Optical study of thin $(As_2Se_3)_{1-x}(AgI)_x$ films

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The optical properties of chalcogenide thin films from the pseudo-binary $(As_2Se_3)_{1-x}(AgI)_x$ system, where x=5, 10, 15, 20, 25, 30 and 35 mol.% were studied with respect to the influence of AgI incorporation. Two techniques – vacuum thermal evaporation (VTE) and pulsed laser deposition (PLD) were applied to prepare the films. The films were amorphous, as revealed by X-ray diffraction (XRD); their morphology and topography studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM) exhibited uniform homogeneous surfaces. The optical transmission and reflection of the deposited $(As_2Se_3)_{1-x}(AgI)_x$ were investigated in the spectral region 300–3300 nm. The values of the optical parameters (refractive index, *n*, and extinction coefficient, *k*) were determined from the spectra. The compositional dependence of the basic optical parameters of the films, specifically their dependence on different AgI contents, was determined. The optical band gap Eg was determined from the Tauc plot $\alpha h\nu = B(Eg - h\nu)^2$ and the Eg^{04} in the strong-absorption region ($\alpha \geq 10^4$ cm^{-1}) from the relationship $\alpha = f(h\nu)$. The dispersion of the refractive indices and extinction coefficients and the observed trends in the band gap variation were discussed with respect to the influence of the AgI and film preparation methods.

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1. Introduction

Chalcogenide glassy semiconductors continue to attract the attention of scientists, because they possess very attractive properties and offer new approaches in engineering. Chalcogenide glasses are transparent in the VIS and IR spectral ranges [1-3], with relatively high refractive index ($2 \leq n \leq 3.7$), low optical losses ($\leq$ 0.3 dB/cm), especially if they are rapid thermal annealed [4]. It is well known that a number of photo-induced phenomena and structural transformations appear upon irradiation with band gap light. This makes them appropriate materials for optical recording [5], diffractive gratings [6], holography and micro-optics [7].

Arsenic selenide glasses are heavily studied materials, due mainly to their unique light induced effects [8, 9]. Superionic conducting glasses containing Ag ions have received much attention because of potential applications for batteries, sensors and displays. AgI-doped arsenic selenide glasses are also of interest, due to the superionic properties of AgI and its use as a sensitive detector. AgI, similar to CuI, is known to cross the As-Se layers, which causes defects in the layer structure pushing atoms out of the layer and causing it to crimp [10].

In this paper, we have studied thin films from the $(As_2Se_3)_{1-x}(AgI)_x$ system and have traced the role of AgI incorporated into the glassy AsSe in respect of their optical properties.

2. Experimental

The samples studied in the present work were $(As_2Se_3)_{1-x}(AgI)_x$ films, prepared by VTE and PLD onto BK7 glasses and single side polished Si wafers. Bulk samples were prepared by the well-known melt-quenching technique.

The thermal evaporation was performed in a Leybold LB 370 vacuum installation, with a residual gas pressure of 1.33×10^{-4} Pa, using a suitable tantalum crucible. The experiments were carried out with a constant geometry of the experimental setup and monitored with a Ni-Ni/Cr thermocouple at evaporation temperatures in the range 850-1000 K. To avoid non-uniformity in the thickness of the films the substrates were rotated during the deposition. In the second case, the PLD system was evacuated to a residual pressure less than 10^{-4} Pa prior to the laser deposition. The depositions were performed using a KrF excimer laser source (λ = 248 nm, $\tau_{FWHM} \geq 7.4$ ns) operating at a repetition rate of 2 Hz. The incident laser fluence was 3.3 J/cm^2. The basic properties of the $(As_2Se_3)_{1-x}(AgI)_x$ films have been thoroughly investigated by different techniques. Films with AgI up to 35 mol% added to As_2Se_3 glass were prepared by the VTE and PLD methods. The thickness of the studied layers ranged from 300 to 1300 nm. Measurement of the thickness was implemented by a Hitachi S4000 scanning electron microscope (SEM), a Dektak profilometer and a White Light Zygo interferometer. The surface topography of the films was investigated by atomic force microscope (AFM), using a NanoScope II in tapping mode. A UV/VIS/NIR Computer Controlled Spectrometer (Perkin Elmer Lambda 900) was used for measuring the optical transmission of the films in the range 300-3300 nm.

3. Results and discussion

The investigation by SEM of all freshly prepared VTE and PLD films revealed their smooth and homogeneous surface, typical of an amorphous phase as seen in Figs. 1 a, b. Cross-section SEM pictures - e.g. Fig.1 c, confirmed the compactness of the films in depth and the lack of inhomogeneities, suggesting good quality and adhesion of the coatings.

