

Photo-induced structural changes in obliquely deposited arsenic-based amorphous chalcogenides: a model for photostructural changes

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ABSTRACT

The effect of bandgap illumination and annealing below the glass transition temperature on the thickness and the optical bandgap of As-based (As_2Se_3 and As_2S_3), obliquely deposited chalcogenide thin films has been studied. It is observed that illumination increases the thickness and decreases the bandgap. By annealing the samples, before and/or after illumination, the trends of changes in thickness and bandgap are reversed. These changes have been explained on the basis of ordering of the structure by annealing, and of repulsion and slip motion by illumination, the latter processes being due to the negative charging of layers by electron accumulation in conduction-band tails.

§1. INTRODUCTION

Illumination of amorphous chalcogenides with light of energy equal to the bandgap of the material causes various changes such as structural transformations (Shimakawa *et al.* 1995). Some of these changes are reversible on annealing near the glass transition temperature. It was first reported nearly 25 years ago that photoillumination causes reversible photodarkening (PD) in amorphous As_2Se_3 and As_2S_3 evaporated films (de Neufville *et al.* 1973–1974) but the process of PD in amorphous chalcogenides is still baffling researchers (Shimakawa *et al.* 1995). Also, by illuminating with light of energy below that of the bandgap (He–Ne laser), As_2S_3 films show reversible photostructural changes (Hisakuni and Ke. Tanaka 1994). It is also reported that illumination with bandgap light causes photobleaching (PB) in as-evaporated Ge-containing chalcogenide films (Street *et al.* 1987).

It is believed that a change in the interaction of chalcogen lone-pair (LP) electrons is responsible for PD. The increase in LP–LP interactions yields a broadening of the valence band, causing a reduction in the bandgap (PD). The models, which have been put forward in support of the above mechanism, can be placed into the following categories. Prolonged illumination causes a change in the atomic (chalcogen) positions (model 1) (Tanaka 1980, Ke. Tanaka 1990), bond breaking and/or bond alternations between the atoms (model 2) (Elliott 1986, Kolobov *et al.* 1997) and a repulsion and slip motion of structural layers due to negative charging (model

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3) (Shimakawa *et al.* 1998). In models 1 and 2, only *particular atoms* have been considered to be excited by photo-irradiation, that is the atomic relaxation inducing PD, or volume expansion (VE) occurs around particular chalcogen atoms. It is, however, difficult to understand why only particular atoms should be excited in a solid. The top of the valence band is formed by LP electrons. It is expected that 'macroscopic or mesoscopic' interactions are dominant for both VE and PD to occur, because all the LP electrons have an equal probability of being excited. Therefore, electrons or holes in the extended states (or in localized band tail states) might be regarded as responsible for VE or PD.

Model 3 recently proposed by Shimakawa *et al.* (1998) assumes that illumination charges the layers negatively, resulting in a Coulomb repulsion between them. This Coulomb repulsion results in an expansion and slip motion. The model can explain the occurrence of VE and PD in a satisfactory manner.

All measurements and the various models have been proposed either for thin films prepared with their substrates perpendicular to the line of evaporation (normally deposited films) or for bulk glasses. For thin films the photo-induced changes can be greatly enhanced by varying the deposition conditions, mainly the angle of deposition. Obliquely deposited films have a columnar structure and a low density of atoms with many voids (Rajagopalan *et al.* 1982) and as a result large changes can be observed with photo-illumination (Singh *et al.* 1979, Rajagopalan *et al.* 1982, Spence and Elliott 1989, Kuzukawa *et al.* 1998). Recently, Kuzukawa *et al.* (1998) have given detailed experimental results of 'giant' changes in Ge- and As-based films and have observed changes up to 13% in thickness and 8% in bandgap with illumination. We were successful in establishing a strong correlation between the changes in volume and bandgap.

