OPTICAL PROPERTIES OF CHALCOGENIDE $(As_2S_{1.5}Se_{1.5})_{0.99}:Sn_{0.01}$ THIN FILMS

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Abstract

In this work, we carried out measurements of optical constants (refractive index n, absorption coefficient α, extinction coefficient k, optical band gap E_g^{opt}) from transmission spectrum at strong and medium absorption regions on a thin film arsenic As-S-Se-Sn system prepared by a conventional melt-quenching technique. Photostructural transformations in amorphous films of $(As_2S_{1.5}Se_{1.5})_{1-x}:Sn_x$ (x = 0.01 at %) were investigated. The value of the photoinduced changing refractive index and band gap were obtained $\Delta n = 0.10$ (±0.02); $\Delta E_g^{opt} = 0.07$ (±0.01) eV. The refractive index and optical band gap before and after light exposure at $\lambda = 700$ nm is $n = 2.52 \div 2.62$ (±0.02) and $E_g^{opt} = 2.09 \div 2.16$ (±0.01) eV.

1. Introduction

Thin films of chalcogenide glasses are currently a subject of systematic research, among other reasons, because of the changes in physical and chemical properties, which take place in samples after illumination or annealing [1–6]. These photo- and thermally- induced processes offer the possibility of using amorphous chalcogenide semiconductors for high-density information storage, high-resolution display devices, fabrication of diffractive optical elements [7] as inorganic photo-resists for sub-micron technology [8]. In particular, As-S-Se system ternary mixed glasses are attractive candidates for all these important technological applications [9–11]. They also exhibit high photosensitivity which allows the direct writing of holographic patterns, such as Bragg gratings [12].

Special interest for the applications of chalcogenide amorphous films is connected with their metal doping, which alter optical, photoelectrical, and photochemical properties of the host material [13–15].

It is considered that the As-S system has a relatively low photosensitivity than the As-Se system, but the chosen As-S-Se system possesses maximum phase shift in infrared. At the same time, the doping of chalcogenide films with tin assists in stabilizing the glassy matrix with respect to light exposure and thermal treatment and increases the refractive index and photosensitivity [16–18].

As to the method for determining the optical constants of thin films, we must consider that, if the optical thickness of the film is sufficient to generate several interference extremes, it is possible to calculate the refractive index and extinction coefficient from the transmission spectrum alone [19].

2. Experimental

The bulk material of $(As_2S_{1.5}Se_{1.5})_{1-X}:Sn_X$ (x = 0.01 at %) was prepared by a conventional melt-quenching technique from elements heated together in an evacuated silica ampoule (T =

900ºC for approximate 30 h). After the synthesis, the melt was water-quenched, resulting in a bulk glass of the required chemical composition $(As_2S_{1.5}Se_{1.5})_{0.99}:Sn_{0.01}$ which was checked using Energy-Dispersive X-ray Spectroscopy. Thin films (thicknesses of 0.49, 0.61, 0.73 μm) were prepared by thermal evaporation from pieces of bulk glass (on VUP 10^{-5} mm Hg onto a glass substrate for t = 30 s to 15 min) and kept at room temperature. The sample thicknesses were measured by a Linnik MII-4 interferometer with an accuracy of 0.005 μm.

The optical transmission spectra at normal incidence were obtained over the 300-800 nm spectral regions by a Specord UV VIS double-beam computer-controlled spectrophotometer under and after exposure (with an accuracy of 0.5%). Chalcogenide thin films were exposed to a quartz halogen lamp with a IR filter (λ = 400-700 nm), a UV lamp with a filter (λ_{max} = 330 nm), Nd:YAG (DPSS) laser (λ = 532 nm), and He-Ne laser (λ = 633 nm). The relatively higher sensitivity was shown for Nd:YAG laser and halogen lamp. The influence of the light exposure on the optical transmission was examined after Nd:YAG laser illumination of the samples for 5, 10, and 30 min and were investigated at room temperature.

In the present work, the envelope method suggested by Swanepoel [19] (with an accuracy of 1%) and the Tauc method [20], which is based on the extremes of interference fringes, were applied for calculating the optical constants.

3. Results and discussion

3.1. Calculation of the refractive index and film thickness

Since the resulting spectrum does not have the transparency region (α = 0 or x = 1) the optical constants are calculated by the formula at strong and medium absorption regions respectively.

