

Optical studies of $(\text{AsSe})_{100-x}\text{Sb}_x$ thin films

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Abstract Thin arsenic-selenium-antimony films $(\text{AsSe})_{100-x}\text{Sb}_x$ ($x = 0, 5, 10, 15$ mol.%) have been deposited on glass substrates by vacuum thermal evaporation (VTE) and pulsed laser deposition (PLD) techniques from the corresponding bulk glassy materials. The refractive index and the film thickness have been determined from the optical transmission spectra by modified Swanepoel method. The optical band gap calculated using the Tauc's approximation showed a narrowing as a function of the increased Sb content from 1.74 eV to 1.53 eV in the VTE films and from 1.64 eV to 1.42 eV in the PLD films. The refractive index of the Sb-doped films strongly increased with the Sb content and reached the largest value for the PLD films. The results verify that both techniques are suitable for deposition of thin glassy films with high optical quality.

1 Introduction

Selenium-based chalcogenide glasses are very promising materials for optical applications since they possess a relatively high refractive index in combination with a good transparency in the infrared region [1–3]. This makes them suitable for fabrication of optical waveguides, transmitting the light in the long-wavelength region.

Recently there has been considerable interest in the study of the effect of As atoms substitution in the As–Se system by other elements, such as Sb [4]. The replacement of As by Sb does not alter the basic structure of the glass drastically since As and Sb are isovalent elements. At the same time the variation of composition influences their optical properties. In this paper the dependence of the optical parameters of VTE and PLD As–Se–Sb thin layers on the deposition technique and glass composition was studied.

2 Experimental

Four compositions of the glassy $(\text{AsSe})_{100-x}\text{Sb}_x$ alloys with ($x = 0, 5, 10, 15$ mol.% Sb), synthesized by melt-quenching technique as described elsewhere [5], were used for thin film preparation by vacuum thermal evaporation (VTE) and pulsed laser deposition (PLD). The VTE process was conducted from a special designed evaporator at a temperature of the evaporation source of 700–800 K, a source-substrate distance of 0.12 m, and a residual gas pressure in the chamber of 1.33×10^{-3} Pa. The substrates were rotated during the evaporation to avoid thickness and composition non-uniformities.

PLD was performed in a high-vacuum deposition chamber using an UV KrF* excimer pulsed laser ($\lambda = 248$ nm,

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$\tau = 25$ ns). The experiments were carried out at room temperature in vacuum 10^{-4} Pa. For the film deposition we applied 4000 subsequent laser pulses at a frequency repetition rate of 5 Hz with a laser beam focused to get an incident fluence of 1.6 J/cm^2 .

The optical transmission and reflection spectra of the thin films were recorded at room temperature in the range from 400 to 2500 nm using a double beam UV/VIS/NIR spectrophotometer (JASCO V-670). The wavelength accuracy of the instrument was ± 0.3 nm in the UV/VIS region and ± 1.5 nm in the NIR region. The experimental data were processed by a computer program based on the Swanepoel method.

3 Results and discussion

The transmission spectra of the thin As–Se–Sb films deposited by both techniques are shown in Fig. 1. The spectra clearly indicate a shift of the absorption edge to longer wavelengths after inclusion of Sb into the As–Se amorphous matrix.

The optical constants and the thickness of the films were calculated from the transmission spectra using a computer program based on the modified Swanepoel method [6]. The thickness of deposited films varies between 666 and

1123 nm and it depends on the Sb content and the deposition technique.

The absorption coefficient α for all investigated films was determined from the transmission and reflection spectra using the equation:

$$\alpha = 1/d[\ln(1 - R)^2/T], \quad (1)$$

where d is the film thickness while R and T stand for the film reflectance and transmittance, respectively. According to Tauc's relation for the allowed non-direct transitions, the photon energy dependence of the absorption coefficient can be described by

$$(\alpha h\nu)^{1/2} = B(h\nu - E_g), \quad (2)$$

where $h\nu$ is the effective photon energy, E_g the optical band gap and B a parameter which depends on the transition probability. The Tauc plots of $(\alpha h\nu)^{1/2}$ versus $h\nu$ for the VTE and PLD films are shown in Fig. 2 and the optical band gap energy E_g was evaluated from the intercept of the energy axis with the linear part of the curve in the high absorbing region ($\alpha \geq 10^4 \text{ cm}^{-1}$), known as Tauc extrapolation [7].

