

PHYSICAL AND OPTICAL PROPERTIES OF AMORPHOUS (As₂(Sb₂)Se₃)_{1-x}:Sn_x THIN FILMS

M.S.Iovu, D.V.Harea, E.P.Colomeico, E.Harea, I.A.Cojocaru

Institute of Applied Physics, Academy of Sciences of Moldova
dyanaharea@yahoo.com

Abstract: *The mechanical properties (the hardness H), the morphology, the ¹¹⁹Sn Mössbauer spectroscopy, and the Temperature Modulated Differential Scanning Calorimetry (MDSC) of amorphous (As₂Se₃)_{1-x}:Sn_x and (Sb₂Se₃)_{1-x}:Sn_x bulk samples and amorphous thin films were investigated in order to elucidate some aspects of the molecular glass structure. From the transmission spectra of amorphous films under study, the optical band gap E_g , absorption coefficient α , and refractive index n were estimated. It was established the degree of modification of the optical parameters under light irradiation and heat treatment of the amorphous thin films with different amount of Sn was studied.*

Keywords: *Chalcogenide glasses, hardness, light-induced phenomena*

I. Introduction

For the development of modern nanotechnologies, nanostructured and functional materials, chalcogenide glasses (ChG) present a big interest. Amorphous films of ChG have been served as a base of many applications in photonics and optoelectronics, especially as inorganic photo-resists for sub-micron technology, optical diffractive elements, sensors and photonic crystals [1-3]. Because the physical characteristics of bulk material, especially of amorphous thin films are not identical on the investigated area, the study of mechanical properties of As₂Se₃:Sn_x and Sb₂Se₃:Sn_x by nanoindentation is of great interests. Moreover, in the last years the research activities have been focused on photo-induced modifications of mechanical properties in bulk ChG and amorphous thin films. It was established that the plasticity of as-deposited and light irradiated amorphous As_xSe_{1-x} are different and depends on the composition [4]. As the composition of a chalcogenide glass determines both the structural units and the mean coordination number of the amorphous solids [5], the effect of the composition the influence of foreign impurity atoms on the light-induced modifications of optical properties of amorphous As₂Se₃:Sn_x and Sb₂Se₃:Sn_x thin films have been studied. Doping of amorphous As₂Se₃:Sn_x and Sb₂Se₃:Sn_x ChG with Sn impurities leads to the interruption of the two-dimensional (2-D) structure and transition is probably due to a more ionic character of the Sn-Se bonds (3-D). This fact strongly affects the mechanical, optical and light-induced properties of the ChG under study.

II. Experimental

The bulk As₂Se₃:Sn_x and Sb₂Se₃:Sn_x (x=0÷10 at.% Sn) materials were prepared from the elements of 6N (As, Sb, Se, Sn) purity by conventional melt quenching method. The thin film samples with thicknesses $d=0.5\div3.0$ μm were prepared by flash thermal evaporation of the synthesized initial glasses in vacuum onto glass substrates held at $T_{\text{subs}}=100$ °C. 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.

III. Results and discussions

Fig.1 shows variations in $T_g(x)$ for the bulk $As_2Se_3:Sn_x$ glasses, and the non-reversing heat $\Delta H_{nr}(x)$. One finds at low additive concentrations of Sn, T_g of the base glass to increase with x , suggesting that that the base glass becomes more connected. However, as x approaches 5% of Sn, T_g s show a threshold behavior.

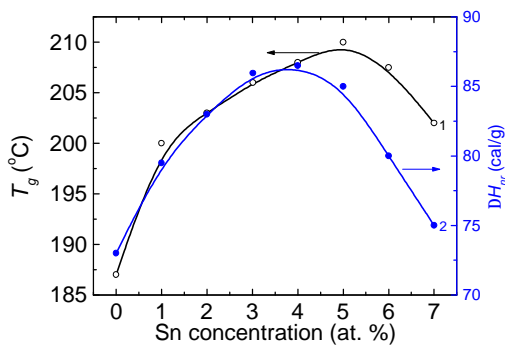


Fig.1. Variations in $T_g(x)$ (1), $\Delta H_{nr}(x)$ for $As_2Se_3:Sn_x$ glasses. The smooth lines are computer fitting.

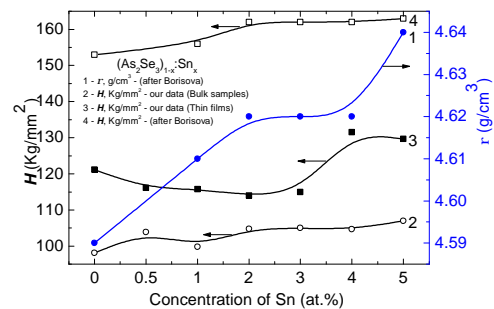


Fig.2. The density (1) and hardness (2 – bulk, 3 – thin films, 4 – bulk after [6]) dependences for the $(As_2Se_3)_{1-x}:Sn_x$ vs. Sn concentration.

