

Annealing induced phase transformations in amorphous As_2S_3 films

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Amorphous arsenic sulphide (As_2S_3) films prepared by ultrafast pulsed laser deposition have been vacuum annealed at a range of different temperatures. Measurements of the glass transition temperature indicate that a crystallization process initiates at annealing temperatures around 170 °C. In combination with Raman scattering analysis, we conclude that phase separation is intrinsic for our as-deposited films. During annealing two sorts of phase transformation are identified: one between different amorphous polymorphs, and another from the amorphous to a crystalline state. We point out a correlation between these two types of transformation and two characteristic time scales identified from measurements of the relaxation of the refractive index, and explain the Arrhenius and non-Arrhenius behaviors leading to the observed temporal characteristics. © 2006 American Institute of Physics. [DOI: 10.1063/1.2353787]

I. INTRODUCTION

Chalcogenide glasses are promising candidates for integrated nonlinear optical components because they offer low switching energies, ultrafast broadband optical response time, and low optical losses.^{1,2} Although films of these materials have been deposited using various methods to create planar waveguides, significant differences have been found to exist between the properties of the bulk glass and as-deposited films, which, for example, result in the films being highly photosensitive—a possible drawback for application in optoelectronics. Furthermore, while the stoichiometry of the film may differ insignificantly from the bulk glass, parameters such as the refractive index (RI) can be markedly different. For example, our experiments show that while bulk As_2S_3 has a refractive index of 2.43 at 1.55 μm , as-grown films produced by pulsed laser deposition (PLD) have values of typically 2.37–2.39 (n_{TE}) depending on deposition conditions, while for thermally evaporated films the index is 2.29–2.32 (n_{TE}). Thus, as-deposited films are in a significantly different physical state from the bulk glass, most likely because they are created in nonequilibrium conditions. The challenge is, therefore, to release the excess internal energy stored in films deposited in nonequilibrium conditions and relax them back to the thermal equilibrium state. The physical properties of the film such as its refractive index should be sensitive to the degree of relaxation towards the bulk glass structure and can be used to monitor changes in the film.³

In the experiments reported here, we have studied the properties of As_2S_3 films produced by PLD. PLD is a useful approach for depositing multicomponent materials because the elemental composition of the target is accurately transferred to the film and hence the stoichiometry of the material is preserved. Deposition onto substrates held at room temperature, which is easily achieved using PLD because of the

absence of radiant sources in the deposition chamber, also generally favors the production of amorphous films. The major drawback of the conventional PLD method that employs low repetition rate, high-energy, nanosecond ultraviolet excimer laser pulses for ablation is the presence of droplets in the plume due to vapor condensation and particulates ejected from the target.⁴ These contaminate the film and cause high propagation losses in optical waveguides. We have shown that a modified approach to PLD which uses high-repetition-rate picosecond duration laser pulses for ablation avoids this problem and allows the deposition of low loss waveguide films in As_2S_3 chalcogenide glass.⁵ The resulting films have been found to be highly photosensitive, have very high surface quality, and have a refractive index closer to that of bulk material when compared with thermally evaporated films. In addition, the thickness uniformity of the films produced by ultrafast PLD is better than $\pm 0.5\%$ over a 100 mm wafer and superior to other deposition methods because the plume undergoes nearly three-dimensional expansion due to the use of a very small focused spot combined with the use of a large scanned area on the target surface. Waveguide losses as low as 0.2 dB/cm in fabricated waveguides have been measured at 1550 nm in these laser deposited films.⁶

Thermal annealing can generally be used to accelerate the relaxation of a film into its equilibrium state since the room temperature relaxation times for nonannealed As_2S_3 film have been reported to be of the order of one year.³ When thermally evaporated As_2S_3 films were annealed near their glass transition temperature T_g , polymerization of the structure through the switching of homopolar bonds to heteropolar bonds was observed to occur.⁷ Although it is well known that the physical properties of chalcogenide film are very sensitive to the preparation conditions and the film history,^{8,9} systematic experiments concerning the effect of thermal annealing on the physical properties of As_2S_3 film prepared by PLD have not been reported.

