EFFECT OF METAL ADDITIVES ON PHOTODARKENING KINETICS IN 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 at.% tin, manganese, samarium and dysposium, separately introduced, was studied in dependence on the impurity type and thermal annealing. Both factors reduce photodarkening and the degree of reduction depends on the type of impurity. The relaxation process may be described by a stretched exponential with the dispersive parameter $0.5 < \alpha < 1$ and time constant increasing by thermal annealing. The results are discussed in the frame of recently proposed "slip-motion" model of photodarkening in chalcogenide glasses.

1. Introduction

The effect of light-induced photodarkening is characteristic of amorphous chalcogenide films and attracts scientific as well as technological interest [1]. The enhancement of the optical absorption in the films is associated with photostructural transformations in amorphous matrix. As the composition of a glass determines both the structural units and the mean coordination number of the amorphous solid the effect of the composition in glassy systems As-S and As-Se on the degree of photostructural transformations has been studied in detail (see [2]). At the same time little attention was devoted to the influence on the photodarkening of foreign impurity atoms introduced in a glass. At present, due to application of metal-doped chalcogenide glasses as optoelectronic materials this problem attracted new interest.

In the present work we report the results of the study of photodarkening effect and its kinetics in amorphous As$_2$Se$_3$ chalcogenide films doped with 0.5 at.% Sn, Mn and rare earths Sm and Dy, separately introduced. Mn, Sm and Dy are well known as effective luminescent additives in chalcogenide glasses for optoelectronic applications. Tin was used for reference, as it was recently shown [3] that it significantly changes the photodarkening kinetics of a-AsSe films and the degree of the changes depends on the Sn content (0.5 to 3.5 at.%). It was also found that metal impurity induced changes in the intermediate order of amorphous matrix dependent on the type of impurity [4]. This particular effect presents special interest as regards the new photodarkening model of Shimakawa et al. [5], which relates the photodarkening (and photoexpansion) to changes in intermediate ordering that restrict mutual slip motion of the structure clusters.

2. Experimental results

The films of about 2 to 3 µm in thickness were prepared by flash thermal evaporation in vacuum onto glass substrates held at $T_{substr} = 100$ °C. A tungstene-lamp provided with an infrared cutting filter was used as a source of light exposure (incident intensity $F_0 = 10^{17}$ cm^{-2} s^{-1}). The total

optical transmittance relaxation of the film was currently registered during the exposure time. Thermal treating effect was examined by annealing the films in vacuum at T_{ann}=100 °C during 30 min. After annealing the optical transmission relaxation under light exposure was registered in the same manner. All As_2Se_3:Me films underwent typical photodarkening under illumination. Red shift of the transmission edge after exposition was clearly observed as well as the corresponding decrease of the transmission in agreement with the literature data.

Relaxation of optical transmission $T(t)/T(0)$ of the As_2Se_3:Me films in dependence on the exposure time t is shown in Fig.1a and 1b for untreated (u) and annealed (a) films, respectively. At a constant light intensity the observed dependencies demonstrate the reduction of film transmittance with the increase of the dose of absorbed photons. Note, that 0.5 at.% of metal impurity significantly weakens the photodarkening effect, especially for Sn and Dy, for which at the end of exposition the photodarkening in untreated films is about three times decreased. In annealed films the specific metal impurity weakens the photodarkening in the same manner, as for untreated films, but this weakening is reduced by a fact of 2/3. It is remarkable that the observed behavior is different from that of a-Si:H, in which the saturation value of photodarkening depends rather on the type of radiation than on the material composition [6]. It appears that addition of metals hinders the photodarkening, i.e. impurity plays the stabilizing role in the glass structure with respect to light exposure. In the annealed films this effect of impurity is weaker.
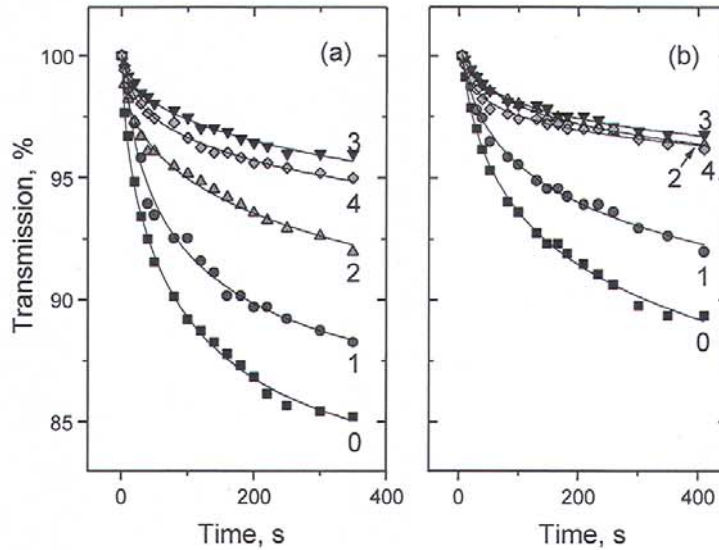

Fig. 1. Photodarkening of untreated (a) and annealed (b) As_2Se_3:Me films with exposure time (symbols). Lines show fitting of the experimental points with the stretched exponential (see text). Numbers of curves correspond to impurity: 0-none, 1-Sm, 2-Mn, 3-Dy, 4-Sn.

