Influence of annealing conditions on the optical and structural properties of spin-coated As$_2$S$_3$ chalcogenide glass thin films

Shanshan Song, Janesha Dua, and Craig B. Arnold

Abstract: Spin-coating of chalcogenide glass is a low-cost, scalable method to create optical grade thin films, which are ideal for visible and infrared applications. In this paper, we study the influence of annealing on optical parameters of As$_2$S$_3$ films by examining UV-visible and infrared spectroscopy and correlating the results to changes in the physical properties associated with solvent removal. Evaporation of excess solvent results in a more highly coordinated, denser glass network with higher index and lower absorption. Depending on the annealing temperature and time, index values ranging from $n = 2.1$ to the bulk value ($n = 2.4$) can be obtained, enabling a pathway to materials optimization.

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References and links

1. Introduction

Chalcogenide glasses have drawn great interest for their high refractive index, low-loss in mid-infrared, a wide range of photo-induced phenomena, and optical nonlinearities [1–3]. They are ideal candidates for various applications in infrared optics, such as lenses, all-optical switching, and laser written waveguides [4,5]. In addition, the photosensitive properties of chalcogenide glasses enable optical tuning of photonic structures, such as tuning for solid-state lasers [6,7] and photonic crystal waveguides [8].

For most applications, thin film deposition with good film quality is a prerequisite. The films are expected to have a composition similar to the bulk glass, a low surface roughness, a reproducible and controlled refractive index and low optical loss. Chalcogenide glass thin films are conventionally prepared by vacuum coating techniques (thermal evaporation or sputtering) or pulsed laser deposition [9,10]. However, less conventional techniques such as spin-coating of glassy films from solution can have certain advantages for realizing large area or thick film deposition while achieving similar optical, physical, and chemical properties of other deposition techniques [11]. Spin-coating approaches have the added advantage that the same solutions can be adopted for other precision dispensing techniques such as mold casting, ink jet or laser direct write [12–14], giving spatial control of the added material. Chern and Lauks first introduced the spin-coating deposition method of preparing chalcogenide films for high resolution photoresists [15,16]. They demonstrated that amorphous films with properties similar to bulk can be deposited from their solutions.

Solvent residue from solution-based deposition can introduce complications in optical properties of the thin films. A review of the literature reveals a range of optical parameters for the same material produced by different studies and different processing methods [17,18]. Heat treatment has a major influence on the amount of organic solvent left in the thin films and therefore on the optical and structural properties of the resulting films. It is important to clarify the relationship between annealing conditions and film properties and this information provides a much needed pathway toward increased stability and optimization of material properties.

In this paper, we examine the influence of annealing conditions on optical properties of spin-coated As$_2$S$_3$ films. Infrared and UV-visible transmission spectra is used to characterize

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the optical properties of films subjected to annealing temperatures ranging from 60 to 180 °C and durations from 1 hour to 20 hours resulting in differing amounts of residual solvent. Results are correlated with density and thermogravimetric analysis, which provide information about the evolution of amine and other components from as-deposited films. Finally, we discuss the effects of the solvent molecules on the glass network by applying the Wemple-DiDomenico (WDD) dispersion model to the measured refractive index data.

2. Experimental

Solutions of As$_2$S$_3$ are prepared by grinding bulk As$_2$S$_3$ pieces into a fine powder and dissolved into n-propylamine solvent at a concentration of 0.8 mol/L. The dissolution is carried out inside a sealed glass container to prevent solvent evaporation. The dissolving process usually takes 7 days and a magnetic stirrer can be used to expedite this process. Exposure of solution to atmospheric moisture is kept to a minimum throughout the preparation procedure since water can lead to precipitation formation [19]. The solution is pipetted onto the substrate, and the substrate is spun at 1000 rpm for 30 seconds. The resulting films are soft-baked immediately after coating under vacuum at 60 °C for 1 hour to remove most of the solvent and then hard-baked at different temperatures ranging from 60 °C up to 180 °C to remove excess solvent and to further densify the glass. Films prepared under these conditions typically have thicknesses around 1 µm and by changing the solution concentration and spin speed, thicknesses from 0.5 to 5 µm can be readily achieved. In this study, the investigated thin films of As$_2$S$_3$ glass are deposited onto either silicon wafers for infrared spectroscopy and density measurement, or onto glass microscope slides for optical spectroscopy. Differential Scanning Calorimeter measurement gives the glass transition temperature $T_g = 185$ °C. For thermogravimetric analysis (TGA), samples are soft-baked at 45 °C for 20 hours and then removed by scraping the solid from glass substrates. TGA is carried out on a Perkin Elmer TGA 7 system. The analysis is performed on 15-20 mg samples in the range 30 to 180 °C at 1 °C/min in a nitrogen-purged atmosphere.