It is known that $\text{As}_x\text{S}_{100-x}$ bulk glass is intrinsically phase separated into small As-rich (As_4S_4) and large S-rich

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clusters for $x > 38$,^{10,11} and displays a global maximum in T_g near $x=40$. However, a similar investigation has not been carried out for films because of the difficulty in measuring T_g of such films. In addition, high annealing temperatures could induce crystallization, which can deteriorate the physical properties of the materials. For example, the inhomogeneities due to crystallization during clad fiber fabrication were found to increase the transmission loss of the fiber by two orders of magnitude.¹² In order to resolve these problems, and to investigate annealing as a method of achieving As_2S_3 glass films with stable physical properties similar to its bulk counterpart, a study on annealing induced change in films is necessary.

In this paper we investigate vacuum annealing of high quality As_2S_3 films prepared by PLD. We measured the glass transition temperature T_g and Raman spectra of the annealed samples. Two sorts of phase transformation were found during the annealing process. One between different amorphous polymorphs, and another is a transformation from an amorphous state into a crystalline state. A correlation between these two kinds of transformations and two different time scales which characterize the relaxation of the RI is also discussed.

II. EXPERIMENTS

Chemically stoichiometric As_2S_3 bulk glass from Amorphous Material Co. was used as the ablation target. High quality As_2S_3 films were deposited by the ultrafast laser ablation method. A detailed description about the laser ablation system and deposition conditions can be found in our previous work.⁵ In order to generate enough material for a differential scanning calorimeter (DSC) to be able to detect phase transformations, a 50 μm thick film was deposited on an aluminum plate before pieces were mechanically removed and sealed into several aluminum boats. The boats were annealed at different temperatures for 15 h, then the T_g measured using DSC at a temperature ramp rate of 10 K/min. A 2.5 μm thick sample was also deposited onto a silicon wafer under the same deposition conditions, cut into smaller pieces, and then annealed in a Heraeus Vacuthem oven at around 100 mbars. Raman scattering spectra were recorded using a quasibackscattering geometry and a 782 nm excitation source. No differences were detectable in the Raman spectra from films deposited on silicon and Al confirming that the substrate had a negligible effect on the structure of our films. An SCI FilmTek 4000 wafer mapper measuring over the wavelength range from 450 to 1650 nm was used to *ex situ* evaluate parameters such as film thickness, refractive index, band gap, etc., based on a least squares fit of the reflection spectra at normal and 70° incidence using a single oscillator Tauc-Lorentz model to represent the refractive index dispersion of the As_2S_3 film. Scanning electron microscopy equipped with energy dispersive x-ray spectrometry (EDX) was used to check the chemical composition of all the samples. The atomic ratio of As in as-grown and annealed films was at $x=40.9\pm 0.2$ for $\text{As}_x\text{S}_{100-x}$.

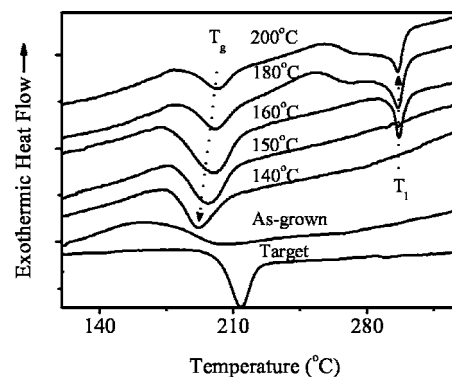


FIG. 1. Glass transition temperature T_g of target, as-grown film, and films annealed at different temperatures for 15 h. Liquidus temperature T_l can be found in some DSC curves as marked by the arrow. The curves are upshifted for clarification.

