THE RELAXATION OF PHOTODARKENING IN Sn DOPED AMORPHOUS As$_2$Se$_3$ FILMS

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Photodarkening relaxation under light exposure of a-As$_2$Se$_3$ amorphous films doped with 0.5-5.0 at.% Sn was studied for its dependence on the concentration of impurities and thermal treatment. Both factors reduce photodarkening with the degree of reduction dependent on the concentration of impurity. The relaxation process may be described by a stretched exponential with the dispersion parameter $0.1 \leq \alpha < 0.6$ and the time constant increasing with tin concentration or thermal annealing. The results are discussed in the frame of the "slip-motion" model of photodarkening in chalcogenide glasses taking into account the peculiarities of the glass structure.

1. Introduction

The effect of light-induced photodarkening is characteristic to amorphous chalcogenides films and presents scientific as well as practical interest [1-4]. The interest is mainly due to considerable changes in the optical absorption edge of the amorphous material associated with the photostructural transformations. The arsenic selenide amorphous films usually become darkened under action of light situated in the region of fundamental optical absorption (h$\nu \geq E_g$) and the so-called photodarkening effect takes place. Because the composition of a chalcogenide glass determines the specific structural units and the mean coordination number [5,6], the effect of the composition in glassy systems As-Se and As-S on the photostructural transformations has been studied in detail [7,8]. In the same time little attention was paid to the influence of foreign impurity atoms introduced in the glass upon, although earlier in 1978 [9] it was remarked that the photodarkening is influenced by doping of amorphous chalcogenide films with Cu impurities. Recently, we have demonstrated that Sn and Mn, and rare earth foreign impurity atoms (Dy, Pr, Sm) influence the photodarkening relaxation in as-deposited and annealed amorphous As$_2$Se$_3$ thin films [10, 11].

In the present paper we report the results of the study of the photodarkening relaxation in pure amorphous As$_2$Se$_3$ thin films and in films doped with various amount of Sn (0.5 to 5.0 at. % Sn). Tin, which is prone to formation of tetrahedrally coordinated sites, affect the network of the host glass by inducing changes in both short-range as well as medium range order. From the X-ray diffraction data, tin in arsenic chalcogenide glasses appears as a network former, which increases the effective thickness of the structural quasi-layers and the inter-layer distance [12]. Tin as a dopant also serves as a model probe atom to permit local structural characterization of the impurity in a chalcogenide glass [13,14] by Mössbauer spectroscopy.

The tin impurity significantly affects the absorption edge making the slope of its exponential part to decrease, widens the photoconductivity spectral interval and retards the recombination of photogenerated holes [15,16]. Furthermore, the particular fact that the metal impurities induce

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changes in photodarkening kinetics, presents special interest regarding the recent photodarkening model [1]. This model takes into account the layered cluster structure of a chalcogenide glass as well as the photoexcited charge carriers in extended states, which are responsible for photodarkening. As a result it was suggested that the foreign metal impurities in chalcogenide glasses induce changes in the intermediate order, which restrict mutual slip motion of the structural quasi-layers.

2. Experimental results

2.1 Experimental details

Tin was introduced in amount of 0.5-5.0 at.% into As_2Se_3 during standard thermal synthesis of the materials prior to deposition. Thin film samples of thickness $L = 2$-$3\ \mu m$ were prepared by flash thermal evaporation in vacuum onto glass substrates held at $T_{subs} = 100\ ^oC$. A He-Ne laser ($\lambda = 0.63\ \mu m, W = 4\ mW$) was used as a source of light. The total transmittance of the film was currently measured during the exposure time with the aid of a registration module. The experimental set-up included a digital build-in PC-card for data acquisition PCI-1713A connected with the photodetector. Special software was elaborated for automatic measurements. The thermal treating effect was examined by annealing of a part of the films in vacuum at $T_{ann} = 120\ ^oC$ during one hour. After the annealing the optical transmission relaxation under light exposure was registered in the same manner.

