

THE EFFECT OF RARE-EARTH IMPURITY ON THE PHOTODARKENING RELAXATION IN AS-EVAPORATED AMORPHOUS $\text{As}_2\text{Se}_3:\text{Pr}$ AND $\text{As}_2\text{Se}_3:\text{Dy}$ FILMS

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The effect of foreign impurity atoms (Dy and Pr) in as-evaporated amorphous As_2Se_3 thin films on the photodarkening relaxation was investigated. The photodarkening amplitude depends on the kind and concentration of rare-earth dopant, as well as on the thickness of the sample. The observed variation of photodarkening amplitude with the sample thickness is due on the amount of absorbed photons generating the photodarkening effect. The photodarkening kinetics is described by a stretched exponential function with the dispersion parameter $\alpha < 0.5$, which indicates high dispersion of the relaxation process in untreated as-deposited chalcogenide films.

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1. Introduction

Special interest for the applications of chalcogenide glassy films is connected with doping of the glass by optically active rare-earth metals, which alter optical, photoelectrical and transport properties of the host material. The films based on arsenic chalcogenides usually become darkened due to photo-structural transformations under action of light from the region of fundamental optical absorption (so called photodarkening). The enhancement of the absorption is caused by the shift of the absorption edge to lower photon energies. It was shown by X-ray diffraction measurements that the rare-earth ions (Dy^{3+} and Sm^{3+}) being introduced in glassy matrix decrease the interlayer distance in structural clusters [1]. Doping of amorphous chalcogenide films by metals assists in stabilising of the glassy matrix with respect to light exposure and thermal treatment [2,3].

At present, due to technical application of chalcogenide glasses as optoelectronic materials this problem have attracted new interest. It was shown in our earlier study that metal impurity has strong retardation effect on the photodarkening and its kinetics in freshly evaporated and especially in annealed amorphous chalcogenide films [4]. It is known from the literature as well that photodarkening process is dependent on the film thickness and angle of deposition onto the substrate. Obliquely deposited films are characterized by loose structure and undergo stronger alteration of optical density under illumination than more dense normally evaporated films [5]. That is why in the present communication both factors, i.e. film thickness and angle of deposition, were controlled along with the effect of impurity.

2. Experimental results and discussion

The metal impurities were introduced in As_2Se_3 glass by adding of rare-earth oxides, i.e. Dy_2O_3 and Pr_6O_{12} . Films of thickness from 0.3 to 6.3 μm were obtained by flash thermal evaporation

in vacuum onto glass substrates. As a source of exposure light a He-Ne laser ($\lambda = 6328 \text{ \AA}$) was used. In the course of exposure the transmittance of the film was measured. By this way the relaxation curves of transmittance in the time interval from 0 to 7×10^3 s were registered during the exposition. Photodarkening relaxation was measured during illumination of a series of thirty samples of as-evaporated amorphous $\text{As}_2\text{Se}_3:\text{Me}$ films varied by the composition (the sort of metal impurity and impurity concentration), by thickness (from 0.3 to 6.3 μm) and by position over the source of evaporation. Two rare-earth impurities were added: Dy and Pr in concentration 0.1, 0.5 and 1.0 at. %. The effect of incident angle of evaporation was controlled by measurement of three samples positioned just over the evaporator (center) and two one-centimeter steps aside (2-nd and 3-rd).

Fig. 1 and Fig. 2 show the concentration dependence of photodarkening kinetics for As_2Se_3 thin films doped with Pr and Dy. Increasing of the rare-earth concentration reduce the photodarkening effect. To obtain a unified approach for comparison, all relaxation curves were fitted to a stretched exponential function

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

using standard computer least-square fitting procedure. This approach proved to be plausible in our previous comparative study of photodarkening relaxation in As_2Se_3 films doped with Sn, Sm, Dy and Mn [2, 3]. Five parameters have been varied, A_0 and t_0 as the initial co-ordinates of the fitting curve*, τ as the relaxation time constant, A as the photodarkening amplitude and α as the dispersion parameter. The parameters of fitting procedure for various samples are summarized in Table 1. The sample codes contain information about the sort and concentration of impurity, sample number (S#), position over the evaporation source (Center, 2-nd, 3-rd) and thickness L in μm .

