

EFFECT OF ANNEALING ON THE STRUCTURE AND OPTICAL PROPERTIES OF a-Se-Sb-Ag THIN FILMS

K. S. Bindra, Nikhil Suri, R. Thangaraj¹

Semiconductors Laboratory, Department of Applied Physics,
Guru Nanak Dev University, Amritsar-143005, India.

Se₇₀Sb₂₀Ag₁₀ bulk sample was obtained using conventional melt quenching technique. Thin films of a-Se₇₀Sb₂₀Ag₁₀ were prepared by vacuum evaporation technique in a base pressure of 10⁻⁴ mbar onto well-cleaned glass substrates. The structure of the as-prepared and annealed films has been studied by X-ray diffraction. These studies show that there is no appreciable change in structure when annealed in the temperature range of 323-363K, however, when annealed above 373K the formation of some polycrystalline structures in the amorphous phases is seen. The optical transmission of these films has been studied as a function of photon wavelength in the range 400-900nm. It has been found that the optical energy gap first increases with annealing temperature upto 323K then continuously decreases with increase in annealing temperature and sharply decreases near crystallization temperature. The temperature dependence of electrical conductivity of the as-prepared and annealed thin films has also been studied. It has been found that the electrical activation energy follows the trend of the optical energy gap as the annealing temperature increases.

Keywords: Chalcogenide glass, Thin film

1. Introduction

Amorphous chalcogenide films have potential and current application in optical memories, photonics crystals and optics [1]. Optically or electrically recorded memories are currently 'hot' scientific topics [2-3]. In recent years, efforts are being made to develop chalcogenide based rewritable optical memories. The mechanism of recording memories is an optically, thermally or electrically induced reversible phase transition between amorphous to crystalline states or vice versa in thin films [4-5]. Thermal processes are known to be important in inducing crystallization in semiconducting chalcogenide glasses [6-7]. Crystallization of chalcogenide films is accompanied by a change in the optical band gap [8-9]. Separation of different crystalline phases with thermal annealing has been observed in ternary glasses [10-12]. The effect of thermal annealing is interpreted on the basis of amorphous-crystalline transformation.

The aim of the present work is to investigate the structural, optical and electrical properties of thermally annealed Se-Sb-Ag thin films. Pure selenium has low sensitivity and short lifetime. In order to overcome this difficulty, several workers have used alloys of Se with certain additives such as Ge, Bi, Sb, As etc. for alloying with Se. We have chosen Sb as an additive material. It has been reported that the addition of small percentage of Sb is sufficient to cause crystallization of Se Mott et al. [13] have reported that the effect of Sb is greater than Te in promoting crystallization of Se. Ag as a second additive has been used due to the nature of the conduction in Ag-doped chalcogenide glasses i.e. electrical conductivity is governed by Ag⁺ ionic conduction since the hole conduction is substantially smaller and electron conductivity is not detected [14-16].

2. Experimental

Bulk samples of Se₇₀Sb₂₀Ag₁₀ were prepared by melt quenching technique. High-purity (99.99%) elements with appropriate atomic percentage were sealed in a quartz ampoule (length ~10cm and internal

¹ Corresponding author: rthangaraj@rediffmail.com

diameter ~ 0.6 cm), in a vacuum of $\sim 10^{-4}$ mbar. The ampoule was kept in a vertical furnace for 48 hrs. The temperature was raised to 1273 K, at a rate of 4-5 K/min. The ampoule was inverted at regular intervals (~ 1 hrs) to make sure homogenous mixing of the constituents, before quenching in an ice bath. The material was separated from the quartz ampoule by dissolving the ampoule into a solution of HF + H₂O₂ for approximately 48h. Using this as source material, thin films were deposited onto chemically cleaned glass substrates by thermal evaporation technique in a vacuum better than 10^{-4} mbar using a Hind High Vacuum coating unit (model 12A4D). The thickness of the films was measured by Tolansky interference method. The film thickness ranged from 1800 to 2000Å. The films were annealed in a vacuum of 10^{-4} mbar at various temperatures (323, 333, 343, 353, 363, 373, 383 and 393 K) for a fixed time (1 hr) and then cooled down to room temperature at the cooling rate of 40 Khr⁻¹. The amorphous/crystalline nature of the as-prepared and annealed thin films were studied using X-ray diffractometer. Differential scanning calorimetric (DSC) measurements were carried on bulk material under pure N₂ atmosphere using Mettler Toledo Star^c (Model No. DSC-200PC) instrument.