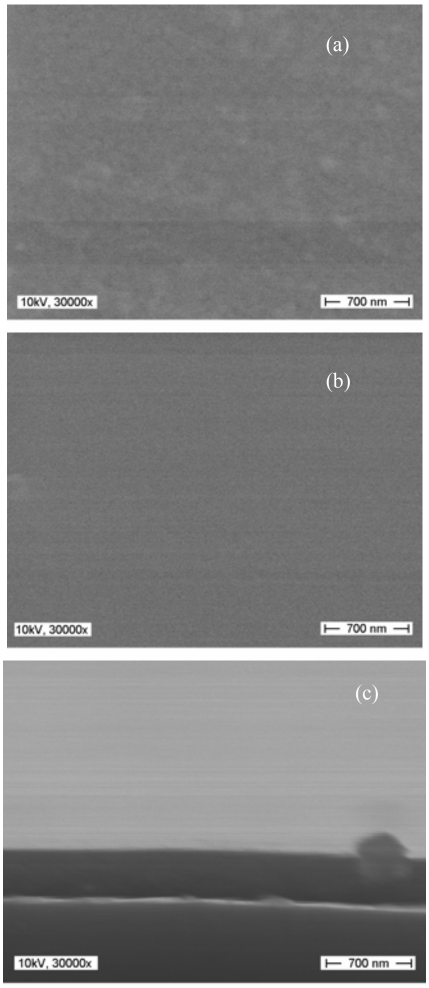


Fig. 1. SEM patterns of VTE (a) and PLD (b) film with compositions $(As_2Se_3)_{65}(AgI)_{35}$ and $(As_2Se_3)_{80}(AgI)_{20}$ respectively; cross section of VTE film with composition $(As_2Se_3)_{85}(AgI)_{15}$ (c).

The root mean-square (rms) roughness was estimated by AFM. The roughness of PLD films was lower, as compared with the VTE films. For example, the rms roughness of the $(As_2Se_3)_{95}$ $(AgI)_5$ film was 0.379 nm at the VTE film and 0.153 nm at the PLD one. The roughness increased with the AgI content in the samples. The VTE sample with 35 mol% AgI showed photosensitivity to the HeNe laser used in AFM and the surface of the film was changed after the scanning.

The results from the XRD investigation show the amorphous character of the films. A typical diffractogramm with a broad halo and lack of sharp peaks is given in Fig. 2.

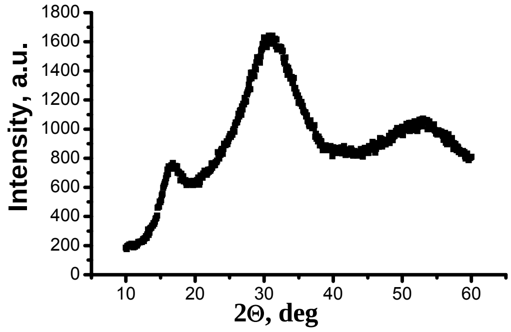


Fig. 2. XRD of a VTE film with composition $(As_2Se_3)_{95}(AgI)_5$

The transmission spectra of the films show very pronounced absorption in the region 300-600 nm. At wavelengths higher than 700 nm, they become transparent. The absorption edge is shifted towards lower wavelengths as the AgI concentration increases, as revealed in Fig.3. This trend is due to the incorporation of the narrow band gap semiconducting AgI into the disordered glassy network of As_2Se_3.

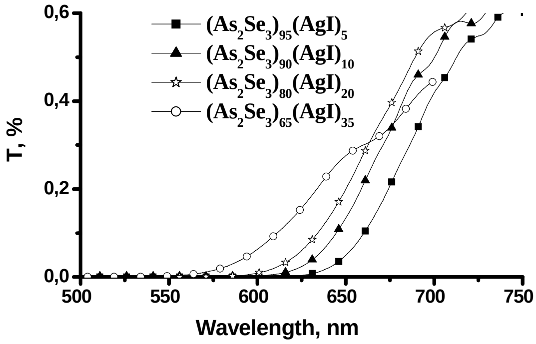


Fig. 3. Transmission spectra of VTE films.

The variation of the absorption coefficient α with the photon energy E was obtained from the transmission spectra.

The optical band gap energy, E_g, is defined using two methods:

- by means of the well-known Tauc's procedure

• taking as the optical gap, E^{04}, the energy at $\alpha = 10^4$ cm^{-1} or higher.

For the amorphous semiconducting materials. E_g can be derived from Tauc's law in the range of strong absorption ($\alpha \leq 10^4$ cm^{-1}):

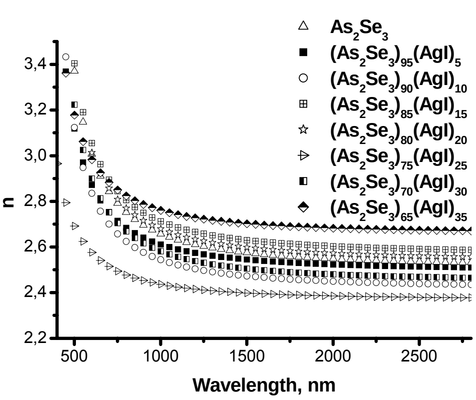
$$\alpha.\ h\nu = B\ (h\nu - Eg)^2 \qquad (1)$$

where $h\nu$ is the photon energy and B the slope of the Tauc edge. The Eg was determined by extrapolation of the linear part of the relation $(\alpha h\nu)^{1/2} = f(h\nu)$ to $\alpha = 0$. The values for Eg and Eg^{04} are shown in Table 1. The values were in the range 1.67 to 1.79 eV. The results show smaller values for PLD samples and marginal changes with AgI content. The small decrease in Eg, observed at the compositions with 20 mol% AgI, could be due to glass network structural transformations.

