fragmentation and delamination of single layers Si, SiO₂, and TiO₂ are shown. The values of SiO₂ and TiO₂ were taken from literature [100].](attachment:image.png)
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Figure 5.15: SEM micrographs of 5 nm (a), 15 nm (b) and 25 nm (c) Si deposited on the insulator structure.

adhesion of the coating to the substrate is weak. We assume that the interface between Kapton® E and SiO₂ fails first.

5.5. Conclusion

In situ optical microscopy, Raman spectroscopy, and resistance measurements were used to determine the cohesive and adhesive properties of ultrathin amorphous and poly-Si films on Kapton® E substrates. The following conclusions can be drawn:

- Amorphous Si films fracture (buckle) at lower (higher) strains compared to poly-Si films. The onset delamination of amorphous Si films can be modeled by the strain energy criterion ($\epsilon_{sed} \propto d^{-0.5}$). The adhesion of poly-Si films to the substrate is very weak and buckling ($\epsilon_b \propto d^2$) is expected as long as $\epsilon_{sed}$ exceeds the onset strain of buckle delamination $\epsilon_b$. The buckle and strain energy models result in an adhesion strength of 33 mJ/m² for amorphous Si and a buckle width of $b=840$ nm for poly-Si which was confirmed by atomic force microscopy measurements.

- The stress transfer length is proportional to the square root of the film thickness which indicates that the stress transfer between substrate and coating is linear elastic.

- The fracture toughness of poly-Si films is higher compared to that of amorphous Si. The determined fracture toughness (poly-Si: $K_{1C}=3.36 \pm 1.37$ MPa m$^{0.5}$; amorphous Si $K_{1C}=1.49 \pm 0.22$ MPa m$^{0.5}$) are independent of the thickness which indicates brittle fracture. The results are in good agreement with $K_{1C}$-values of micrometer-sized Si films reported in literature.

- The aluminum-induced layer exchange mechanism was applied to crystallize the Si films and caused small Si crystallites on top of the coating and plastic deformation of the substrate. This may lead to stress concentrations in the
coating and local strain variations. Consequently, the resulting strength and toughness values of the poly-Si films scatter but provide an indication of the order of magnitude.

- Generally, onset fracture can be delayed by a reduction in the film thickness and compressive residual stress, given that the adhesion is sufficient.
6. Cohesive and adhesive failure of amorphous and crystalline Ge$_2$Sb$_2$Te$_5$ films

The cohesive properties of the phase-change material Ge$_2$Sb$_2$Te$_5$ (GST) were investigated. The onset strains of fragmentation of 20 nm - 400 nm thick as-deposited amorphous and crystalline GST films were determined by in situ resistance measurements, optical microscopy, and reflectance anisotropy spectroscopy (RAS) during uniaxial tensile loading. By comparing the results of the applied methods RAS was introduced as a promising tool to determine the onset strain of fragmentation of brittle films. The fracture strength $\sigma_f$ and fracture toughness $K_{IC}$ of the films were calculated. Amorphous GST fractures at larger strains than crystalline GST. However, due to the small Young’s modulus it is less tough than crystalline GST (amorphous: $K_{IC} = 0.4 \pm 0.2$ MPa m$^{0.5}$; crystalline: $K_{IC} = 0.8 \pm 0.2$ MPa m$^{0.5}$).

Parts of this chapter are based on a work submitted to Acta Materialia.

6.1. Introduction

Phase-change materials exhibit a prominent optical and electrical contrast between the amorphous and crystalline phase and they can be reversibly and rapidly switched between both phases. The reflectivity contrast [20] is exploited in rewritable optical data storage. The electrical resistivity changes up to several orders of magnitude upon the phase transition [21] and offers great potential as non-volatile electronic memory. Moreover, it has been demonstrated recently, that the phase-change material GST is a promising candidate for non-volatile display [46, 48] and data visualization applications [48]. Using thin GST films in the nanometer range and transparent conductors enable color changes upon phase change on both, rigid and flexible substrates.

Although phase-change materials have extraordinary properties some challenges still remain. Using phase-change materials for dynamic random access memory (DRAM) for example is still demanding due to the required fast switching time and extremely high cycle numbers. The endurance of the devices is often limited by void formation at the electrode contact due to the thickness reduction upon crystallization [28] which is 6.5% for GST [27]. Moreover, for thin GST films the large density change upon crystallization leads to a pronounced mechanical stress and might result in cracks in the film. Atomic force microscopy measurements of laser-induced crystallized GST for example show cracks in the crystalline region for laser pulses.
Cohesive and adhesive failure of amorphous and crystalline Ge$_2$Sb$_2$Te$_5$ films

in the ns-µs range [116]. Another failure mechanism which applies to display applications on flexible substrates is bending or straining of the substrate which might induce cracks in the GST film.

Consequently, it is of great interest to determine the mechanical properties of GST films, especially at film thicknesses relevant for the application. In literature most researchers focused on the investigation of the Young’s modulus of amorphous, metastable cubic, and stable hexagonal GST. Here various methods such as wafer curvature [27], nanoindentation [117], microtensile measurements [118], and micromechanical resonating beams [119] were applied. Young’s moduli between 10 GPa and 25 GPa for amorphous GST and values between 25 GPa and 60 GPa for crystalline GST were obtained [27, 117–119] depending on the method, the film thickness and the annealing temperature. Choi et al. [118] performed uniaxial microtensile tests of 500 nm amorphous GST and investigated the average crack spacing in the film as a function of strain. They determined an onset strain of fragmentation of 0.6%. However, no analysis of the crack evolution was carried out and only one film thickness and no crystalline GST was characterized.

In this chapter the cohesive and adhesive properties of amorphous and crystalline GST films in the thickness range from 20 nm to 400 nm are presented. Various in situ methods such as optical microscopy, resistance measurements, and reflectance anisotropy spectroscopy (RAS) are applied during uniaxial loading of the samples to determine the onset strain of fragmentation. RAS measures the difference in reflectance of linearly polarized light between two perpendicular directions (x, y) in

\[ \epsilon = 0 \]

\[ \epsilon < \epsilon_{on} \]

\[ \epsilon > \epsilon_{on} \]

Figure 6.1.: Illustration of a thin film on a substrate applied to uniaxial tensile load. (a) No strain \( \epsilon \) is applied and the atoms are arranged in their initial cubic structure. (b) The film is strained and the atomic structure is distorted in tensile direction. Brittle films exhibit only elastic deformation of the atoms while ductile materials also show plastic deformation. (c) The strain \( \epsilon \) exceeds the onset strain of fragmentation \( \epsilon_{on} \) and cracks are visible in the thin film. The atoms at the cracks are not bonded anymore and the stress in the film is released close to the cracks. Hence, the atomic structure starts to relax and elastic deformation of the film in tensile direction decreases.
the surface plane [120]:

\[ \frac{\Delta r}{r} = 2 \cdot \frac{r_x - r_y}{r_x + r_y} \]  

(6.1)

Note that the reflectance \( r \) is a complex number and here, we focus on the real part of the RA signal. This method is amongst others applied to monitor the growth of semiconductors [121], to determine the adsorption on surfaces [122], or to characterize the mechanical properties of a material [101, 123, 124]. The latter is possible because RAS is very sensitive to small lattice parameter changes. Uniaxial tensile strain below the onset strain of fragmentation results in these lattice parameter changes because the atomic structure is distorted in loading direction as depicted in Figure 6.1 (b). Hence, the band structure is affected and asymmetries in the reflectance of polarized light parallel and perpendicular to the strain direction are induced. Consequently, straining of a material results in a characteristic RA signal. In the elastic strain regime this RA feature increases linearly with strain till it saturates at the yield point [101, 124]. However, this method is limited to materials which show strain-induced optical anisotropy. Here, we demonstrate that RAS is additionally a promising tool to determine the onset strain of fragmentation of brittle films. As shown in Figure 6.1 (c) cracks in the film due to straining occur perpendicular to the loading direction and consequently, result in an anisotropy in the reflectance of polarized light parallel and orthogonal to the strain direction. Optical microscopy is additionally used to determine the onset strain of delamination and to monitor the evolution of the crack patterns. That allows to calculate the fracture strength and fracture toughness of the amorphous and the crystalline GST films.

### 6.2. Materials and Methods

GST films of 20 nm, 30 nm, 50 nm, 100 nm, 200 nm, and 400 nm were produced by direct current magnetron sputtering (PVD Products) using a power of 20 W. The background pressure in the chamber was better than \( 8 \cdot 10^{-5} \) Pa and during the depositions, an Ar flow of 20 sccm and a pressure of 0.67 Pa were used. In order to achieve homogeneous film thicknesses the substrate was rotated with 30 rpm. The polyimide substrates (Kapton® E from DuPont™) with a thickness of 50 µm were cleaned in acetone and isopropanol and baked in a furnace for at least 6 h at 200 °C prior to deposition.

All GST films were amorphous as-deposited as confirmed by Raman spectroscopy. Crystallization was performed under argon atmosphere in a furnace. The samples were annealed at 200-210 °C for 6 min with a heating rate of 30 °C/min. The phase transition to the rocksalt crystalline (fcc) phase is at around 160 °C for 250 nm thick films for heating rates of 30 °C/min [125]. XRD was carried out to analyze the crystalline structure. A \( \theta-2\theta \) scan from 3° to 120° was performed with a step size of 0.008°.

The residual stress \( \sigma_{\text{res}} \) of the films was determined by measuring the curvature of the polyimide substrates with the GST films by optical microscopy and calculating \( \sigma_{\text{res}} \) using Stoney’s equation [98]. For uniaxial tensile tests, the samples were mounted
Cohesive and adhesive failure of amorphous and crystalline Ge$_2$Sb$_2$Te$_5$ films into a tensile machine (Kammrath & Weiss GmbH). Each sample was 5 mm wide and the strain rates were 5.3·10$^{-5}$/s (optical microscopy and RAS measurement) and 1.1·10$^{-4}$/s (resistance measurements). In situ confocal light microscopy (WITec CRM200) was performed with a 100x objective to observe the crack patterns during stepwise loading. The mean crack distance $L$ was calculated with a Matlab routine [99]. The analysis of the crack evolution leads to fracture strength and fracture toughness values of the GST layers.

An electrical resistance module was used in a constant current mode to record the change of the normalized resistance $R/R_0$ of all films during uniaxial loading. The settings were the same as those described in Chapter 5. Due to its low specific resistance, the resistance change of amorphous GST was monitored indirectly by measuring the resistance of a conductive, thin Pt capping layer during loading. Hence, GST films with a 3 nm Pt capping layer were sputtered without breaking the vacuum in between for in situ resistance measurements of amorphous GST. A direct current power of 41 W, a pressure of 0.67 Pa, and an Ar flow of 20 sccm were used for Pt.

RAS was performed in an energy range from 1.5 to 5.5 eV in intervals of 0.02 eV and with an integration time of 1 s per energy step. The spot size at the sample surface was 2 mm and the loading direction of the tensile machine was set in x-direction in Equation 6.1. The RA data was recorded during continuous loading at a single photon energy of the sample to track the evolution of one feature. Alternatively, data was obtained stepwise which means a whole spectrum in the range from 1.5 to 5.5 eV was acquired while straining was briefly interrupted. For all RAS measurements the Kapton® E substrates were roughened on the back side to prevent a reflection from this surface.

6.3. Results

Here, first the results of a XRD measurement are introduced followed by the residual stress measurements. Subsequently, the cohesive and adhesive properties of thin GST films as well as of the layer structure to tune the color appearance are presented. Finally the results of the reflectance anisotropy spectroscopy of all films are introduced.