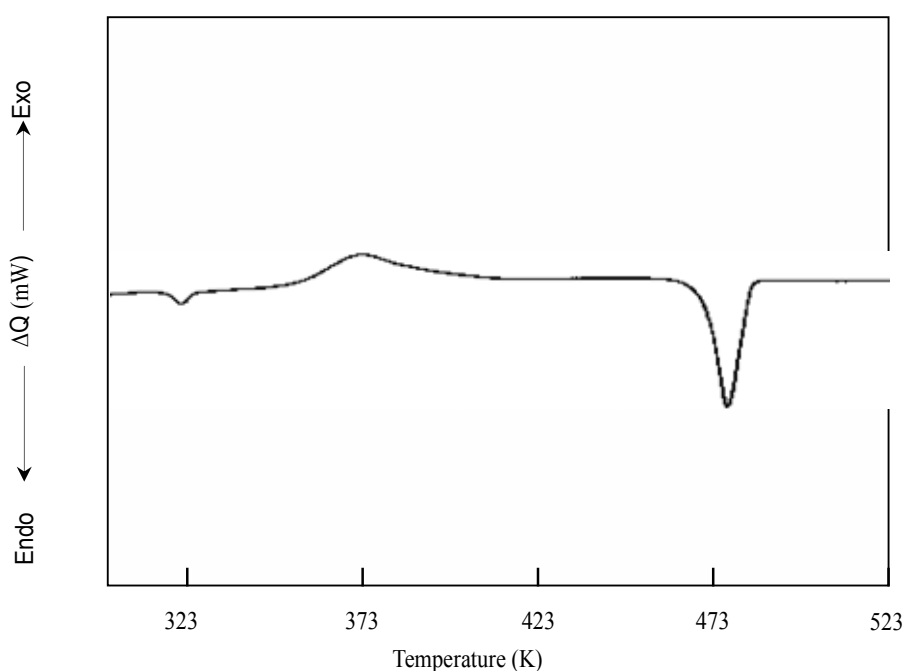


Fig. 1. DSC thermogram for Se₇₀Sb₂₀Ag₁₀ at heating rates of 15 K/min

The optical transmission spectrum was recorded at room temperature for as-prepared and annealed films using UV-visible spectrophotometer (UV-160A Shimadzu, Japan) in the wavelength range 400-900nm. The absorption coefficient (α) was calculated using equation $\alpha = 1/t \ln(100/T)$, where, t is thickness of film and T is transmittance. The optical energy gap was obtained from a plot of $(\alpha hv)^{1/2}$ vs hv and taking the intercept on the energy axis, where α is the absorption coefficient. The conductivity measurements were carried out in the temperature range 263-333K in a running vacuum of 10^{-3} mbar. Electrical contacts with an electrode gap of ~ 2 mm in a coplanar geometry were made using silver paint. The current was measured using a digital picoammeter (DPM-111 Scientific Equipments, Roorkee). The ohmic nature of the contact was verified by straight line passing through the origin of voltage versus current plot.

3. Result and discussion

3.1 Structure

A typical DSC thermogram for the bulk at a particular heating rate of 10 Kmin⁻¹ is shown in fig 1. Similar thermograms were obtained at other heating rates of 5, 15, 20 Kmin⁻¹ (not shown here). It can be seen from the above figure that the thermogram show three distinct peaks corresponding to glass transition (T_g), peak crystallization (T_p) and the melting (T_m) temperatures.

X-ray diffraction data reveals the amorphous nature of the as-prepared specimens as shown in fig 2. The figure does not show any diffraction peaks and the broad features indicate that the thin films are amorphous in nature. The analysis of XRD results, using standard ASTM data cards, reveals the formation of polycrystalline phases in number of annealed films. The films annealed at 323, 333, 343, 353 and 363K do not show any sharp peak in the XRD pattern, thus indicating the absence of any crystalline phase. (fig 2) However, XRD pattern of films annealed at 373 and 393K indicates the formation of poly-crystalline structure in the amorphous phases. (fig 2)