III. RESULTS AND DISCUSSION

Figure 1 shows data from DSC that allows the value of T_g for the target, the as-grown film, and films annealed at different temperatures. The position of the dip in the DSC scans around 200 °C is defined as T_g . It can be seen that the target has a narrow glass transition at 213 °C, while the as-grown film has a broad glass transition range starting at around 158 °C and reaching a minimum at around 204 °C. This broad feature suggests that the structure of the as-grown film is inhomogeneous with a distribution of different cluster sizes, bond states, and possible compositions.¹³ After annealing at several temperatures for 15 h, the transition becomes narrow again. The T_g increases with increasing T_a , and then saturates for T_a more than 180 °C. However, all values of T_g for the annealed films were less than that of the target.

Moreover, when T_a was increased to 160 °C, a sharp transition appeared around 296 °C. We cannot definitively assign this transition to a particular form of As-S compound on the basis of the techniques available to us, but there are two possibilities. Firstly, and perhaps most likely, is that orpiment (crystalline As_2S_3) has been formed during annealing, since its melting temperature was reported to be 296 °C in Ref. 14. Unfortunately, Refs. 15 and 16 suggest a higher melting temperature at 310 °C and this places some doubt on this interpretation. Alternatively, the melting point of As_2S_5 is quoted as 300 °C (Ref. 17) though we have no particular information on a reaction route that would lead to the formation of a substantial fraction of As_2S_5 in the films. Interestingly, it has been reported that in bulk As_2S_3 glass, crystallization does not occur even after prolonged storage at or near T_g .¹⁸

As shown in the top two curves of Fig. 1, further increasing the annealing temperature up to 180 °C induces a broad shoulder centered at 270 °C. This is quite close to the melting point of α -realgar As_4S_4 at 267 °C,¹⁴ and consequently, we conclude that there is crystalline As_4S_4 (α -realgar) phase in high temperature annealed samples. The α -realgar could have been crystallized from polymerization of arsenic clusters with As_2S_3 units or formed from the reverse reaction of pararealgar known to occur at temperatures above 160 °C. One may argue that these two high temperature endothermic peaks represent

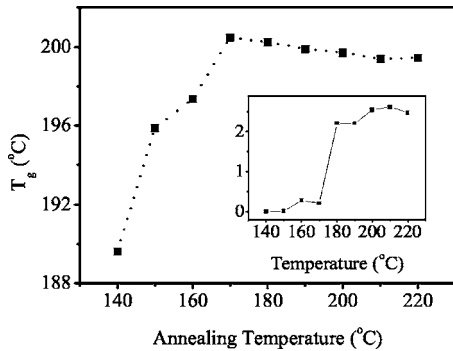


FIG. 2. T_g as a function of T_a . The inset shows the ratio of the integrated area of crystal melting transition around 295 °C to that due to the glass transition as a function of T_a .

glass phase transitions, for example, an As-deficient phase has a liquidus temperature T_l close to 300 °C. However, our near chemically stoichiometric films were sealed in Al boats for DSC measurements and the formation of As clusters would be necessary if such an As-deficient phase was present in order to maintain the chemical stoichiometry. Since we did not observe any endothermic peaks corresponding to glass transition of As clusters, we believe the contribution of the melting state of any As-deficient phase to the endothermic peaks is small, if not negligible.

The change of T_g as a function of the T_a for the films is shown in Fig. 2, from where it is evident that the increase of T_a up to 170 °C will lead to the increase of T_g . However, T_g becomes saturated or slightly decreases with any further increase of T_a . The trends in the evolution of T_g is remarkably similar to the chemical composition dependence of T_g in As_xS_{100-x} and As_xSe_{100-x} bulk glasses, where there is a phase separation region around $x=40$.^{10,11,19} The chemical composition of our as-grown and annealed samples is located in this region. However, our EDX measurements do not show any change in the chemical composition that correlates with T_a . The physical origin of the similarity is unclear, but may correlate with structural change between different polymorphs.