The influence of the Sb content on the optical band gap of amorphous $(\text{AsSe})_{100-x}\text{Sb}_x$ films prepared by PLD and VTE is presented in Fig. 3. The decrease of the band gap

Fig. 1 Transmission spectra of $(\text{AsSe})_{100-x}\text{Sb}_x$ thin films prepared by (a) VTE and (b) PLD

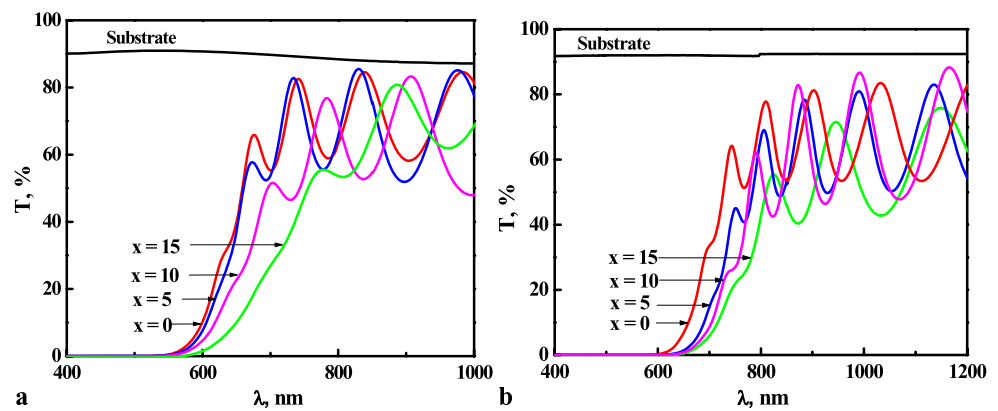
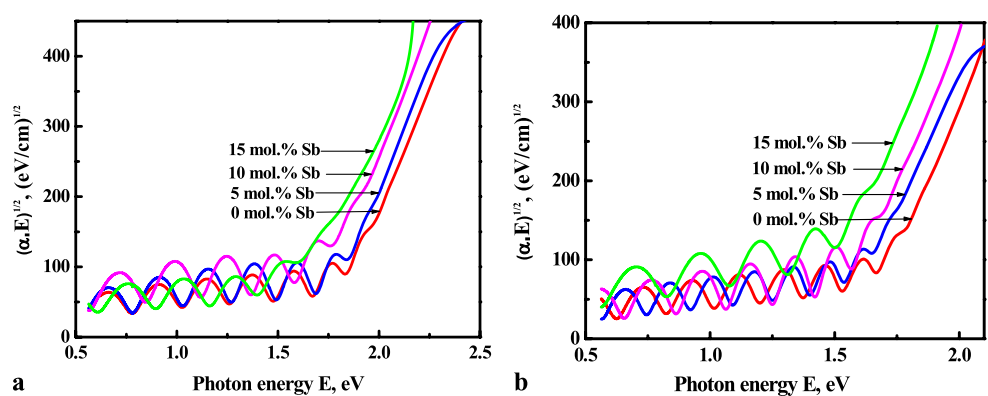


Fig. 2 Experimentally inferred graphs of $(\alpha h\nu)^{1/2}$ vs. $h\nu$ for (a) VTE and (b) PLD films



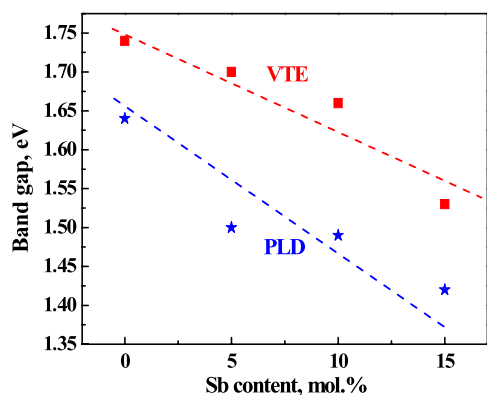


Fig. 3 Composition dependence of the optical band gap of amorphous (AsSe)_{100-x}Sb_x films prepared by VTE and PLD