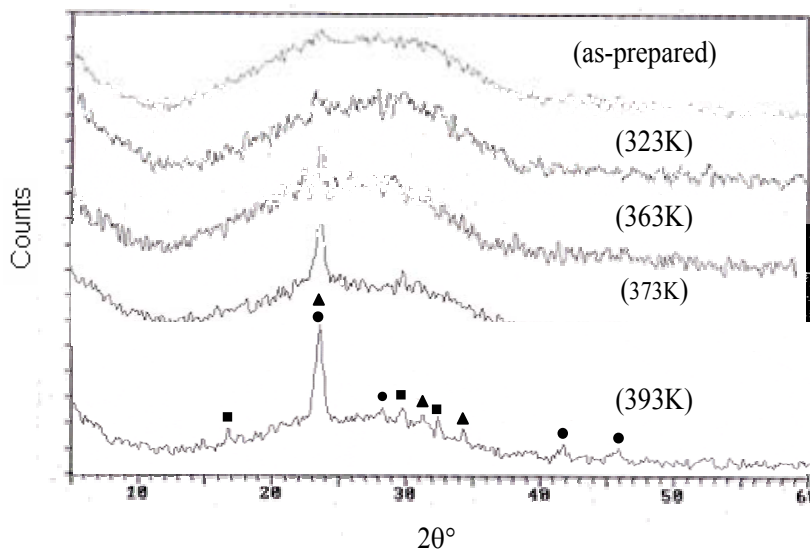


Fig 2. X-ray diffraction curves of the as-prepared and annealed $\text{Se}_{70}\text{Sb}_{20}\text{Ag}_{10}$ samples. (■ peaks of Sb_2Se_3 , ● peaks of Se and ▲ peaks of Ag_2Se).

3.2 Optical and electrical properties

The spectral dependence of transmittance (T) as a function of wavelength for as-prepared and annealed films of $\text{a-Se}_{70}\text{Sb}_{20}\text{Ag}_{10}$ with different annealing temperatures were studied. The absorption coefficient α increases with increase in the photon energy for as-prepared and annealed films. In the absorption process, a photon of known energy excites an electron from a lower to higher energy state, corresponding to an absorption edge. In chalcogenide glasses, a typical absorption edge can broadly be ascribed to one of the three processes: residual below-gap absorption, Urbach tails and interband absorption. Chalcogenide glasses have been found to exhibit highly reproducible optical edges, which are relatively insensitive to preparation conditions [17]. The Tauc plots [17] of $(\alpha h\nu)^{1/2}$ versus $h\nu$ for some of the as-prepared and annealed films are shown in fig 3. The values of optical energy gap (E_g^{opt}) are determined by taking the intercept on x-axis.

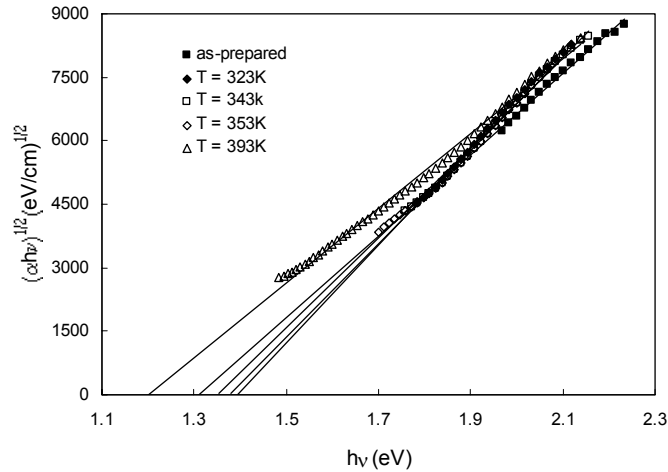


Fig. 3. The absorption coefficient plotted as $(\alpha hv)^{1/2}$ versus $h\nu$ for the as-prepared and annealed $\text{Se}_{70}\text{Sb}_{20}\text{Ag}_{10}$ thin films.

The electrical conductivity of the as-prepared and annealed thin films of $\text{Se}_{70}\text{Sb}_{20}\text{Ag}_{10}$ was measured as function of temperature in the range 263- 333K. The result of these measurements is plotted in fig 4. It is clear from this figure that $\ln \sigma$ vs $1000/T$ curves are straight lines for all the samples indicating that the conduction in these glasses is through an activated process having a single activation energy in the above temperature range and follows Arrhenius equation $\sigma = \sigma_0 e^{-\Delta E_a/kT}$, where σ_0 is the pre-exponential factor, ΔE_a is the activation energy, k is the Boltzmann constant and T is absolute temperature. The values of activation energy ΔE_a were calculated for all the samples using the curves of fig 4.