Density measurements are conducted using spin-coated As$_2$S$_3$ thin films on square silicon chips. The silicon wafers are first spin-coated and then cut into 10 × 10 mm square chips to insure similar film thicknesses (± 5%).

The infrared transmission spectra of the films are measured with a Nicolet Fourier transform infrared (FTIR) spectrometer using a cooled mercury cadmium telluride (MCT) detector with a resolution of 4 cm$^{-1}$. Absorption bands associated with the solvent n-propylamine are examined as a function of annealing temperature and duration using this technique.

The UV-VIS transmission spectra are measured using an Ocean Optics HR4000 high-resolution spectrometer. The optical spectra of the films show a periodic variation of the transmission value as a function of wavelength. This effect is caused by the interference between multiple reflections at the two surfaces of the film, and is influenced by both the film’s thickness and its refractive index at that particular wavelength. The optical band gap, $E_g$ is determined from the absorption coefficient values using Tauc’s extrapolation in the strong absorption region [20], i.e., from the relationship $\alpha (h\nu) = K (h\nu - E_g)^{1/2} / h\nu$, where $K$ is a constant, and the optical band gap is defined as the intercept of the plot of $(\alpha h\nu)^{1/2}$ against $h\nu$. Using Swanepoel’s method on the transmission spectra [21,22], the refractive index dispersion for the films are calculated.

The refractive index as a function of wavelength are analyzed on the basis of the Wemple-DiDomenico dispersion model [23,24], which is based on the single-oscillator approach:

$$n = 1 + \frac{E_1 E_i}{E_0 - (h\nu)^2}$$
where \( h \) is Planck’s constant, \( h\nu \) is the photon energy, \( E_o \) is the single-oscillator energy and \( E_d \) is the dispersion energy or oscillator strength. Plotting \( (n^2-1)^{-1} \) against \( (h\nu)^2 \) allows one to determine the oscillator parameters by fitting a straight line to the experimental points. By extrapolating the fitting line towards \( h\nu = 0 \), one can obtain the static refractive index \( n(0) \).

The WDD model also relates the dispersion energy, \( E_d \), to other physical parameters of the material through the following empirical relationship [23,24]:

\[
E_d (\text{eV}) = \beta N_c N_e
\]

(2)

where \( N_c \) is the effective coordination number of the cation nearest-neighbor to the anion, \( Z_a \) is the formal chemical valency of the anion, \( N_e \) is the effective number of valence electrons per anion and \( \beta \) is a two-valued constant with either an ionic or a covalent value (\( \beta_i = 0.26 \pm 0.03 \text{ eV} \) and \( \beta_c = 0.37 \pm 0.04 \text{ eV} \), respectively). For \( \text{As}_2\text{S}_3 \) being studied, it is assumed that \( Z_a = 2, \beta = 0.37 \pm 0.04 \text{ eV} \) and \( N_e = 9.3 \), which is determined by the glass stoichiometry. Based on these assumptions, any difference in \( E_d \) derived by the WDD model will be likely due to the difference in \( N_c \), the arsenic effective coordination number, which indicates the structure of the glass network.

3. Results and discussion

We measure the transmission spectra of the films annealed at different temperatures. In the strong absorption region, the optical band gap can be determined by Tauc's extrapolation [20]. In the weak and medium absorption region, the refractive index dispersion can be calculated using Swanepoel’s method [21,22].