For Mössbauer spectroscopy we have synthesized a glass sample of $As_2Se_3(^{119}Sn)$ containing 1 wt % of ^{119}Sn. Here the purpose was to examine the local chemical environment of the Sn dopant in the As_2Se_3 base glass.

2.2. Mössbauer investigation

Using the Mössbauer spectroscopy of a glass sample of As_2Se_3:(^{119}Sn) containing 1 wt % of ^{119}Sn, we have examined the local chemical environment of the Sn dopant in the As_2Se_3 base glass. Fig. 1 shows the Mössbauer spectrum of the glass sample recorded at 78 K with an emitter of ^{119m}Sn in a $CaSnO_3$ matrix.
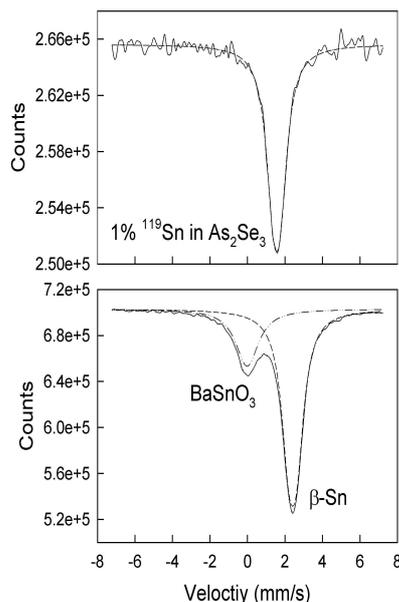
Fig. 1. ^{119}Sn spectra of indicated samples taken at 78 K using a standard constant acceleration. (drive and NaI detector with Pd filter).

The spectrum reveals a single line with an isomer shift of 1.55(2) mm/s. The shift is characteristic of tetrahedral Sn(Se$_{1/2}$)$_4$ local environment. For comparison it is shown the spectrum of beta-Sn and BaSnO$_3$ taken at 78 K under identical conditions. The BaSnO$_3$ absorber reveals a single line with an isomer shift of –0.03(1) mm/s. This is expected since the emitter and absorber are identical and the resonance must be observed at zero velocity. Beta-Sn has a large positive isomer shift of 2.40(2) mm/s.

2.3. Photodarkening

The transmission spectra around the fundamental absorption edge measured for all thin film compositions before and after exposure were characteristic for amorphous chalcogenide films. All As$_2$Se$_3$+Sn$_x$ films underwent typical photodarkening under illumination. A red shift of the absorption edge as well as the corresponding decrease of the transmission was clearly observed in agreement with the data published in literature.

