

Physical Aging of Arsenic Trisulfide Thick Films and Bulk Materials

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Differential scanning calorimetry (DSC) measurements were performed at different heating rates under nonisothermal conditions to probe the glass transition kinetics of As₂S₃ bulk glass and thick films. We found that, for films, the glass transition temperature (T_g) increases with increasing annealing temperature, and sharp crystalline-like melting endothermic peaks appear in samples annealed at 160°C. Such sharp endothermic peaks could also be found for samples annealed at 140°C for 300 h, indicating a very slow crystallization process. The activation energy for the molecular motions and rearrangements around T_g could be estimated as 2.12 eV for films and 2.3 eV for the bulk, respectively.

I. Introduction

THE As₂S₃ chalcogenide glasses offer large third-order optical nonlinearities, ultra-fast broad-band optical response time, and low optical losses, and thus are promising for many technological applications.^{1,2} However, As₂S₃ films are well known to exhibit physical properties that are different from their bulk counterparts. For instance, the as-grown films prepared by laser ablation or thermal evaporation always include molecular clusters and cross-linked bonds, which degrade the network of the glass. Moreover, different phases of these clusters may coexist in the films.^{3–5} Although thermal annealing can accelerate the structural relaxation of amorphous films, complete transformation from homopolar to heteropolar bonding cannot be achieved. As a result, there are always structural differences between the film and the bulk material.⁶

On the other hand, as the glass state is characterized by the lack of thermodynamic equilibrium, all the physical properties of the glasses are time dependent, and this behavior is generally referred to as a physical aging phenomenon.^{7,8} To avoid the changes in physical properties caused by physical aging, a material with completely saturated aging should be used in chalcogenide-based devices. However, natural physical aging requires years at low temperatures; therefore, γ -ray irradiation, photo-exposure, and thermal annealing are usually applied to accelerate the relaxation process.^{8,9}

We are particularly interested in obtaining high-quality films with the same physical properties as bulk material by thermal annealing. Our previous investigation has shown that thermal annealing is an effective way to increase the refractive index of the film close to that of the bulk material.⁵ However, the different glass transition kinetics, which can be investigated in terms of glass transition temperature and thermal relaxation activation energy,⁷ are not yet resolved. The present paper will

focus on this point using differential scanning calorimetry (DSC). To identify the physical parameters that are uniquely related to the aging process, one must freeze the phase transformation to a large degree because the phase transformation and physical aging processes may occur simultaneously upon thermal annealing. On the basis of our previous annealing results, the characteristics for phase transformation are 100 min at 150°C.⁵ We therefore expected that the phase transformation process is almost complete after 15 h of annealing, and thus the effect of phase transformations during the DSC measurements will be negligible. We, therefore, comparably studied the physical aging of the bulk and annealed films, and derived their respective activation energy and different crystallization behaviors.

II. Experimental Procedure

A high-quality As₂S₃ thick film was deposited on an aluminum plate by the ultra-fast laser ablation method, using chemically stoichiometric As₂S₃ bulk glass from Amorphous Material Co. (Garland, TX) as the ablation target.¹⁰ The amorphous state of the bulk and films was checked by X-ray diffraction with Cobalt K α radiation ($\lambda = 0.178897$ nm). The homogeneity and composition of the samples were verified through scanning electron microscopy in a JEOL 6400 (JEOL, Tokyo, Japan) equipped with energy-dispersive X-ray spectrometry (EDX). The thick film was mechanically removed and weighed before being sealed into several aluminum boats. The boats were annealed at several different temperatures, and then the calorimetric measurements were performed in a Shimadzu DSC 50 (Kyoto, Japan) at a temperature ramp rate of 10 K/min except when otherwise stated. The atomic ratio of As in as-grown and annealed films was at $x = 40.9 \pm 0.2$ for As_{*x*}S_{100–*x*}. The same annealing treatments were applied to the bulk glasses stored for 18 months, and the results of DSC measurements were used as references.