The isomer-shift of the line in the Mössbauer spectroscopy experiments has been previously assigned to Sn that is tetrahedral coordinated to 4 Se near-neighbors as in a $Sn(Se_{1/2})_4$ local structure [7]. Apparently, introduction of Sn additive in As_2Se_3 base glass promotes growth of $Sn(Se_{1/2})_4$ units and leads the base glass to become As-rich. The latter leads of forming $As_2(Se_{1/2})_4$ and As_4Se_4 structural units. It was established that the hardness H of amorphous $As_2Se_3:Sn_x$ thin films is generally higher than the hardness of bulk samples of the same chemical composition (Fig.2). The hardness H of bulk $(As_2Se_3)_{1-x}:Sn_x$ varies between $H=150\div 160$ kg/mm² when the Vickers shape of the used indenter was used. For both bulk samples and thin films the hardness is lower according to the data [6]. This fact may be connected with some technological specifics in preparing the ChG. The microscopically studies show that all as-deposited Sb_2Se_3 and $Sb_2Se_3:Sn_x$ are amorphous (Fig.3). The heat treatment and light exposure modify the morphology. Some crystalline clusters appear and which are distributed non-uniformly on the sample. The number and the size of clusters after the heat treatment and light exposure increase when increasing the concentration of tin impurity in Sb_2Se_3 films.

The light-induced effect (“photodarkening” or “photoblanching”) in amorphous chalcogenide thin 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.

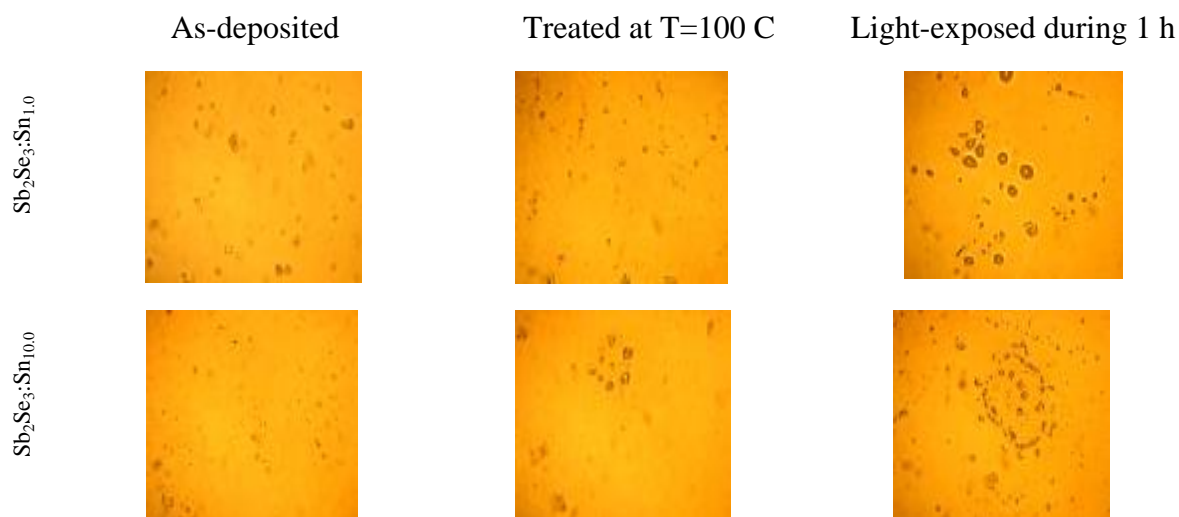


Fig.3. The morphology of the surface for the as-deposited (a), heat treated at $T=100^{\circ}\text{C}$, and light-exposed during 1 h of the amorphous (b) $\text{Sb}_2\text{Se}_3:\text{Sn}_x$ films.

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. Usually during the illumination the amorphous $\text{Sb}_2\text{S}_3:\text{Sn}_x$ thin films became less transparent and the refractive index n increase [8]. The dispersive curves of the refractive index $n=f(\lambda)$ for amorphous $\text{Sb}_2\text{Se}_3:\text{Sn}_x$ films, determined from the transmission spectra for different concentrations of Sn and for as-deposited, heat treated and light-exposed are presented on the Fig.4 and Fig.5, respectively. It was established that increasing of Sn amount in amorphous Sb_2Se_3 films, as well as the heat treatment and light-exposure increase the refractive index n .

