

# OPTICAL PHOTOINDUCED ABSORPTION IN $\text{As}_2\text{S}_3$ THIN FILMS DOPED WITH RARE-EARTH IONS

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## Abstract

In the present paper we have focused our study on relaxation of photodarkening in  $\alpha\text{-As}_2\text{S}_3$  doped with rare-earth ions ( $\text{Dy}^{3+}$ ,  $\text{Pr}^{3+}$ ,  $\text{Nd}^{3+}$ ). It was shown that the degree of photostructural transformation depends on the species and concentration of rare-earth ions. The relaxation process of photodarkening is described by a stretched exponential function with the dispersion parameter  $0 < \alpha < 1.0$ . The obtained results can be taken into account for chalcogenide glasses doped with rare-earth ions used as fiber optics amplifiers operating at the 1.3  $\mu\text{m}$  and 1.5  $\mu\text{m}$  telecommunication windows.

## 1. Introduction

The illumination of amorphous chalcogenide films with photon energy from the region of fundamental optical absorption ( $h\nu \geq E_g$ ) causes changes in optical transmission, refractive index, microhardness, density, and other physical properties. These photoinduced phenomena have stimulated a variety of potential applications in photonics and optoelectronics, especially, of a new class of inorganic photoresist [1, 2]. Special interest for the applications of chalcogenide glass films is attributed to doping with optically active rare-earth ions, which alter optical, photoelectrical, and transport properties of the host material. The choice of rare-earth ions ( $\text{Nd}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Pr}^{3+}$ ) is determined by the fact that these dopants are actually used in industrial applications in photonics and optical fiber telecommunication systems [3, 4]. At the same time, insignificant attention has been given to the influence on photodarkening of foreign impurity atoms introduced in the glass, although it was shown that the photodarkening is influenced by doping of  $\text{As}_2\text{Se}_3$  amorphous chalcogenide films with Sn and rare-earth ions ( $\text{Er}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Ho}^{3+}$ ,  $\text{Nd}^{3+}$  and  $\text{Pr}^{3+}$ ) [5-7]. It was established that doping of amorphous chalcogenide films by metals contributes to stabilizing a glassy matrix with respect to light exposure and thermal treatment.

X-ray diffraction measurements have shown that the rare-earth ions ( $\text{Dy}^{3+}$  and  $\text{Sm}^{3+}$ ) in glassy matrix decrease the interlayer distance in structural clusters [8]. According to the “slip-motion” model [9], the metal impurities that influence the structure of the glass matrix must be shown in the photodarkening process. In the present paper, we analyze the relaxation of photodarkening in  $\alpha\text{-As}_2\text{S}_3$  doped with rare-earth ions ( $\text{Dy}^{3+}$ ,  $\text{Pr}^{3+}$ , and  $\text{Nd}^{3+}$ ).

## 2. Experimental

The glasses were synthesized from the elements of 6N (As, S) purity by adding of rare-earth oxides by the conventional technique. The rare-earth oxides were supplied by ALFA

Aesar. Thin films of thickness from 0.3 to 6.3  $\mu\text{m}$  were prepared by “flash” thermal evaporation in vacuum onto glass substrates held at  $T_{\text{substr}}=100^\circ\text{C}$ . In order to initiate the photostructural transformations in the thin film samples a red ( $\lambda=0.63\ \mu\text{m}$ ,  $W=0.6\ \text{mW}$ ) and a green ( $\lambda=0.54\ \mu\text{m}$ ,  $W=0.75\ \text{mW}$ ) continuous He-Ne lasers were used simultaneously as sources of light exposure. Some experiments were carried out with nanosecond pulsed  $\text{N}_2$  laser ( $\lambda=0.34\ \mu\text{m}$ , repetition rate 100 Hz, pulse energy 0.1 mJ) as an exciting light source. The relaxation of the transmission curves was measured both at 0.63  $\mu\text{m}$  and 0.54  $\mu\text{m}$  wavelengths during the excitation (for  $\text{As}_2\text{S}_3$  the optical gap  $E_g=2.4\ \text{eV}$ ). The laser spot on the sample was about 1 mm in diameter. The experimental set-up included a digital build-in PC-card for data acquisition PCI-1713A connected with the registration module.

### 3. Results and discussion

It was shown that in chalcogenide glasses the absorption edge is broader than in crystalline analogues and this is caused by a broad energy distribution of electronic states in the band gap due to disorder and defects. The absorption edge in the high absorption region ( $\alpha>10^4\ \text{cm}^{-1}$ ) is described by the quadratic function

$$\alpha \propto \frac{1}{h\nu} (h\nu - E_g)^2. \quad (1)$$

When plotted in the Tauc coordinates  $(\alpha \cdot h\nu)^{1/2}$  vs.  $(h\nu)$  [10] gives the value of the optical gap,  $E_g$ , determined as the energy difference between the onsets of exponential tails of the allowed conduction bands [11]. For amorphous  $\text{As}_2\text{S}_3$  the value of band gap was found to be  $E_g = 2.35 \pm 2.4\ \text{eV}$  [2].