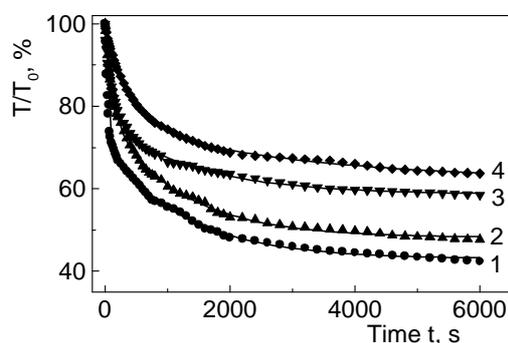


Fig. 1. The relaxation curves of photodarkening for $\text{As}_2\text{Se}_3:\text{Pr}$ thin films. 1- As_2Se_3 ($L=3.6 \mu\text{m}$), 2- $\text{As}_2\text{Se}_3 + 0.1$ at. % Pr ($L = 2.1 \mu\text{m}$), 3- $\text{As}_2\text{Se}_3 + 0.5$ at. % Pr ($L = 1.5 \mu\text{m}$), 4- $\text{As}_2\text{Se}_3 + 1.0$ at. % Pr ($L=1.2 \mu\text{m}$).

For the obtained relaxation curves rather wide scatter of parameters is observed for samples of the same composition. For doped samples the reason for this dispersion may be that the concentration and distribution uniformity of impurity is not adequately preserved along the film at deposition. But the relaxation curves are significantly different in the case of non-doped As_2Se_3 as well. The main reason comes from the difference in thickness, particularly for the samples with submicrometer thickness. For these samples the effect of interference of light reflected at the front and the rear film boundaries significantly changes the amount of absorbed light leading to strong dependence of the photodarkening at a fixed laser wavelength on the film thickness (see Fig. 3).

Comparison of the parameters of the relaxation curves for samples deposited at different incident angles have shown that in the considered limits of distance from the center over the evaporator the greatest effect of photodarkening is observed for the central samples, in contrast to the results reported in the literature for obliquely deposited films [5]. Slight decrease of the

* t_0 reflects the difference in the time scales of the experimental and fitting curves; its mean value is usually less than 1-2 % of the time domain, i.e. lies within the error limits of the chart-recorder.

photodarkening amplitude with the distance from the center is due to decreasing of the film thickness. This is true both for pure and doped As_2Se_3 films. We may conclude that no structure-caused position dependence is observed in our case.

Table 1. Stretched exponential parameters of As_2Se_3 :Me thin films.

Thin film composition	Sample position	L , μm	A_0	t_0 , s	τ	α	A
As_2Se_3	S1, Center	6.25	0.21	0	2430	0.29	0.81
As_2Se_3	S2, Center	4.9	0.63	2.9	1627	0.36	0.39
As_2Se_3	S3, Center	0.6	0.23	7.3	3456	0.56	0.78
As_2Se_3	S4, Center	0.4	0.77	0	121	0.35	0.23
As_2Se_3	S5, Center	0.3	0.15	-2.6	4500	0.61	0.9
$\text{As}_2\text{Se}_3+0.1$ at.% Dy	S6, Center	1.1	0.64	-31	397	0.4	0.45
$\text{As}_2\text{Se}_3+0.1$ at.% Dy	S7, 2-nd	0.75	0.73	0	534	0.26	0.28
$\text{As}_2\text{Se}_3+0.1$ at.% Dy	S8, 3-rd	0.72	0.89	-183	192	0.43	0.3
$\text{As}_2\text{Se}_3+0.5$ at.% Dy	S9, Center	3.4	0.36	-14	216	0.61	0.9
$\text{As}_2\text{Se}_3+0.5$ at.% Dy	S10, 2-nd	3.1	0.39	-3.7	297	0.58	0.71
$\text{As}_2\text{Se}_3+0.5$ at.% Dy	S11, 3-rd	3.25	0.63	1.9	446	0.36	0.38
$\text{As}_2\text{Se}_3+1.0$ at.% Dy	S12, Center	1.9	0.49	-13	498	0.41	0.57
$\text{As}_2\text{Se}_3+1.0$ at.% Dy	S13, 2-nd	1.9	0.52	1.1	607	0.4	0.49
$\text{As}_2\text{Se}_3+1.0$ at.% Dy	S14, 3-rd	1.6	0.60	-4.7	413	0.43	0.44
$\text{As}_2\text{Se}_3+0.1$ at.% Pr	S15, Center	2.1	0.48	9.5	604	0.36	0.5
$\text{As}_2\text{Se}_3+0.1$ at.% Pr	S16, 2-nd	1.85	0.58	0	346	0.47	0.54
$\text{As}_2\text{Se}_3+0.1$ at.% Pr	S17, 3-rd	1.5	0.58	0	377	0.37	0.42
$\text{As}_2\text{Se}_3+0.5$ at.% Pr	S18, Center	1.5	0.57	4	411	0.51	0.45
$\text{As}_2\text{Se}_3+0.5$ at.% Pr	S19, 2-nd	1.5	0.61	-25	308	0.79	0.71
$\text{As}_2\text{Se}_3+1.0$ at.% Pr	S20, Center	1.2	0.81	-12	788	0.56	0.22
$\text{As}_2\text{Se}_3+1.0$ at.% Pr	S21, 2-nd	1.2	0.57	-5	791	0.31	0.45
$\text{As}_2\text{Se}_3+1.0$ at.% Pr	S22, 3-rd	1.2	0.64	0.4	716	0.32	0.37