III. Results and Discussion

Figure 1 shows the DSC curves of bulk glass, as-grown, and annealed films at several different temperatures. Defining the middle point of the endothermic peak as the glass transition temperature, the bulk glass has a sharp glass transition at 211°C, while the as-grown film has a broad transition. In both cases, we did not find exothermic crystallization and endothermic crystalline melting peaks, suggesting that no crystalline composition exists in the initial materials and thus the crystallization process of As₂S₃ upon heating is very slow. After 15 h annealing, the DSC curve of the film sample annealed at 140°C shows a well-defined glass transition peak at 185°C, which is 25°C lower than the bulk material. As the annealing temperature was increased, T_g also increased, reaching 200°C for 180°C annealing—still significantly below that of the bulk glass. Moreover, a signal representing an endothermic melting crystalline peak appears in the sample annealed above 160°C, indicating that a substantial amount of crystalline phase had formed.

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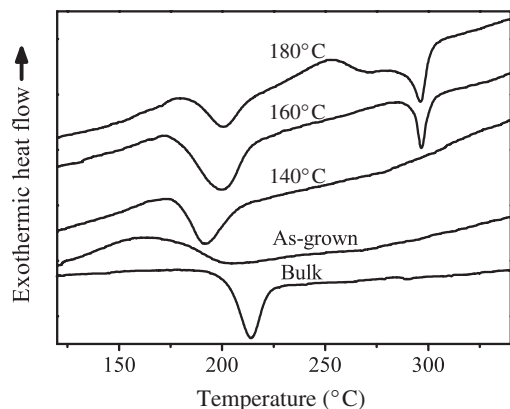


Fig. 1. Differential scanning calorimetry curves of the *bulk*, as-grown, and annealed films at several different temperatures for 15 h.

It is well known that T_g depends on the connectivity and consequently on the rigidity of the vitreous network, and the width of the glass transition is related to the width of the time relaxation distribution.^{7,8} The broad distribution of the glass transition is consistent with the existence of different clusters in the as-grown films. These clusters may melt and rebound to each other upon thermal annealing, leading to an increasing T_g for the film.

To determine whether the crystalline phase can be formed during low-temperature annealing, we annealed the samples at 140°C with different annealing times. The DSC results are shown in Fig. 2. With increasing annealing time, T_g clearly shifts to a higher temperature, approaching its bulk counterpart. Moreover, an endothermic crystalline melting peak appears in the sample annealed for 200 h, and this peak becomes stronger with further prolonged annealing, suggesting that the crystalline phase could be formed even at a lower annealing temperature at a very slow rate.

We also noted a characteristic low-temperature shoulder appearing before the sharp crystalline melting peak in the DSC trace of the 180°C annealed sample in Fig. 1, and before the stronger endothermic relaxation peak in the DSC traces of the 200- and 300-h annealed samples in Fig. 2. Similar double-peak relaxation effects were observed recently in both 10-year natural physical aging Ge-Se and γ -ray-irradiated As-Se glasses.^{7,8} This was ascribed to microphase separation of the samples under various conditions. From Figs. 1 and 2, we infer that the optimal thermal annealing conditions should be an annealing temperature below 160°C and time below 100 h. Even then, we still could not obtain the films with the same T_g as the bulk materials. This is consistent with Tanaka's results; namely, thermal annealing cannot induce complete transformations from homopolar to

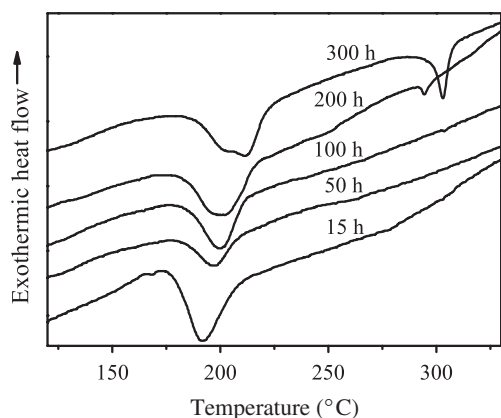


Fig. 2. Differential scanning calorimetry curves of the films annealed at 140°C for different times.

heteropolar bonds, and there are gross structural differences between bulk glass and the annealed film.⁶

On the basis of our previous investigation, the structural relaxation time for the amorphous-amorphous transformation at 140°C is typically 100 min⁵; therefore, we expect that most of the phase transformation would be completed by annealing for 15 h. By changing the heating rates during DSC measurements for samples annealed at 140°C for 15 h, we can probe that part of the physical aging of the films that only involves molecular motions or bond rearrangement.^{7,8} The results follow the well-known dependence of glass transition parameters on heating rate, e.g. T_g , and the thermal enthalpy increase with increasing heating rate.

