JOURNAL OF MATERIALS SCIENCE **38** (2003) 937–940

Photo-induced changes in optical properties of As_2S_3 and As_2Se_3 films deposited at normal and oblique incidence

P. BHARDWAJ
Department of Electronic Science, University of Delhi South Campus, Benito Juarez Road, New Delhi 110021, India
P. K. SHISHODIA
Department of Physics & Electronics, Zakir Hussain College, University of Delhi, New Delhi 110002, India
R. M. MEHRA
Department of Electronic Science, University of Delhi South Campus, Benito Juarez Road, New Delhi 110021, India
E-mail: rammehra@netscape.net

Photostructural transformations in amorphous chalcogenide films have been a subject of intensive research so far. In this paper we discuss the changes in the optical properties of typical As-based chalcogenide glasses ($As_2S_3$and As_2Se_3) on exposure to ultraviolet (UV) light. An attempt has been made to systematically investigate the optical parameters like extinction coefficient, refractive index and optical bandgap of the films by measuring the same for as-grown and UV-exposed amorphous films of As_2S_3 and As_2Se_3 prepared by vacuum evaporation technique. © *2003 Kluwer Academic Publishers*

1. Introduction

Reports on photo induced transformations in chalcogenide glasses [1, 2] have triggered a lot of research activity in this field. From amongst several photo-induced phenomena investigated so far in these glasses photo darkening and photo induced volume expansion have aroused most interest. Exclusive research has been put into photo induced changes and structure related properties of these materials [3–6]. However, for opto-electronic applications, a comprehensive study on the spectral dependence of optical parameters of semiconductor thin films is essential as it enables one to precisely model the spectral response of optoelectronic devices. The same is also important for the design and manufacture of multilayer. Here, we report a systematic study of similar light induced (ultraviolet light) changes in the optical properties of typical As-based chalcogenide glasses (As_2S_3 and As_2Se_3).

2. Experimental details

The normal and oblique films of As_2S_3 and As_2Se_3were prepared by vacuum evaporation of the source material. The oblique films were deposited at an angle of 80°, this being the angle between the normal to the substrate and direction of incidence of the evaporated atoms. The evaporation was carried out on the glass substrates at room temperature in a vacuum of about 1×10^{-6} Torr from a molybdenum boat heater. A surface profiler (DekTak 3) was used to measure the thickness of the films. Arrangements were made to deposit films of equal thickness. Film thickness was monitored to be about 1 μm. The samples were annealed below their glass transition temperatures (423 K for As_2Se_3 and 453 K for As_2S_3) for 2 h in vacuum of about 1×10^{-6} Torr. The annealed films were illuminated with 80 watt Hg vapor lamp with quartz envelope ($\lambda \sim 250$ to 350 nm) for 2 h.

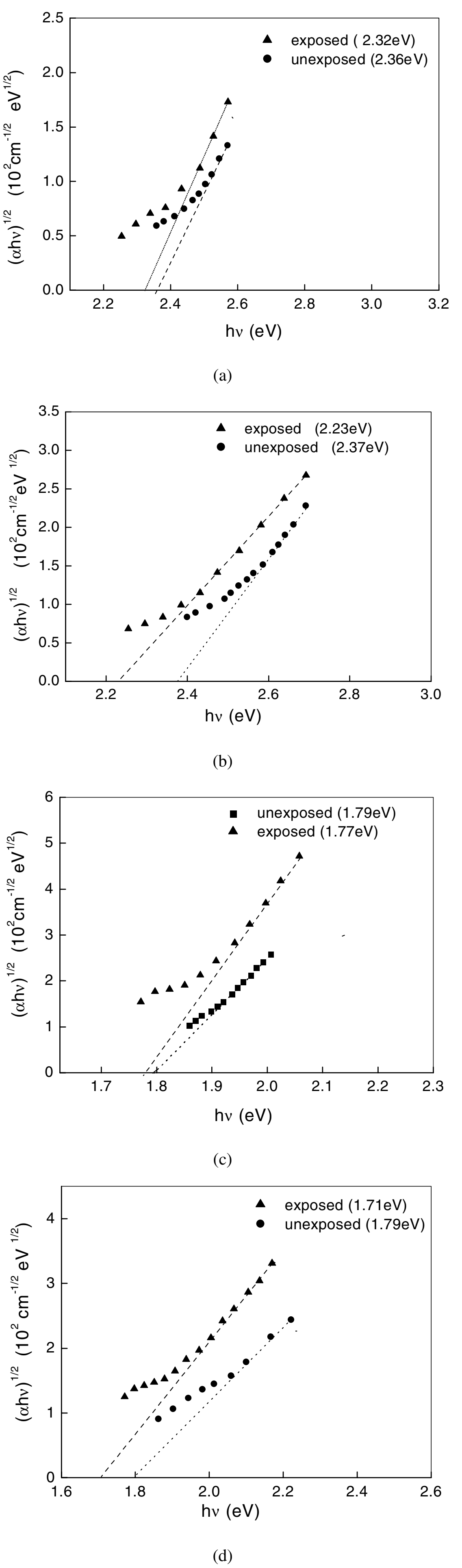
The optical transmission measurements were performed on thin films using UV-VIS spectrophotometer (Shimadzu 1240).