It follows then that film thickness is the most important factor, which influences the photodarkening effect, for it depends on the amount of absorbed energy of light $I_A/I_0 = 1 - \exp(-kL)$, where k is the absorption coefficient and L is the film thickness. This amount is characterized by the amplitude A , determined from the fitting procedure.

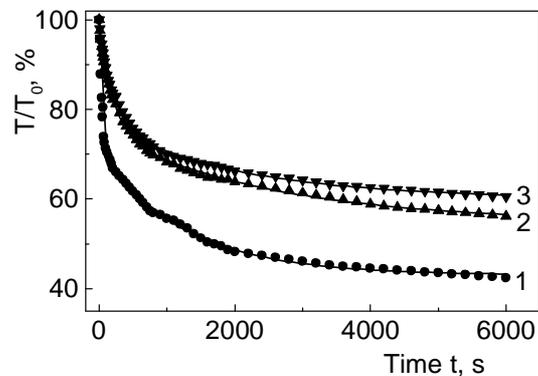


Fig. 2. The relaxation curves of photodarkening for As_2Se_3 :Dy thin films. 1- As_2Se_3 ($L=3.6$ μm), 2- $\text{As}_2\text{Se}_3+0.1$ at. % Dy ($L=1.1$ μm), 3 - $\text{As}_2\text{Se}_3+0.5$ at. % Dy ($L=2.25$ μm), 4- $\text{As}_2\text{Se}_3+1.0$ at. % Dy ($L=1.9$ μm).

In Fig. 4 the values of the A parameter for all As_2Se_3 samples, pure and doped with Dy and Pr, are plotted in semilogarithmic co-ordinates $-\ln(1-A)$ vs. L . In ideal case this plot should give straight lines with the slope determined by the absorption coefficient k .

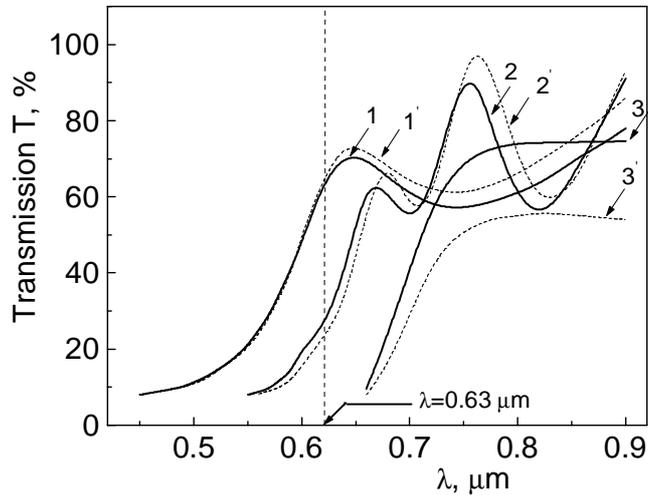


Fig. 3. Transmission spectra of unexposed (1,2,3) and light exposed (1', 2', 3') As_2Se_3 samples of various thicknesses. Great interference - induced difference of transmission at a fixed laser wavelength is clearly seen. Thin film thickness, μm : 1-0.3; 2-0.6; 3-6.25.