![Fig. 1. Determination of optical band gap \( E^\infty \) for \( \text{As}_2\text{S}_3 \) films spin-coated from \( n \)-propylamine solutions and annealed at different temperatures for 1 hour: (a) Tauc’s extrapolation, the optical band gap is defined as the intercept of the plot of \( (\alpha h\nu)^{1/2} \) against \( h\nu \); (b) \( E^\infty \) as a function of annealing temperature.](image)

The optical band gaps \( E^\infty \) of the films as a function of the annealing temperature are determined through Tauc’s extrapolation as presented in Fig. 1. As expected, the annealing temperature has a significant effect on the optical band gap, with increased temperatures corresponding to a red-shift of the optical band gap. \( E^\infty \) stabilizes at 2.24 eV with annealing above 150 °C. Using Swanepoel’s method on the transmission spectra, the refractive index dispersion for the films are calculated and shown in Fig. 2(a) and the indices at 900 nm are shown in Fig. 2(b) for different annealing conditions. An increase of the annealing...
temperature leads to films with larger refractive indices. This behavior is consistent with the reduced optical band gap, indicating a higher relative permittivity. Furthermore, the refractive index increases with longer annealing duration at the same temperature until saturation. The saturation index is the same for temperatures below approximately 150 °C. Above this temperature, films rapidly reach saturation at higher refractive index approaching the accepted bulk value. These saturated refractive indices between 2.3 and 2.4 agree well with indices reported for As$_2$S$_3$ films deposited using other techniques, such as thermal evaporation (n = 2.2-2.4), PECVD (n = 2.3), and pulsed laser deposition (n = 2.4) [5,17,25].

![Fig. 2](image_url)

**Fig. 2.** (a) The refractive index dispersion for the films spin-coated from $n$-propylamine solutions and treated with different annealing conditions; (b) refractive indices at 900 nm wavelength as a function of annealing temperature and time.

![Fig. 3](image_url)

**Fig. 3.** Infrared transmission spectra of films spin-coated from solutions of As$_2$S$_3$ in $n$-propylamine with different heat treatment: (a) Soft bake at 60 °C for 1 hour, and then thermal anneal at 60, 90, 120, 150 and 180 °C. (b) A close-up view of the spectra emphasizing the bands related to $n$-propylamine residue.

FTIR is used to verify the presence of residual solvent in the films and the effects of film annealing on optical loss in the infrared range. After spinning and soft-baking, the thin films are annealed at different temperatures for duration range from 1 hour to 20 hours in order to evaporate residual $n$-propylamine in the films. The infrared transmission spectra of the
resulting films are shown in Fig. 3. The spectra exhibit peaks between 2290 and 2380 cm\(^{-1}\), which are related to the fluctuation of water and CO\(_2\) levels in the uncontrolled atmosphere of the measurement chamber. The FTIR spectra also show an absorption band in the 2200-3200 cm\(^{-1}\) range, the intensity of which decreases as the annealing temperature and duration increases. This broad absorption band can be assigned to N-H stretch and a narrower but stronger band between 2800 and 3000 cm\(^{-1}\) can be assigned to aliphatic C-H stretches confirming the presence of residual solvent in the film annealed at low temperatures [26]. Annealing at higher temperature or for longer duration leads to an attenuation in these bands, indicating a decrease in the organic solvent content of the film. The films are found to be free of organic content after an annealing at 150 °C in vacuum, as indicated by the disappearance of these bands in the spectra. These films exhibit a nearly uniform transmittance of over 80% across the 2.5-5 μm wavelength range. On the other hand, for annealing temperatures at or below 90 °C, extended duration is needed to remove the remaining solvent.

To understand the physical difference between high temperature (at or above 150 °C) and low temperature annealing, we study the evolution of different constituents from as-deposited films as a function of temperature. Thermogravimetric analysis is carried out in the range 30-180 °C at 1 °C/min in a nitrogen atmosphere, as shown in Fig. 4. Three regimes of weight loss are observed. From 50 to 120 °C, 4.0% weight loss is found as a result of loss of amine. The sample weight remains stable in the range 120-150 °C. Above 150 °C, 2.3% weight loss is caused by H\(_2\)S evolution. According to elemental analysis, the stoichiometry of as-deposited As\(_2\)S\(_3\) is proposed to be As\(_2\)S\(_{3+x}\)(C\(_3\)H\(_7\)NH\(_3\))\(_{2x}\) [26]. After low temperature annealing with removal of occluded amine, a hydrogenated arsenic sulfide As\(_2\)S\(_{3+x}\)H\(_{2x}\) is left behind. Further high temperature annealing above 150 °C leads to loss of H\(_2\)S and results in a glass containing only arsenic and sulfur.

