

Optical properties and photoconductivity of amorphous $\text{As}_2\text{Se}_3:\text{Sn}$ thin films

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Abstract — From scientific point of view, because the composition of chalcogenide glass (ChG) determine the kind of structural units and the mean coordination number, in the present work the amorphous films of the $\text{As}_2\text{Se}_3:\text{Sn}_y$ ($y=0\div 10.0$ at.% Sn) chalcogenide system was investigated. The transmission and photoconductivity spectra, photo-darkening relaxation and holographic characteristics of the amorphous films under study were measured. It was demonstrated that with increasing the concentration of tin in amorphous $\text{As}_2\text{Se}_3:\text{Sn}_y$ the effect of persistent photoconductivity was observed. The values of degree of modifications of the refractive index Δn under light irradiation and heat treatment were revealed. As a result of investigation of the photoinduced phenomena it was established that the more sensitive to light irradiation are the amorphous films of $\text{As}_{60}\text{Se}_{40}$ and $\text{As}_{50}\text{Se}_{50}$ compositions which exhibit big modifications of the refractive index ($(\Delta n/n) = 0.394$). The correlation between the photostructural and holographic characteristics was established.

Keywords: Amorphous materials, mechanical properties, optical transmission, refractive index, photo structural transformations.

EXPERIMENTAL

INTRODUCTION

The effect of light-induced photo-structural transformations is characteristic for many amorphous chalcogenides films, and they have been served as a base of many applications in photonics and optoelectronics, especially as inorganic photo-resists for sub-micron technology [1]. Special interest is connected of doping of chalcogenide glasses (ChG) with metal impurities, which alter optical, photoelectrical and transport properties of the host material [2-4]. At the same time it was shown that doping of ChG by tin impurities assist in stabilizing the glassy matrix in respect to light exposure and thermal treatment [5,6]. The interest in optical properties of amorphous semiconductors has been stimulated also by their possible applications as optical fibers in telecommunication systems and integrated optics for fabrication of different diffractive elements with high resolution.

It was shown that the addition of tin impurity in amorphous As_2Se_3 films can provide a pronounced effect on electrical, transport properties, optical and photo-induced phenomena [3-8]. In this paper the experimental results on some mechanical properties, optical, photoelectrical, and photo-induced characteristics of thermally evaporated thin films (thickness $\sim 1.0\div 3.0$ μm) of $\text{As}_2\text{Se}_3:\text{Sn}_x$ are presented. The transmissions spectra were used for calculate the absorption coefficient α , the optical band gap $E_{g, opt}$, as well as the dependence of the refractive index on composition, and its modifications Δn under light irradiation and heat treatment.

The glasses $\text{As}_2\text{Se}_3:\text{Sn}_x$ ($x = 0$ to 10.0 at.% Sn) were synthesized using initial materials of high purity (6N) of As, Se and Sn. More detail regarding the technology of preparation of different compositions of ChG are presented in [9]. Usually the synthesis of ChG is performed in quartz ampoules evacuated to a pressure of $p = 10^{-5} \div 10^{-6}$ Torr, placed horizontally in a furnace, equipped with rotating and vibrating devices. In the synthesis process the ampoule with the melt is rotate around its axis at a speed of 2÷3 rot/min with continuous vibration. The amorphous $\text{As}_2\text{Se}_3:\text{Sn}_x$ were obtained by thermal flash evaporation in vacuum ($p = 5 \cdot 10^{-5}$ Torr) of the initial synthesized material onto the glass substrate held at $T_{substr} = 100\div 120$ °C. The thickness of the amorphous films was in the range of $d \sim 1\div 3.0$ μm . For optical transmission a UV/VIS (300÷800 nm) and 61 NIR (800÷3500 nm) Specord's CARLZEISS Jena production were used. The investigation of the mechanical properties of $\text{As}_2\text{Se}_3:\text{Sn}_x$ ($x = 0 - 10.0$ at.% Sn) bulk and amorphous thin film samples was performed at PMT-3 device using Bercovici indentor. The hardness was calculated using the expression:

$$H_B = (1570 * P) / l^2, \quad (1)$$

where P- is the applied load, and L – is the height of triangle of remaining imprints[10]. Both in the case of the bulk samples and for amorphous thin films the applied load was 10g, and the depth of deposited imprints does not exceeded 20% of films thickness.