Relaxation of the relative optical transmission *T(t)/T(0)* of the amorphous As$_2$Se$_3$:Sn thin films in dependence of the exposure time *t* for untreated and annealed films is shown in Fig. 2a and Fig. 2b, respectively. 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. From Fig. 2a it is shown that as low as 0.5 at.% of tin impurity significantly reduces the photodarkening effect in as-deposed amorphous As$_2$Se$_3$ films. The decrease of photodarkening is characteristic for amorphous As$_2$Se$_3$ films doped with tin up to 2.0 at.% Sn. For higher concentration of tin the effect of reducing the phodarkening by impurity decreases. In annealed undoped and slightly doped (up to about 2 at.% Sn) amorphous As$_2$Se$_3$ films the photodarkening is rather weak while at higher impurity concentrations (4 and 5 at.% Sn) approaches that in undoped unannealed films. It appears that for the glass composition up to 2.0 at.% Sn the heat treatment plays a stabilizing role against the photostructural transformations if compared to the glass compositions with tin concentration more than 2.0 at.%.
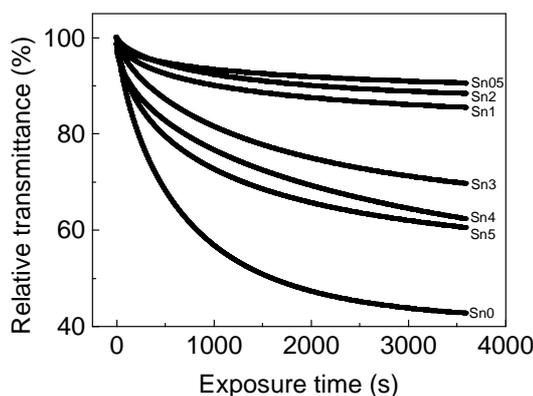
Fig. 2a. Photodarkening kinetics of as-deposited As$_2$Se$_3$:Sn films with exposure time. The digits attached to Sn denote the amount of Sn impurity introduced into the source material, in at.%
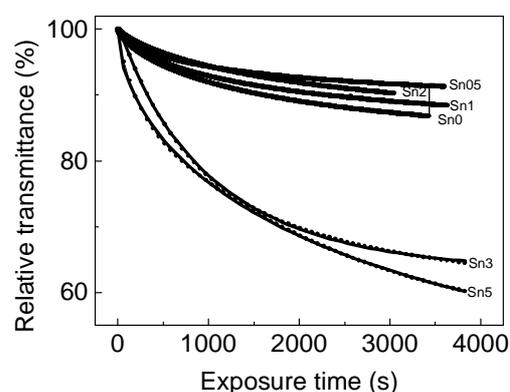
Fig. 2b. Photodarkening kinetics of annealed at T=100 ^{o}C As$_2$Se$_3$:Sn films with exposure time.

3. Discussion of the results

The photodarkening phenomenon in chalcogenide glass films under illumination has no clear explanation up to now in spite of detailed investigation and a series of models advanced. The red shift of the absorption edge that indicats 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. Several models have been put forward to substantiate this broadening considering a particular individual atom as an initial object of photoexcitiation [7,8]. Recently, a novel model for photodarkening in a-$As_2Se(S)_3$ has been proposed [1,18,19], in which photoexcited charge carriers in extended states are considered as responsible for photodarkening. Unlike to the previous ideas 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 the enlargement of the interlayer distance (leading to photoexpansion) and slip motion along the layers. This latter process alters the interaction of lone-pair electrons between the layers leading to photodarkening effect. M. Popescu [20], in his structural model proposed for explanation of photodarkening phenomena, has pointed out that distortion in the second and third coordination spheres should be taken into account as important factors.

The model of Shimakawa et al. [1,18] offers a good basis for consideration of the effect on photodarkening of impurity atoms with coordination different from that of the host glass atoms, as in the case of tin. The disappearance of phodarkening effect when a certain amount of the first group metal is added to a-As_2Se_3 may be referred to as an example [9]. The foreign metal atoms provide bridging between the layers and hence reduce the slip motion, thus hindering the photodarkening. We suggest that this consideration is applicable in the case of tin impurity in a-As_2Se_3.

To obtain a unified basis for comparison of the transmission relaxation $T(t)$ curves we used the so called stretched exponential presentation for the relaxation curves in Fig. 2a and Fig. 2b in the form:

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

Here t is the exposure time, τ is the apparent time constant, A characterizes the exponential amplitude, t_0 is the initial time, A_o is the final transmission ratio, and α is the dispersion parameter ($0<\alpha<1$). As a background for Eqn. (1) two groups of mechanisms are usually considered [21]. The first one includes diffusion-controlled processes with random distribution of transport parameters in a disordered glass. The second group combines the relaxation hierarchy of several successive steps with a distribution of relaxation times. Approximation of the experimental decays with the aid of a standard computer fitting procedure proved to be attainable for all curves (χ^2 better than 4×10^{-3}). The parameters of the stretched exponential A_0, A, τ and α have been determined for all compositions of the untreated and annealed films (for $t_0 = 0$).

The difference of the influence of tin impurity and that of annealing on photodarkening in As_2Se_3 films is illustrated in Fig. 3, which presents the relative transmittance decrement A in dependence on the impurity content in the films. The parameter $A = 1-A_0$ characterizes the "steady-state" optical losses due to photodarkening.