This thermogravimetric analysis helps to explain the annealing behavior shown in Figs. 2 and 3. In the lower temperature regime between 50 °C and 150 °C the excess amine is evaporated from the film resulting in a lower absorption and corresponding increased index of refraction. Saturation in these properties occurs when most of the occluded amine is removed from the film. The evaporation of excess amine results in a glass with hydrogen compensated sulfur dangling bonds remaining in the amorphous network. Such bonds are stable over time but cause a decrease in the index relative to the bulk As\(_2\)S\(_3\). Above 150 °C, H\(_2\)S evolution justifies the increase in steady-state refractive index. This decomposition removes excess hydrogen from the glass resulting in a film with a stoichiometry and properties that are more closely aligned with the bulk material.

Fig. 4. Thermogravimetric analysis of As\(_2\)S\(_3\) spin-coated from n-propylamine solution. Sample pre-baked at 45°C for 20 hours.
Table 1. Density of spin-coated As$_2$S$_3$ films annealed at different annealing conditions after soft-baking

<table>
<thead>
<tr>
<th>Annealing condition</th>
<th>Density (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60 °C for 1 hr</td>
<td>3.0 ± 0.3</td>
</tr>
<tr>
<td>90 °C for 1 hr</td>
<td>3.4 ± 0.3</td>
</tr>
<tr>
<td>90 °C for 2 hr</td>
<td>3.4 ± 0.3</td>
</tr>
<tr>
<td>90 °C for 3 hr</td>
<td>3.4 ± 0.3</td>
</tr>
<tr>
<td>90 °C for 20 hr</td>
<td>3.5 ± 0.3</td>
</tr>
<tr>
<td>150 °C for 1 hr</td>
<td>3.6 ± 0.3</td>
</tr>
<tr>
<td>180 °C for 1 hr</td>
<td>3.8 ± 0.3</td>
</tr>
</tbody>
</table>

Density measurements provide information about the film structure through direct characterization of the film compactness at different temperatures (Table 1). With higher annealing temperature, longer duration, and the consequent removal of solvent, the film density increases from 3.0 to 3.8 g/cm$^3$. This increase in density is associated with film densification and a volume change. We observe a decrease in film thickness of up to 20% after annealing. The density of the spin-coated films annealed at 150 °C for 1 hour or at 90 °C for 20 hours agrees with the reported value for bulk As$_2$S$_3$ glass within the error of the measurement [27].

According to Lorentz-Lorenz relation, the refractive index $n$ is related to the density of a dielectric through Eq. (3), where the constant $K$ depends on the polarizability of the molecules constituting the dielectric. Therefore, any change in the density will lead to a change in the refractive index, as described by Eq. (4).

An increase of about 27% in density in annealed films would account for an increase of approximately 15% in refractive index, according to Eq. (4). This prediction agrees with the refractive indices at long wavelength calculated from UV-visible transmission spectra, as shown in Fig. 2.

To further probe the structure of the spin coated glass network, we apply the Wemple-DiDomenico (WDD) model to refractive index dispersion calculated by Swanepoel’s method. According to Eq. (1), we plot $(n^2-1)^{-1}$ against $(h\nu)^2$ and make least-square linear fits to the experimental points, as shown in Fig. 5. The intercept on the $(n^2-1)^{-1}$ axis gives the static refractive index $n(0)$ while $E_o$ and $E_d$ could be derived from the intercept on the $(h\nu)^2$ axis and the slope of the linear line. Table 2 lists the values of the dispersion parameters for the films with different annealing conditions, as well as the values for $n(0)$. As shown in Table 2, the static refractive index follows the same trend as the refractive index measured at 900 nm and increases with higher temperature and longer duration of annealing.
Fig. 5. Plot of refractive index factor $(n^2-1)/n$ vs. $(\hbar\nu)^2$ for As$_2$S$_3$ films prepared by spin-coating and different heat treatment. As expected, the experimental dispersion of the refractive index departs from the linear behavior given by Eq. (1) for photon energies outside the transparent region [23,24].