In the present work, photo-induced effects on the thickness and the optical bandgap of obliquely deposited As-based (As_2Se_3 and As_2S_3) chalcogenide thin films have been studied. We have also observed the effects of pre- and post-illumination annealing on these changes. A correlation between the changes in thickness and optical bandgap for illumination, as well as for annealing, has been established. The observed 'giant' changes in PD and VE in obliquely deposited films are explained on the basis of the 'repulsion and slip' model.

§2. EXPERIMENTAL DETAILS

Thin films of amorphous As_2Se_3 (a- As_2Se_3) and amorphous As_2S_3 (a- As_2S_3) were deposited by conventional evaporation at room temperature onto Si and glass (Corning 7059) substrates. The samples were deposited at an angle of 80° , this being the angle between the normal to the substrate and the direction of incidence of the evaporated atoms, as the density of atoms is found to be a minimum and changes in the properties are expected to be maximum at this deposition angle (Rajagopalan *et al.* 1982). As_2Se_3 and As_2S_3 films were illuminated with halogen and Hg lamps (40mWcm^{-2}) respectively in vacuum (about 1×10^{-4} Torr) for 2h through an infrared cut-off filter. The samples were also annealed before and after illumination at 433 K for As_2Se_3 and 463 K for As_2S_3 , that is below their respective glass transition temperatures, for 2h in vacuum (about 1×10^{-6} Torr). Two sets of samples were used for thickness and bandgap measurements. One set was annealed before illumination (type I) and the other set was illuminated without annealing (type II). This was done to observe the effects of pre-illumination annealing.

Thickness and optical bandgap were estimated for as-deposited samples, after pre-illumination annealing, after illumination and after post-illumination annealing.

Optical bandgaps were estimated from ultraviolet–visible–infrared spectroscopy studies using Tauc plots (Mott and Davis 1979). For thin-film thickness measurements, a non-contact optical spectrometric film thickness measurement system (VLM 8000, DaiNippon Screen) with a beam spot of 10 μm diameter and an accuracy of $\pm 10 \text{ \AA}$ was used. Si was used as the substrate for thickness measurements owing to its high optical reflection coefficient and flatness. The flatness of the substrate exerts a large influence on the reliability of the optical thickness measurements. The thickness was measured at nine points within a diameter of 5 mm and the average taken. Illumination was confined to the same spot of diameter 5 mm.

The interference film thickness gauge used for thickness measurements consists of a reflecting microscope, a halogen light source, an interference spectroscope and a data-processing computer. The interference spectroscope consists of a diffraction grating and a charge-coupled device image sensor. The film thickness d was obtained from the reflectivity spectrum, using the peak-and-valley method, in the wavelength range 400–800 nm. The accuracy of the measurements was improved by fitting a theoretical spectral profile, which was generated by computer with the known optical parameters of the film and substrate, to the experimental profile in the same wavelength range. The thickness was also measured with a mechanical thickness gauge (Dektak IIA) for comparison purposes.

§3. EXPERIMENTAL RESULTS

Figures 1–4 show the relative change $\Delta d/d$ in thickness and relative change $\Delta E_g/E_g$ in optical bandgap after various treatments for a-As₂Se₃ and a-As₂S₃ thin films respectively. The solid and broken lines represent the relative changes in thickness and optical bandgap respectively. Figure 1 shows the experimental results for the a-As₂Se₃ films under type I measurement conditions. The film thickness

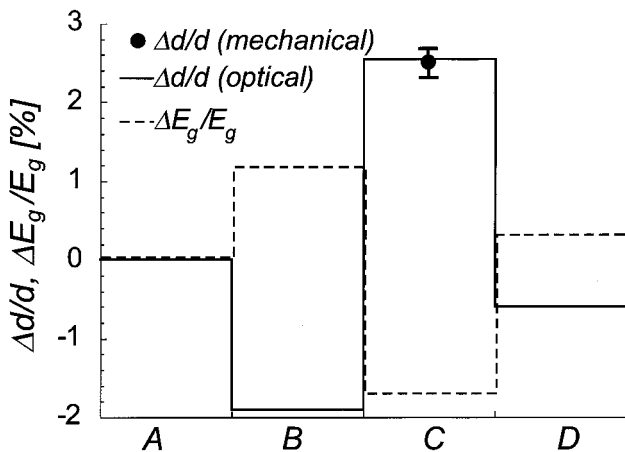


Figure 1. Variation in relative changes in thickness d and optical bandgap E_g of a-As₂Se₃ for type I measurement conditions. Measurement conditions are as follows: A, as deposited; B, after pre-illumination annealing; C, after illumination; D, after post-illumination annealing. The full circle represents the thickness estimated by mechanical measurement.