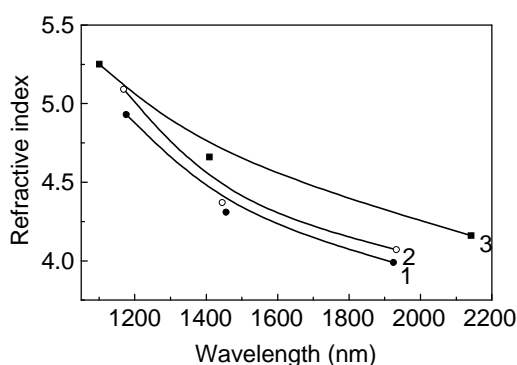


Fig.4. The dispersion curves of the refractive index for amorphous Sb_2Se_3 (1), $\text{Sb}_2\text{Se}_3:\text{Sn}_{0.01}$ (2), and $\text{Sb}_2\text{Se}_3:\text{Sn}_{0.5}$ (3) thin films.

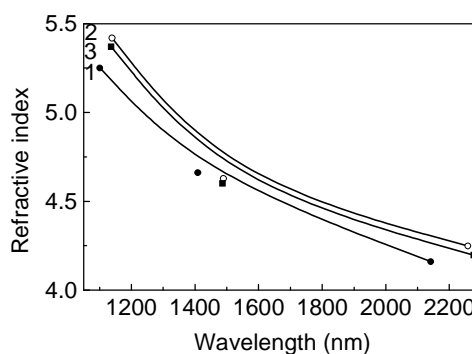


Fig.5. The dispersion curves of the refractive index for amorphous $\text{Sb}_2\text{Se}_3:\text{Sn}_{0.5}$ thin films. 1 – as-deposited; 2 – illuminated, 3 – heat treated.

Fig.6 represents the dependence of the excess absorbance induced by light absorption during the exposition for the As_2Se_3 films without Sn and doped with 2.0 at.% Sn for untreated (untr) and annealed (ann) samples. It was established that the effect of Sn concentration and of the heat treatment is of the same order. The dependence of the refractive index n ($I=720$ nm) and transmittance T under light exposure ($I=630$ nm) vs. Sn concentration of amorphous $\text{As}_2\text{Se}_3:\text{Sn}_x$ thin films are shown in the Fig.7. Increasing the Sn concentration linearly increase the refractive index n . The relaxation of photodarkening in amorphous $\text{Sb}_2\text{Se}_3:\text{Sn}_x$ and $\text{As}_2\text{Se}_3:\text{Sn}_x$ thin films have been studied using the procedure described in [7,8].

It was shown that the transmission relaxation $T(t)$ we used so called stretched exponential presentation in the form: $T(t)/T(0) = A_0 + A \exp[-(t-t_0)/\tau]^{(1-\alpha)}$. Here t is the exposure time, τ is the apparent time constant, A characterizes the exponent amplitude, t_0 and A_0 are the initial coordinates, and α is the dispersion parameter ($0 < \alpha < 1$). In order to explain the light-induced phenomena in amorphous $\text{Sb}_2\text{Se}_3:\text{Sn}_x$ and $\text{As}_2\text{Se}_3:\text{Sn}_x$ we have been used the model for photodarkening proposed in [9], in which the photoexcited charge carriers in extended states are considered as responsible for photodarkening. Unlike to the previous conceptions the new model takes into account the layered cluster structure of a chalcogenide glass. 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 latter process alters interaction of lone-pair electrons between the layers leading to photodarkening effect. The obtained experimental results in framework of the slip-motion model [9] may be used to estimate the behavior of Sn impurity in the photodarkening process in amorphous $\text{Sb}_2\text{Se}_3:\text{Sn}_x$ and $\text{As}_2\text{Se}_3:\text{Sn}_x$ thin films.

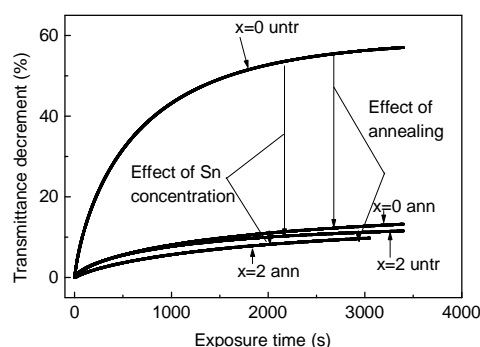


Fig.6. Excess absorbance induced by light absorption during the exposition for the As_2Se_3 films without Sn and doped with 2.0 at.% Sn for untreated and annealed samples.