6.3.1. Phase analysis

The Young’s modulus of hexagonal GST can be up to twice as large as that of cubic GST [119]. Hence, to choose the correct Young’s modulus of crystalline GST from literature it is important to know which phases are included in the annealed GST films. In Figure 6.2 XRD patterns of Kapton® E with and without annealed 400 nm GST film are shown. Kapton® E exhibits broad XRD peaks which partly overlay the XRD signals of crystalline GST. Here, the spectra are only presented up to 50° as some reflections are not measurable at high angles because of the disordered structure. Moreover, at these high angles the peaks are difficult to distinguish because of their broad appearance due to small grain sizes and the high density of peaks. Reflections of the cubic fcc structure were clearly identifiable and a lattice constant
Cohesive and adhesive failure of amorphous and crystalline Ge$_2$Sb$_2$Te$_5$ films

Figure 6.2.: XRD spectra of a Kapton substrate (gray spectrum) and 400 nm crystalline GST on Kapton (red spectrum) are presented.

of $a=6.00$ Å was determined which is consistent with literature [126]. These peaks are labeled in Figure 6.2. A peak fit of the hexagonal reflections was not feasible as hexagonal and trigonal phases are not distinguishable by the angular position of the reflection but by the intensity. However, as the sample is texturized here, the peak intensity does not provide information on the phase. Therefore, a quantitative analysis of the ratio of cubic and hexagonal phase cannot be provided. Nevertheless, the XRD spectrum indicates that both phases hcp and fcc are included in annealed GST films. Literature values of Young’s moduli of GST strongly differ. Therefore, the inaccuracy of the Young’s modulus taken in this work does not originate from the unknown phase-ratio but from discrepancies in literature. Won et al. [119] has demonstrated that the Young’s modulus of hexagonal GST is larger than that of cubic GST. Here, we use a Young’s modulus of 10-20 GPa for amorphous GST and $E_f$=30-40 GPa for crystalline GST which is consistent with literature [27, 117–119].

6.3.2. Residual stress

The determined residual stresses of all films are summarized in Table 6.1. The residual stress is tensile and decreases as a function of film thickness. Crystalline GST films exhibit larger residual stresses than amorphous films because of the density increase upon crystallization. Calculating the elastic strain values from the residual stress in the linear elastic regime yields unreasonably high values for ultrathin films

<table>
<thead>
<tr>
<th>film thickness $d$ (nm)</th>
<th>$\sigma_{res}$ amorphous (GPa)</th>
<th>$\sigma_{res}$ crystalline (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.78 ± 0.25</td>
<td>1.13 ± 0.36</td>
</tr>
<tr>
<td>30</td>
<td>0.57 ± 0.18</td>
<td>0.68 ± 0.20</td>
</tr>
<tr>
<td>50</td>
<td>0.30 ± 0.10</td>
<td>0.32 ± 0.10</td>
</tr>
<tr>
<td>100</td>
<td>0.15 ± 0.05</td>
<td>0.16 ± 0.05</td>
</tr>
<tr>
<td>200</td>
<td>0.08 ± 0.02</td>
<td>0.12 ± 0.04</td>
</tr>
<tr>
<td>400</td>
<td>0.05 ± 0.02</td>
<td>0.09 ± 0.03</td>
</tr>
</tbody>
</table>
Cohesive and adhesive failure of amorphous and crystalline Ge$_2$Sb$_2$Te$_5$ films below 50 nm. Hence, the validation method for these ultrathin films is questioned and is not used for the calculations in the following for the thinnest layers.

### 6.3.3. Cohesive and adhesive properties

**GST thin films**

Typical crack patterns of amorphous and crystalline GST at various strain values are depicted in Figure 6.3. The patterns resemble those of amorphous and poly-Si presented in Figure 5.3 in Chapter 5. Also here cracks in the crystalline film deviate from straight paths as they have to propagate through the grain boundaries in contrast to those in amorphous GST. Compared to the crack patterns of Si films, GST films exhibit smaller mean crack distances which indicates that the films are more brittle. Generally, buckling was not observed for amorphous GST up to strain values of 20% while crystalline films show delamination as presented in the right micrograph of Figure 6.3 (b).

Characteristic evolutions of crack patterns are obtained upon uniaxial tensile loading of thin brittle films. In Figure 6.4 the mean crack distances against applied strain are presented for amorphous (a) and crystalline (b) thin films. Cracks in the very thin films (20 nm and 30 nm) cannot be observed by optical microscopy, *in situ* AFM, and SEM measurements as the crack openings are too small. While for optical microscopy the resolution is not sufficient, detection of the cracks by *in situ* SEM is challenging because of charging effects of the polyimide substrate and carbon redeposition onto the film during scanning. For AFM measurements straining was briefly interrupted at various strain values and small areas of the film were scanned. However, as this method takes more time compared to SEM and optical microscopy

![Figure 6.3.](image)

**Figure 6.3.:** (a) Exemplarily, light micrographs of crack patterns of 100 nm amorphous GST at various strains are shown. The cracks are perpendicular to the loading direction and buckling is not observed. (b) Optical micrographs of crack patterns of 100 nm crystalline GST at various tensile strains are presented. In contrast to amorphous GST films, cracks do not channel through the whole film after reaching the critical length but stop at obstacles like e.g. grain boundaries.
Cohesive and adhesive failure of amorphous and crystalline Ge$_2$Sb$_2$Te$_5$ films

Figure 6.4.: Mean crack distance as a function of strain of (a) amorphous and (b) crystalline GST films.

measurements stress relaxation in the substrate occurs during the measurements which further decreases the crack openings. Generally, the onset strain of fragmentation determined by optical microscopy decreases as a function of film thickness. Furthermore, the saturated mean crack distance in the third regime is larger for thicker films.

Figure 6.5 shows the normalized resistance curves as a function of strain. The onset strain of fragmentation occurs as soon as the normalized resistance $R/R_0$ deviates from the ideal resistance change $R/R_0 = (1 + \epsilon)(1 + 2\nu_fe)$ (black line). In literature a 5% deviation from the ideal behavior is often taken as a measure

Figure 6.5.: Normalized resistance plotted versus strain for (a) amorphous GST films with 3 nm conductive Pt top layers and (b) crystalline GST films. The black solid line corresponds to the ideal resistance change while the dashed black line shows a 5% deviation of this ideal behavior. Exemplarily, for 100 nm crystalline GST an error bar is plotted to demonstrate scattering effects which occur between several measurements.
Cohesive and adhesive failure of amorphous and crystalline Ge$_2$Sb$_2$Te$_5$ films

for first cracking (dashed black line) [102]. The resistance of amorphous GST, which is less conductive than crystalline GST (amorphous: $(3-6) \cdot 10^3 \Omega \text{cm}$; cubic: $(1-4) \cdot 10^{-1} \Omega \text{cm}$ [18]), was measured indirectly by a thin Pt capping layer. To detect the first cracks in amorphous GST the thickness of the Pt layer should neither be too thick nor too thin. On the one hand, the first crack in amorphous GST films will not induce a crack in the Pt capping layer, if it is too thick. On the other hand, very thin Pt films built islands on the GST films and consequently Pt might induce cracks in the GST films. The second case can be excluded by measuring the resistance change upon straining of a single Pt film. This resistance curve follows the ideal resistance change (black line) to larger strains than all GST films as can be seen in Figure 6.5 (a). Hence, the method seems reliable. The resistance curves of amorphous GST films dramatically increase as soon as they deviate from the ideal behavior. This indicates that a crack propagates immediately through the whole film as soon as it appears. For 50 nm amorphous GST the slope of the normalized resistance is less steep. It might be that the crack opening of this thin film is too small to instantly induce a crack in the Pt film which propagates immediately through the whole film.

The normalized resistance curves of crystalline GST films (see Figure 6.5 (b)) deviate from the ideal resistance change as soon as the films are strained. At low strains the slopes of the normalized resistance curves are the same for all crystalline GST films. This slope further increases at one strain value depending on the film thickness. The deviation from the ideal behavior may have two possible origins: On the one hand, crystalline films may exhibit small cracks which start to open as soon as the film is loaded. At higher strain values the slope of the normalized resistance increases due to new cracks which occur in the film. On the other hand, straining of the crystalline films may result in a piezoresistive effect.

For both cases, the deviation from the initial resistance slope indicates the formation of first cracks such that these strain values are taken as onset strains of fragmentation. For 100 nm crystalline GST scattering in data is demonstrated by an error bar which results from three different resistance measurements. Generally, the onset strain of fragmentation decreases as a function of film thickness for amorphous and crystalline GST films.

Tunable color coatings

Figure 6.6 presents optical micrographs of crack patterns of amorphous (b) and crystalline (c) GST embedded in a tunable color coating (a) similar to that introduced in Chapter 3. The patterns differ from those of single amorphous and crystalline GST films. In contrast to single films the appearance of first individual cracks was difficult to observe. Instead several tiny cracks were detected at one strain value which can be explained as follows: For both phases the crack openings at low strain values are very small such that they cannot be observed in the optical microscope. Increasing the uniaxial tensile strain causes further crack opening and several short fractures are simultaneously visible in the optical microscope as can be seen in Figure 6.6 (b) and (c) at 3.3 % strain. Upon loading the crack density increases and the tiny cracks grow until they intersect with other cracks. At high strain values sharp microscope images could not be taken as can be seen in Figure 6.6 (b) and (c) at 13.3 % strain. This indicates differences in height of the film which might be
Cohesive and adhesive failure of amorphous and crystalline Ge$_2$Sb$_2$Te$_5$ films

Figure 6.6: (a) Illustration of a tunable color coating similar to that introduced in Chapter 3 is shown. Light micrographs of crack patterns of 18 nm amorphous (b) and crystalline (c) GST embedded in the tunable coating are depicted.

explained by delamination of the film.

The crack distances are very narrow and the cracks are very short. Therefore, it is challenging to determine the mean crack distance. Figure 6.7 depicts the mean crack distance of the multilayer films for amorphous and crystalline GST as a function of strain. The onset strain of fragmentation is most probably overestimates as several tiny first cracks were detected at one strain value. Nevertheless, first cracks in crystalline GST were observed at lower strains than in amorphous GST. This trend is in good agreement with single amorphous and crystalline GST layers.

Figure 6.7: Mean crack distance as a function of applied tensile strain for amorphous and crystalline 18 nm GST embedded in the layer structure presented in Figure 6.6 (a).
6.3.4. Reflectance anisotropy spectroscopy

**GST thin films**

Reflectance anisotropy (RAS) measurements were performed to measure the yield point and onset strain of fragmentation. In Figure 6.8 a simulation of the light penetration depth in amorphous and crystalline GST as a function of photon energy is presented. The penetration depth describes the depth $d$ at which the intensity of the light decays to $1/e$ of its surface value ($d = \lambda/(4\pi k)$). The imaginary parts of the refractive index $k$ of amorphous and crystalline GST were taken from literature [127]. Especially, for thin amorphous and crystalline GST films below 50 nm thickness the penetration depth needs to be taken into account. For these thin films the reflectance anisotropy spectra might origin not only from the film but also from the Kapton® E substrate.

Several representative RA spectra taken at different strains are presented in Figure 6.9. Those of amorphous GST films are shown on the left while those of crystalline films are on the right in Figure 6.9. For comparison spectra of different film thicknesses (30 nm, 100 nm, and 400 nm) are plotted. The solid lines represent the spectra during tensile loading and the dashed lines those during unloading of the samples. Loading of the films results in the appearance of RA features with negative amplitude which are called crack features in the following. For all films the position of the crack features are marked with small black arrows in the figure. Generally, the following description of the crack features in RA are valid:

- For each film thickness the signal appears at a different photon energy which indicates that it is not a materials property. For 100 nm amorphous GST it is for instance at 2.8 eV while 400 nm amorphous GST shows the crack feature at approximately 2.2 eV.

- The crack feature does not appear at the beginning of straining but at a strain value dependent on the film thickness and phase of the sample. For 100 nm amorphous GST e.g. it occurs at approximately 1% strain.

![Simulated light penetration depth versus photon energy of amorphous and crystalline GST.](image)

**Figure 6.8.** Simulated light penetration depth versus photon energy of amorphous and crystalline GST.
Figure 6.9: RA-spectra of amorphous ((a), (c), (e)) and crystalline ((b), (d), (f)) GST films at different strain values. Exemplarily, only the spectra of 30 nm ((a), (b)), 100 nm ((c), (d)), and 400 nm ((e), (f)) GST films are shown. All solid lines represent tensile loading and the dashed lines unloading of the sample. The RA spectra of all crystalline GST films reveal a feature at 5.06 eV. Moreover, the RA spectra of amorphous and crystalline GST films show crack features which are indicated by black arrows. The absolute amount of the crack feature increase as a function of strain. Exemplarily, circles indicate the energy position of the crack feature of 100 nm amorphous GST for different strain values.