According to the Swanepoel's method [19], which is based on the idea of Manifacier et al. [21] of creating the envelopes of interference maxima and minima (Fig. 1), the first approximate value of the refractive index of the film *n,* in the spectral region of strong and medium absorption, can be calculated by the expression:

$$n = [N+(N^2-s^2)^{1/2}]^{1/2}, \quad (1)$$

where $s = 1.52$ (refractive index of the substrate) and

$$N = 2s\frac{T_{max}-T_{min}}{T_{max}T_{min}}+\frac{s^2+1}{2}. \quad (2)$$

Here T_{max} and T_{min}, are the transmission maximum and the corresponding minimum at a certain wavelength λ (Fig. 1).

Alternatively, one of these values is an experimental interference extreme and the other one is derived from the corresponding envelope; both envelopes were computer-generated using the origin version 7 program using more than one procedure. On the other hand, the necessary values of the refractive index of the substrate *s* are obtained from the transmission spectrum of the substrate T_S using the well-known Eq. [3] (and Fig. 1)

$$s = \frac{1}{T_S}+\left(\frac{1}{T_S^2}-1\right)^{1/2}. \quad (3)$$

Absorbance is given by the formula

$$\alpha = -\frac{Ln(x)}{d}, \quad (4)$$

where

$$\tilde{o} = \frac{(n+1)^3(n+s^2)}{16n^2s}T_0, \quad (5)$$

where T_0 is taken from the transmission spectrum at strong absorption.

The values of the refractive index n are calculated from the basic equation of interference extreme: $2nd = m\lambda$, where m is an integer for maxima and half-integer for minima.

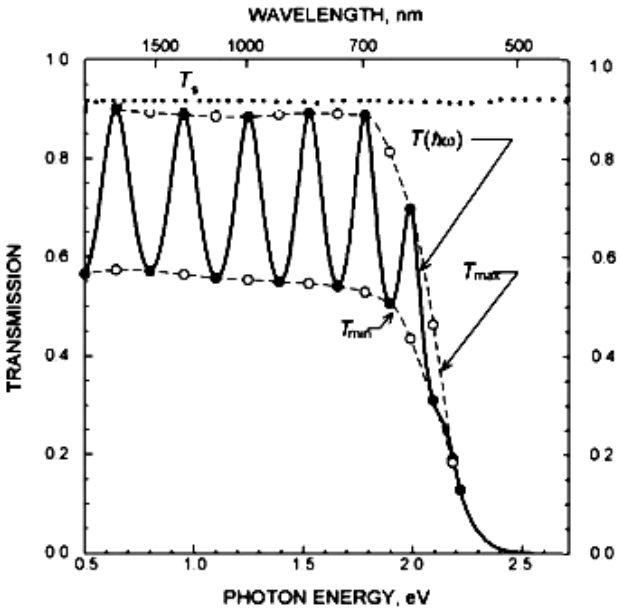


Fig. 1. Transmittance spectra for a thin film on a glass substrate with transmission Ts.

The transmittance T from Fig. 1 is a complex function: $T = T(\alpha, \lambda, s, d, n)$ But if we know s, the equation is simplified: $T = T(x, n)$, where x is the absorptive of the substance. The optical constants are calculated by formulae (1)-(5) and are all listed in the table.

3.2. Optical transmission and Tauc's plots

Transmission spectra of the given chalcogenide thin films onto glass substrate and glass substrate (refraction index $s = 1.52$) and dependences $T = f(\lambda)$, dispersion of refractive index $n = f(\lambda)$, Tauc's plots $(\alpha h\nu)^{1/2} = f(h\nu)$ and determination the optical band gap with the respective thicknesses of 0.49, 0.61, and 0.79 μm is shown below (Figs. 2-5).

Illumination of amorphous chalcogenide thin films by band gap light leads to appreciable changes in their optical and chemical properties and, as a result of illumination, the optical absorption edge shifts to longer wavelengths (see Fig. 2). It is the phenomenon of photodarkening. The displacement of the absorption edge under light exposure takes place for all films under study, and is accompanied by the respective modification in the refractive index (Fig. 3). Figure 4 represents the absorbance coefficient as a function of photon energy which shows increasing absorbance after exposure to the same quantity of photon energy. Figure 5 shows the optical band gap determined by the Tauc method of extrapolation.