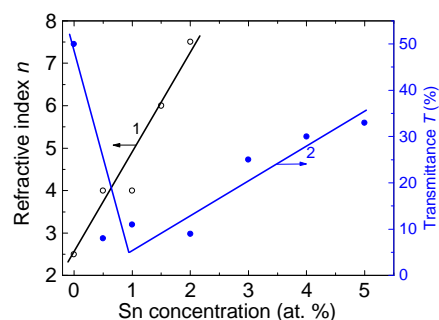


Fig.7. The dependence of the refractive index n ($I=720$ nm) and transmittance T under light exposure ($I=630$ nm) vs. Sn concentration of amorphous $\text{As}_2\text{Se}_3:\text{Sn}_x$ thin films

The effect of Sn impurity is manifested mainly through retardation of the photodarkening process. The time constant of the process in undoped films is several times increased after doping. The presence of Sn impurity strongly enhances the annealing effect in comparison with undoped film. The difference in photodarkening time constant for the untreated and annealed films became wicker. This fact clearly indicates the strong retardation of the slip motion of the structure layers due to presence of Sn impurity. Because the tin tends to create directional bonds when are introduced in the host glass some bridging bonds should appear between the layers. The structure of the glasses that contains tin impurity requires therefore some excess slip forces, i.e. leads to greater exposition doses and time constants. Furthermore, creation of clusters such as of SnSe_2 type may

lower the density of the typical for AsSe lone-pair defects (i.e. D-centers) thus lowering the charge state of the layers and, finally, the photodarkening.

IV. Summary

The optical transmission spectra of amorphous $\text{Sb}_2\text{Se}_3:\text{Sn}_x$ and $\text{As}_2\text{Se}_3:\text{Sn}_x$ thin films were used in order to determine the optical band gap E_g and the refractive index n , and its modification under light exposure and heat treatment. Photodarkening and its relaxation under light exposure in amorphous $\text{Sb}_2\text{Se}_3:\text{Sn}_x$ and $\text{As}_2\text{Se}_3:\text{Sn}_x$ thin films was studied in dependence on the Sn concentration and thermal treating. It was shown that Sn impurity effectively reduces photodarkening. Doping of amorphous chalcogenide films by tin impurities assist in stabilizing the glassy matrix with respect to light exposure and thermal treatment.

V. Acknowledgment

The authors are acknowledged the support under regular Project no. 11.817.05.03A.

VI. References

1. Aggarwal I.D., Sanghera J.S. Development and applications of chalcogenide glass optical fibers at NRL, *Journal of Optoelectronics and Advanced Materials*, Volume 11, Issue 3, 2002, pp. 665-678.
2. Andriesh A.M., Iovu M.S., In Series; *Optoelectronic Materials and Devices*, Volume 1, 2004, *Non-Crystalline Materials for Optoelectronics*, Eds. G.Lucovsky & M.Popescu, INOE Publishing House, Bucharest 2004, pp. 155-210.
3. Freeman D., Madden S., Luther-Davies B. Fabrication of planar photonic crystals in a chalcogenide glass using a focused ion beam, *Optics Express*, Volume 13, Issue 8, 2005, pp. 3079-3086.
4. Trunov M.L. Light-induced plasticity in chalcogenide glasses: evolution of plastic properties under irradiation, *Journal of Optoelectronics and Advanced Materials*, Volume 7, Issue 3, 2005, pp. 1223-1229.
5. Boolchand P., Georgiev D.G., Goodman B. *Journal of Optoelectronics and Advanced Materials*, Volume 3, Issue 3, 2001, pp. 703-720.
6. Borisova Z.U. *Chalcogenide semiconducting glasses*, Leningrad, 1983 (in Russian).
7. Boolchand P., Georgiev D.G., Iovu M.S. Molecular structure and quenching of photodarkening in $\text{As}_2\text{Se}_3:\text{Sn}$ amorphous films, *Chalcogenide Letters*, Volume 2, Issue 4, 2005, pp. 27-34.
8. Iovu M.S., Harea D.V., Colomeico E.P. Some optical properties of thermally deposited $\text{Sb}_2\text{Se}_3:\text{Sn}$ thin films, *Journal of Optoelectronics and Advanced Materials*, Volume 10, Issue 4, 2008, pp. 862-866.
9. Shimakawa K., Yoshida N., Ganjoo A., Kuzukawa Y., Singh J. A model for the photostructural changes in amorphous chalcogenides", *Philosophical Magazine Letters*, Volume 77, Issue 3, 1998, pp. 153-158.