- The crack feature has a negative amplitude and the absolute value of the amplitude increases as a function of straining. Unloading of the sample results
in a decrease of the absolute value of the amplitude.

- As a guide to the eye small circles in the RA spectra of 100 nm amorphous GST represent the photon energy position of the feature at each strain value. The feature shifts to larger photon energies with increasing strain until it saturates at 2.8 eV at approximately 2% strain. Upon unloading the energy position of the feature shifts back to smaller photon energies. This shift to larger energies upon loading and the reversible behavior upon unloading is valid for all films.

- For films thicker than 50 nm the crack feature of amorphous and crystalline GST films of the same film thickness resemble each other. The RA spectra of amorphous and crystalline 20 nm and 30 nm films differ from each other. This might be due to the penetration depth of the light which is in the same order of magnitude as the film thickness. Consequently, not only the film properties but also the substrate properties are measured. The RA spectra of 20 nm amorphous GST are similar to that of the Kapton® E substrate. Hence, an interpretation is challenging and the spectra are not included in the analysis.

In addition to the crack feature all crystalline GST films show another signal at 5.06 eV. This signal grows in amplitude with increasing strain and is called elastic feature in the following. Independent of film thickness all crystalline GST films show the elastic feature at 5.06 eV which indicates that it is a material property. Moreover, also this feature is reversible and disappears upon unloading.

**Tunable color coatings**

Figure 6.10 shows RA spectra of amorphous (a) and crystalline (b) 18 nm thick GST films embedded in the tunable color coating. Upon uniaxial tensile loading of the sample the whole spectrum shifts to lower intensities and several features in the RA spectra occur. The absolute value of the pronounced feature at 1.76 eV for amorphous (2.06 eV for crystalline) GST increases as a function of strain. Unloading of the sample results in a shift back to larger intensities. However, upon unloading the spectrum does not return to the initial position of the spectrum at 2% tensile strain.
6.4. Discussion

6.4.1. Residual stress

The residual stresses of crystalline GST films are more tensile than those of amorphous GST films. This trend was also observed by Pedersen et al. [27]. They showed that the stress change upon crystallization is only 9% of the theoretically calculated stress change which would be expected due to the large film thickness change upon crystallization. The observed result can be explained by a viscous flow in the amorphous phase which relieves the stress as explained by Pedersen et al. [27]. The authors show that upon annealing crystalline GST the stress relief rate is minor and cannot explain the discrepancy between measurement and calculation. Hence, they assume that the stress is relieved in the amorphous phase during growth of crystalline nuclei.

The intrinsic tensile stress in the amorphous phase is formed during the fabrication process and might be caused by the working gas pressure during sputter deposition [128]. The thickness dependent trend of the residual stress shown here is probably related to the coalescence of the islands and the atomic peening of the film during sputter deposition [129].

6.4.2. Cohesive and adhesive properties of GST films

Figure 6.11 presents the fracture strength of amorphous and crystalline GST as a function of film thickness. The fracture strength was calculated from fragmentation kinetics in the defect-controlled regime in analogy to Chapter 5 and in analogy to literature [107, 108]. Generally, amorphous films exhibit a smaller fracture strength
Cohesive and adhesive failure of amorphous and crystalline Ge$_2$Sb$_2$Te$_5$ films

Figure 6.11.: Fracture strength values as a function of film thickness of amorphous and crystalline GST are presented. The error bars result from uncertainties of the Young’s moduli. Fitting Griffith’s ($\sigma_f \propto d^{-0.5}$) law to the data results in bulk fracture strength values which are indicated as shaded areas. than crystalline films. However, Figure 6.4 demonstrates that crystalline GST fractures at lower strains than amorphous GST. This apparent contradiction can be solved by considering that the Young’s modulus of crystalline GST ($E_f$=30-40 GPa [119]) is two to three times larger than that of amorphous GST ($E_f$=10-20 GPa [119]) which results in a higher fracture strength of crystalline GST. The film thickness dependence of the fracture strength can be modeled according to Griffith’s law ($\sigma_f = a \cdot d^{-0.5} + b$). This law assumes that the dominant factor determining the fracture strength is defect growth throughout the film thickness. Thicker films result in smaller fracture strength values because a larger film volume exhibits a higher number of volume defects. Consequently, the probability of critical defects at a certain stress is larger for thicker films. However, the fracture strength converges against a bulk fracture strength value which corresponds to the fit parameter $b$ and is plotted as shaded areas in Figure 6.11. The fitparameter $a$ includes the fracture toughness $K_{1C}$ and an unknown geometry factor.

In Figure 6.12 (a) the fracture toughness values of amorphous and crystalline GST are shown as a function of strain. These values were evaluated by an energy-based approach in analogy to Chapter 5. A two-dimensional shear lag model derived by Frank et al. [30] was used to derivate the fracture toughness. The model is valid in the strain regime $\epsilon_c < \epsilon < \epsilon_b$, with $\epsilon_c$ the crossover strain where the stress relaxation zones start to overlap and $\epsilon_b$ the onset strain of delamination. For amorphous GST the model is applied in the strain regime $\epsilon_c < \epsilon < \epsilon_{sat}$ as at larger strains no further cracks occur. To calculate the fracture toughness, first the stress transfer length $\xi = L_c/2$ needs to be identified. As the decrease in onset strain of fragmentation as function of strain is low (see Figure 6.4) it is challenging to determine $L_c$. Consequently, in contrast to Si the critical length $L_c$ was determined from the mean crack distance at saturation $L_c = 1.5 \cdot L_{sat}$ [107]. At low strains $K_{1C}$ increases as a function of strain which is expected as first cracks occur at the largest defects and consequently result in a reduced effective fracture toughness. The fracture toughness
Cohesive and adhesive failure of amorphous and crystalline Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} films

Figure 6.12: (a) Fracture toughness $K_{1C}$ plotted as function of strain for amorphous and crystalline GST determined by the model introduced by Frank et al. (b) The $K_{1C}$-values obtained by the model of Frank et al. and Beuth are plotted as a function of film thickness. Generally, crystalline GST is tougher than amorphous GST.

saturates at higher strain values as soon as the stress in the film reaches the fracture strength of the film. Exemplarily, for each film thickness one error bar is plotted which result from uncertainties of the Young’s moduli. Compared to these uncertainties, a variation in $L_c$ has a minor influence on the calculated fracture toughness but changes the evolution of the fracture toughness as a function of strain.

In Figure 6.12 (b) the $K_{1C}$-values obtained at $\epsilon_c$ and $\epsilon_b$, or respectively $\epsilon_{sat}$ for the model of Frank et al. are compared to the values calculated with the model of Beuth [111]. This model relies on linear elastic response of substrate and coating and the residual stress of the film was considered in the calculated $K_{1C}$ values. For both models the obtained values scatter but are independent of the film thickness which indicates that there is no plastic deformation in the films. For amorphous GST an average fracture toughness of $K_{1C}=0.4 \pm 0.2 \text{ MPa m}^{0.5}$ is obtained and for crystalline GST the value is $K_{1C}=0.8 \pm 0.2 \text{ MPa m}^{0.5}$. Compared to other thin brittle films with $K_{1C}$ values around 1-5 MPa m\textsuperscript{0.5} [30, 85] these values are small. The difference in
Cohesive and adhesive failure of amorphous and crystalline Ge$_2$Sb$_2$Te$_5$ films

$K_{IC}$ values can be explained by the small Young’s modulus of GST compared to other brittle materials. Polymers also exhibit a small Young’s modulus and a reduced fracture toughness, but they are still used as substrate material for flexible electronics. Consequently, in some applications the criteria of maximum strain to fracture ($\varepsilon_{max} \propto K_{IC}/E_f$) and the energy release rate which is the maximum stored energy ($K^2_{IC}/E_f$) are more important. For flexible electronics e.g. the strain to fracture value is more important as it describes the failure of the device. Comparing the strain to fracture values of GST (amorphous GST: $K_{IC}/E_f=(30\pm15) \cdot 10^{-6} \cdot m^{0.5}$; crystalline GST: $K_{IC}/E_f=(23\pm6) \cdot 10^{-6} \cdot m^{0.5}$) with those of Si (amorphous Si: $K_{IC}/E_f=(18\pm3) \cdot 10^{-6} \cdot m^{0.5}$; crystalline Si: $K_{IC}/E_f=(20\pm8) \cdot 10^{-6} \cdot m^{0.5}$) shows that the values are comparable.

6.4.3. Onset strain of fragmentation and delamination of GST films

In this subsection first the reflectance anisotropy measurements are presented because they help to understand the anomaly in resistance measurements of the crystalline GST films. Subsequently, these results are compared to the onset strains of fragmentation determined by optical microscopy and resistance measurements. Finally, the onset strain of delamination is shown.

The onset strains of fragmentation of amorphous GST were obtained from RA spectra at the strain value where the crack feature starts to grow. Figure 6.13 (a) presents the intensity value of Re($\Delta r/r$) at the respective energy value of the crack feature as a function of strain. The films of all thicknesses first possess the same linear change of the anisotropy signal behavior during loading. The strain value where the RA signal deviates from the linear behavior depends on the film thickness and is taken as onset strain of fragmentation. Thicker films start to deviate at lower strain values from the initial linear behavior than thinner films.

The origin of this deviation can be explained as follows: Crack formation in the film always appears perpendicular to the loading direction. Hence, an anisotropy in the reflectance of the linearly polarized light between two perpendicular directions is induced. With increasing strain more and more cracks form, the anisotropy augments, and the intensity of the crack feature increases. A mean crack distance of 970 nm obtained from Figure 6.4 and a crack opening of 80 nm determined by \textit{in situ} atomic force microscopy measurements were used to simulate the behavior of linear polarized light at the cracks.

Figure 6.14 shows the electromagnetic response of a 100 nm amorphous GST slit array with a period of 970 nm to an incident transverse magnetic plane wave. The electromagnetic response has been modelled using the finite-element modelling software COMSOL Multiphysics. The surface plot shows the x-component of the electric field and the arrows indicate the relative electric field. This image can be seen as snapshot where incoming and reflected light interfere. The incident light couples to surface plasmon polaritons (SPP) at the upper (air/GST) and lower (GST/Kapton® E) surface which is enabled by the fundamental mode of the slit array [130]. Due to the significantly altered SPP dispersion relation at the GST/Kapton® E interface the coupling between the SPP modes of the upper
and lower surface can be considered weak. In analogy to transmissive gratings the overall electromagnetical response depends in general on the geometrical parameters of the slit array. Here, the crack distance ($\overline{L} > \lambda$) and crack opening ($a < \lambda$) are constant and the film thickness acts as critical coupling parameter.

Figure 6.15 compares the measured and simulated RA spectra of 50 nm, 100 nm, and 400 nm amorphous GST. The spectral position of the crack feature is in good agreement for measurement and simulation. With increasing film thickness the crack feature shifts to smaller photon energies. However, the exact shape of the spectra differ for measurement and simulation. The simulation assumes a perfect periodic grating but in reality crack openings and crack distances vary. Consequently, the measurement averages grating structures with slightly different periodicity which explains why the spectra are smoother than those of the simulations. Moreover, for the simulation we assume that the cracks are perfectly oriented to the polarization of the light. During the measurement a deviation of some degrees may easily occur which might also influence the RA spectra.
Cohesive and adhesive failure of amorphous and crystalline Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} films

Figure 6.14.: Simulation of an incident transverse magnetic field at $E_{\text{photon}}=2.70$ eV ($\lambda=460$ nm) on a 100 nm amorphous GST slit-array with period $L=970$ nm and slit width $a=80$ nm. The surface plot indicates the x-component of the electric field and the arrows present the relative electric field.