Optical constants of virgin samples of amorphous $(As_2S_{1.5}\ Se_{1.5})_{0.99}$:$Sn_{0.01}$ thin films before/after (at saturation of 10 and 30 min) light exposure (at λ = 700 nm of transmission spectra).

d, μm	n±0.02	E_g^{opt}±0.01 eV	$\alpha x10^4 cm^{-1}$	Δn±0.02	ΔE_g^{opt}±0.01 eV
0.49	2.52/2.62	2.16/2.09	0.10/0.13	0.10	0.07
0.61	2.53/2.62	2.14/2.08	0.15/0.17	0.09	0.06
0.73	2.50/2.58	2.17/2.09	0.14/0.16	0.11	0.08

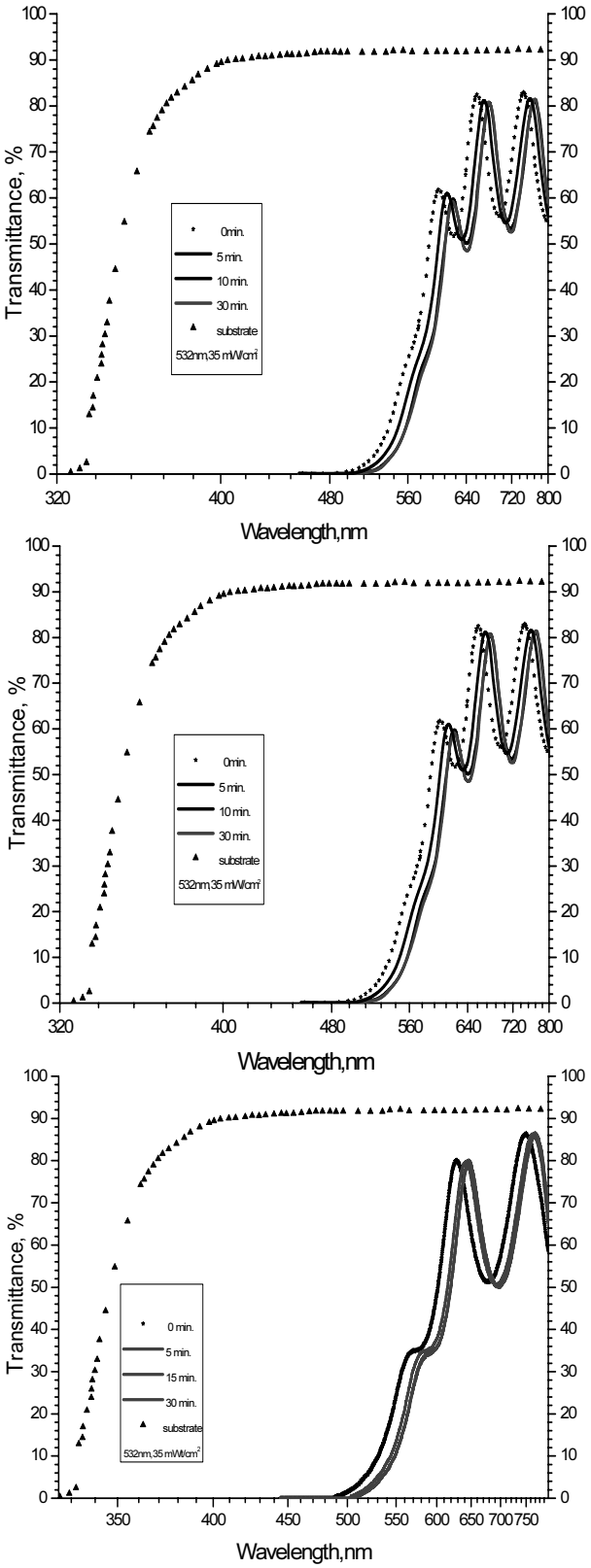


Fig. 2. Transmission spectra of thin films $(As_2S_{1.5}Se_{1.5})_{0.99}$:$Sn_{0.01}$ before and after exposure for thicknesses of 0.49, 0.61, and 0.73 μm (from bottom); T_S is the transmittance of the glass substrate.