decreases (*thermal contraction*) and the bandgap increases (*thermal bleaching*) by annealing. On illumination, the thickness is found to increase (VE) and the bandgap decreases (PD). Post-illumination annealing decreases the thickness and increases the bandgap. Figure 2 shows the experimental results for a-As₂Se₃ films under type II conditions. As is obvious from the figure, the thickness increases (VE) and the bandgap decreases (PD) on illumination. Annealing the sample after illumination contracts the film and increases the bandgap.

Figure 3 shows the results for a-As₂S₃ under type I conditions. The behaviours are similar to those observed for a-As₂Se₃ (figure 1). Figure 4 shows the results for a-As₂S₃ under type II conditions. Again, the behaviours are qualitatively the same as observed for a-As₂Se₃ (figure 2).

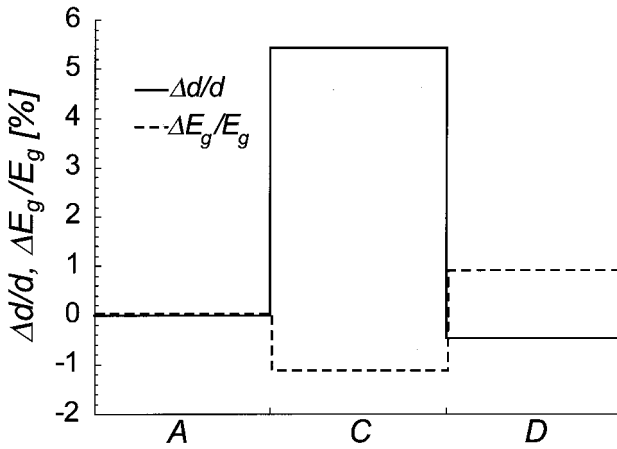


Figure 2. Variation in relative changes in thickness d and optical bandgap E_g of a-As₂Se₃ for type II measurement conditions. Measurement conditions are as follows: A, as deposited; C, after illumination; D, after post-illumination annealing.

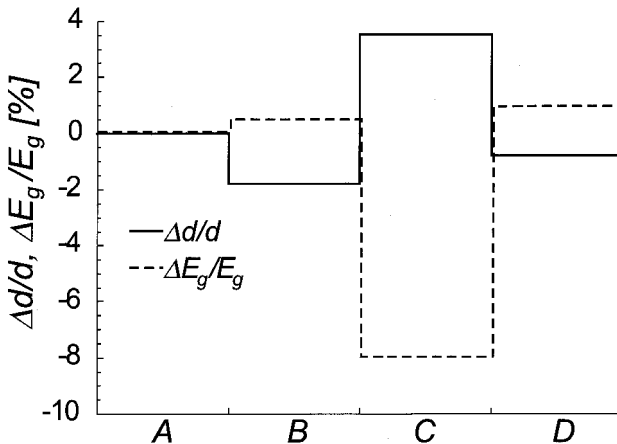


Figure 3. Variation in relative changes in thickness d and optical bandgap E_g of a-As₂S₃ for type I measurement conditions. The measurement conditions are the same as for figure 1.