To obtain a unified basis for comparison of the transmission relaxation curves $T(t)$ we used so called stretched exponential presentation for the relaxation curves in Fig.1a,b, 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 exponent amplitude, t_0 and A_0 are the initial coordinates, and α is the dispersive parameter ($0<\alpha<1$). As a background for Eq.(1) two groups of mechanisms are usually considered [7]. 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. Assumption of random distribution of states leads to the exponent $\alpha=0.5$. Approximation of the experimental decays with the aid of a standard computer fitting procedure proved to be attainable for all curves, as it is shown in Fig. 1a,b by solid lines. The parameters of the stretched exponential t_0, A_0, A, τ and α for all compositions of the untreated and annealed films are summarized in Table 1. The t_0 parameter describes the deviation of the onset of the fitting time scale; it may be neglected as it amounts to less than 3 % of the interval. The parameter A_0 as well as $A=1-A_0$ characterizes the 'steady-state' transmission value, with A describing the growth of optical losses at photodarkening (about 20 to 30 %).

The influence of metal impurity on the kinetic parameters τ and α of the stretched exponential for various additives in untreated and annealed As_2Se_3:Me films is illustrated by Fig. 2. It is seen that α parameter is close to 0.5 for untreated As_2Se_3 and As_2Se_3:Sm films and increases up to 0.8...0.9 for other metal additives and after annealing. The time constant τ of the photodarkening process in virgin as well as annealed films increases in the series Sm-Mn-Sn-Dy of metal impurity. This means that in films containing impurity the photodarkening process proceeds many times slower, especially in annealed films.
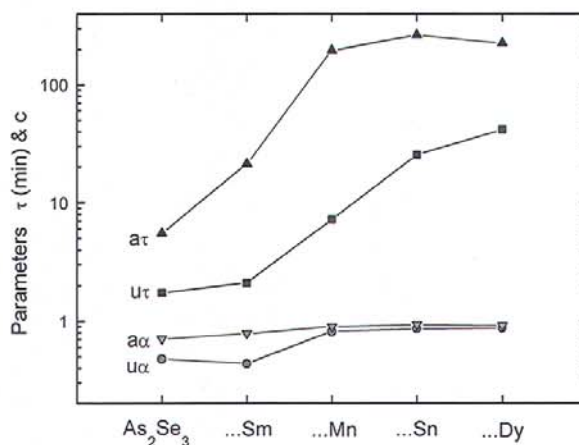

Fig.2. The dependence of the kinetic parameters τ and α on metal additives for untreated (u) and annealed (a) films. The lines are drawn as a guide for eye.

3. Discussion

The photodarkening phenomenon in chalcogenide glass films under illumination has received no satisfactory explanation up to now, although several promising models have been proposed. The red shift of the absorption edge 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 put forward to substantiate this broadening considered a particular individual atom as an initial object of photoexcitation [1,2]. Recently, a novel model for photodarkening in a-$As_2Se(S)_3$ has been advanced [1,5], in which photoexcited charge carriers in extended states are treated as responsible for photodarkening. Unlike 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 created 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. Note that one of the present authors (M. Popescu, [8]) in his structural model proposed for explanation of photodarkening phenomena has pointed out that distortions in the second and third coordination spheres should be taken into account as important factors.

The model of Shimakawa et al. [5] offers a good basis for consideration of the influence on photodarkening of impurity atoms with coordination different from that of the host glass atoms, as in the case of metals under study. The disappearance of phodarkening effect when a certain amount of the 1st 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 metal impurity in a-As_2Se_3 as well.

Table 1. Parameters of the stretched exponentials obtained by fitting the experimental points calculated curves (shown in Fig.1 by symbols and lines, respectively).