The reflectance anisotropy of crystalline GST was recorded at a photon energy of 5.06 eV during continuous loading (see Figure 6.13 (b)). At low strains the films of all thicknesses exhibit a linear increase in intensity as a function of strain, which is perfectly reversible upon cyclic loading. The strain value where the signal starts to

Figure 6.15.: Measurement (a) and COMSOL simulation (b) of RA spectra of 50 nm, 100 nm, and 400 nm amorphous GST films. The thickness-dependent trend of the spectral position of the crack feature is identical for measurement and simulation. For the simulation crack openings of 80 nm and crack distances of 970 nm were assumed. The measured spectra were recorded at approximately 5% strain.
deviate from this linear behavior differs for each film thickness. It is taken as yield point where the elastic deformation stops. Here, the change of the RA spectra at strains larger than the yield point is difficult to interpret as the crack feature might influence the signal. Generally, a saturation of the RA signal corresponds to plastic deformation [101] and a decrease of the signal results from relaxation of the film due to crack formation. Here, the decrease of the RA signal is not only caused by stress relaxation but also by the overlying crack feature signal.

The RA feature at 5.06 eV can be attributed to the piezo-optic tensor and reflect critical points in the electronic band structure of metastable cubic GST. The electronic band structure of cubic GST was calculated in literature [53]. It is very complex and the authors were not able to determine all critical points. Moreover, the results are based on calculations for the lowest energy structure where intrinsic vacancies are ordered. At real conditions they are randomly distributed in the material. Consequently, it is challenging to find a transition in the band structure which corresponds to the RA feature at 5.06 eV. However, numerous conductive bands around 5 eV [53] at the Γ-point and a high density of states at this energy [131] indicate that several transitions may be accessible. That would also explain that the RA signal at 5.06 eV is much broader than usually observed for a single transition [101].

To demonstrate that the strain where the reflectance anisotropy features appear can be attributed to the onset strain of fragmentation we compare these strain values with the onset strain of fragmentation determined by optical microscopy and resistance measurements. Figure 6.16 (a) presents the onset strains of fragmentation of amorphous GST and Figure 6.16 (b) those of crystalline GST films. The values obtained by RAS are in excellent agreement with those of the two other methods. This indicates that the method is reliable. Moreover, optical microscopy and

![Figure 6.16.](image)

**Figure 6.16.** Thickness-dependent onset strain of fragmentation of amorphous (a) and crystalline (b) GST films determined by RAS, optical microscopy, and resistance measurements. Here, continuously means that the RA data were recorded during continuous loading at a single photon energy. Stepwise means that a whole spectrum was acquired while the straining was briefly interrupted.
Cohesive and adhesive failure of amorphous and crystalline Ge$_2$Sb$_2$Te$_5$ films

resistance measurements could not be used to determine the formation of cracks in 20 nm and 30 nm thin GST films while this was partly feasible for reflectance anisotropy spectroscopy.

The RA measurements help to interpret the resistance measurement of crystalline GST. The RA feature at 5.06 eV corresponds to elastic deformation. This speaks against the thesis that the deviation of the normalized resistance from the ideal resistance change at low strains in Figure 6.5 (b) is caused by small intrinsic cracks which open upon straining. Consequently, this deviation results from a piezoresistive effect. From the slope of the initial resistance curves a piezoresistive gauge factor of \( GF = \Delta R/R \cdot \epsilon^{-1}=10-20 \) is calculated which is in the same order of magnitude as that of polycrystalline Si (\( GF=\pm30 \)) but much smaller than p-type silicon with \( GF=200 \) [132].

A comparison of the onset strain of fragmentation of amorphous and crystalline GST (Figure 6.16 (a) and (b)) shows that crystalline GST starts to fracture at lower strains than amorphous GST which might origin from the larger residual tensile stress of crystalline GST. Generally, thinner films exhibit a higher resistance against fracture than thicker films.

It was challenging to determine the onset strain of delamination of crystalline GST as the cracks appear not straight through the films (see Figure 6.3 (b)) and as the mean crack distance is very small. Figure 6.17 presents the onset strain of delamination of crystalline GST determined by optical microscopy. The delamination behavior follows the strain energy criterion where thinner films delaminate at higher strains \( \epsilon \) than thicker films [104] (see Equation 5.1). A fit of the onset strain of delamination as a function of film thickness is shown in Figure 6.17. Here, the Poisson’s ratio \( \nu_f \) of the film was taken as \( \nu_f=0.3 \) [133]. The Poisson’s ratio of the substrate is assumed to be the same as that of Kapton® HN (\( \nu_s=0.34 \) [73]). The fit yields the energy release rate \( G_0 \) and the residual stress \( \sigma_{\text{res}} \) as fit parameter. Both values depend on the Young’s modulus which we assume to be between 30-40 GPa. The residual stress obtained from the fit is slightly larger than those measured

\[
\begin{align*}
E_f=30 \text{ GPa:} & \quad G_0=1.42 \text{ J/m}^2 \\
& \quad \sigma_{\text{res}}=0.61 \text{ GPa} \\
E_f=40 \text{ GPa:} & \quad G_0=1.90 \text{ J/m}^2 \\
& \quad \sigma_{\text{res}}=0.81 \text{ GPa}
\end{align*}
\]

\[\text{Figure 6.17.: Onset strain of delamination of crystalline GST determined by optical microscopy. The data is fitted by the strain energy criterion. For amorphous GST no buckling could be observed up to a strain of 20\%.}\]
by substrate curvature. This indicates either that the residual stress determined experimentally is underestimated or that the Young’s modulus of crystalline GST taken from literature is overestimated. The determined energy release rate is in the same order of magnitude as that of typical surface energies such as of Si [134]. Amorphous GST does not exhibit any buckling up to a strain of 20%.

**Tunable color coatings**

Figure 6.18 presents the evaluation of the RA spectra shown in Figure 6.10. In analogy to amorphous single GST films also here, the intensity values $\text{Re}(\Delta r/r)$ of RA features as a function of strain are shown. For amorphous and crystalline films respectively, two features were analyzed. The onset strain of fragmentation which is the strain value where the signal deviates from the initial linear behavior is not as obvious as those of single amorphous GST films (see Figure 6.13 (a)). This can be explained as follows: First cracks of these layered structures do not channel through the whole film as soon as they reach their critical length. Instead they are very short (see Figure 6.6) and hence, do not cause a large anisotropy in the spectra. However, for both, amorphous and crystalline GST films embedded in the tunable color coatings the evaluated onset strains of fragmentation of both crack features yield the same value. The onset strain of fragmentation of amorphous GST is at $\epsilon=2.4\%$ and that of crystalline GST is at $\epsilon=1.6\%$.

The onset strain of fragmentation determined by RAS and optical microscopy are compared in Figure 6.19. Generally, the strain at onset fragmentation measured by optical microscopy is lower than that measured by RAS which might be explained by the first small cracks in the film which do not cause a large anisotropy. However, for both methods the same trend is observed. The color coating that includes crystalline GST cracks at lower strains than that with amorphous GST. This trend was

![Figure 6.18.](image)

**Figure 6.18.**: Evolution of the RA signals of amorphous (blue graphs) and crystalline (orange and red graphs) GST embedded in the layer structure. The $\text{Re}(\Delta r/r)$ value was recorded at two photon energies for amorphous and crystalline GST respectively as the spectra exhibit two features at different photon energies (see Figure 6.10).
Cohesive and adhesive failure of amorphous and crystalline Ge$_2$Sb$_2$Te$_5$ films

![Graph showing onset strain of fragmentation for amorphous and crystalline GST films](image)

**Figure 6.19.:** Onset strain of fragmentation of amorphous and crystalline GST embedded in the tunable color coating determined by optical microscopy and RAS.

also detected for single amorphous and crystalline GST films. Both color coatings fracture at lower strains than single GST layers.

### 6.5. Conclusion

In conclusion we have investigated the cohesive and adhesive properties of amorphous and crystalline GST films in the film thickness range from 20 nm to 400 nm by uniaxial tensile tests. Different *in situ* methods such as optical microscopy, resistance measurements, and reflectance anisotropy spectroscopy were applied.

- Generally, thinner films start to fracture at higher strains than thicker films due to a size effect in fracture strength. Amorphous films exhibit a higher onset strain of fragmentation than crystalline films. Nevertheless, amorphous samples show a lower fracture strength and fracture toughness than crystalline films. This is due to the small Young’s modulus of amorphous GST. Also crystalline GST has a small Young’s modulus compared to other brittle materials such as Si or Ta. This explains why the fracture toughness values of GST (amorphous: $K_{1C}=0.4 \pm 0.2$ MPa m$^{0.5}$; crystalline: $K_{1C}=0.8 \pm 0.2$ MPa m$^{0.5}$) are smaller compared to those of other brittle films. However, the maximum strain to fracture of GST is similar to that of Si.

- The adhesion of amorphous GST films to Kapton® E is good and the films do not delaminate up to a strain of 20 %. Crystalline GST starts to delaminate at lower strains and the film thickness dependence of the delamination follows the strain energy criterion.

- It was demonstrated that RAS is a reliable tool to determine the onset strain of fragmentation. This method is even feasible for very thin films where optical microscopy, atomic force microscopy, and scanning electron microscopy are limited because of the small crack openings of the films. Note that the sensitivity of RAS as onset strain of fragmentation detector strongly depends...
Cohesive and adhesive failure of amorphous and crystalline Ge$_2$Sb$_2$Te$_5$ films on the crack pattern. Short cracks were first detected by optical microscopy compared to RAS. This was demonstrated for the tunable color coatings.

- The appearance of an elastic feature of crystalline GST proves that the phase transition from amorphous to crystalline does not cause intrinsic cracks in the film but that first cracks occur upon loading. Moreover, the RA signal decreases at strains larger than the yield point strain because crack formation results in relaxation of the atomic structure.

- Resistance measurements of crystalline GST show a piezoresistive effect which is in the same order of magnitude as that of polycrystalline Si.
The aim of this thesis is to lay the materials foundations to develop new concepts for static and tunable color devices which are described in the previous chapters. In contrast, this chapter focuses on possible applications of the introduced color coatings. In the first part the long-term color stability of static and tunable color coatings is investigated. In the second part the switching speed, endurance, and resolution of phase-change materials are compared to existing display technologies. Moreover, the influence of mechanical properties on possible applications is discussed. Note that the presented color coatings are prototypes and here we discuss which properties need to be improved for future applications.

7. General discussion

7.1. Long-term color stability

7.1.1. Static color coatings

In Chapter 2, three different color coatings based on metal, insulator, and semiconductor layers as underlying substrate materials were developed. For the application as decorative coatings, solar cells, or photodetectors, it is of great importance that the absorption resonance remains stable for at least several years. A shift of the depth or spectral position of the absorption resonance affects the Lab values which were calculated from the reflectance spectra. Hence, we compare the color appearance of the coatings 2.5 years after deposition with the color measurements performed directly after fabrication.

Figure 7.1 presents photographs of the three different sample structures on a smooth and rough substrate taken 2.5 years after fabrication. Compared to the color appearance of the structures shown in Figure 2.2, the appearance of the metal structure has changed completely. The sample surfaces exhibit inhomogeneous color appearances. Spots which deviate from the initial colors are visible which occur especially at the edge of the samples. This indicates that gold has diffused into the thin amorphous Si capping layer. Transition metals undergo direct interstitial diffusion in amorphous Si. Au diffuses faster in amorphous Si than in crystalline Si, because in the latter Au atoms are temporary trapped at intrinsic defects which is not the case for amorphous Si [135]. The diffusion coefficient of Au in amorphous Si was measured between 400 °C and 800 °C and exhibits an Arrhenius-like behavior with an activation energy of 1.5 eV [136]. Extrapolating the diffusion coefficient at room temperature (21 °C) from this data results in a value of 6.39·10⁻³⁰ cm²/s. This value is small compared to the diffusion coefficient $D$ of Au in amorphous Ge at room temperature ($D=5.91·10^{-18}$ cm²/s [137]). Nevertheless, for long-term stability of the color appearance a diffusion barrier between Si and Au or a replacement of Au
Figure 7.1.: I-IX: 0, 3, 5, 7, 10, 15, 20, 25, and 30 nm of Si deposited on the different sample structures on the polished side (smooth surface) and on the unpolished side (rough surface) of a silicon wafer. The photographs were taken 2.5 years after fabrication. The semiconductor and insulator structures seem to exhibit the same color appearance as directly after deposition (see Figure 2.2). However, the color appearance of the metal structure changed: Au atoms diffused into the Si capping layer.

by TiN is required. The photographs of the insulator and semiconductor structures indicate that the color appearance has not changed after 2.5 years (see Figure 7.1). However, for a quantitative analysis reflectance measurements have been performed as presented in Figure 7.2.