We integrated the dips in the DSC data around 200 and 296 °C and plot the ratio of their areas against T_a in the inset in Fig. 2. Although we cannot determine exactly what fraction of the material transfers into the crystalline states by this approach, a sharp increase in the crystallized fraction is clearly evident, suggesting that a substantial amount of crystalline material had been formed at 170 °C. A trace of the crystalline phase was also observed at $T_a=150$ °C, evident from the small fluctuation in the DSC data around 290 °C.

Typical Raman scattering spectra are shown in Fig. 3. These spectra were obtained using 0.2 mW pump power at 780 nm with a resolution of 1 cm^{-1} . A weak feature at 188 cm^{-1} and another broad and strong feature at 342 cm^{-1} dominate the Raman spectrum of the target. For the films, some separated or additional peaks appear. On the basis of the previous assignments,^{9-11,20} the peaks at 188, 211, 220, and 360 cm^{-1} are ascribed to $\alpha(\beta)$ - As_4S_4 , and 303 and 342 cm^{-1} to the orpiment phase As_2S_3 . The appearance of the peaks corresponding to As_4S_4 indicates the existence of phase separation in all the films. The absence of S-S vibra-

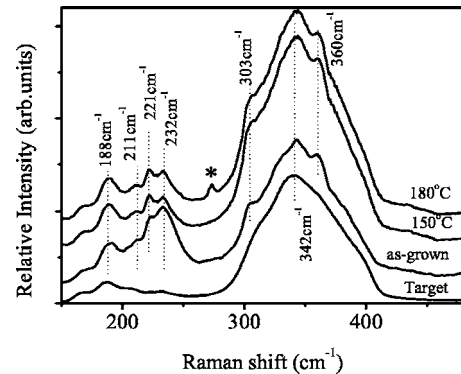


FIG. 3. Raman scattering spectra of the target, as-grown film, and the films annealed at 150 and 180 °C for 15 h, respectively. The curves are displaced vertically for clarification.

tions at 494 cm^{-1} is puzzling given that S-S bonds are necessary in order to form As_4S_4 and maintain the chemical stoichiometry. Indeed, ¹²⁹I Mossbauer spectroscopy measurement has provided evidence of the existence of an internal surface dressing the S-rich cluster.²¹ The weak vibration at 494 cm^{-1} in thermally evaporated films was ascribed to S-S bonds,²² which, however, cannot be observed in our experiments. We suppose that this weak vibration may be smeared out by the strong background from the silicon 520 cm^{-1} Raman peaks in our samples. Another available explanation is that S reacts with silicon wafer forming Si-S bond, whose signature is hidden in the broad band between 300 and 400 cm^{-1} although this seems unlikely anywhere but the silicon surface.

An interesting change in intensity happens at 232 cm^{-1} , which is assigned to As-As vibration in pararealgar, As_4S_4 , or to As clusters.^{20,23} A strong vibration at this position is found for as-grown films, which then becomes weak after vacuum annealing. The decrease of the intensity at 232 cm^{-1} could indicate a transformation of the pararealgar phase into α -realgar As_4S_4 upon annealing as deduced above from the DSC data. Among the different polymorphs of α , β , and pararealgar- As_4S_4 , pararealgar is the most voluminous.²⁴ As a result, such a transformation should be accompanied by a decrease in the thickness of the film. Indeed, in all our experiments we have observed a decrease in film thickness upon annealing, as shown in the right axis of Fig. 4, although this could also result from pure bond angle relaxation of the

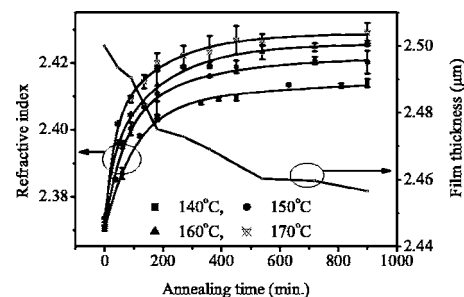


FIG. 4. The left axis is the refractive index of As_2S_3 film at 1.55 μm as a function of annealing time. The squares and their error bars are experimental results, and the dotted lines are fitting results using an exponential growth function. The right axis shows the typical thickness change for a film annealed at 160 °C.