The effect of Sn doping on the amplitude of photodarkening is strong at low doping levels up to 2 at. % Sn; with further growing of Sn content the effect becomes smaller, and at about 4-5 at.% Sn it tends to the value characteristic for undoped films. The effect of annealing is much stronger for the undoped sample than for that doped with Sn. The time constant τ of the photodarkening process increases both in doped and thermally treated films comparative to that of the as-deposited film. In annealed films the photodarkening proceeds much slower than in untreated and undoped films. The time constant is of the same order of magnitude in all the samples and seems to be dependent of the impurity concentration. This type of behavior is different from that observed in amorphous AsSe:Sn films [12], in which the time constant rapidly increased with the Sn content in the case of the annealed films. The dispersion parameter α remains much less than unity for all the examined films indicating a large degree of dispersion.
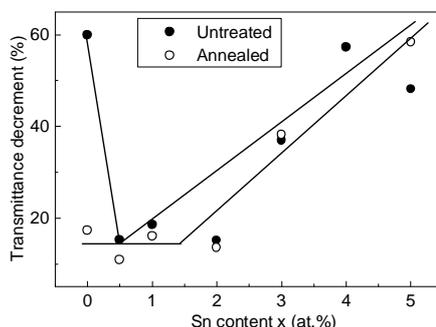
Fig. 3. The dependence of the transmittance decrement on the tin content in amorphous
As$_2$Se$_3$:Sn$_x$ films.

In the absence of tin, the arsenic chalcogenide glass is formed of corrugated and disordered layer domains with some correlation between them. This correlation leads to a rather compact packing with low inter-configurational distance. When Sn is added then, due to the tetrahedral disposal of the sp^3 bonds with the chalcogen, the dopant atom inserted into the network increases the thickness of the layered configuration as revealed by the significant shift of the FSDP towards lower angles. This insertion corresponds in fact to the introduction in the network of the structural units of the type $SnSe_2$. The effect is greater for higher dopant content but only up to a certain concentration, because, further, the separation of the reciprocally ordered configurations is interrupted by more and more interconnection between layers and a transition to three-dimensionally (3D) connected network follows. The transition is preceded by the appearance of structural units of the type SnSe. Then, the direct consequence of this transition will be reflected in the intensity of the FSDP which gradually disappears. For the glasses As$_2$Se$_3$:Sn the transition towards 3D network seems to start very early (at ~2 at.% Sn) compared to the glasses As$_2$S$_3$:Ge, where the transition starts for more than 25 at.% Ge. The interruption of the two-dimensional structure and transition is probably due to a more ionic character of the Sn-Se bonds compared to Ge-Se bonds. The ionic component gives a higher structural mobility in the network and, therefore, a higher instability of the glass. Thus, we can expect that the tin impurity strongly affect the network of the host glass inducing changes in both short-range as well as medium-range order, in particular they exert significant influence on the structural layers and the character of their relative motion.

The central message from the Mössbauer spectroscopy result is that the group IV additive removes Se from the base glass to form tetrahedrally coordinated $Sn(Se_{1/2})_4$ local unit in the base glass. This has the obvious consequence that the base glass becomes Se deficient which would result in the creation of more As-rich local units such as As_4Se_4 units. A related issue raised by the present result is how are the As-rich and Sn-centered local units present in the base glass network. Specifically do they form part of the base glass network composed of $As(Se_{1/2})_3$ pyramids? Or do they nanoscale phase separate, from the backbone of the glass? In the previous work [22] on As_xSe_{1-x} binary glasses we suggested that the nanoscale phase based on As-rich units separate from the backbone of the glasses. The suggestion was based on the experimental fact that T_g of the glasses show a threshold behavior near x = 0.40. By systematically adding more Sn in the stoichiometric glass, one could address the issue of how do the $Sn(Se_{1/2})_4$ local units connect in the base glass. This could be done by establishing the compositional dependence of the glass transition in glasses of the type-$[As_2Se_3]_{1-y}Sn_y$.