Figure 7.2.: Exemplarily, reflectance spectra of the insulator structure (a) and the semiconductor structure (b) are shown. The reflectance of samples with 5 nm, 10 nm, 15 nm, and 20 nm Si capping layers were measured directly after deposition (2013) and more than two years later (2016).

Here, the colors of the graphs correspond to the measured colors of the samples. Dashed lines represent measurements performed directly after fabrication and solid
Table 7.1.: Color difference $\Delta E$ of the insulator and semiconductor structure directly after deposition (2013) and 2.5 years later (2016).

<table>
<thead>
<tr>
<th>Insulator structure</th>
<th></th>
<th>Semiconductor structure</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Si thickness (nm)</td>
<td>$\Delta E$</td>
<td>Si thickness (nm)</td>
<td>$\Delta E$</td>
</tr>
<tr>
<td>0</td>
<td>5.73</td>
<td>0</td>
<td>0.98</td>
</tr>
<tr>
<td>3</td>
<td>2.86</td>
<td>3</td>
<td>0.59</td>
</tr>
<tr>
<td>5</td>
<td>2.44</td>
<td>5</td>
<td>0.62</td>
</tr>
<tr>
<td>7</td>
<td>5.42</td>
<td>7</td>
<td>0.68</td>
</tr>
<tr>
<td>10</td>
<td>9.69</td>
<td>10</td>
<td>1.01</td>
</tr>
<tr>
<td>15</td>
<td>7.11</td>
<td>15</td>
<td>1.34</td>
</tr>
<tr>
<td>20</td>
<td>4.61</td>
<td>20</td>
<td>1.12</td>
</tr>
<tr>
<td>25</td>
<td>6.40</td>
<td>25</td>
<td>1.08</td>
</tr>
<tr>
<td>30</td>
<td>3.88</td>
<td>30</td>
<td>1.13</td>
</tr>
</tbody>
</table>

lines those determined 2.5 years after deposition. Generally, the spectra are shifted to lower reflectance compared to the measurements performed directly after deposition. Moreover, the spectral position of the absorption resonance slightly shifted to longer wavelengths for the insulator structure (a) and semiconductor structure (b). To evaluate the color change over time the color difference $\Delta E$ between the color appearance directly after deposition and 2.5 years later was calculated as presented in Table 7.1. The insulator structure exhibits considerably larger $\Delta E$ values than the semiconductor structure. Here, a shift of the absorption resonance to different wavelengths has a larger influence on the color appearance as the resonances are narrower.

Several measurements of the same sample with the photospectrometer resulted in deviations of $\Delta E=1.21 \pm 0.85$. This value was derived from both measurements at different parts of the sample, and measurements which were each performed after a new calibration of the photospectrometer. The deviations of the colors of the semiconductor structure measured 2013 and 2016 are smaller than this error. Consequently, this structure has not significantly changed its color. However, the $\Delta E$ values determined for the insulator structure cannot be explained from the inaccuracy of the instrument. The color tolerances in industry depend on the application: In the automotive industry parts with $\Delta E$ values below 1.4 are automatically delivered while values below 1.7 need further consideration [138]. In commercial reproduction on printing presses color reproduction is not as strict as that in automotive industry. Here, $\Delta E$ between 3 and 6 are accepted [139]. In average, the color change of the insulator structure is below $\Delta E=6$, but it should be improved in the future by replacing the materials.

The results presented here give a hint on the color stability of the three different static color coatings. However, more testing methods depending on the application of the coating should be performed to verify the long-term color stability. Possible methods are e.g. annealing or cooling cycles to determine the temperature-dependent color stability.
7.1.2. Tunable color coatings

GST and Si films embedded in the coatings introduced in Chapter 3 change color upon amorphization or crystallization. The corresponding $\Delta E$ value is large (GST: $\Delta E=25.45$; Si: $\Delta E=47.18$) and proves that a different color is observed upon phase-change for both systems. These samples were fabricated in April and May 2014 and the color stability of the coatings was evaluated 2 years later in April 2016.

Figure 7.3 depicts reflectance spectra of amorphous and crystalline layer structures measured directly after deposition (2014) and two years later (2016). The colors of the graphs corresponds to the measured colors of the samples. For both materials, GST (a) and Si (b), the deviations of the reflectance spectra recorded at different dates are marginal. Table 7.2 presents $\Delta E$ values calculated from the reflectance spectra shown in Figure 7.3. The amorphous and crystalline layered structures based on GST exhibit a long-term color stability as the $\Delta E$ values are on the same order of magnitude as the inaccuracy of the photospectrometer. This proves that a thin Ti-TiN diffusion barrier, which was deposited between Au and GST, prevents interdiffusion and guarantees a better long-term stability. The color difference of the tunable color coating based on Si is a bit larger than the inaccuracy of the photospectrometer. Especially, the crystalline sample exhibits a pronounced color change which is caused by diffusion. The sample was annealed to 800°C to crystallize Si and at this temperature diffusivities of the embedded materials are large. The microscope image in Figure 3.9 (a) exhibits small dots inside and outside the laser-amorphized region which might be caused by diffusion. As these dots are not observed for the as-deposited film (see Figure 3.9 (b)) it can be assumed that they are induced by annealing. Hence, the annealed crystallized sample is more susceptible to interdiffusion which results in a more pronounced color change. However, the color difference of the graphs of the crystalline Si structures in Figure 7.3 (b) is difficult to observe by human eye although the $\Delta E$ value exceeds one. The color difference between the amorphous and crystalline phase of the color coating is still pronounced 2 years after deposition: $\Delta E=40.42$ for the Si color coating.

Figure 7.3.: Measured reflectance spectra of the tunable color coatings based on GST (a) and Si (b) are presented. The spectra determined directly after deposition (2014) and 2 years later (2016) do not deviate from each other.
Table 7.2.: Color difference $\Delta E$ of the tunable color coatings based on Si and GST directly after deposition (2014) and 2 years later (2016).

<table>
<thead>
<tr>
<th></th>
<th>GST</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>phase</td>
<td>$\Delta E$</td>
<td>phase</td>
</tr>
<tr>
<td>amorphous</td>
<td>1.69</td>
<td>amorphous</td>
</tr>
<tr>
<td>crystalline</td>
<td>1.48</td>
<td>crystalline</td>
</tr>
</tbody>
</table>

and $\Delta E=25.47$ for the tunable GST coating.

7.2. Application of the tunable color coating

7.2.1. Introduction

Display technologies can be divided into two types based on differences in their light source: Active lighting displays include emissive and transmissive modes and passive lighting displays work in reflectance. The latter are superior for outdoor applications and provide excellent readability under sunlight. Moreover, compared to active lighting displays the energy consumption is reduced as images are displayed by reflecting the light. Paper-like display technologies which have already been commercialized have the drawback that the low switching time makes them unfeasible for video content. However, new technologies with high potential for the application in mobile electronic devices have been developed. It is assumed that the market for electronic papers increases by a compound annual growth rate of 16.4% during the period 2015 to 2020 [140].

The color coatings based on ultrathin semiconductors introduced in this work are prototype devices. As they work in reflectance and have a low power consumption due to their stable color appearance they are potential future candidates for reflective display technologies.

In this chapter we investigate possibly necessary improvements of tunable color coatings based on ultrathin phase-change materials by comparing them to the properties of existing electronic papers. Here, the focus is on resolution, power consumption, switching speed, cycling numbers, and mechanical properties. Therefore, first a short overview of various electronic paper technologies is given [141, 142].

Electrophoretic displays: Positively charged black particles and negatively charged white particles can be positioned vertically by applying a controlled electric field. A desired gray scale can be obtained by manipulating the electrical field properly. This display technology based on bistability is heavily employed in e-Reader applications. Colors of the display are not ideally realized by a color filter because the brightness is reduced. The drawback of this technology is the low switching time and the difficulty to display a desired gray scale by simple and short drive waveforms. Besides vertical electrophoretic displays also horizontal electrophoretic displays exist. Here, homogeneously distributed particles in a pixel absorb light and produce a dark state. Light is transmitted through the pixel onto a reflector in the light state where all particles are collected into a laterally small area. Moreover, a hybrid vertical and horizontal electrophoretic technology was realized which is called electrokinetic and
has higher switching speeds. Electronic papers based on electrophoretic displays are heavily applied e.g. in Amazon’s kindle.

**Electrofluidic displays:** These displays contain colored oil which is confined inside the pixel. Above the oil film the pixel is filled with water and below a fluoropolymer coating exists on top of a lower transparent electrode and a white reflective substrate. A thin oil film is formed on the fluoropolymer coating because the fluoropolymer is hydrophobic. Applying a voltage between water and electrode results in a polarized water/fluoropolymer interface. Hence, the polymer is water wettable and the oil film is pushed to the side. This effect strongly depends on the voltage and a larger voltage yields a smaller area which is covered by the oil. The switching speed of these displays exceeds those of electrophoretic displays and the power consumption is low as no backlight is required. However, the display is not bistable. Electrofluidic displays are developed and produced by the company Gamma Dynamics.

**Microelectromechanical systems (MEMS):** MEMS are used to modulate light by changing the length of an optical cavity. A deforming membrane which changes the cavity length and a film stack that defines the color appearance are implemented in the device. In the open state light is reflected in a specified wavelength range and a color is visible. In the collapsed state the gap between membrane and film stack is closed and only UV light reflection occurs. The color states are defined by RGB areas. The disadvantage of this technology is the complex fabrication for large scale modules and the limited viewing angle. The company Qualcomm commercialized the MEMS display Mirasol.

**Electrochromic displays:** These displays are based on materials which reversibly change color when a voltage is applied. There is a large variety of chemistry, performance, and construction of display devices based on electrochromic materials. Generally, electrochromic materials are placed on patterned transparent electrodes which work as pixels. The fabrication is cheap and the driving voltage to tune the color is low. However, the durability and speed are low. In the past these displays were e.g. applied as smart Valentines gift card sold by Marks & Spencer in the UK [143].

**Photonic crystals:** The propagation of electromagnetic light interacts with the spacing of periodic nanostructures and results in selective transmission or reflection of the light. Tuning the spacing of the structure changes the color appearance of the photonic crystal. Two displays based on photonic structures are in development. Systems that control the interspacing of metal nanoparticles in electrophoretic colloidal suspension by applying a voltage are developed by the company Nanobrick. The company Opalux fabricates an expandable electroactive polymer which includes silica beads. Both systems are not commercialized as some challenges still remain. Currently, only unit pixels or simple segments are fabricated but matrix addressing still needs to be demonstrated. Hence, white color is difficult to create as it requires RGB pixels.

### 7.2.2. Resolution

Nowadays, displays of mobile devices exhibit vivid colors and high resolutions. The iPhone 6s Plus has e.g. a resolution of 401 ppi (pixels per inch) [144] while the Galaxy S6 and S6 edge from Samsung are equipped with a display that has 577 ppi.
Table 7.3.: Comparison of the display resolution of electronic papers introduced in subsection 7.2.1 with the color device developed by Hosseini et al. and our device.

<table>
<thead>
<tr>
<th>Display technology</th>
<th>state</th>
<th>Resolution (ppi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>electrophoretic</td>
<td>on the market:</td>
<td>300 [148]</td>
</tr>
<tr>
<td></td>
<td>Amazon Kindle Paperwhite</td>
<td></td>
</tr>
<tr>
<td>electrofluidic</td>
<td>R&amp;D:</td>
<td>75-300 [149]</td>
</tr>
<tr>
<td></td>
<td>Gamma Dynamics</td>
<td></td>
</tr>
<tr>
<td>MEMS</td>
<td>R&amp;D:</td>
<td>75-300 [150]</td>
</tr>
<tr>
<td></td>
<td>Qualcomm Mirasol</td>
<td></td>
</tr>
<tr>
<td>Electrochromic</td>
<td>on the market</td>
<td>comparable to</td>
</tr>
<tr>
<td></td>
<td></td>
<td>inkjet printer [151]</td>
</tr>
<tr>
<td>Photonic crystal</td>
<td>R&amp;D:</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Nanobrick</td>
<td></td>
</tr>
<tr>
<td>ultrathin GST</td>
<td>research:</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>Schlich et al. [46]</td>
<td></td>
</tr>
<tr>
<td>GST with ITO electrode</td>
<td>R&amp;D:</td>
<td>254000</td>
</tr>
<tr>
<td></td>
<td>Hosseini et al. [48, 152]</td>
<td></td>
</tr>
</tbody>
</table>

[145]. Human eyes will generally not resolve individual pixels in printed images with a resolution between 300 and 600 ppi [5].