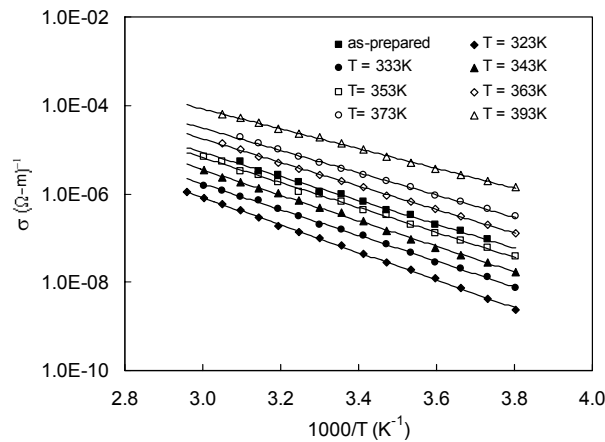


Fig. 4. Arrhenius plot for the as-prepared and annealed $\text{Se}_{70}\text{Sb}_{20}\text{Ag}_{10}$ thin films.

Figure 5 shows the variation of activation energy and optical energy gap with different annealing temperature. It can be observed that both E_g^{opt} and ΔE_a follow the same trend i.e. they increase when annealed at 323K, then decrease at comparatively slower rate, and finally when annealed above peak crystallization temperature decrease sharply. The increase in these quantities with annealing temperature may be explained on the basis of density of states model in amorphous solids proposed by Mott and Davis [13]. According to this model, the width of localized states near the mobility edges depends on the degree of disorder and defects present in amorphous structure. In particular it is known that unsaturated bonds together with some saturated bonds (like dative bonds [18]) are produced as a result of insufficient number of atoms deposited in the amorphous films [19]. These unsaturated bonds are responsible for the formation of some

defects in the films, which produce localized state in the amorphous solids. The presence of a high concentration of localized states in the band structure was responsible for low values of optical energy gap and electrical activation energy in case of as-prepared amorphous films and those annealed below glass transition temperature (T_g). The unsaturated defects are gradually annealed out [20], producing a large number of saturated bonds. The reduction in the number of unsaturated defects decreases the density of localized states in the band structure [21] and consequently increases ΔE_a and E_g^{opt} .

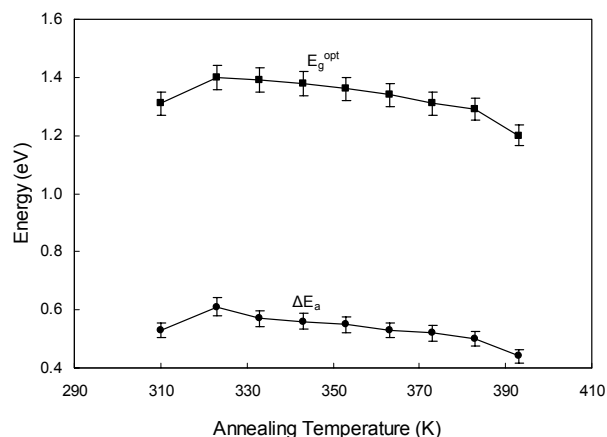


Fig. 5. Variations of activation energy and optical energy gap with different annealing temperature.

Thermal annealing above T_g is known to be important in inducing crystallization in semiconducting chalcogenide glasses [22-24]. During annealing temperature higher than T_g , the indirect optical energy gap and electrical activation energy decreases and the width of localized states tails increases with increase in annealing temperature. These results can be interpreted by assuming the production of surface dangling bonds around crystallites [25] during the process of crystallization. It has been suggested by many authors [26] that nearly ideal amorphous solids crystallize under heat treatment and that in the process of crystallization, dangling bonds are produced around the surface of the crystallites. Further heat treatment causes the crystallites to breakdown [26] into smaller crystals, thereby increasing the number of surface dangling bonds. These dangling bonds are responsible for the formation of some types of defects in the highly polycrystalline solids. As the number of dangling bonds and defects increase with an increase in annealing temperature, the concentration of localized states in the band structure also increases gradually. Hence, the heat treatment of the films causes an increase in the energy width of localized states thereby reducing the optical energy gap and causes a rapid increase in the electrical conductivity and consequently, a decrease in the electrical activation energy for conduction.