Ozawa developed a simplified version of the Kissinger crystallization kinetics theory, which can be used for DSC measurements. The heating rate and glass transition peak temperature exhibit the relationship $d(\ln(\beta))/d(1/T_g) = -E/R$ where β , E , and R are the heating rate, the activation energy, and the universal gas constant, respectively.¹¹⁻¹⁴ According to this equation, the $\ln\beta$ versus $1/T_g$ plot should be a straight line and the activation energy involved in the molecular motions and rearrangements around T_g can be extracted from the slope of this plot.

Some factors, such as the thermal history of the sample and the heating/cooling scan used in DSC experiments, could lead to a considerable difference in glass transition activation energy.¹⁵ However, in this paper, emphasis is on the relative difference of physical aging between the film and the bulk material when the same thermal annealing procedure is applied. An understanding of this difference is important to achieve high-quality films for photonic applications. The plots of $\ln\beta$ versus $1/T_g$ are shown in Fig. 3 for As_2S_3 bulk material and films annealed at 140°C for 15 h. The activation energy estimated from this relationship is 2.12 eV for the film and 2.3 eV for the bulk material. These are comparable to dissociation energies of As-S (2.0 eV) and S-S (2.2 eV) covalent bonds prevalent in the glass-like network of this material.¹⁶

To understand the crystallization behavior of the film and bulk, we reheated the samples to 240°C, which is higher than T_g , and annealed them for 2 h in order to form a large number of crystalline nuclei. These reheated samples were subjected to the same calorimetric scans as before. For the reheated bulk As_2S_3 glass, a linear relationship between the heating rate and T_g still appeared with an activation energy of 2.52 eV, but T_g slightly shifted to a low temperature as shown in Fig. 3, indicating a slight aging for an 18-month stored bulk glass. However, no exothermic crystallization and endothermic crystalline melting peaks were observed in the corresponding DSC curves, indicating that the bulk material is strongly resistant to crystallization. On the other hand, the endothermic crystalline melting peak was clearly visible for the reheated As_2S_3 film, indicating that a

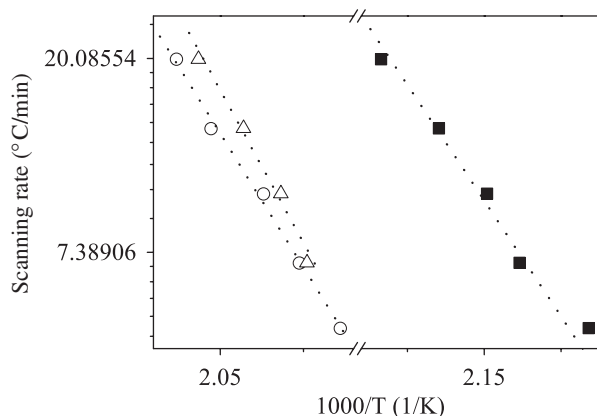


Fig. 3. Plots of T_g versus $\ln\beta$ for As_2S_3 bulk (O) and films annealing at 140°C for 15 h (■), as well as the reheating bulk material at 240°C for 2 h (Δ). The heating rates of β are 5, 7, 10, 14, and 20 K/min, respectively.

number of nuclei had formed during the annealing process. Moreover, when we changed the heating rate for the DSC measurements, the linear relationship of $\ln\beta$ versus $1/T_g$ was completely absent for the reheated films. These results suggest that the studies of the deterioration of device using As_2S_3 films must consider the film's unique crystallization behavior, although at present the physical mechanisms leading to crystallization is not understood.

IV. Summary

We have compared the different glass transition kinetics of As_2S_3 thick films and bulk material by DSC measurements. We found that T_g of the film increases with increasing annealing temperature, and sharp crystalline melting endothermic peaks appear in the DSC curves of the films annealed above $160^\circ C$ as well as at lower temperatures for 300 h, indicating that the crystallization process is very slow during thermal annealing. The activation energy of viscous flow involved in the molecular motions and rearrangements around T_g could be estimated as 2.12 eV for films and 2.3 eV for the bulk, respectively. Moreover, the importance of the different crystallization behaviors between the film and bulk must be emphasized when seeking to achieve high-quality stable films for device application.

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