3. Results and discussion

The amorphous nature of the films was confirmed by the absence of any sharp peak in X-ray diffractograms. Transmission spectra were used for calculating the optical parameters. The bandgap, of the films was estimated using Tauc's relation

$$\alpha = (B/h\nu)(h\nu - E_{\text{opt}})^n \qquad (1)$$

where B is a constant, E_{opt} is the optical bandgap energy, hν is the photon energy and n depends on electronic transitions in k-space and takes the values $^1/_2$, 1, 2 and 3. Fig. 1 shows the changes in the optical bandgap of As_2S_3 and As_2Se_3films on illumination. As can be seen from the figures, the changes in the obliquely deposited films are more significant as compared to those in normally deposited films. Besides a decrease in bandgap an increase in thickness (~9–10%) was also observed.



(a)

(b)

(c)

(d)

Figure 1 The optical band gap E_g of (a) As_2S_3-Normal (b) As_2S_3-80° (c) As_2Se_3-Normal (d) As_2Se_3-80° thin films.

These changes are in agreement with the earlier reported results [7]. Different models [8, 9] have been put forward in support of these phenomena however, the 'repulsive layer' model proposed by Shimakawa *et al.* [10] has been able to explain these changes in a satisfactory manner. This model provides a more satisfactory explanation as according to it in chalcogenide glasses having a layered structure, the clustered layers get negatively charged due to electron accumulation by illumination. The layers in turn repel each other leading to photo volume expansion (PVE). The photodarkening in turn can be attributed to the slip motion that follows the PVE. While in case of other models, photo-irradiation excitation of only particular atoms has been considered i.e. photostructural changes like photodarkening and volume expansion occurs around particular chalcogen atoms due to atomic relaxation and it is difficult to understand why only particular atoms should be excited in a solid.

The structural changes, on the other hand, accompany the change in refractive index (n), besides the change in bandgap and hence these effects can be useful for devices, such as optical memory applications. Refractive index and extinction coefficients have been calculated using the method suggested by Swanepoel [11–13]. In this method the transmission spectrum of the films is obtained as a function of wavelength. In case of the films having uniform thickness, interference effects give rise to transmission spectrum having fringes. Envelopes are drawn through the maxima and minima of the transmittance curve and values of T_M (transmission maxima) and T_m (transmission minima) are taken at a particular wavelength. The refractive index (n) is obtained using the following expressions,