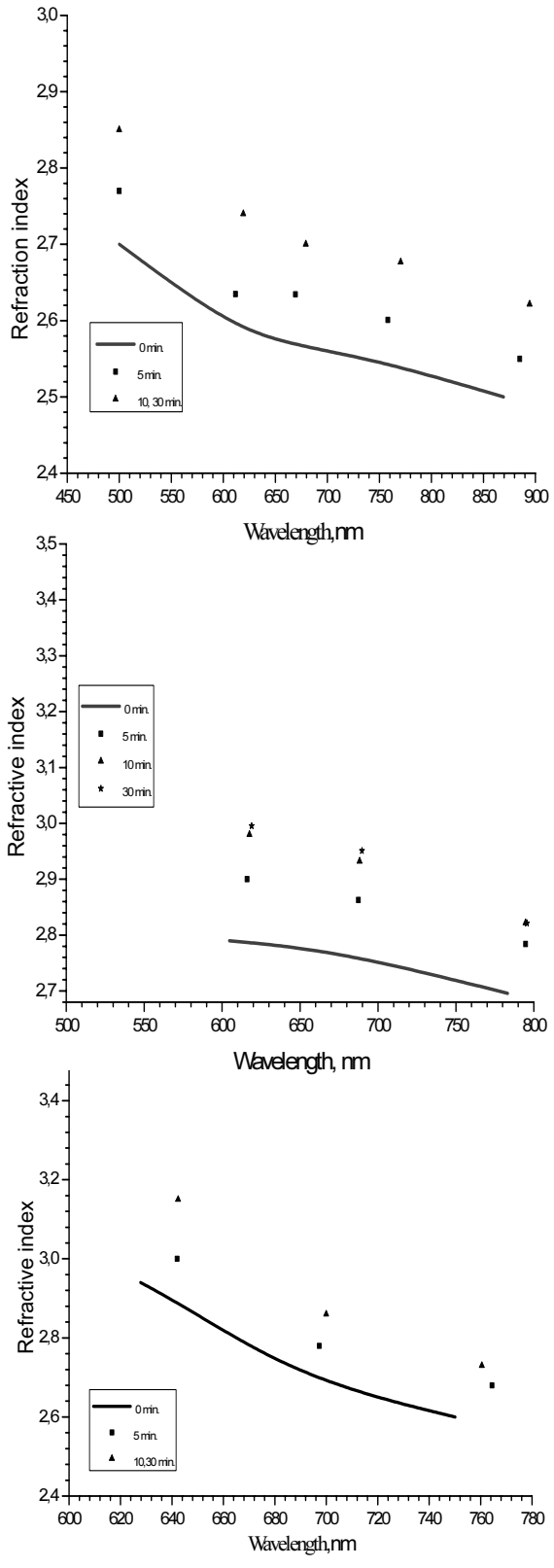
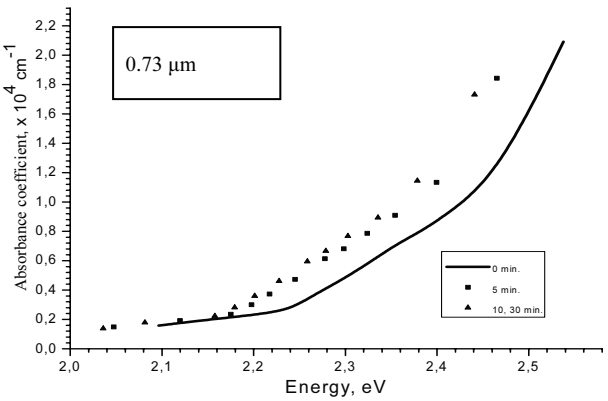
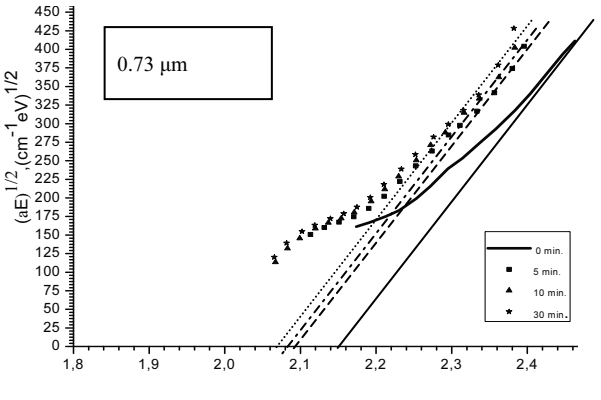
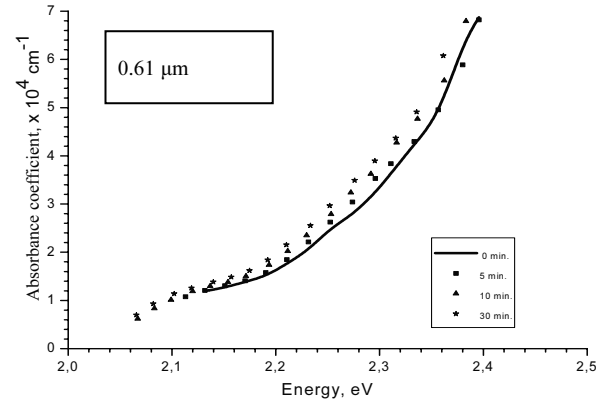
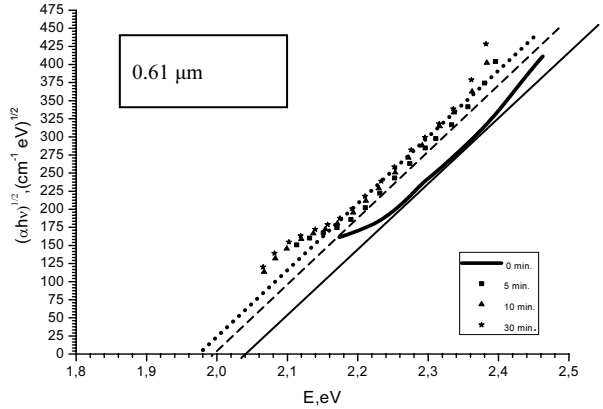


