PHOTOPLASTICAL EFFECTS IN AMORPHOUS As_2Se_3:Sn_X CHALCOGENIDES

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Abstract: In this paper the experimental results on some mechanical properties and photo-induced characteristics of thermally evaporated amorphous As_2Se_3:Sn_x (x=0,10 at.% Sn) thin films (d~2.0 mm) are presented. Investigation of photoplastical effect was performed *in-situ,* during illumination the bulk and thin film samples during indentation, as well as their indentation after illumination with green laser (λ = 532 nm) with power P = 50 mV/cm^2. The hardness was calculated from load-displacement curves by Oliver-Pharr method. A sharp increasing of hardness is registered when the tin concentration exceed the value of 3% ÷ 4% Sn. The hardness H of $(As_2Se_3)_{1-x}$:Sn_x films varies between H=115,130 kg/mm2. It was established that the hardness H of amorphous thin films is generally higher than the hardness of bulk samples of the same chemical composition. In this work, we focus our investigations on the mechanical characteristics of high-purity As_2Se_3:Sn_x thin films.

1. Introduction

Amorphous materials represent a new class of advanced materials exhibiting attractive combinations of properties such as high strength/hardness and excellent wear/ corrosion resistance [1–4]. These distinguished properties are primarily due to disordered atomic arrangement in the amorphous materials resulting in absence of grain boundaries and defects in the microstructure. While the non-equilibrium nature of amorphous materials offers outstanding properties, it also presents significant challenges in the processing of such materials.

The elements of group sixteen of the periodic table, are known as the chalcogens. The interest in chalcogenide As-Se films is engendered by their low optical losses, broad transparency range in the mid-IR, and good mechanical and physicochemical properties.

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 [5-6].

Photoplastical effect is manifested by hardening of illuminated materials [7], as well as by their softening [8]. Photoplastical effect depends on a number of factors such as: radiation power, temperature and wavelength. Study of spectral dependence of photoplasticity showed the maximum effect under samples illumination with wavelength close to the band gap value [9]. Photoplasticity in chalcogenide films were studied in [10-12], where the effect was observed during samples illumination with wavelength comparable to band gap value. Nature of photoplastical effect is carried out definitively yet. The effect was attributed to thermal expansion of the film due to absorption of exciting light, as well as recombination of electrons and holes under photo excitation.

The properties of glass can be varied and regulated over an extensive range by modifying the composition, production techniques. 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 [13-19].

2. Experimental

In this paper the experimental results on some mechanical properties of thermally evaporated amorphous As_2Se_3:Sn_x (x=0,10 at.% Sn) thin films (thickness d~2.0 mm) are presented.

The glasses As_2Se_3: Sn_x (x = 0 to 10.0 at.% Sn) were synthesized from the starting elements of 6N (As, Se, Sn) purity by a conventional melt quenching method. For both the practical application and scientific study of chalcogenide glasses, glass purity is of utmost importance. High purity glass ensures repeatability of experimental work, particularly when dealing with active properties of the glasses. Varying levels of trace impurities, even at levels of a few parts per million can alter the spectroscopic behavior of a glass. Similarly, impurities are a major concern for optical components. The starting components elements As_2Se_3 and Sn were mixed in quartz ampoules and then evacuated to pressure of P~10^{-5} torr, sealed and heated to temperature T=900 °C at the rate of 1 °C/min. The requirement for the sealed atmosphere is dictated by the volatile nature of many of the precursors which if melted in open atmosphere can result in large compositional changes or completes removal of components with low vapor pressures. This process also has the effect of trapping any impurities in the precursors within the glass as thus the precursor purity limits the ultimate quality of the glass that is produced. The quartz tubes were held at this temperature for 48 hours for the homogenization and then slowly quenched in the heating furnace. The amorphous As_2Se_3: Sn_x thin films were obtained by thermal flash evaporation in vacuum (p = 5 10^{-5} Torr) of the initial synthesized material onto the glass substrate held at T_{substr}=100÷120 °C. The thickness of the amorphous films was in the range of d~1÷3.0 mm.

3. Results and Discussions

Physical properties (e.g. density, hardness, glass transition temperature, electrical conductivity etc.) of amorfous As-Se films have been reviewed previously by Borisova [20,21].

The investigation of bulk, thin films and illuminated thin films samples was performed using nanohardnes tester NHT CSM. The hardness was calculated from load-displacement curves by Oliver-Pharr method. *In-situ* illumination of samples was carried with green laser (λ = 532 nm) with power P = 50 mV/cm^2. For change the direction of incident laser beam the optical glass prism was used (Fig.1). Maximum indentation load was 5mN, which allowed maximal penetration depth does not exceed 15% of film thickness.