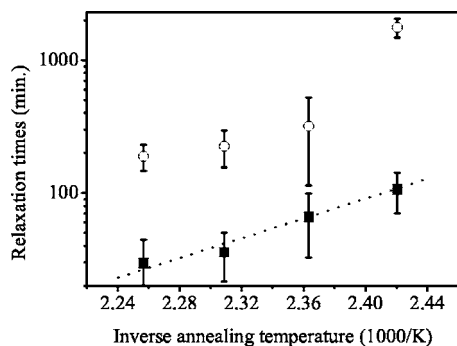


FIG. 5. The two kinds of relaxation times and their error bars vs inverse T_a . The solid squares correspond to a group of short times, and the open circles to the second group at long times.

amorphous structures. Alternatively, the data are also consistent with the Kolobov-Adriaenssens conclusion⁴ that heating could switch homopolar As-As bonds to heteropolar S-As-S bonds. If this resulted in the formation of crystalline α -realgar, then this explanation is also consistent with the DSC data.

The peak at 273 cm^{-1} found in high temperature annealed films marked by the star corresponds to the vibration in crystalline As_4S_4 or As-rich glass.¹⁰ Since EDX measurements do not show any observable change of the chemical composition, and given the DSC data, then this peak most likely comes from the formation of As_4S_4 microcrystals.

For the RI measurements (Fig. 4), we annealed the films on Si substrates below $180\text{ }^\circ\text{C}$. The RI of the film was found to increase with increasing annealing time. At $140\text{ }^\circ\text{C}$, the RI reaches 2.41 after 500 min annealing, and this time scale can be reduced to 300 min at $170\text{ }^\circ\text{C}$. Several different functions were tried to fit these experimental data; finally, the best fitting was achieved with the double exponential function. Two time scales from the double exponential function imply that two different relaxation processes occur during annealing. The Arrhenius plots in Fig. 5 reveal that a group of short relaxation time processes follow a linear relation, from which the activation energy was estimated to be 0.32 eV. Another group of long relaxation time processes show strong non-Arrhenius behavior at $150\text{ }^\circ\text{C}$. In combination with Figs. 1–3 we argue that the short time scale corresponds to structural relaxation within the amorphous state itself and the long time scale to the transformation from the amorphous states into the crystalline state. This is consistent with Angell's paper,²⁵ where he pointed out that the relaxation time of the amorphous-crystal transformation is much longer than that of amorphous-amorphous transformation. When Arrhenius behavior in the physical properties of a glass such as As_2S_3 exists, the appearance of crystalline As_2S_3 creates nucleation centers in the matrix which disrupt the As_2S_3 glass network making it more fragile and this results in the appearance of the non-Arrhenius behavior.^{10,11,26}

IV. CONCLUSIONS

In summary, we have vacuum annealed amorphous As_2S_3 films deposited by ultrafast laser ablation at different

temperatures. DSC measurements indicate that T_g increases with increasing T_a up to $170\text{ }^\circ\text{C}$, and then a crystallization process appears. Raman scattering analysis suggests that our films are intrinsically phase separated, and two sorts of phase transformation occur during the annealing process. One is between different amorphous polymorphs, and another is transformation of the amorphous state into a crystalline state. These two sorts of transformations correlate with two different time behaviors identified via studies of the relaxation of the refractive index. Finally, one should note that from these studies, it would appear that thermal annealing of As_2S_3 films deposited by pulsed laser deposition does not necessarily relax the films into a state characteristic of the bulk glass and hence is unlikely to lead to a material stable enough for optoelectronic applications.

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