The results of the present work together with the slip-motion model of Shimakawa et al. [1, 18] may be used to estimate the behavior of tin impurity in the photodarkening process. It is seen from the experiment that the effect of impurity is manifested mainly through retardation of the photodarkening process due to the impurity of presence. Thermal treating is also known as an important factor to act upon the structure of an amorphous solid and to transfer the energy necessary for reconstruction and removal of constraints. The time constant of the process in undoped films is several times increased after doping and annealing. This fact clearly indicates the strong retardation of the slip motion of the structure layers due to presence of impurity. Because the tin tends to create

directional bonds when are introduced in the host glass, and, especially, during the annealing process, some bridging bonds should appear between the layers. The structure of the glasses that contain tin impurity requires therefore some excess slip forces, i.e. greater exposition doses. Larger time constants will be characteristic. Furthermore, creation of clusters such as of $SnSe_2$ type may lower the density of the typical lone-pair defects (i.e. D-centers) for AsSe, thus lowering the charge state of the layers and, finally, the photodarkening. This effect is particularly important at high Sn content in our case up to $x = 2.0$ at.% Sn, when impurity approaches the dissolution limit and actually changes the number of structural units in the glass. In the untreated films, as it was pointed out earlier [12], the changes in the structure after introducing Sn impurity occur first of all in the layers, that is why the slip mobility is retained, while the enlargement of the interlayer distance promotes the slip motion slightly decreasing the time constant of the process. The observed difference in the behavior of AsSe:Sn films and As_2Se_3:Sn films may be attributed to non-stoichiometric character of AsSe whose structure contains numerous homopolar bonds.

The fact that the photodarkening kinetics may be described by a stretched exponential may be considered as an indication of dispersion in kinetic mechanism, i.e. the time dependence of the process rate [21]. The data allow to conclude that formation of photoinduced absorption is limited by a dispersive process with the exponent $\alpha \cong 0.5$. In our case, it is the dispersive character of hole transport that may cause the dispersive character of the relaxation after photogeneration. Indeed, the transport of photoexcited holes is included in the model in the stage when the layer clusters are charged due to capture of charge carriers. Charge transport in chalcogenide glasses is known as highly dispersive due to wide distribution of capture times in multiple-trapping process [23]. For glasses like a-As_2Se_3 the dispersive parameter α of hole transport is close to 0.5, in accordance with the value found from the stretched exponential of the photodarkening kinetics. A discussion on photo-conductivity and transport properties in As-Se thin films is given in [24]. The fact that α is increasing with addition of metal impurities indicates that the dispersion of the transport is decreased. This is in general accordance with both the stabilization of the structure and expected alteration of defect center density.

Finally, we want to mention that for the first time the influence of charged defects on the photodarkening in chain and layered chalcogenide structures was considered by Bercha et al. [25].

4. Summary

Photodarkening and its relaxation under light exposure in amorphous films of As_2Se_3:Sn (0.5 to 5.0 at.% Sn) were studied in relation to the concentration and thermal annealing. It was shown that tin impurity effectively reduces photodarkening and the degree of reduction becomes stronger up to 2.0 at.% Sn, then photodarkening is increased again. Thermal treatment of the films at 120 ^{o}C, in vacuum, reduces the photodarkening, especially the glass composition with tin content up to 2.0 at.% Sn.

The optical transmission relaxation of the As_2Se_3:Sn films under illumination may be described by a stretched exponential with the dispersive parameter $0.1 \leq \alpha \leq 0.6$. This fact indicates the presence of strong dispersion in the photodarkening process. In the frame of the "slip-motion" model this dispersion may be naturally attributed to the multiple-trapping of photoinduced holes. In particular, due to its tetrahedral coordination, tin should reduce the flexibility of the layer network, hence retarding the photodarkening phenomenon. Doping of amorphous chalcogenide films by tin impurities assists in stabilizing the glassy matrix with respect to light exposure and thermal treatment.

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