The resolution of the color coating based on ultrathin phase-change materials is limited by the diameter of the laser beam. Here, the spot we have amorphized or crystallized had a diameter of approximately 270 µm, which corresponds to a resolution of 94 ppi. The resolution can easily be increased since diffraction-limited spot sizes of 1 µm are achieved by stronger focusing. However, for display application color switching should be induced by electrical pulses. This was realized by Hosseini et al. [48] and Rios et al. [146] with a pixel size below 100 nm. This resolution of 254000 ppi is even better than the recently presented static images with pixel sizes of 250 nm, which display the whole color spectrum [147]. They have been fabricated by NanoDrip printing and are based on red, green, and blue colloidal quantum dots. Table 7.3 compares the display resolutions of our device with that of Hosseini et al. [48] and the electronic paper technologies introduced in subsection 7.2.1. The resolution of our color coating where color switching is induced by a laser is comparable to electronic papers on the market.

7.2.3. Power consumption

The power consumption of mobile devices dedicated to the display is dramatically increasing. In 2008, only 34% of the power consumption of a multimedia application was used by its display while in 2014 it was already 54% [153]. Hence, display
Table 7.4.: Required voltage pulses to switch the various display technologies are presented. Note that the size or number of pixels are only known for some of the listed technologies. Hence, it is difficult to compare the values.

<table>
<thead>
<tr>
<th>Display technology</th>
<th>bistable</th>
<th>Voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td>electrophoretic</td>
<td>yes</td>
<td>15 V [142]</td>
</tr>
<tr>
<td>electrofluidic</td>
<td>yes</td>
<td>15 V [149]</td>
</tr>
<tr>
<td>MEMS</td>
<td>yes</td>
<td>5 V [153]</td>
</tr>
<tr>
<td>Electrochromic</td>
<td>min. to hours</td>
<td>0.5-1 V [151]</td>
</tr>
<tr>
<td>Photonic crystal</td>
<td>yes</td>
<td>&lt; 10 V (50 µm gap) [154]</td>
</tr>
<tr>
<td>ultrathin GST</td>
<td>yes</td>
<td>-</td>
</tr>
<tr>
<td>GST with ITO electrode</td>
<td>yes</td>
<td>5 V [48]</td>
</tr>
</tbody>
</table>

Technologies with low power consumption like that of electrophoretic displays are needed. In Table 7.4, the required voltage pulses of the different technologies are listed.

It is difficult to compare the power consumption of the color coating based on GST which was introduced in Chapter 3 with the other technologies as our coating was switched by a laser and not electrically. Electrically-induced switching of such a micrometer-sized area would require much larger energies than those of the nanometer-sized pixels [22, 155] introduced by Hosseini et al. The authors have estimated that a display of 300 cm$^2$ area with 250 nm x 250 nm pixels consumes 7.2 J for reamorphization which is only slightly larger than the energy consumption of electrochromic displays which would require 2.0 J for a 300 cm$^2$ screen [142]. In contrast, the same display with 10 µm sized phase-change material pixels would require 7500 J [155]. Consequently, the power consumption of displays based on ultrathin phase-change materials are competitive to those on the market if the pixel-size is confined to nanometric areas.

### 7.2.4. Switching speed

Human eyes can discriminate consecutive images for a switching speed of up to 20 Hz and beyond this threshold they perceive the images as continuous [156]. Usually, the refresh rate of displays based on phase-change materials is limited by their crystallization time. However, for the tunable color coating introduced in this thesis it is limited by the experimental setup which allows a maximum laser pulse rate of only 960 Hz (see Table 7.5). The resulting switching speed of 2 Hz is too low for


<table>
<thead>
<tr>
<th>Display technology</th>
<th>Switching speed (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>electrophoretic</td>
<td>$\approx 10 \ [142]$</td>
</tr>
<tr>
<td>electrofluidic</td>
<td>$&gt; 33 \ [149]$</td>
</tr>
<tr>
<td>MEMS</td>
<td>$\approx 10^3 \ [153]$</td>
</tr>
<tr>
<td>Electrochromic</td>
<td>$\approx 10^3 \ [142]$</td>
</tr>
<tr>
<td>Photonic crystal</td>
<td>$&gt; 10 \ [154]$</td>
</tr>
<tr>
<td>ultrathin GST</td>
<td>amorphization $&gt; 10 \cdot 10^6$ (60 fs pulse)</td>
</tr>
<tr>
<td></td>
<td>crystallization 2 (60 fs pulses at 960 Hz)</td>
</tr>
<tr>
<td>GST with ITO electrode</td>
<td>amorphization $\approx 8 \cdot 10^6$ (125 ns pulse)</td>
</tr>
<tr>
<td></td>
<td>crystallization $&lt; 8 \cdot 10^6$ ($x \cdot 125$ ns pulse)</td>
</tr>
</tbody>
</table>

Electronic paper applications but can be sped up straightforwardly by using higher repetition rates.

Generally, amorphization and crystallization of GST and consequently color switching can be on the Megahertz scale as demonstrated by Hosseini et al. [48], which is much faster than the switching time of existing display technologies and overcomes the drawback of electrophoretic displays. Consequently, display technologies based on phase-change materials enable playbacks of video content. Besides PCMs also electrofluidic, MEMS, and electrochromic displays are able to play video content.

### 7.2.5. Cycling numbers

For a video device typically $10^9$ switches are required before the device fails [141]. These demands are fulfilled for electrofluidic and MEMS displays as presented in Table 7.6. The cycling number of electrophoretic displays was taken from a book written in 1975 [157]. We assume that nowadays longer lifetimes can be achieved. Color switching of ultrathin PCMs was demonstrated for 6 respectively 130 cycles which is not sufficient for the application. Here, ablation, diffusion, and void formation due to the large density change upon phase change might limit the lifetime [28]. However, the color coatings based on GST are prototypes and by choosing appropriate material systems higher switching numbers will be feasible. It was demonstrated that memory devices based on Sb-rich Ge-Sb-Te phase-change materials show $10^{11}$ cycles [28] which would be sufficient for video devices.
Table 7.6.: Display lifetimes strongly depend on their feasible number of cycles which are presented here for the various display technologies.

<table>
<thead>
<tr>
<th>Display technology</th>
<th>cycling number</th>
</tr>
</thead>
<tbody>
<tr>
<td>electrophoretic</td>
<td>$&gt;10^7$ [157]</td>
</tr>
<tr>
<td>electrofluidic</td>
<td>$10^9$ [141]</td>
</tr>
<tr>
<td>MEMS</td>
<td>$12 \cdot 10^9$ [153]</td>
</tr>
<tr>
<td>Electrochromic</td>
<td>$\approx 40\cdot10^6$ [142]</td>
</tr>
<tr>
<td>Photonic crystal</td>
<td>-</td>
</tr>
<tr>
<td>ultrathin GST</td>
<td>6</td>
</tr>
<tr>
<td>GST with ITO electrode</td>
<td>130</td>
</tr>
</tbody>
</table>

7.2.6. Mechanical properties

Omodani defined [158] four grades of display flexibility: Elastic but in a rigid form, curved, bendable, or foldable displays. Elastic displays, which are used in rigid forms, are applied in mobile devices. All introduced display technologies fulfill the requirements of elastic displays in rigid forms. Curved displays are shaped during the fabrication but are not flexible during use. Flexibility is provided for bendable or foldable displays, but here we focus on bendable displays as foldable displays are very challenging to realize.

Flexible or rollable display technologies with a bend radius of <0.5 cm must be at most 100 $\mu$m thick as thicker devices would result in mechanical degradation over time [142]. Subtracting the substrate thickness and the backplane only 40 $\mu$m are left for the active pixel layer. This argument already eliminates some display technologies. Flexible MEMS displays are unlikely because of the complexity of their structure and the inorganic dielectrics [142]. Moreover, they require a good vacuum level in the cell gap such that the membrane can move freely and the viewing angle is limited due to the nature of interference colors. Prototypes of bendable electrophoretic displays were realized by Polymer Vision but they stopped their research due to financial challenges. Electrofluidic technologies developed by the company Gamma Dynamics satisfy the major requirements for flexible displays and they already offer rollable active-matrix displays [149].

Color coatings based on phase-change materials on flexible substrates were demonstrated by Hosseini et al. [48]. They fabricated flexible display films in both reflective and semi-transparent mode and showed that the color appearance is similar to that of rigid substrates. Consequently, these coatings are potential candidates for wide-viewing-angle displays. The color stability as a function of incident angle is demonstrated in the simulations shown in Figure 7.4. The reflectance remains stable up to angles of 40° for both color coatings (our device: (a), (b) and Hosseini’s device: (c), (d)).
General discussion

Figure 7.4.: Simulated reflectance spectra as a function of incident angle of light are presented. Amorphous (a) and crystalline (b) GST embedded in the color coating introduced in this work show stable reflectance spectra as a function of incident angle up to 40°. The same applies to the reflectance spectra of amorphous (c) and crystalline (d) GST films embedded in the color coatings introduced by Hosseini et al. For the reflectance simulation in (c) and (d) an ITO thickness of 180 nm was assumed.

Hosseini et al. did not discuss the influence of bending and straining on the durability of the color coating. As shown in Chapter 6 GST films are brittle and fracture at uniaxial strains depending on the thickness and phase of the film. As color coatings based on display technologies require very thin GST films below 20 nm thickness the onset strain of fragmentation exceeds 1.5% strain (see Figure 6.19). Moreover, patterning of the films to enable electro-tunable pixels might improve the mechanical properties of the display device.

7.3. Conclusion

In conclusion, reflective bistable displays based on ultrathin phase-change materials are possible competitors for existing reflective display technologies. The resolution of the devices is comparable and even exceeds that of existing display technologies. The power consumption is slightly larger than that of electrochromic displays but might be reduced further by choosing appropriate material systems [159] or by doping the phase-change material [160]. Switching speeds of some Megahertz were demonstrated and would even allow to play video content. The durability of switchable color coatings based on phase-change materials needs to be enhanced. High cycle numbers of memory devices based on Sb-rich Ge-Sb-Te phase-change materials were observed [28] and would be sufficient for display applications. Moreover, flexible displays based on GST were demonstrated but further research needs to be conducted to better understand the influence of mechanical strain on the lifetime of the device.

Full color tuning of a display based on phase-change material is challenging. Red colors are particularly difficult to achieve by interference coatings as the color matching functions considerably overlap and because of the heightened sensitivity in
the blue region (see Figure 1.1). Therefore, RGB colors caused by light interference at ultrathin phase-change materials are unlikely. They could be obtained by e.g. a color filter but more challenges remain. Three separate pixels would be required such that only one-third of the incoming light can be reflected and therefore, the brightness of the display is limited. Still, not only binary displays are feasible by phase-change materials. Continuous gray-scaling pixels were demonstrated by inducing different levels of crystallization [146]. Hence, continuous color switching will also be achieved for other colors besides gray. As displays based on phase-change materials require three times more power (7.2 J) than electrochromic display technologies (2.0 J), display applications with low refresh rates are feasible:

- Phase-change materials are promising candidates for electronic shelf labels which allows stores to use digital price tags. Supposed that the power consumption is so little that multiple-year battery lifetimes are accomplished this offers superior product management. Price updating is achieved automatically, the resolution is sufficient and as the display works in reflection the readability in a store environment is given. Over time these e-labels enable cost saving as manual updating of prices at the shelf is not required anymore [142].