RESULTS AND DISCUSSION

The surface morphology was investigated for both bulk and amorphous $As_2Se_3:Sn_x$ ($x = 0 - 10.0$ at.% Sn) thin films. The experimental results of investigation of hardness for bulk and $As_2Se_3:Sn_x$ amorphous thin films are presented in Fig.1. In the Fig.1 also are presented the experimental results obtained earlier by Borisova [11]. The hardness values on bulk samples depending of Sn concentration in the $As_2Se_3:Sn_x$ glasses and vary between 100 and 110 kg/mm^2 . According to [11,12] the hardness of the $As_2Se_3:Sn_x$ amorphous thin films presents a non monotonous character in dependence on the Sn concentration. A sharp increasing of hardness is registered when the impurity concentration exceed the value of 3% ÷ 4% Sn.

The hardness of the films is generally higher than the hardness of bulk samples of the same chemical composition, which is known from the study of the mechanical properties of the films. the bulk $As_2Se_3:Sn_x$ varies between 150 and 160 kg/mm^2 due to the shape of the used indenter (in [11,12] was used Vickers indenter). Curves shape and hardness variation during of changes in chemical composition of samples have similar values.

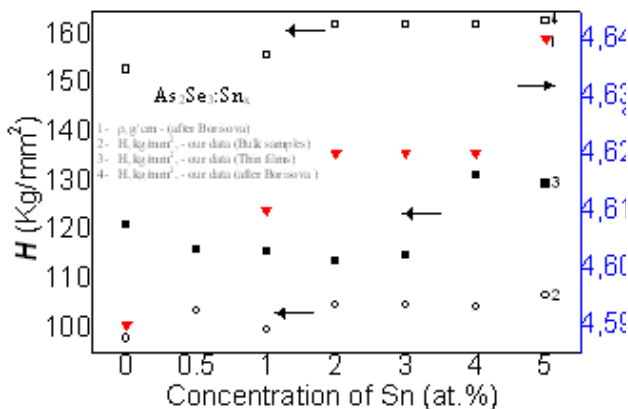


Fig.1. The density (1) and hardness(2) dependences for the $As_2Se_3:Sn_x$ ($x = 0 \div 10.0$ at.% Sn) vs. concentration of Sn. (2): hardness of bulk samples, (3) – the hardness for the amorphous films after our original data, and (4) – the hardness of the $As_2Se_3:Sn_x$ bulk samples after Borisova [11,12].

Tab.1. The values of hardness of bulk samples and amorphous thin films of $As_2Se_3:Sn_x$ ($x = 0 - 10.0$ at.% Sn).

Concentration Sn, %	Hardness of massive samples H, Kg/mm^2	Hardness of thin films H, Kg/mm^2
0	98,1112	121,1521
0,5	103,9009	116,092
1	99,84	115,7833
2	104,7696	113,9348
3	104,9942	115,0021
4	104,68	131,5123
5	106,9551	129,6286

Fig.2 represents the transmission spectra for as-deposited amorphous As_2Se_3 (1), $As_2Se_3:Sn_{0.5}$ (2) and $As_2Se_3:Sn_{2.0}$ (3) thin films. Increasing of the tin concentration in $As_2Se_3:Sn_x$ ChG shifts the absorption edge towards longer wavelength and decrease the absolute value of the transmission. As it seen from Fig.2 the transmission spectra represent a curve with maximums and minimums, and which allow us to determine the values of the refractive index n , and the dispersion of the refractive index $n=f(\lambda)$.

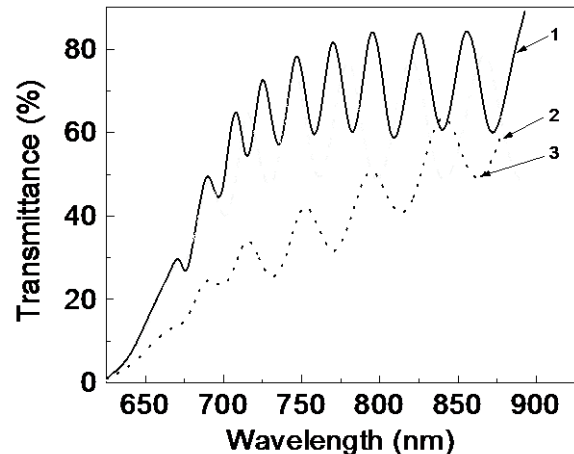


Fig.2. The transmission spectra for as-deposited amorphous $As_2Se_3:Sn_{0.5}$ (2) and $As_2Se_3:Sn_{2.0}$ (3) thin films.

Usually the optical transmission $T(\lambda)$ for thin films is determined by the expression:

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

where R - is the optical reflection, k - the absorption coefficient, and d - the thickness of the amorphous film. In the visible region the reflection R is constant and for calculations of the absorption coefficient was taken the value $R = 20\%$ [13,14].

As was mentioned above the increasing of Sn concentration in amorphous As_2Se_3 thin films shifts the absorption edge in the red region of the spectra and decreases the optical band gap [13].