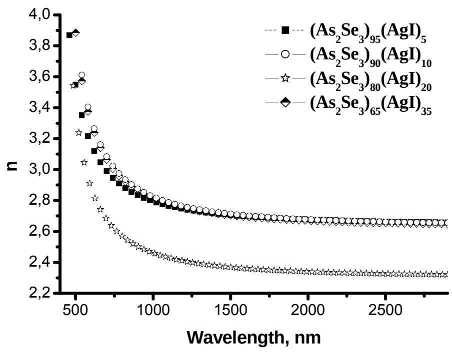
Table 1. Results for the optical band gaps of VTE and PLD films.

Composition	VTE films		PLD films	
	Eg, eV	Eg^{04}, eV	Eg, eV	Eg^{04}, eV
As_2Se_3	1.67	1.97		
$(As_2Se_3)_{95}(AgI)_5$	1.68	2.01	1.58	1.80
$(As_2Se_3)_{90}(AgI)_{10}$	1.69	2.04	1.60	1.84
$(As_2Se_3)_{85}(AgI)_{15}$	1.74	2.05		
$(As_2Se_3)_{80}(AgI)_{20}$	1.72	2.00	1.54	1.68
$(As_2Se_3)_{75}(AgI)_{25}$	1.76	2.03		
$(As_2Se_3)_{70}(AgI)_{30}$	1.77	2.05		
$(As_2Se_3)_{65}(AgI)_{35}$	1.79	2.10	1.64	1.90

The optical constants n (refractive index) and k (extinction coefficient) of the films were calculated from the transmission spectra, using (i) the Swanepoel method [11], (ii) a computer program developed by Konstantinov [12] and (iii) the Sellmeier equation which gives an empirical relationship between the refractive index n and the wavelength λ for a particular transparent medium. The spectral dependences $n(\lambda)$ are presented in Fig.4 a, b.



(a)



(b)

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

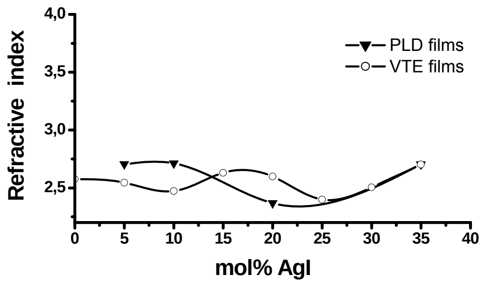
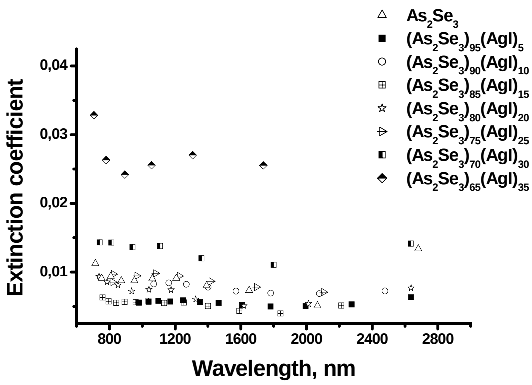


Fig.5. Refractive index at wavelength λ = 1500 nm as a function of AgI content in the As_2Se_3 glass

The dependence of refractive index n on the $(As_2Se_3)_{1-x}(AgI)_x$ film composition is shown in Fig. 5. It is seen that the refractive index for the two types of film varies in the range 2.4 – 2.71.

The spectral dependence k(λ) is shown in Fig.6 a, b.



(a)

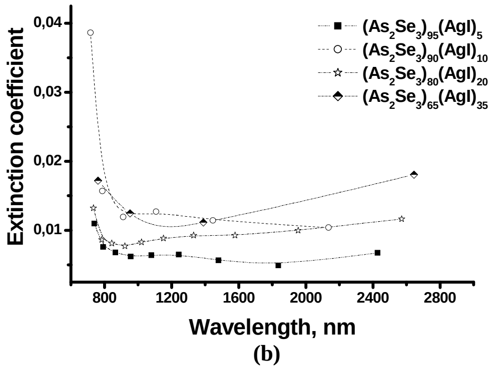


Fig.6. Spectral distribution of the extinction coefficient in VTE films (a) and PLD films (b).

The results obtained from the study reveal the good dielectric properties of films from the As_2Se_3-(AgI) system.

3. Conclusions

The results from the investigation of the optical properties of $(As_2Se_3)_{1-x}(AgI)_x$ films can be summarised as follows:

- Films obtained by the PLD method are smoother than VTE films
- The roughness increases with increasing AgI content
- Marginal changes in *Eg* and *n* with AgI content are associated with structural changes due to the AgI incorporation.

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