- As demonstrated by Hosseini et al. [48], the color appearance of phase-change material displays is provided both, indoors and outdoors in bright sun light. Consequently, they might be used for electronic conference room booking systems [161], for management of parking spaces [161], or for displaying temporary road works in a city. The latter is imaginable as a sign at a city entry to inform which roads are closed. As these road works often last for several months an update of the signs is seldom and power consumption is reduced.

- Moreover, displays based on phase-change materials might be applied to announce performances in a theater or to inform when a soccer game starts in a stadium.

- Numerous other applications with low refresh rates such as advertisement posters or guides in exhibitions or museums are possible.
8. Conclusion

This thesis comprises the development of static and tunable color coatings based on ultrathin Si and GST films and their optical properties are investigated. Furthermore, a variety of different methods are applied to investigate the mechanical properties of ultrathin amorphous and crystalline Si and GST films. Here, major achievements of this project are summarized and remaining open questions are defined.

This thesis lays the materials foundations for static and tunable color coatings. Color coatings based on strong interference are attractive because of the considerable reduction in layer thickness compared to conventional optical coatings based on transparent films. In the first part of this thesis we demonstrate that the underlying material of these coating systems is not limited to metals but can be replaced by any material. The required non-trivial phase-shift at the interface between substrate material and lossy dielectric top layer and the high reflection of the substrate material can be tuned by the thickness and number of layers. Color coatings with substrate materials of metal, semiconductor, and insulator thin films were fabricated with Si top layers in the thickness range from 3 nm to 30 nm.

Metal structure: Deep and narrow absorption resonances result in bright color appearance and the optical properties are robust with respect to incident angles between 0° and 80°. However, long-term color stability is prevented by interdiffusion of the Au and Si thin films.

Insulator structure: Due to the low reflectance of the Si substrate wafer only two layers of insulators are sufficient to mimic the effective optical constant of a highly reflective metal. Consequently, the resulting color appearance can compete with that of the metal structure. The absorption resonance remains prominent for incident angles of the light from 0° to 60°. Compared to the metal structure, the long-term color stability is dramatically enhanced but still needs to be improved for the application as e.g. decorative coating. This structure is advantageous for coloring glass where the color appearance depends on the position of the light source.

Semiconductor structure: For amorphous underlying semiconductors the absorption resonances are not as deep and narrow as those of the other two structures. Moreover, the reflectance depends stronger on the angle of incidence of the light but is constant between 0° and 30°. However, a long-term color stability is observed. Simulations have shown that deep and narrow absorption resonances can be obtained by exchanging the amorphous Si and Ge underlying layers by crystalline ones.

The long-term color stability of static color coatings based on ultrathin semiconductors will be improved by minimizing the number of thin films and choosing appropriate material systems. Gold could e.g. be exchanged by TiN which is less...
reflective but similar to Au the imaginary part of the refractive index strongly varies as a function of the wavelength. Hence, deep absorption resonances are expected for ultrathin Si on TiN as presented in the simulation in Figure 8.1. This material can be fabricated by sputter deposition and exhibits reduced material costs in contrast to Au. Moreover, it is well-known as a diffusion barrier for Si [162].

From the investigations of the static color coatings we learn that the absorption coefficient of the dielectric and the underlying material requires a strong variation with the wavelength to obtain deep and narrow absorption resonances.

This result is exploited for tunable color coatings based on strong interference. Reversible color switching between blue and gray is obtained by switching a thin GST phase-change material on top of a metal between the amorphous and crystalline phase. A single femtosecond laser pulse is sufficient to amorphize the GST film and crystallization is achieved by 60 fs long pulses for 16 s at a repetition rate of 40 Hz. The color appearance and contrast can be tuned by the thickness of the GST film and by choosing the appropriate underlying metal. To use GST e.g. for blue ray discs an optical contrast of more than 87% can be achieved by optimizing the thickness of GST and the SiO$_2$ top layer on Al.

Si does not show a large natural optical contrast between the amorphous and crystalline phase. Nevertheless, we present that ultrathin Si on Ag changes color upon phase-change with an optical contrast as large as 92% at wavelengths around 572 nm.

The mechanical properties of amorphous and crystalline ultrathin Si and GST films were investigated as they influence the functionality of static and tunable color coatings on flexible substrates. Here, polyimide substrates with a maximum service temperature of 400°C were used for uniaxial tensile tests. Hence, ideal sputter parameters of Si and Al were evaluated to reduce the crystallization temperature.

![Figure 8.1: Simulated reflectance spectra of various ultrathin Si films on TiN [38, 52]. The colors of the graphs correspond to the simulated color appearance of the samples.](image-url)
of Si below 400 °C by metal-induced crystallization. Generally, high sputter powers and low argon flows diminish the crystallization time and temperature.

The onset strain of fragmentation of amorphous and crystalline Si and GST was determined by various methods such as optical microscopy, resistance measurement, Raman spectroscopy, and reflectance anisotropy spectroscopy. In contrast to crystalline layers cracks in amorphous films are straight and propagate through the whole film as soon as they nucleate. While crystalline GST films fracture at lower strains than amorphous GST films, the opposite is the case for amorphous and crystalline Si films. This observation can be explained by the residual stress of the layers. The large compressive stress of crystalline Si films helps to delay crack initiation while the large tensile stress of crystalline GST films has the opposite effect. The determined fracture toughness values of GST are lower than those of Si but the onset strains of fragmentation of both materials are similar: The onset strain of fragmentation of amorphous (crystalline) GST is larger (smaller) than that of amorphous (crystalline) Si. A reduction in film thickness significantly improves the fracture behavior of both materials due to a size effect. In terms of adhesion, we show that GST films have superior properties compared to Si films. For amorphous GST films delamination is even not observed up to strain values of 20%.

Static color coatings based on ultrathin Si on the insulator structures crack at strain values below the onset fracture strain of single ultrathin Si films. Here, the Si film thickness does not have a large impact on the onset strain of fragmentation and delamination as Si is much thinner compared to the whole layer stack thickness. Note that the static color coating delaminates at larger strain values than ultrathin Si films which is caused by the better adhesion of SiO₂ to Kapton® E.

Crack initiation in the tunable color coatings with 18 nm amorphous and crystalline GST films occurs at lower strains than in single GST films which might be caused by a size effect. The layer stack with amorphous GST possess a higher onset fragmentation strain than that with crystalline GST in analogy to amorphous and crystalline GST single films.

Another scientific achievement of this thesis is the successful introduction of reflectance anisotropy spectroscopy as a tool to determine the onset strain of fragmentation. In thin brittle films such as GST, no plastic deformation is observed. Crystalline GST shows an increasing feature in the RA spectra upon loading which indicates elastic straining of the film. A comparison with other methods, such as optical microscopy or resistance measurements proves, that first cracks are observed in the film as soon as the elastic feature in RA decreases. This can be explained by the stress relaxation of the film due to crack formation. Amorphous GST does not exhibit a RA feature. Nevertheless, the onset strain of fragmentation is observed by this method as cracks form perpendicular to the loading direction and induce an anisotropy for linearly polarized light. It is demonstrated that RAS is even more sensitive to first cracks in ultrathin films than the other applied methods.

Data storage applications have similar requirements as display applications such as large durability, low power consumption, or fast switching speeds. GST
fulfills these requirements and is exploited in rewritable optical data storage. Consequently, flexible display applications based on ultrathin phase-change materials exhibit superior optical properties compared to displays based on conventional semiconductors such as Si. The required power consumption to switch GST is only slightly larger than that of existing displays such as electrochromic displays [48]. Moreover, reversible color switching is demonstrated and the number of cycles can be enlarged by preventing ablation and diffusion by choosing appropriate materials systems. Fast amorphization times in the megahertz-regime are demonstrated in this thesis and here, the crystallization time is limited by the experimental set-up. Generally, GST can be crystallized in some hundred nanoseconds as demonstrated by e.g. Hosseini et al. [48].

It will be challenging to obtain RGB colors in displays based on phase-change materials. Especially, red colors are difficult to achieve by interference coatings because of the heightened sensitivity in the blue regime of the color matching functions. However, displays based on GST are not only limited to binary colors but intermediate colors can be obtained by inducing different levels of crystallization [146].

Taking into account that GST is as brittle as Si which is demonstrated in this thesis it might be challenging to exploit GST in flexible display devices. A loss of integrity of the ultrathin GST film might cause failure of the entire display. Consequently, the mechanical properties of other phase-change materials should be investigated in the future to find an ideal candidate for flexible display applications. Compared to GST, AgInSbTe exhibits a lower density increase upon crystallization [27]. Hence, the residual stress in the crystalline phase is reduced and the cohesive properties are likely to be improved.
Appendix

A. Appendix

In this chapter two tunable color coatings based on elastomers are introduced. In the first part stretch-tunable distributed Bragg reflectors (DBRs) made of two alternating elastomers on different flexible substrate materials are described. Straining these DBRs result in decreasing thicknesses of the layers and consequently, in a shift of the stopband to smaller wavelengths. In the second part an electro-tunable interference device based on an elastomer sandwiched between two electrodes is introduced. First test measurements which were performed with a conductive flat punch in a nanoindenter are described. Moreover, the surface roughness of Kapton® E substrates is presented.

A.1. Stretch-tunable distributed Bragg reflectors based on elastomers

Tunable color coatings based on elastomers have potential applications in sensors and display devices. Elastomers are perfect candidates for these devices as they can be stretched with strains going beyond 100% [163]. Various color devices based on elastomers have been demonstrated such as elastomer diffraction gratings with voltage-induced tunable periodicity [164] or color switching of polymer opals by altering the thickness by an applied voltage [165]. Kolle et al. [166] showed color tuning of stretch-tunable DBRs. However, full color tuning was not achieved (only from red to green) and only microscope images which depicted some defects were presented.

We reproduced these DBRs on two different substrate materials and on a large scale. The alternating polymer layers were fabricated from Polydimethylsiloxane (PDMS) from Dow Corning and Polystyrene-block-polyisoprene-block-polystyrene (PSPI) from Sigma Aldrich in analogy to Kolle’s work. The films were produced by spin coating and the thickness was adjusted by the ratio of solvent and elastomer and the rotation speed of the spin coater. The DBR was not fabricated by continuous spin-coating of all elastomer films as during spin coating impurities were incorporated into the films. Instead PDMS/PSPI bilayers with sacrificial layer of poly(4-styrene-sulfonic acid) (PSS) were spin-coated on a Si wafer. Subsequently, bilayers of good quality were transferred and stacked on an elastomer substrate.

First, PSS was spin coated on a Si substrate. An 18% concentration in water was used and spin coating was performed at 4000 rpm for 30 s. Subsequently, PDMS was mixed with the curing agent (10:1) and diluted in heptane (4.8%). Spin coating was performed at 4000 rpm for 30 s and crosslinking of the PDMS was induced (70 °C for
2 hours) on a hot plate. The resulting layer thickness of 144 ± 7 nm was measured by ellipsometry. Finally, 301 nm thick PSPI was spin coated onto this film. Thinner PSPI films were not achieved as they dewet on the PDMS film due to low surface energy of PDMS (19.8 mN/m [167]). PSPI was diluted in toluene (4.3%) and a spin speed of 4000 rpm for 30 s was applied.

The sacrificial PSS film was dissolved in warm water at 50 °C and the bilayers were transferred with the help of a self-made frame to the desired substrate. The substrate material has a significant impact on the reflectance spectra of the DBR. Simulations have shown that substrates with constant low reflectance over the whole visible wavelength range such as carbon result in a higher and more defined stopband. Two different commercial available VHB tapes were chosen as substrate material: A transparent VHB tape (4910F) and a gray VHP tape (4941P) from 3M. On both elastomer substrates 10 bilayers of PDMS/PSPI were transferred and the reflectance of the DBRs was measured during uniaxial tensile tests.