Fig.3. represents the dispersion curves for amorphous layers of $As_2Se_3:Sn_x$ the dependence of the refractive index n of the concentration of tin, respectively. Significantly increase the concentration of tin leading to an increase of refractive index n . At concentrations of 2.0 at. % Sn, the refractive index n increases from $n=2.5$ to a value of $n = 4.5$.

The high values of the refractive index n of the amorphous $As_2Se_3:Sn_x$ thin films with high concentration of tin may be caused with the peculiarities of the structure of the ChG with high concentration of Sn. According to [6] the tin impurities increase in As_2Se_3 increase the transition temperature T_g and leads to the transition from the 2-D glass network to 3-D glass network, e.g. the trigonal structural units characteristic for As_2Se_3 are replaced by the tetragonal structural units.

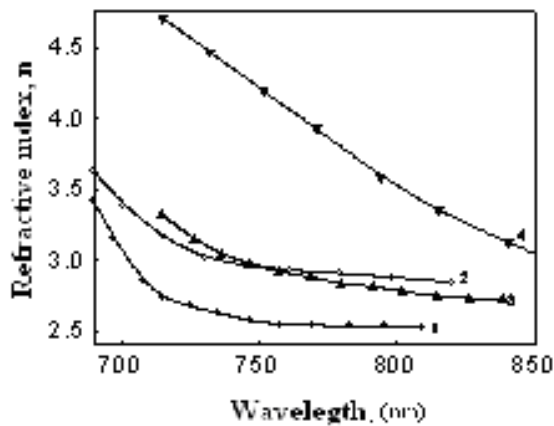


Fig.3. The dispersion curves of the refractive index $n=f(\lambda)$ for as-deposited amorphous As_2Se_3 (1), $As_2Se_3:Sn_{0.5}$ (2), $As_2Se_3:Sn_{1.0}$ (3), and $As_2Se_3:Sn_{2.0}$ (4) thin films;

Photocondarkening relaxation was measured for as-deposited amorphous $As_2Se_3:Sn_y$ ($y=0\div 10.0$ at.% Sn) thin films. The relaxation of the relative optical transmission $T(t)/T(0)$ of the amorphous $As_2Se_3:Sn_x$ films is shown in Fig.4. The experimental data show that for the films with increasing the tin concentration in $As_2Se_3:Sn_y$ the photodarkening is less pronounced, and almost is absent for the films with increasing of Sn concentration.

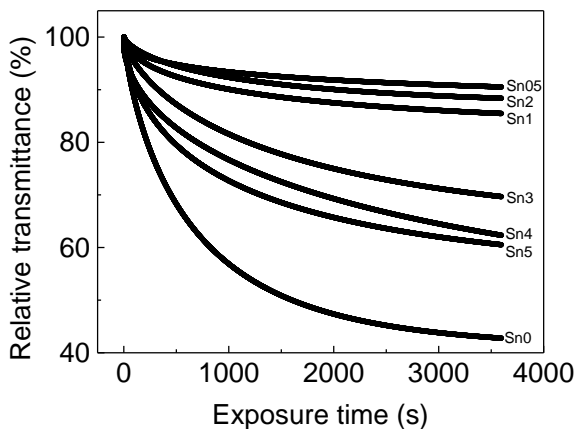


Fig.4. Photodarkening kinetics of as-deposited $As_2Se_3:Sn_x$ films with exposure time. The figures against the curves denote the amount of Sn impurity introduced into the source material, in at. %

At a constant light intensity the presented dependences characterize the decay of the film optical transmittance with the increase of the dose of absorbed photons. To obtain a unified basis for comparison of the transmission relaxation $T(t)$ curves we used so called stretched exponential presentation for the relaxation curves in the form:

$$T(t)/T(0) = A_0 + A \exp[-(t-t_0)/\tau]^{(1-\beta)}$$

Here t is the exposure time, τ is the apparent time constant, $A=I-A_0$ characterizes the “steady-state” optical losses due to photodarkening, t_0 and A_0 are the initial coordinates, and β is the dispersion parameter ($0 < \beta < 1$). For explanation of photodarkening in $As_2Se_3:A:Sn_x$ the

photoexcited charge carriers in extended states are considered as responsible for photodarkening. Unlike to the previous conceptions this model takes into account the layered cluster structure of a chalcogenide glass. According to this model, during exposure the layer is negatively charged due to capture of photoexcited electrons, and repulsive forces are built between the layers. These forces cause enlargement of the interlayer distance (leading to photoexpansion) and slip motion along the layers. This process alters interaction of lone-pair electrons between the layers leading to photodarkening effect.