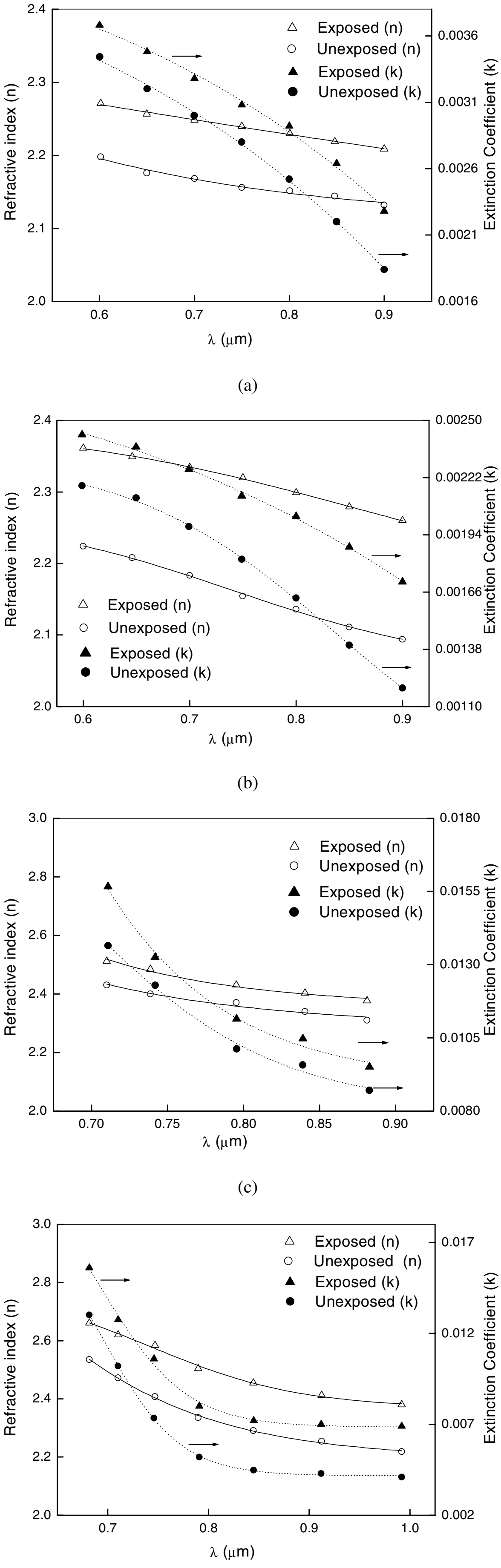
$$n = \left[M + (M^2 - s^2)^{\frac{1}{2}}\right]^{\frac{1}{2}}$$

$$\text{where } M = \frac{2s}{T_m} - \frac{(s^2+1)}{2} \text{ for transparent region}$$

$$\text{and } M = \frac{s^2+1}{2} + 2s\frac{T_M - T_m}{T_M T_m} \text{ for weak and medium absorption region}$$

where s is the refractive index of the substrate. The refractive index of the substrate was calculated in the wavelength range 0.4 μm–0.9 μm and was found to be same throughout.

Illumination of As_2S_3 and As_2Se_3 films (both normal and oblique films) with UV light also results in an increase in their refractive indices, the results of which are summarised in Fig. 2. The changes in extinction coefficient also indicate similar trends (Fig. 2), the changes being more significant in case of obliquely deposited films. The increase in refractive index is due to increase in absorption, which is a direct consequence of the observed decrease in bandgap. Thus refractive index is inversely related to the bandgap of the films. The photoinduced changes are greatly enhanced by changing the angle of deposition because of the low density of atoms with many voids [14] in case of oblique films and as a result, large changes can be observed with photo



(a)

(b)

(c)

(d)

Figure 2 The spectral response of the refractive index (*n*) and extinction coefficient (*k*) of (a) As_2S_3-Normal (b) As_2S_3-80° (c) As_2Se_3-Normal (d) As_2Se_3-80° thin films.

TABLE I Optical parameters of normally and obliquely grown as As_2S_3 and As_2Se_3 films

	% Change in optical parameters		
Type of film	E_g	*n*	*k*
As_2S_3-N	~1.7%	3–4%	3–4%
As_2S_3-80°	~6%	6–8%	4–6%
As_2Se_3-N	~1.1%	2.5–3.5%	1–2%
As_2Se_3-80°	4.5%	5–7%	3–5%

E_g: Bandgap, *n*: Refractive index, *k*: Extinction coefficient.

illumination. The table above indicates the extent of increase/decrease in these parameters.

