

Some optical properties of thermally deposited $\text{Sb}_2\text{Se}_3:\text{Sn}$ thin films

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The optical properties of amorphous Sb_2Se_3 and $\text{Sb}_2\text{Se}_3:\text{Sn}_x$ ($x=0.01, 0.5, 10$ at. Sn %) prepared by vacuum evaporation on glass substrates was determined from transmission spectra. The band gap was found to be $E_g=1.30$ eV for amorphous Sb_2Se_3 and decrease with increasing of tin concentration up to $E_g=1.0$ eV for $\text{Sb}_2\text{Se}_3:\text{Sn}_{10.0}$. The maximum modifications of the refractive index under the light irradiation Δn ($\Delta n=0.20$) occur for the composition $\text{Sb}_2\text{Se}_3:\text{Sn}_{0.01}$. That allows us to conclude that doping of amorphous Sb_2Se_3 films with small concentrations of tin initiate the photostructural transformations under light irradiation, and make these materials suitable for registration of optical information.

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1. Introduction

The optical properties of chalcogenide glasses present a great scientific interest for the establishment of the general legitimacy of interaction of the optical irradiation with the amorphous solids, as well as a practical interest. The effect of light-induced photostructural transformations is characteristic for many amorphous chalcogenides films, and have been initiated a lot of applications of amorphous material in photonics and optoelectronics, especially as inorganic photo-resists for sub-micron technology [1]. Special interest for the applications of chalcogenide amorphous films is connected with doping with metal impurities, which alter optical, photoelectrical and transport properties of the host material [2-4]. At the same time doping of chalcogenide films by tin impurities assist in stabilizing the glassy matrix with respect to light exposure and thermal treatment [5,6].

The crystalline antimony selenide (Sb_2Se_3) is a layer-structured semiconductor with melting temperature $T_g=590$ °C [7]. The basic structural units are the $\text{SbSe}_3/2$ -pyramides. Sb_2Se_3 is a direct band gap semiconductor with orthorhombic crystal structure, and present a great interest due to its switching effects and its potential applications in photovoltaic devices [8-10]. Polycrystalline and amorphous Sb_2Se_3 films extend the possibilities of its application in photonics and optoelectronics [11,12]. The addition of the impurity such as Sn in amorphous Sb_2Se_3 films can provide a pronounced effect on electrical, transport properties, optical and photoinduced phenomena [13,14]. For the Sb_2S_3 , Sb_2Se_3 and Sb_2Te_3 also were demonstrated the amorphous-to-crystalline phase change induced by CW Ar^+ laser [15]. The photo-thermal processes are found to be responsible for the phase change in all antimony chalcogenides. It was found that the more potential candidate for use as the worm kind of storage devices is the Sb_2Se_3 films, having a minimum threshold power (about 100 W/cm²). The chalcogenide glasses

containing antimony also were investigated in order to obtain chemical microsensors and sensitive membranes for the detection of Cd^{2+} and Cu^{2+} ions in solutions [16,17]. In this paper are presented the experimental results of optical transmission spectra of thermally evaporated thin films (thickness ~ 1 μm) of Sb_2Se_3 and $\text{Sb}_2\text{Se}_3:\text{Sn}_x$ ($x=0.01, 0.5, 10$ at.%). The refractive index changes for different amorphous films in the $\text{Sb}_2\text{Se}_3:\text{Sn}_x$ ($x=0.01, 0.5, 10$ at. Sn %) under the light exposure and heat treatment is estimated.

2. Experimental

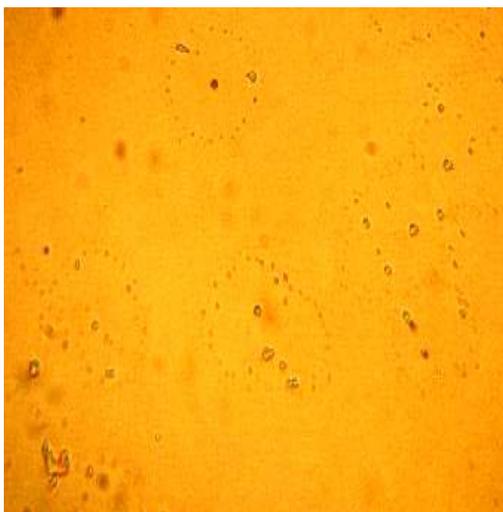
The Sb_2Se_3 and $\text{Sb}_2\text{Se}_3:\text{Sn}_x$ ($x=0.001, 0.5$ and 10 at.% Sn) were fabricated by "flash" thermal evaporation in vacuum ($p=10^{-5}$ Torr) of the initial synthesized material onto the clean glass substrates. The thickness of the films was about $d\sim 1$ μm . For optical transmission a UV/VIS (300÷800 nm) and 61 NIR (800÷3500 nm) Specord's CARLZEISS Jena production were used.