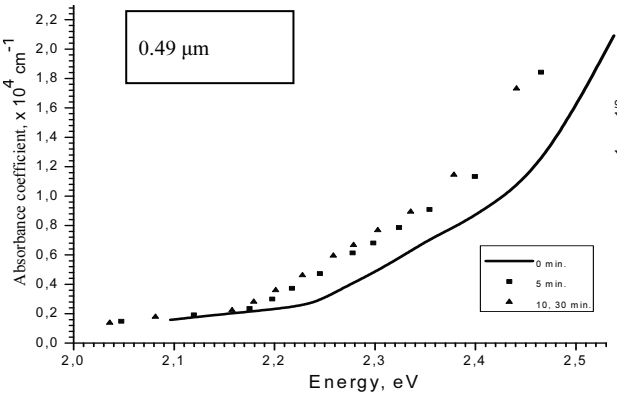
Fig. 3. Dispersion of refractive index of $(As_2S_{1.5}Se_{1.5})_{0.99}$:$Sn_{0.01}$ for thicknesses of 0.49, 0.61, and 0.73 μm (from bottom).











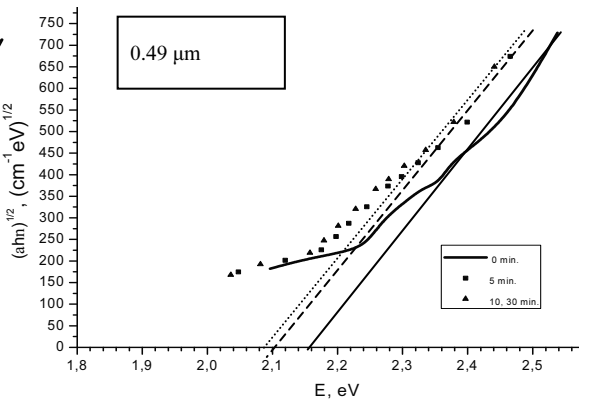


Fig. 4. Tauc's plot with inserting thicknesses.

Fig. 5. Determination the optical band gap with inserting thicknesses.

Conclusions

Photostructural transformations in amorphous $(As_2S_{1.5}Se_{1.5})_{1-x}:Sn_x$ (x = 0.01 at %) thin films were investigated. The influence of the light exposure on the optical transmission was examined after Nd:YAG laser illumination of the samples for 5, 10, and 30 min. As a result of illumination, the photostructure transformations as photodarkening in the material were observed. It means that the optical absorption edge ΔE_g^{opt} shifts to longer wavelengths. Average results of calculation of optical constants of thin films $(As_2S_{1.5}Se_{1.5})_{0.99}:Sn_{0.01}$ showed that before illumination: n = 2.52 ± 0.02 (at λ = 700 nm of transmission spectra); E_g^{opt} = 2.16 ± 0.01 eV. And after light exposition the results are: n = 2.62 ± 0.02 (at λ = 700 nm of transmission spectra); E_g^{opt} = 2.09 ± 0.01 eV; ΔE_g^{opt} = 0.07 ± 0.01 eV; Δn = 0.10 ± 0.02.

These large changes in refractive index and a small shift of the optical absorption edge allows using this material in the form of thin films of this composition for recording diffractive elements and channel waveguides.

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