The hardness was calculated using the expression:

$$H_B = (1570 * P) / L^2, \qquad (1)$$

where P- is the applied load, and L – is the height of triangle of remaining imprints [22]. 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.

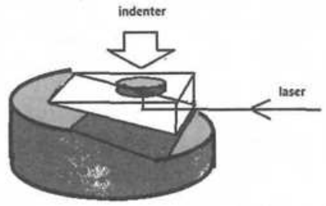

Fig.1. The experimental set-up for investigation of the photoplastical effect in chalcogenide glasses.

Fig.2 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 the base glass becomes more connected. However, as x approaches 5% of Sn, T_g show a threshold behavior [16].

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 [16]. 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.3).

The experimental results of investigation of hardness for bulk and As_2Se_3:Sn_x amorphous thin films are presented in Fig.3, and are in good agreement with experimental results obtained earlier by Borisova [20]. The hardness values of bulk samples depending of Sn concentration in the As_2Se_3:Sn_x glasses and vary between 1300 and 1700 MPa. The hardness of the amorphous As_2Se_3:Sn_x thin films presents a nonmonotonous character in dependence on the Sn concentration. An increasing of hardness is registered when the impurity concentration is around of 4% Sn.

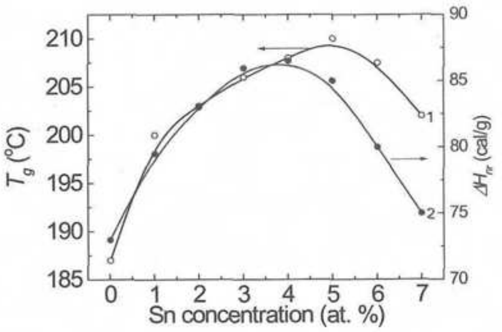

Fig.2. Variations in $T_g(x)$ (1), $\Delta H_{nr}(x)$ for As_2Se_3:Sn_x glasses. The smooth lines are computer fitting.

The hardness H of $(As_2Se_3)_{1-x}$:Sn_x films varies between 1730,1780 MPa. For both bulk samples and thin films the hardness is higher according to the data [20,21]. This fact may be connected with some technological specifics in preparing the ChG.

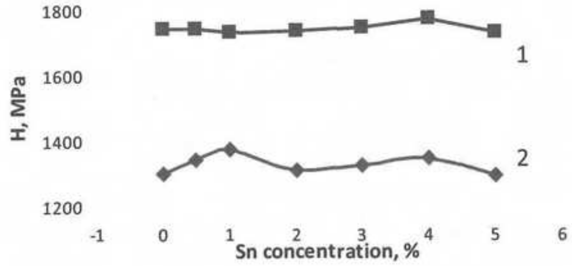

Fig.3. The hardness H of $(As_2Se_3)_{1-x}$:Sn_x. samples, thin films (1) and bulk (2).

In the present paper we report the experimental results on investigation of the photoplastical effect in amorphous As_2Se_3:Sn_x thin films (fig.4, Table 1). In the paper [16] on the base of the "slip-motion" model was shown that the photo-excited carrier play an important role in the processes of photoinduced phenomena in amorphous semiconductors. Athermal light-induced plasticity in cristalline semiconductors under light illumination causes decrease of hardness. This effect was interpreted in terms of increasing of the mobility of dislocations due to photoinduced increase of carrier concentration. In our experiments the photomechanical properties of As_2Se_3:Sn_x was performed at NHT-SCM nanohardness tester.

The nanohardness testers operate dynamic mod of data collection, and calculate hardness values using projected imprint area when indenter is unloaded. During in-situ illumination of studied films, hardness decreasing was observed (Table 1 and Fig.4). Photoelastic effect becomes more visible when Sn concentrations increase. Under the illumination the nanohardness of amorphous As_2Se_3:Sn_x thin films decrease. This effect is more pronounced for the compositions with Sn concentration more than 1.0 at. %. Decreasing of nanohardness under illumination also was observed for as-deposited and annealed amorphous $As_{40}Se_{60}$ thin films [22].