The influence of the light exposure on the optical transmission was examined by illumination of the samples during 1 hour by light with the intensity $F=50000$ Lux. The thermal treating effect was examined by annealing of a part of the films in vacuum at $T_{ann}=100$ °C during one hour. After the annealing and light exposure the optical transmission was registered in the same manner.

3. Results and discussion

The microscopically studies show that all as-deposited Sb_2Se_3 and $\text{Sb}_2\text{Se}_3:\text{Sn}_x$ are amorphous (Fig. 1a). The heat treatment and light exposure modify the morphology. Some crystalline clusters appear and which are distributed non-uniformly on the sample (Fig. 1b). The number and the size of clusters after the heat treatment and light

exposure increase when increasing the concentration of tin impurity in Sb₂Se₃ films.



a



b

Fig. 1. The morphology of the surface for the as-deposited (a) and after light exposure (b) Sb₂Se₃:Sn₁₀ films.

Fig. 2 shows the transmission spectra for as-deposited amorphous Sb₂Se₃ and Sb₂Se₃:Sn₁₀ films. The transmission spectra for Sb₂Se₃:Sn_{0.01} and Sb₂Se₃:Sn_{0.5} is situated in the intermediate region. The optical transmission T for thin films is determined by the expression:

$$T = \frac{(1-R)^2 \exp(-kd)}{1-R^2 \exp(-2kd)}, \quad (1)$$

where R is the optical reflection, k is the absorption coefficient, and d is the thickness of the amorphous film. Usually in the visible region the reflection is constant ($R \approx 20\%$).

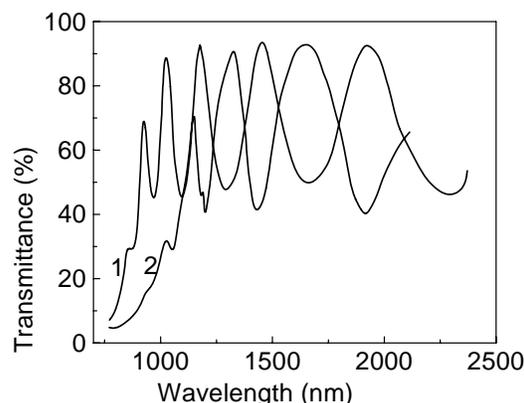


Fig. 2. The transmission spectra of amorphous Sb₂Se₃ (1, $d=0.8\mu\text{m}$) and Sb₂Se₃:Sn_{10.0} (2, $d=0.9\mu\text{m}$) thin films.

In the assumption that $R^2 e^{-2\alpha d} \ll 1$ from the equation (1) we can obtain the absorption coefficient, α

$$\alpha = \frac{1}{d} \ln \frac{(1-R)^2}{T} \quad (2)$$

The optical band gap E_g for as-deposited amorphous films was calculated from the relation:

$$(\alpha h\nu)^{1/2} = A(h\nu - E_g), \quad (3)$$

where A – is a constant. A plot $(\alpha \cdot h\nu)^{1/2} \sim h\nu$ (Tauc plot) yields a straight line and the extrapolation of the photon energy axis $(\alpha \cdot h\nu)^{1/2} \rightarrow 0$ give the values of the optical band gap, E_g .

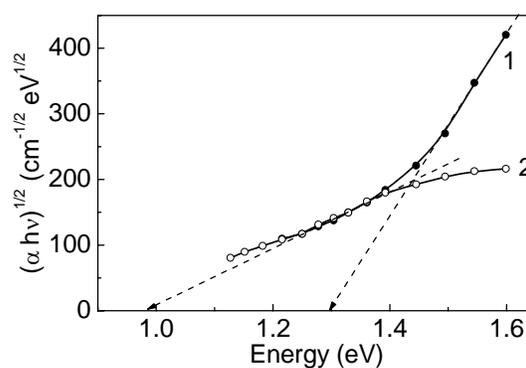


Fig. 3. The absorption edge of amorphous Sb₂Se₃ (1, $d=0.8\mu\text{m}$) and Sb₂Se₃:Sn_{10.0} (2, $d=0.9\mu\text{m}$) thin films.