As is evident from the results S-containing chalcogenides are found to exhibit larger photostructural changes compared to Se-based samples. The likely reason for this behaviour could be the involvement of intermolecular (weaker bonds between non-bonded chalcogen atoms in neighbouring layers) or intra-molecular (primary covalent bonds) bond breaking mechanisms and size of the chalcogen. The degree of intermolecular bonding is known to increase from S → Se → Te [15] as a result the local flexibility of structures is progressively reduced. Thus greater structural flexibility in case of S-based chalcogenides makes the intermolecular bonds more susceptible to photoinduced rupture, resulting in greater degree of photostructural changes. Intra-molecular bond-breaking mechanisms (e.g. STE (Self-Trapped Exciton) and RCN (Random Covalent Network) transformations) may also be responsible in part for photo-induced changes. According to STE model the only photoinduced defect, which could give rise to appreciable photostructural changes, is the P_4^+ and C_1^- pair (P = pnictogen and C = Chalcogen), which is formed by the bond-switch P—C → P—P. As the magnitude of such changes depends on the difference in the bond lengths associated with P—C and P—P, S-containing chalcogenides are expected to show larger photostructural changes because sulphur has smaller covalent radius than other chalcogenides, consequently the bond length is greater for it.

4. Conclusion

A study of photoinduced changes on the thickness and optical constants (Bandgap, refractive index, extinction coefficient) of As-based (As_2S_3 and As_2Se_3) films deposited at normal and oblique incidence (80°) has been presented. It was observed that the illumination with ultraviolet light is found to significantly increase the thickness, refractive index and extinction coefficient and decrease the bandgap of both the films. However, these changes are more pronounced in As_2S_3 than in As_2Se_3.

The more prominent changes observed in obliquely deposited films have been explained on the basis of the existence of columnar structure and the presence of voids facilitating easier motion of layers in these films.

Acknowledgement

One of the authors Priyamvada Bhardwaj acknowledges the financial support from UGC, India.

References

1. K. TANAKA, *Rev. Solid State Sci.* **4** (1990) 641.
2. G. PFEIFFER, M. A. PAESLER and S. C. AGGARWAL, *J. Non-Cryst. Solids* **130** (1991) 111.
3. K. TANAKA, *Phys. Rev.* B **57** (1998) 5163.
4. Y. KUZUKAWA, A. GANJOO and K. SHIMAKAWA, *J. Non-Cryst. Solids* **227–230** (1998) 715.
5. K. STARBOVA, J. DIKOVA and N. STARBOVA, *ibid.* **210** (1997) 261.
6. K. SHIMAKAWA, A. KOLOBOV and S. R. ELLIOT, *Adv. Phys.* **44** (1995) 475.
7. Y. KUZUKAWA, A. GANJOO and K. SHIMAKAWA, *Phil. Mag.* B **79**(2) (1999) 249.
8. A. V. KOLOBOV, H. OYANAGI and K. TANAKA, *Phys. Rev.* B **55** (1997) 726.
9. KE. TANAKA, *Rev. Solid State Sci.* **4** (1990) 641.
10. K. SHIMAKAWA, N. YOSHIDA, A. GANJOO, Y. KUZUKAWA and J. SINGH, *Phil. Mag. Lett.* **77** (1998) 153.
11. J. C. MANIFACIER, J. GASSIOT and J. P. FILLARD, *J. Phys.* E **9** (1976) 1002.
12. R. SWANEPOEL, *ibid.* **16** (1983) 1214.
13. *Idem., ibid.* **17** (1984) 896.
14. R. A. STREET, J. KAKALIOS, C. C. TSAI and T. M. HAYES, *Phys. Rev.* B **35** (1987) 1316.
15. R. M. MARTIN, G. LUCOVSKY and K. HELLIWELL, *ibid.* **13** (1976) 1383.

Received 18 April
and accepted 5 November 2002