The photodarkening phenomenon in chalcogenide glass films under illumination has no plain explanation up to now in spite of detailed investigation and a series of models advanced for interpretation of it. The red shift of the absorption edge indicating the narrowing of the optical gap of the film at photodarkening, is believed to be due to broadening of the valence band, the top of which is formed mainly by states of lone-pair electrons of the chalcogen atom. The non-monotony dependence of the parameters of the stretched exponential for $As_2Se_3:Sn_x$ samples is connected with the transition towards from 2D to 3D network with increasing the concentration of Sn. Creation of clusters such as $SnSe_2$ type lowering the density of the typical for AsSe lone-pair defects (D-centers), the charge state of the layers also is lowering, and the photodarkening phenomena is quenched.

Fig.5. represents the spectral distribution of the stationary photoconductivity of the amorphous $As_2Se_3:Sn_x$ thin films. The threshold located at 1.4 eV for all compositions is well distinguished, and which can be associated with a group of located states in the forbidden gap of the host material induced by the tin impurity.

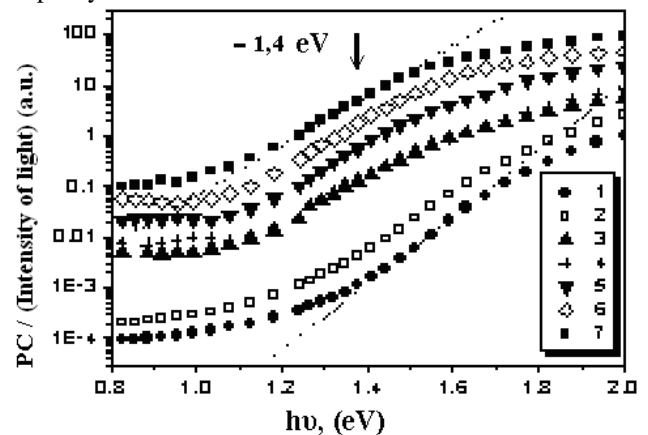


Fig.5. Photocurrent spectra of $As_2Se_3:Sn_x$ thin films at the temperature $T=310$ K for compounds x , at. % Sn: 1-0.0, 2-0.5, 3-1.0, 4-2.0, 5-3.0, 6-4.0, 7-5.0.

The persistence photoconductivity have been studied in As_2Se_3 amorphous layers doped with Sn impurities by combining methods for measuring the stationary photocurrent, transient photocurrent and photo capacitance. For photocurrent spectra and photo capacitance distribution energy of states of defects in the

band gap of amorphous layers $As_2Se_3: Sn_x$ ($x > 0.5$ at.% Sn) has been assessed. It was established that these states significantly contribute to the persistent photoconductivity.

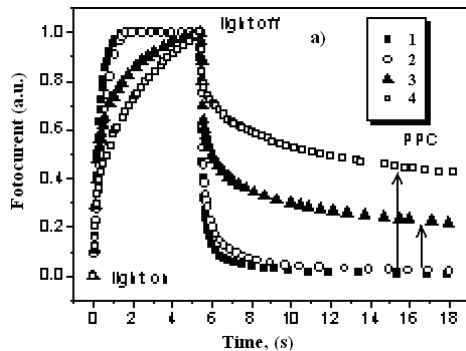


Fig.6. Relaxation of the stationary photocurrent for amorphous $As_2Se_3: Sn_x$, x : 1-0.0, 2- 0.5, 3-1.0, 4-3.0, $T=290$ K.;

The persistent photoconductivity (Fig.6) in the studied materials is caused of deeply localized defects states. Energy distribution of defects states with the center located at 1.4 eV, which have a lower energy than the band gap excitation energy was observed in all amorphous $As_2Se_3: Sn$ (Fig.5). With increasing of the Sn content in the amorphous $As_2Se_3: Sn$ thin films the percentage of the persistent conductivity increase (Fig.6), and this is a good opportunity for use this materials as modern photodetectors.

ACKNOWLEDGMENTS

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CONCLUSION

From optical transmission spectra of amorphous layers of $As_2Se_3: Sn_y$ were calculated values of refractive index n which depends on the composition of the glassy system. It was established that the Sn impurities reduce the photo-darkening, effect and increase the refractive index. The modifications of the refractive index under the light exposure and heat treatment also were investigated. Increasing of the Sn concentration in amorphous $As_2Se_3: Sn_y$ thin films make more

pronounced the effect of persistent photoconductivity. The experimental results on optical and photoelectrical properties on the amorphous $As_2Se_3: Sn$ thin films shows that they are perspective for elaboration of effective photo detectors and registration media for optical and holographic information.

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