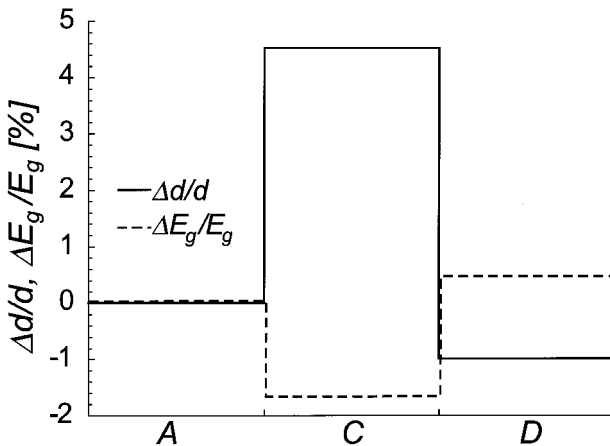


Figure 4. Variation in relative changes in thickness d and optical bandgap E_g of a-As₂S₃ for type II measurement conditions. The measurement conditions are the same as for figure 2.

The above results indicate that, for As-based glasses, photo-illumination always expands the films and decreases the bandgap while annealing before or after illumination is found to contract the films and increase the bandgap. We observe that illumination increases the thickness (VE) and shrinks the bandgap (PD), irrespective of the thermal treatment of the sample before illumination. By post-illumination annealing, it is observed that the changes are nearly reversible and this effect is also independent of the thermal treatment of the sample before illumination.

It should be noted that we have also confirmed the thickness changes, as an example for a-As₂Se₃, by mechanical measurement. This datum is shown by the full circle in figure 1. It can be seen that the results obtained from both these techniques agreed within the experimental error ranges of each. This suggests that the optical measurement technique as adopted in the present work gives reliable results.

As can be seen from the figures, we have observed 'giant' changes in obliquely deposited glasses, of up to 8% in thickness and up to 6% in bandgap with illumination. Other workers (Singh *et al.* 1979, Rajagopalan *et al.* 1982, Spence and Elliott 1989, Kuzukawa *et al.* 1998) have also observed large changes in Ge-based, obliquely deposited films.

§4. DISCUSSION

As shown in the previous section, illumination increases the thickness and decreases the bandgap whereas annealing decreases the thickness and increases the bandgap for both As₂Se₃ and As₂S₃ thin films. This suggests a correlation between the two types of change. These observations are different from those observed in obliquely deposited Ge-based chalcogenide films (Kuzukawa *et al.* 1998) where illumination contracts the films and increases the bandgap and annealing increases the thickness and decreases the bandgap.

When the substrate is held at an angle to the direction of evaporation, the deposited atoms create a shadow (or a void) in their vicinity and thus the atoms are deposited in a columnar way. As many of the atoms are surrounded by voids,

they have much free space in which to move during illumination or annealing. It has been shown that As_2S_3 films, when deposited at an oblique incidence, also have a columnar structure (Starbova *et al.* 1997).

Spence and Elliott (1989) in their study on the effect of illumination on obliquely deposited Ge-based chalcogenides have observed large changes in bandgap with illumination and have proposed that O assisted bond reconstruction and light-induced surface oxidation results in an increase in the bandgap, even for samples in air. Singh *et al.* (1979) in their work on the changes in thickness of obliquely deposited Ge-based chalcogenide thin films have observed up to 11% contraction in thickness with illumination and they attribute this to a rearrangement of the bonds on exposure to light followed by a collapse of the columnar structure of the films. Rajagopalan *et al.* (1982) have, on the other hand, concluded that the changes in bandgap are due to photo-induced volume changes induced by void collapse. It should be noted here that the changes observed in As-based films show the opposite behaviour to that of Ge-based films. This difference will be discussed in a future publication.

Owing to the porous and columnar structure of obliquely deposited films, it is generally assumed that the collapse of voids by illumination results in giant changes (Singh *et al.* 1979, Rajagopalan *et al.* 1982). The pronounced change observed in small-angle X-ray scattering intensity with illumination (Spence and Elliott 1987a,b, Rayment and Elliott 1983) also led many to believe that giant photocontractions in obliquely deposited glasses are a direct consequence of gross structural changes caused by illumination, which Rayment and Elliott (1983) suggested arose from the collapse of voids. However, it was shown by Spence and Elliott (1987b) from their extended X-ray-absorption fine-structure measurements that there is no change in nearest-neighbour bond length on illumination, indicating that changes in thickness (or volume) do not arise from this effect.