The value of the optical band gap for amorphous Sb₂Se₃ films was $E_g=1.3$ eV. This value is in a good agreement with those obtained for the Sb₂Se₃ hollow nanospheres ($E_g=1.33$ eV) [18], and other published data for amorphous Sb₂Se₃ films ($E_g=1.25$ eV). Increasing the

Sn concentration in Sb_2Se_3 decrease the optical band gap, and for amorphous $Sb_2Se_3:Sn_{10}$ films $E_g=1.0$ eV.

For the semiconductor transparent thin film the transmission spectra, when the thickness d is comparable with the wavelength λ represents the pattern, presented on the Fig.4. For normal incident light the dependence of transmission T vs. wave-length λ , the refractive index n and the thickness d mathematically can be expressed as [19]:

$$T = \frac{(1-R)^2}{1+R^2-2R\cos\delta}, \quad (4)$$

were $\delta = \frac{4\pi}{\lambda}nd$ and $R = \left(\frac{n-1}{n+1}\right)^2$.

From (4) follow that in the transparence region of the spectra at the wavelengths

$\lambda_{max} = \frac{4nd}{m}$, $m=2, 4, 6, \dots$ we have the maxima, and at

the wavelengths $\lambda = \frac{4nd}{m}$, $m=1, 3, 5, \dots$ we have the minima.

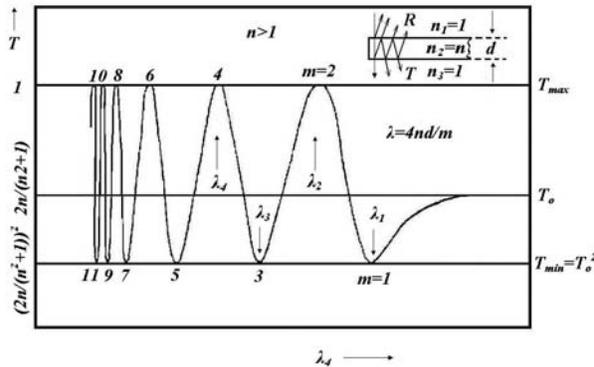


Fig. 4. The transmission spectra of thin film Semiconductor layer.

For each λ_m and λ_{m-1} , corresponding to the neighbor extremes in the transmission spectra, we can calculate the refractive index n :

$$n = \frac{\lambda_m \lambda_{m-1}}{2d(\lambda_{m-1} - \lambda_m)} \quad (5)$$

The dispersive curves of the refractive index n for amorphous Sb_2Se_3 films are presented on the Fig. 5. Light exposure and heat treatment slightly change the refractive index of Sb_2Se_3 .

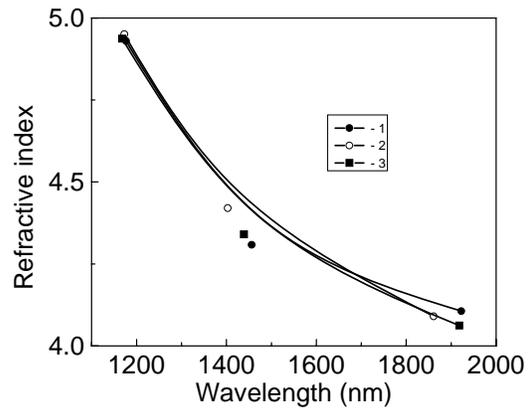


Fig. 5. The dispersion curves of the refractive index for amorphous Sb_2Se_3 thin films. 1 – as - deposited; 2 – illuminated, 3 – heat treated.

The refractive index depends on the Sn concentration in amorphous Sb_2Se_3 films, on light irradiation, and heat treatment. In the wavelengths region 1100÷2000 nm tin impurities (up to 0.5 at.% Sn) increase the refractive index (Fig.6), than for 10.0 at.% Sn, decrease. This may be due to the formation of new structural units, like SnSe and SnO_2 . For small concentrations of tin ($x=0.01$ and 0.5 at.% Sn) illumination and heat treatment increase the refractive index n .

The maxima changes in the refractive index Δn (about $\Delta n=0.20$) occur for the composition $Sb_2Se_3:Sn_{0.01}$ and $Sb_2Se_3:Sn_{0.05}$. That allows us to conclude that doping of amorphous Sb_2Se_3 films with small concentrations of tin initiate the photostructural transformations under light irradiation, and make these materials suitable for registration of optical information. The similar effect was observed for the amorphous Sb-Se-In films. Increasing of In atoms in Sb-Se-In films improve the optical information recording characteristics [20].