Table 2. Values of static refractive indices, $n(0)$, WDD dispersion parameters, $E_o$ and $E_d$, and As effective coordination number, $N_c$, for As$_2$S$_3$ films prepared by spin-coating and different heat treatment

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Time (hr)</th>
<th>$n(0)$ (± 0.01)</th>
<th>$E_o$ (eV) (± 0.05)</th>
<th>$E_d$ (eV) (± 0.03)</th>
<th>$N_c$ (± 0.3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>1</td>
<td>2.02</td>
<td>5.16</td>
<td>15.89</td>
<td>2.3</td>
</tr>
<tr>
<td>90</td>
<td>1</td>
<td>2.11</td>
<td>4.95</td>
<td>17.17</td>
<td>2.5</td>
</tr>
<tr>
<td>90</td>
<td>2</td>
<td>2.13</td>
<td>4.86</td>
<td>17.14</td>
<td>2.5</td>
</tr>
<tr>
<td>90</td>
<td>3</td>
<td>2.18</td>
<td>4.96</td>
<td>18.48</td>
<td>2.7</td>
</tr>
<tr>
<td>90</td>
<td>20</td>
<td>2.21</td>
<td>4.77</td>
<td>18.58</td>
<td>2.7</td>
</tr>
<tr>
<td>120</td>
<td>1</td>
<td>2.20</td>
<td>4.75</td>
<td>18.20</td>
<td>2.6</td>
</tr>
<tr>
<td>120</td>
<td>2</td>
<td>2.24</td>
<td>4.69</td>
<td>18.75</td>
<td>2.7</td>
</tr>
<tr>
<td>120</td>
<td>3</td>
<td>2.23</td>
<td>4.74</td>
<td>18.73</td>
<td>2.7</td>
</tr>
<tr>
<td>120</td>
<td>20</td>
<td>2.23</td>
<td>4.74</td>
<td>18.73</td>
<td>2.7</td>
</tr>
<tr>
<td>150</td>
<td>1</td>
<td>2.24</td>
<td>4.78</td>
<td>19.21</td>
<td>2.8</td>
</tr>
<tr>
<td>150</td>
<td>20</td>
<td>2.24</td>
<td>4.78</td>
<td>19.21</td>
<td>2.8</td>
</tr>
<tr>
<td>180</td>
<td>1</td>
<td>2.32</td>
<td>4.78</td>
<td>20.87</td>
<td>3.0</td>
</tr>
</tbody>
</table>

According to Eq. (2), any difference in $E_d$ will be likely due to the difference in the As effective coordination number, $N_c$, since we assume that $\beta$, $Z_a$, and $N_e$ are constant. As reported [28], the glass network of As$_2$S$_3$ consists of locally two-dimensional structural layers, formed by AsS$_3$ pyramidal units linked through a common two-fold coordinated S, and interacting with each other by weak intermolecular bonds. Therefore, $N_c > 3$ can be expected as a result of those As atoms acting as bonding points between layers. The As effective coordination number $N_c$ for bulk As$_2$S$_3$ glass is reported to be 3.2 [24]. However, as shown in Table 2, the calculated $N_c$ for spin-coated As$_2$S$_3$ films is lower than 3.0, depending on the annealing condition. $N_c$ increases with higher temperature and longer duration of annealing and ranges from 2.3 to 3.0. This low $N_c$ is a result of solvent and hydrogen remaining in the material, and different amorphous structure in spin-coated films as compared to melted, bulk glass. Chern et al. [29] showed that solvent molecules are linked to S atoms through the –NH$_2$ amine radical. The solvent molecules in the glass matrix break the continuous random network model expected for these films and contribute to increase the structural randomness in the spin-coated films and fill in the voids around the AsS$_3$ pyramidal units. There is a weaker interaction between structural layers forming the amorphous network in the spin-coated films than in bulk glass, causing the lower $N_c$ observed. Above 150 °C the solvent is fully removed.
and the change in coordination is associated with the removal of hydrogen from the glass network resulting in a greater interaction between structural units.

4. Conclusions

In this paper, we examine the influence of annealing conditions on optical properties of spin-coated As$_2$S$_3$ thin films, by analyzing refractive index dispersion, optical band gap and absorption in infrared. Optical parameters are closely related to the amount of solvent residue, film density and glass structural network. For films annealed in the low temperature regime (<150 °C) the evolution of excess solvent enables one to select any desired index with the range of $n = 2.1 - 2.3$ by controlling the duration of the anneal. Above this temperature regime, there is a structural change in the amorphous material associated with the removal of hydrogen from the glass network leading to a film with a higher index ($n = 2.3 - 2.4$) that is comparable to bulk As$_2$S$_3$. Armed with a better understanding of the evolution of optical properties in these materials and how to control them, spin-coatable and solution processed chalcogenides can be used where reliable and stable properties are required. The additional processing flexibility offered by these deposition methods open the door to many new applications in optics and photonics where traditional processing is either undesirable or not possible.

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