Untreated As_2Se_3:Me films					
Film	t_0, s	A_0, %	A, %	τ, min	α
As_2Se_3	0.35	82.12	19.19	1.72	0.479
As_2Se_3:Sm	8.58	85.97	13.82	2.08	0.437
As_2Se_3:Mn	-5.15	81.55	28.61	7.18	0.813
As_2Se_3:Dy	-12.69	82.80	28.27	41.23	0.869
As_2Se_3:Sn	-6.1	82.77	27.39	25.27	0.857
Annealed As_2Se_3:Me films					
Film	t_0, s	A_0, %	A, %	τ, min	α
As_2Se_3	-4.89	78.72	30.37	5.47	0.703
As_2Se_3:Sm	5.23	77.87	31.48	21.13	0.78
As_2Se_3:Mn	-13.03	80.49	31.62	193.87	0.888
As_2Se_3:Dy	-8.36	81.14	32.41	262.7	0.926
As_2Se_3:Sn	0.85	81.28	32.24	222.4	0.91

The metals Mn, Sm and Dy are well known effective luminescent emitters. They enter the host glass as ions Mn^{2+}, Sm^{2+} or Sm^{3+} and Dy^{3+}, and, due to charge and large ion dimensions, induce deformations in the host matrix. The Sn environment in As-Se glasses was determined from Mössbauer spectroscopy studies [10]. Sn was found to be tetrahedrally coordinated. From the X-ray investigation of the first diffraction peak (FSDP) in As_2Se_3 glasses doped with 0.5 at.% of Sn, Mn, Sm and Dy it was concluded [11] that disordered layers of the glass structure are locally distorted by insertion of the metal atoms that make bonds with selenium. A high covalency of the Me-Se bond gives rise to strong directional bonds and the layers become more rigid while high metal ionicity diminishes the stiffness of the layers. The Sm and Dy atoms with higher electronegativity determine a shift of the interlayer distance towards a lower value, i.e. large rare-earth atoms play the role of network modifiers that smooth the disordered As_2Se_3 layers allowing for a better packing at a smaller thickness. The Mn and especially Sn, which exhibit lower electronegativity induce a shift of the interlayer distance towards higher values [12]. This effect can be ascribed to the role of network former played by the more covalent atoms. The disordered layers are stiffed by the insertion of the atoms with directional bonds. In this case the interlayer distance is increased due to the increase of the effective thickness of the layers. With these properties of impurity we may expect, that metal strongly affects the network of the host glass inducing changes in both short-range as well as medium-range order, in particular it exerts significant influence on the structural layers and the character of their relative motion.

The results of the present work together with the slip-motion model of Shimakawa et al. [5] may be used to estimate the behavior of metal 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 impurity presence. The time constant of the process in undoped films is several times increased with a factor of several units, the strongest effect was found for Dy. Thermal treating is known to be an important factor that acts upon the structure of an amorphous solid and transfers the energy necessary for reconstruction and removal of constraints. The presence of metal impurity strongly enhances the annealing effect in comparison with undoped film. In the frame of the model [5] this fact clearly indicates the strong retardation of the slip motion of the structure layers due to presence of impurity. Because metals tend to create directional bonds when are

introduced in a- As_2Se_3 and, especially, during the annealing process, it results that some bridging bonds should appear between the layers. The structure that contains metal impurity, requires, therefore, some excess slip forces, i.e. leads to greater time constants. Moreover, higher exposition dose is needed to get the same PD effect as in pure films.

The fact that the photodarkening kinetics can be described by a stretched exponential could be considered as indication of dispersion in kinetic mechanism, i.e. the time dependence on the process rate [7]. The data allow to conclude that formation of photoinduced absorption is limited by a dispersive process with the exponent $0.5 \leq \alpha \leq 1.0$ (see also [13]). 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 [14]. For a-As_2Se_3 glass the dispersive parameter α of hole transport is close to 0.5, in accordance with the value found from the stretched exponential behaviour of photodarkening kinetics. The fact that α is increasing towards unity with addition of metals indicates that the dispersion of the transport is decreased. This is in general accordance with the stabilization of the structure. In particular, a specific path of impurity conduction has been detected for films doped with Mn and Dy [4].

4. Conclusions

Photodarkening relaxation under exposure of a-As_2Se_3 amorphous films doped with metals Sn, Mn, Sm and Dy was studied in dependence on the type of impurity and thermal treatment. It was shown that impurity reduces photodarkening and the degree of reduction depends on the type of impurity. Thermal treatment of the films at 100 °C in vacuum reduces the photodarkening, especially in doped a-As_2Se_3 films.

The optical transmission relaxation of the a-As_2Se_3:Me films under illumination may be described by a stretched exponential with the dispersive parameter $0.5 \leq \alpha \leq 1.0$ and time constant increasing with embedding of impurity by thermal annealing. In the frame of the model [5] the dispersion could be naturally attributed to multiple-trapping of photoinduced holes. The effect of metal additives on the photodarkening kinetics, especially on its response to thermal treatment is in agreement with the model developed in the paper [5]. Addition of metal impurity should reduce the flexibility of the layer network, hence retarding the photodarkening phenomenon. Doping of amorphous chalcogenide films by metals assists in stabilizing the glassy matrix with respect to light exposure and thermal treatment.

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