after addition of antimony is attributed to structural transformation in the As–Se films due to Sb incorporation. According to P. Němec et al. the basic structural units in As₅₀Se₅₀ glass are AsSe₃ pyramids [8]. The addition of Sb into the As–Se matrix decreases the number of the AsSe₃ units by replacing them with SbSe₃ structural units. The atomic substitution of arsenic by antimony probably causes an increase of disorder and defects concentration, which results in reduction of the width of the optical gap. This can be explained by Mott and Davis model of the density of states in amorphous solids. According to this model, the width of localized states depends on the degree of disorder and defects present in the amorphous structure. As a result of incorporation of insufficient number of “foreign” atoms in the amorphous chalcogenide backbone structure, unsaturated bonds together with some saturated bonds (like dative bonds) are generated. These unsaturated bonds are responsible for the formation of narrow tails of localized states at the valence and conduction bands in the band structure, which leads to the decrease in the optical gap of the material [9].

The higher values of E_g of the VTE layers compared to PLD ones is due to the physical peculiarities of the deposition technique, inducing differences in the composition

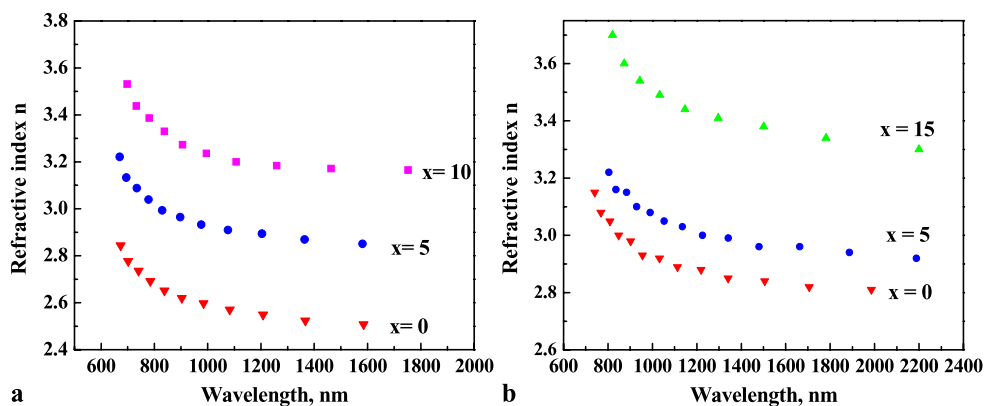
and structure of the obtained films. Indeed, as known thermal evaporation from single source could result in compositionally non-uniform films. On the other hand, the different structure of PLD and VTE thin layers can be assigned to difference in the energy of the particles deposited on the substrates. As the energy of these particles in the case of PLD is very high, they are more reactive and have better migration ability. As a result the obtained amorphous PLD films possess a lower degree of disorder, which makes them closer to the equilibrium state of the amorphous solid.

Figure 4 shows the spectral dependence of the refractive index $n(\lambda)$ of PLD and VTE films. The values of the refractive index for both types of films vary in the range of 2.5–3.5 and increase with the addition of antimony. This tendency is probably related to the structure and the higher polarizability of the larger Sb atoms (with an atomic radius of 145 pm) as compared to As atoms (with an atomic radius of 115 pm). The refractive index of the PLD films is slightly higher in comparison with the VTE films, which could be explained by peculiarities in their structure. This is in agreement with the data reported in [10].

4 Conclusions

Thin amorphous (AsSe)_{100-x}Sb_x films were obtained by VTE and PLD and their optical properties were investigated. The observed decrease of the optical band gap with the increase of Sb concentration is attributed to structural transformation and bond rearrangement in the films. The atomic substitution of As by Sb probably causes an increase of disorder and of the amount of defects present in amorphous structure and thereby decreases the optical band gap. The refractive index calculations show that the PLD films have a slightly higher index of refraction as compared to the VTE films. The increase of the refractive index with Sb content in both types of films is probably connected to the larger polarizability of the incorporated Sb atoms.

Fig. 4 Spectral dependence of the refractive index of (a) VTE and (b) PLD films



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