The assumption that the 'giant' photo-induced changes in obliquely deposited films is a consequence of the collapse of voids by illumination cannot explain the results of the present work, in which induced changes can be nearly annealed back to the original state.

The expansion and slip motion model proposed recently by Shimakawa *et al.* (1998) can explain volume changes satisfactorily in normally deposited films, and we shall try to use this model to explain the 'giant' changes as observed in obliquely deposited films. First of all, we would like to discuss the model briefly.

Amorphous As-based chalcogenides have a layered structure. It was suggested that photocreated electrons reside in the layers during illumination, causing a Coulomb repulsion between the layers. The accumulation of electrons in the layers arises because photocreated holes are more mobile than electrons in amorphous chalcogenides and they diffuse away to a non-illuminated area through the valence band or their tail states. The photocreated electrons reside in the conduction-band tails. The repulsive Coulomb interaction increases the distance between layers, giving rise to VE. This interaction is indicated by arrows E in figure 5. It is expected, however, that PD is not induced at this stage. It was made clear by Ke. Tanaka (1998), based on experimental results, that the rate of VE is greater than PD, indicating that there is no direct correspondence between VE and PD. It is believed that, in conjunction with the occurrence of the interaction E between adjacent clusters, a slip motion along the layer is generated. This slip motion is indicated with arrows S in figure 5. It should be noted, here, that the slip motion is directly related to PD

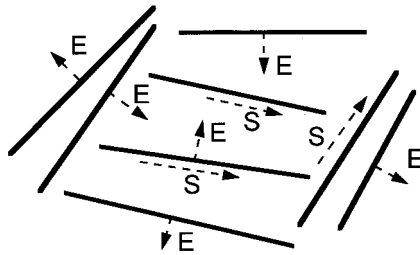


Figure 5. Schematic illustration of the expansive (E) and slip (S) motion of the layers for chalcogenide films (Shimakawa *et al.* 1998).

(Watanabe *et al.* 1988). Both the interactions E and S are caused by the same repulsive force between the layers but only interaction S is directly related to PD. When the adjacent layers are separated by slipping from their equilibrium positions, an increase in the energy of the highest occupied states in the valence band is expected owing to an increase in the LP-LP interactions. This leads to a widening of the valence band, but the conduction band remains almost unchanged (Watanabe *et al.* 1988). Thus, the changes in volume and bandgap can be explained by this mechanism.

Obliquely deposited As-based films have a layered structure with many voids and a larger free volume compared with normally deposited films. In fact, the density of atoms for obliquely deposited Ge-based films has been found to be nearly half of that in normally deposited films (Pandaya *et al.* 1975). On annealing the obliquely deposited films, it is expected that the voids will collapse, but not completely. This will result in contraction of the volume and bleaching of the bandgap. On illuminating obliquely deposited films, owing to the larger free volume and easy motion of the layers (fluidity), the repulsive motion of the layers, leading to VE, will be larger than for normally deposited films. The slip motion will also be enhanced, and the changes in the bandgap larger.

§5. CONCLUSIONS

We have studied the effect of photo-illumination and annealing on the thickness and the optical bandgap of As-based (As_2Se_3 and As_2S_3), obliquely deposited thin films. It was observed that, on annealing, the thickness decreases and the bandgap increases while illumination is found to increase the thickness and decrease the bandgap. Annealing the samples before or after illumination always shows an effect which is opposite to that of illumination. We have observed 'giant' changes in both thickness and bandgap with illumination. It is also observed that post-illumination annealing causes the changes to revert to nearly the initial conditions.

These giant changes have been explained on the basis of the presence of voids and an easy motion of layers in the films, resulting in an easier expansion and slip motion of the layers.

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