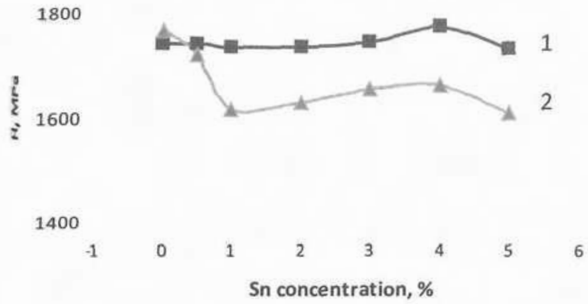

Fig.4. The hardness H of $(As_2Se_3)_{1-x}$:Sn_x as-deposited thin films(1) and iluminated(2)

A microscopic model of this phenomenon is based on the assumption of the athermal decrease in the viscosity of the films during irradiation, which is close to the viscosity of vitreous semiconductors near their glass transition temperature T_g [23]. It was suggested that the photoviscous effect, that is, the athermal decrease of viscosity of non-crystalline chalcogenide upon illumination is the key for a considerable photoinduced effects in different amorphous chalcogenide films [24].

Table 1. The hardness vs. Sn concentration for amorphous As_2Se_3:Sn_x thin films.

Nr.	Film composition	H (MPa) As-deposited films	H (MPa) Illuminated films	H (MPa) Bulk samples
1	As_2Se_3	1780	1768	1300
2	As_2Se_3:$Sn_{0.5}$	1762	1783	1341
3	As_2Se_3:$Sn_{1.0}$	1734	1614	1376
4	As_2Se_3:$Sn_{2.0}$	1735	1628	1311
5	As_2Se_3:$Sn_{3.0}$	1745	1656	1327
6	As_2Se_3:$Sn_{4.0}$	1774	1660	1347
7	As_2Se_3:$Sn_{5.0}$	1732	1607	1297

Fig.5 represents the changes of the surface morphology of the as – deposited amorphous As_2Se_3:$Sn_{0.1}$ thin film under the indentation load after light illumination (a) and before light illumination (b, upper patterns). For comparison, in the downside of the Fig. 5 the pictures of the light-induced anisotropic plasticity in amorphous $As_{20}Se_{80}$ thin films are shown: a – the image of non-irradiated film surface, and b – the image of this surface by irradiated linearly polarized laser beam (l = 633 nm) [23]. In both cases it is observed that after light irradiation the plasticity of the investigated amorphous films increase.

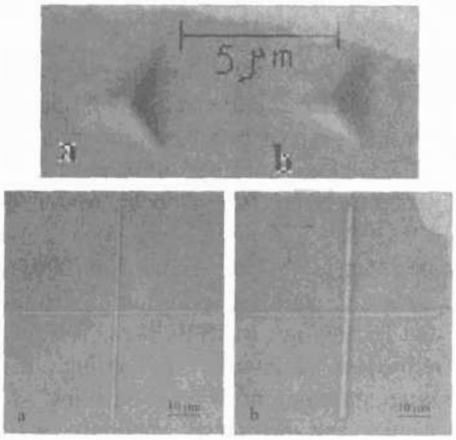

Fig.5. The surface morphology of the as – deposited amorphous As_2Se_3:$Sn_{0.1}$ thin film under the indentation load after light illumination (a) and before light illumination (b, upper patterns). For comparison, in the downside of the figure the pictures of the light-induced anisotropic plasticity in amorphous $As_{20}Se_{80}$ thin films are shown: a – the image of non-irradiated film surface, and b – the image of this surface by irradiated linearly polarized laser beam (l = 633 nm) [23].

For explanation of this phenomena the authors [25] the mechanical model of anisotropic plasticity in chalcogenide glasses have been proposed, according to which the anisotropic softening consists in the weakening of mechanical compliance in the direction to be orthogonal to the light polarization.

5. Conclusion

The mechanical properties of chalcogenide glasses play critical role for their realistic applications and are intimately connected with their structure as well as physical and chemical properties. The paper reports the effect of additives Sn on the micro-hardness and related thermo-mechanical properties of glassy As-Se alloy. We have found that that micro-hardness of binary As-Se alloy is changed significantly after the incorporation of Sn additives as chemical modifiers. Possible explanations of "metal-induced effects" on thermo-mechanical properties of glassy As-Se alloy are also discussed. The interrelation between mechanical properties of As_2Se_3 chalcogenide glasses and thin films on their base has been determined. The necessity of the combined studies of the mechanical properties for the prediction of the wear resistance has been shown. The effect of the additional stress originating under friction should be taken into account in the explanation of the deviations from the found relationships between wear resistance and mechanical parameters.

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