4. Conclusion

Amorphous thin films of $Se_{70}Sb_{20}Ag_{10}$ were prepared by vacuum evaporation technique. The structure of the as-prepared and annealed films has been studied by X-ray diffraction. The optical energy gap and electrical conductivity measurements were carried out on these thin film samples. It may be concluded from the above studies that there is not any appreciable change in structure, when annealed in temperature range of 323-363K, however, when annealed above 373K the formation of some polycrystalline structures in the amorphous phases is seen. The optical energy gap of these films has been studied as a function of photon wavelength in the range 400-900nm. The temperature dependence of electrical conductivity of as-prepared and annealed thin films has also been carried out in the temperature range of 263-333K. It has been found that the optical energy gap and the electrical activation energy increases when annealed at 323K then continuously decreases with increase in annealing temperature and sharply decreases above crystallization temperature. It has been observed that the variation of both optical energy gap and the activation energy with annealing temperature follow the same trend.

References

- [1] P.J.S. Ewen, in A.V. Kolobov (Ed), Photo-induced Metastability in Amorphous Semiconductors, Wiley, VCH Weinheim, 2003, p. 365.
- [2] A.V. Kolobov, P. Fons, A.I. Frenkel, A.L. Ankudinov, J. Tominaga, T. Uruga, *Nat. Mater.* **3** 703 (2004)
- [3] M.H.R. Lankhorst, *Nat. Mater.* **4** 347 (2005)
- [4] T. Kawaguchi, in A.V. Kolobov (Ed), Photo-induced Metastability in Amorphous Semiconductors, Wiley, VCH Weinheim, 2003, p. 182.
- [5] S.R. Elliott, *Physics of Amorphous Materials*, Longman Scientific and Technical, Harlow, 1990 p 57.
- [6] J. M.del Pozo, L. Diaz, *J. Non-Cryst. Solids* **243** 45 (1999)
- [7] A.H. Moharram, M.S. Rasheedy, *Phys. Stat. Sol. A*, **169** 33 (1998)
- [8] Z.H. Khan, M. Zulfequar, M. Hussian, *Japanese J. Appl. Phys.* **37** 23 (1998)
- [9] M. Chen, K.A. Rubin, R.W. Barton, *Appl. Phys. Lett.* **49** 502 (1986)
- [10] A.H. Moharram, *Appl. Phys. A*. **66** 515 (1998)
- [11] A. Abu El-Fadl, M. M. Hafiz, M.M. Wakaad, A.S. Aashour, *Physica B* **382** 110 (2006)
- [12] A.M. Salem, S.H. Moustafa, *Fizika A* **13** 137 (2004)
- [13] N.F. Mott, E.A. Davis: *Electronic processes in Non-Crystalline Materials*, Clarendon Press, Oxford, (1971).
- [14] Z.U. Borisova, *Glassy Semiconductors*, Plenum Press, New York, (1981).
- [15] K. Tanaka, *J. Non-Cryst. Solids* **164-166** 1179 (1993).
- [16] M. Ohto, M. Itho, K. Tanaka, *J. Appl. Phys.* **77** 1034 (1995).
- [17] J. Tauc, *Amorphous and Liquid Semiconductors*, Ed. By J. Tauc Plenum Press, New York, 1974 p.159
- [18] S.R. Ovshinsky, D. Adler, *Contem. Phys.* **19** 109 (1978)
- [19] M.L. Theye: In Proc. 5th Int. Publisher Conf. on Amorphous and Liquid Semiconductor, Vol. 1, ed. by J. Stuke, W. Brenig (Garmisch-Partenkirchen 1973) p. 479.
- [20] S. Hasegawa, S. Yazalici, T. Shimiza, *Solid State Commun.* **26** 407 (1978)
- [21] A.S. Maan, D.R. Goyal, S.K. Sharma, T.P. Sharma, *J. Non-Cryst. Solids* **183** 186 (1995)
- [22] M.M. Ibrahim, M.A. Abdel-Rahim, *Phys. Scr.* **38** 762 (1988)
- [23] S. Shgetomi, H. Ohkubo, *Thin Solid Films* **199** 215 (1991)
- [24] M.A. Abdel-Rahim, A.H. Moharram, M. Dongel, M.M. Hafiz. *J. Phys. Chem Solids* **51** 355 (1990)
- [25] S. Chaudhuri, S.K. Biswas, *J. Non-Cryst. Solids* **54** 179 (1983)
- [26] S. Hasegawa, M. Kitagawa, *Solid State Commun.* **27** 855 (1978)