Though strongly scattered, especially for thin films (as it was discussed above), the points show clear tendency to increase the ordinate with increasing the film thickness. Estimation of absorption coefficient from the slope of linear fit to the points gives a reasonable value of about $k = 3 \times 10^3 \text{ cm}^{-1}$ for indoped As_2Se_3 . For As_2Se_3 doped with Pr and Dy slightly greater k values were obtained due to increase of impurity absorption. We may conclude that the observed variation of photodarkening amplitude for various samples is due mainly to the difference in film thickness, which regulates the amount of absorbed photons generating the photodarkening effect. Besides the thickness dependence of the position of optical absorption edge, the thickness dependence of the photodarkening in As_2Se_3 thin films was also explained by the strain induced by the lattice mismatch between the film and the substrate [6].

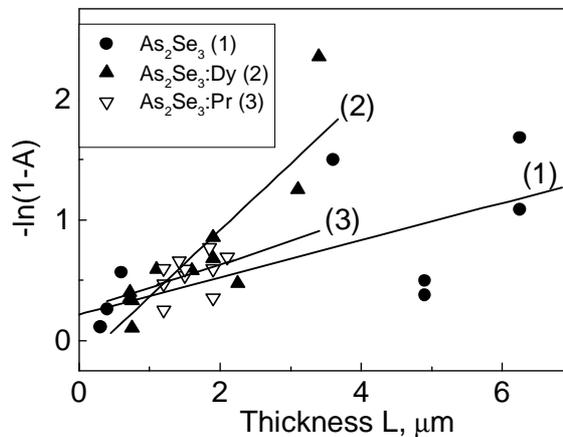


Fig. 4. Semi logarithmic plot of photodarkening amplitude vs. film thickness ($-\ln(1-A)$ vs. L) for all As_2Se_3 samples, pure and doped with Dy and Pr.

According to measurements of the relaxation time constant (see Table 1) most slow relaxation is inherent to undoped As_2Se_3 (the mean value is about 1500 s). Adding of Pr and Dy decreases this value to about 500 s and 400 s, respectively (Table 2). Speeding up of relaxation at introducing of metal impurity in thermally untreated samples has been reported in our previous publication [2,3]. No monotonous concentration dependence was observed in the explored range of impurity concentration (up to 1.0 at. % of Pr and Dy), with the relaxation time constant first decreasing respective to As_2Se_3 for 0.1 and 0.5 at. %, and then increasing for 1.0 at. % for both Pr and Dy impurity. As in the previous communication [2,3], we can suppose that in untreated films the changes in the structure after introducing of impurity occur first of all in the layer clusters and enlargement of interlayer distance promotes the slip motion, thus leading to decrease of the time constant of the process.

The dispersive parameter α for most measured samples is less than 0.5, the fact that indicates high dispersion of the relaxation process in untreated as-deposited chalcogenide films. In the previous communication we preliminary associated this dispersion with the dispersive transport of photoexcited holes at the initial stage of the photodarkening process, as it is considered by the slip-motion model [5].

Table 2. Mean relaxation time values for thermally untreated As_2Se_3 :Me films.

Composition	Mean relaxation time, s
As_2Se_3	1515
As_2Se_3 :0.1 at.% Pr	563
As_2Se_3 :0.5 at.% Pr	358
As_2Se_3 :1.0 at.% Pr	765
As_2Se_3 :0.1 at.% Dy	393
As_2Se_3 :0.5 at.% Dy	320
As_2Se_3 :1.0 at.% Dy	506

3. Summary

In conclusion, the comparative study of the effect of metal impurity on the photodarkening kinetics is obscured by strong influence of the film thickness on the amplitude of photodarkening. This influence results from the exponential dependence of the absorbed light energy on film thickness and leads to significant scatter of photodarkening amplitude due to slight thickness difference. The dependence of the effect on the deposition angle in the studied angle interval is insignificant and is reduced to the film thickness dependence as well. Nevertheless, the effect of impurity is clearly revealed in decreasing of relaxation time constant in comparison with indoped As_2Se_3 .

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References

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