Figure A.1 presents photographs of the DBR on a gray VHB substrate. With increasing strain the color changes from violet to red, green and blue. However, due to small thickness variations in the films and the rough VHB substrate the color change is not homogeneous. At 35.1% strain e.g. some areas of the sample appear orange while other parts of the sample are more strained and the color appearance changed to green. Due to the substrate roughness some parts of the DBR attach better to the substrate than other parts. Consequently, lateral dimensions of these areas are more efficiently changed than other parts. The dark spot in the middle of each photograph results from reflectance measurements. VHB is resistant to heat or ultraviolet light [168]. Consequently, this spot is induced in the thin elastomer films.

In Figure A.2 photographs of the 10-bilayer DBR on a transparent VHB tape are depicted at different strain values. Also here the color changes from violet to red, orange, green and blue. However, the colors are less pronounced compared to the DBR on gray VHB tape. In analogy to the DBR on gray tape the two dark spots are induced by the detection beam during reflectance measurements.

The reflectance of both DBRs at different strain values are presented in Figure A.3. The colors of the graphs correspond to the measured colors of the sample. The spectral position of the stopband shifts to shorter wavelengths as a function of in-
Figure A.2.: Photographs of a 10-bilayer DBR with transparent VHB substrate are shown. Each photograph is labeled by its strain value. The color appearance is less pronounced compared to the DBR on the gray VHB substrate.

Increasing strain due to the thinning of the layers. The decreasing peak height with increasing strain is mainly caused by defects in the film which are induced by the detection beam as described above.

Compared to the DBR introduced by Kolle et al. our DBRs exhibit some advantages:

- The initial stopband height of the DBR transferred to the gray VHB tape is higher than that of the multilayer stack presented by Kolle et al. He achieved a maximal reflectance of approx. 50% while our layers exhibit a reflectance of 60%. The number of layers in the DBR was the same in both cases, however, a dark substrate material such as the gray VHB tape results in an increase of the peak.

- Kolle et al. only presented microscope images of their DBR with an image height of 140 µm so that the size of their fabricated DBR is unknown. The initial size of the DBRs shown here was 1 cm² and most probably much larger than that presented by Kolle et al.

Figure A.3.: Reflectance spectra of a 10-bilayer DBR on gray (a) and transparent (b) VHB substrates at various strain values. The spectral position of the stopband shifts to shorter wavelength with increasing strain. The colors of the graphs correspond to the measured colors of the samples.
• Full color tuning from violet, red, orange, green to blue with strain values up to 80% were achieved.

Figure A.4.: (a) Illustration of an electro-tunable DBR with two sets of electrodes AA and BB. The DBR is drawn as blue oval. (b) Applying a voltage to AA results in an increasing thickness of the DBR layers and a shift of the stopband to longer wavelengths. The opposite is the case when a voltage is applied to the electrodes BB.

Although some improvements have been demonstrated during this work still some challenges remain. PSPI should be replaced by an elastomer which is stable under heat treatment and ultraviolet light. Moreover, spin coating should be performed in a clean room environment to prevent dust in the layer structure.

Figure A.4 (a) shows an illustration of a possible electro-tunable DBR structure. A gray elastomer (e.g. VHB tape) is used as actuator between two sets of electrodes: AA and BB. These electrodes can be made of carbon black nanoparticles. The DBR is plotted in blue and is attached to the top electrode B. Applying a voltage between the electrodes BB results in an electrostatic attraction of the two electrodes and the center of the actuator is compressed. Consequently, the DBR area increases and the spectral position of the stopband shifts to shorter wavelength (see Figure A.4 (b)). The opposite case can be achieved by applying a voltage between the electrodes AA. The applied voltage can be minimized by using a thin prestrained actuator material [163].
A.2. Voltage-induced color change in elastomers

Electro-tunable thin film color coatings based on the elastomer PDMS are shown in Figure A.5. The corresponding simulated color appearance as a function of PDMS film thickness is presented. Electrodes made of ITO and Ti (a) result in less pronounced colors compared to electrodes made of Pt and Au (b). As PDMS exhibits a Poisson’s ratio close to $\nu=0.5$ its volume remains constant upon compression or straining. Therefore, open pores should be integrated into the PDMS to ensure that the PDMS thickness decreases as soon as a voltage is applied to the rigid electrodes. Compared to dielectric elastomer actuators with compliant electrodes the film thickness of PDMS in this color coating is much smaller. Therefore, thickness variations can be obtained at considerably smaller applied voltages. Unfortunately, these experiments could not be performed as the PDMS films exhibited some defects like dust or air bubbles. An applied voltage yielded a short circuit of the electrodes and heating of the PDMS film. Hence, the PDMS film thickness expanded and did not as expected decrease as a function of applied voltage.

To evaluate the feasibility first test experiments were performed with a conductive flat punch in a CSM nanoindenter. With the optical microscope in the nanoindenter a defined position on the sample can be chosen where no defects are visible to perform the measurement. Figure A.6 shows a schematic drawing of the setup. A 50 nm sputtered Pt film on a Si wafer acts as lower electrode. PDMS was spin-coated with 3000 rpm for 30 s onto this Pt film. An isolated wire connected the conductive flat punch of the nanoindenter and the Pt electrode to an external power supply (0–30 V). The sample was isolated from the stepmotor of the nanoindenter by a plastic plate which served as a sample holder. Moreover, a fuse with maximal current of 0.1 A between flat punch and power source prevented a short circuit at the sample. Consequently, a damage of the nanoindenter could be excluded.

The nanoindenter was used in a constant load mode with a constant load of 3 µN.
Appendix

**Figure A.6.** The thickness decrease of a thin PDMS film as a function of applied voltage is measured with a conductive flatpunch. A voltage is applied between the flat punch and the Pt film during constant load. The current is measured and an embedded fuse prevents a breakthrough.

To 5 \( \mu \text{N} \) and a maximal load of 5 \( \mu \text{N} \). The loading rate was set to 120 \( \mu \text{N/min} \) and the unloading rate to 240 \( \mu \text{N/min} \). Moreover, 3000 nm/min were set for the arrival and retract speed of the flat punch. During constant load different voltages were applied and the displacement was measured.

Young’s moduli of PDMS samples depend on the base to curing agent ratio and values between 0.55 MPa for a ratio of 33:1 and 3.58 MPa for a PDMS ratio of 5:1 were reported [169]. Moreover, a linear behavior between curing temperature and Young’s modulus of PDMS was demonstrated [170].

Here, we fabricated two different PDMS films. Sample A was fabricated in analogy to PDMS films for the stretch-tunable DBR films. A base to curing agent of 10:1 was used, PDMS was diluted in heptane (16.67 %), and the film was post-baked for 2 hours at 70 °C on a hot plate. A resulting film thickness of 730 nm was measured by ellipsometry. To evaluate the effect of Young’s modulus on the decrease of film thickness upon applied voltage sample B was fabricated with different settings. A

![Diagram](attachment:image.png)

**Figure A.7.** Displacement curves as a function of time are plotted for sample A (a) and sample B (b) during constant load. An alternating voltage between 0 V and 30 V was applied between the Pt lower electrode and the flat punch during constant load which yields in alternating displacements. For sample B the displacements are much larger compared to sample A as the Young’s modulus of the PDMS film is smaller.
base to curing agent of 30:1 and a dilution in heptane of 11.11% was used. Moreover, the PDMS was cured at room temperature for 48 hours and the resulting film thickness was 560 nm.

Figure A.7 shows displacement curves as a function of time for sample A (a) and sample B (b). The red dashed graphs are displacement measurements without applied voltages. The orange and blue graphs show displacement measurements during which the voltage was altered between 0 V and 30 V. As soon as the voltage increased the displacement of the flat punch grew because the flat punch was attracted to the lower Pt electrode. When the voltage was set back to 0 V the electrodes stopped to attract each other and the displacement went back to the initial position. For sample A the displacement changed 2 nm upon applying 30 V while the displacement of sample B increased by approx. 20 nm. This trend is expected as the thickness decrease is inversely proportional to the Young’s modulus [171]. A thickness decrease from 560 nm to 540 nm corresponds to 3.6% thickness change. A PDMS film of 600 nm thickness with Au and Pt electrodes as presented in Figure A.5 (b) would result in a color change from rose to green upon 3.6% thickness decrease.

However, if the displacement of the flat punch is caused by the attraction of both electrodes the load should remain constant. This is not the case as presented in Figure A.8. The load decreased upon increasing the voltage to 30 V between flat punch and Pt thin film and a load maximum is observed as soon as the voltage is switched back to 0 V. Changing the instrument adjustments such as the force feedback loop parameters did not prevent the observed changes in load. Note that CSM recommends load Kp values below 8 and load Ki values below 500.

As the load curve only varies initially when the voltage value changes but remains constant during applied constant voltage we assume that the measured displacements are real. Consequently, the feasibility of thin PDMS color coating is proved. For future investigations patterned PDMS thin films without defects should be fabricated to increase the breakdown voltage. This could be achieved in a clean room environment or a glove box.
A.3. Surface roughness of Kapton E

Kapton® E substrates were used for mechanical testing of thin Si (see Chapter 5) and GST (see Chapter 6) films. It has been shown that these polyimide substrates have smoother surfaces and reduced defect density compared to Kapton® HN polyimide substrates [30]. Hence, Frank et al. have measured larger fracture strength of coatings deposited on Kapton® E substrates compared to the same coatings on Kapton® HN substrates.

Consequently, in this work we chose Kapton® E as substrate material to exclude substrate roughness effects on the result. AFM measurements of a Kapton® E substrate resulted in a root-mean-squared surface roughness of $R_{\text{rms}} = 2.8 \text{ nm}$ which is lower or in the same order of magnitude as that of Kapton® HN ($R_{\text{rms}} < 10 \text{ nm}$) [172]. However, the measurement also exhibited some structures on the surface as can be seen in Figure A.9 (a). These worm-like structures have an average height of $8.8 \pm 3.0 \text{ nm}$ and a full width at half maximum of $30.1 \pm 6.0 \text{ nm}$. Although the structures are very small they might influence the measured tensile strength of thin films which’s thicknesses are in the same order of magnitude. For thicker films the influence of the worm-like structures is minor.

These structures either occurred recently due to aging of the Kapton® E sheets or they have always been on the surface but were not detected before because the film roughness was larger than the substrate roughness.

In conclusion, especially uniaxial tensile measurements of very thin films presented in this work might be a conservative estimate of fracture strength and fracture toughness and enhanced values might be obtained for smoother substrate surfaces.

![Figure A.9.](image)

**Figure A.9.** (a) Atomic force microscope (AFM) image of a Kapton® E substrate. Bright worm-like structures are visible on the surface. (b) A line scan over such a structure is shown.
A.4. RA signal in the elastic strain regime

As described in Chapter 6 RAS can be used to determine the onset strain of fragmentation of amorphous and crystalline GST films. For crystalline GST films an RA feature at 5.06 eV increases as a function of strain in the elastic regime. It deviates from this linear behavior as soon as the first cracks in the film appear. To demonstrate that the linear increase of the RA feature at low strains is perfectly reversible we performed cyclic loading experiments of a 30 nm crystalline GST film on a Kapton® E substrate. During loading and unloading cycles the RA signal was recorded at 5.06 eV. Figure A.10 (a) presents the measured RA signal and the elastic strain as a function of time. Tensile straining of the sample results in a linear increase of the RA signal, the intensity of the signal is constant if straining is interrupted and unloading the sample yields a decrease of the RA signal. Figure A.10 (b) presents the same RA data as in (a) but as a function of strain for cyclic loading. Here, loading and unloading of the sample can only be distinguished by the color of the graphs which demonstrated that the signal increase in the elastic regime is perfectly reversible.

![Figure A.10](image)

**Figure A.10.** (a) Measured RA signal and applied strain as a function of time for 30 nm crystalline GST. The RA signal increases for tensile loading and decreases for unloading the GST film. (b) The same RA data as in (a) but as a function of strain are presented. To distinguish between loading and unloading cycles they are plotted in various colors.
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Bibliography


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- **Dong, Hao** is a former student at ETH Zürich. During his Master project *Stretch-tunable Distributed Bragg Reflector* he prepared and analyzed DBRs on two different substrates. These results are presented in the Appendix.

- **Frank, Stephan** is a former PhD student at the Laboratory for Nanometallurgy. He wrote the Matlab script *FractureBucklingAnalysis* to analyze the mean crack distance in tensile tested films.

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