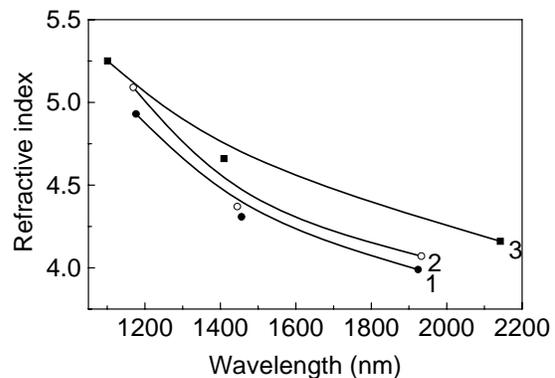


Fig. 6. The dispersion curves of the refractive index for amorphous Sb_2Se_3 (1), $Sb_2Se_3:Sn_{0.01}$ (2), and $Sb_2Se_3:Sn_{0.5}$ (3) thin films.

For the amorphous films with low concentrations of tin in Sb_2Se_3 (≤ 0.5 at. % Sn) the refractive index n increases under the light irradiation ($\Delta n > 0$, Fig. 7). i.e. the photodarkening effect take place.

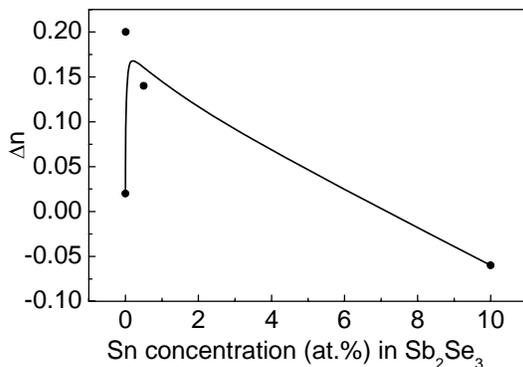


Fig. 7. Variation of the refractive index under the light exposure Δn vs. Sn concentration in amorphous Sb_2Se_3 thin films.

At the same time, at high concentration of tin (10 at. % Sn) in Sb_2Se_3 , the light irradiation decreases the refractive index ($\Delta n < 0$). That means that in this case the photobleaching effect take place.

Fig. 8 shows the dependence of the refractive index n on wavelength λ for as-deposited (1), illuminated (2) and heat treated (3) amorphous $\text{Sb}_2\text{Se}_3:\text{Sn}_{0.5}$ films. Light exposure and heat treatment in the same way increase the refractive index n .

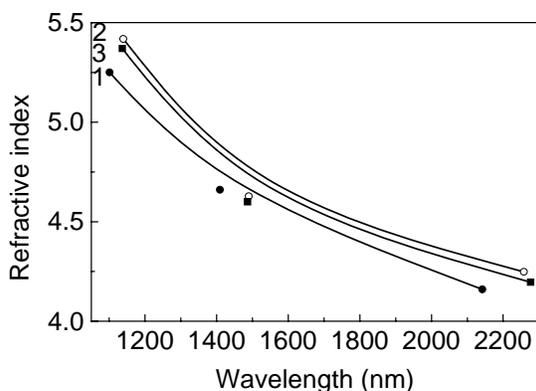


Fig. 8. The dispersion curves of the refractive index for amorphous $\text{Sb}_2\text{Se}_3:\text{Sn}_{0.5}$ thin films. 1 – as-deposited; 2 – illuminated, 3 – heat treated.

The increases of the refractive index under illumination and heat treatment, as was mentioned above can be used for optical storage devices with high capacities [13-15]. Moreover, changing the composition of the amorphous Sb_2Se_3 thin film using the different concentrations of tin impurities, we can create conditions for “negative”, as well as “positive” information recording process (Fig.7).

4. Summary

The optical absorption spectra of amorphous Sb_2Se_3 and $\text{Sb}_2\text{Se}_3:\text{Sn}$ ($x=0.01, 0.5, 10$ at. Sn %) thin films were used in order to determine the optical band gap and the refractive index. The band gap was found to be $E_g=1.30$ eV for amorphous Sb_2Se_3 and decrease with increasing of tin concentration up to $E_g=1.0$ eV for $\text{Sb}_2\text{Se}_3:\text{Sn}_{10.0}$. The maximum modifications of the refractive index under the light irradiation Δn ($\Delta n=0.20$) occur for the composition $\text{Sb}_2\text{Se}_3:\text{Sn}_{0.01}$. The obtained experimental results allow us to conclude, the amorphous $\text{Sb}_2\text{Se}_3:\text{Sn}$ are perspective for registration of optical information.

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