The optical absorption edge spectra of amorphous  $\text{As}_2\text{S}_3$  (curve 1) and doped with Dy (curve 2) thin films are presented in Fig. 1. As in the case of bulk glasses, doping of the evaporated  $\text{As}_2\text{S}_3$  thin films affects strongly the optical absorption edge spectra, being evidenced by the pronounced shift to lower energy values [13]. The optical gap  $E_g$  determined by extrapolation of the straight-line portions of the  $(\alpha \cdot h\nu)^{1/2}$  vs.  $(h\nu)$  graphs was found to be 2.34 eV for  $\text{As}_2\text{S}_3$ . This value is in a good agreement with previously reported data [12]. Doping of  $\text{As}_2\text{S}_3$  glass with rare-earth ions shifts the absorption edge in the red region of the spectra and was found to decrease  $E_g$ . The optical gap value is dependent on the nature and concentration of the metal ion dopant [13].

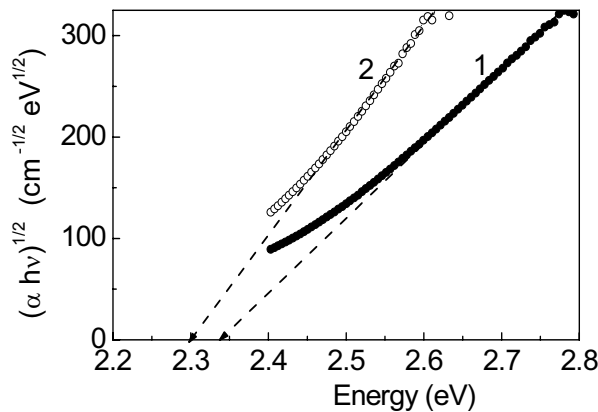


Fig. 1. The absorption coefficient for as-deposited amorphous  $\text{As}_2\text{S}_3$  (1) and  $\text{As}_2\text{S}_3+0.1\ \text{at. \% Dy}$  (2) thin films.

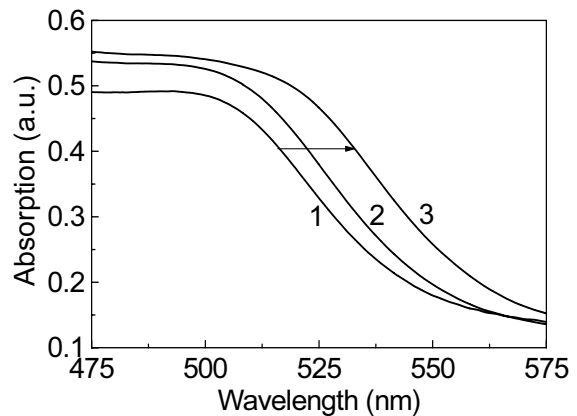


Fig. 2. The absorption spectra of as-deposited  $\text{As}_2\text{S}_3$  thin films ( $L=8.55\ \mu\text{m}$ ) (1), irradiated during 20 min (2), and irradiated during 3600 min (3).

Irradiation of  $\text{As}_2\text{S}_3$  thin films prepared by thermal evaporation was found to cause a photodarkening effect, as shown by measurements of the absorption edge of thin films ( $L=8.85\text{ }\mu\text{m}$ ) before and after irradiation (Fig. 2). The irradiation causes a shift of the absorption edge in the Urbach region to lower energies. This shift is of  $\Delta\lambda=6.3\text{ nm}$  when the film is irradiated for 20 min, and increases to  $\Delta\lambda=16.8\text{ nm}$  when the film is irradiated for 6 hours. From Raman measurements, it was established that irradiation treatment for 20 and 40 min causes the decrease in the intensity of bands at  $364\text{ cm}^{-1}$  and  $495\text{ cm}^{-1}$  and those in the frequency region  $100\text{ to }250\text{ cm}^{-1}$  [13]. When the irradiation time was increased to 6 hours the glass exhibited a broad Raman spectrum with a pronounced feature at  $231\text{ cm}^{-1}$ , which may be attributed to As clustering in the glass [14].

These changes may be interpreted in terms of optical polymerization of  $\text{As}_4\text{S}_4$  structural units into the glassy network, as reported previously in the study of photoinduced changes in the infrared spectrum of amorphous  $\text{As}_2\text{S}_3$  films [15].

The experimental data show that the metal impurities influence the photodarkening. The degree of reduction or increasing of the process depends on wavelength of the light excitation, and on the concentration and species of rare-earth impurity. Figs. 3 and 4 show the relaxation curves for amorphous  $\text{As}_2\text{S}_3$  films doped with  $\text{Dy}^{3+}$  and  $\text{Pr}^{3+}$  ions.

For the amorphous  $\text{As}_2\text{S}_3$ :Dy samples, as in the case of  $\text{As}_2\text{Se}_3$  ones, the small concentrations of rare-earth ions significantly reduce the photodarkening effect. At the same time, high concentrations of rare-earth ions (0.25 at. %  $\text{Pr}^{3+}$  and 1.5 at. % Nd) increase the sensitivity of photostructural transformations. This is illustrated in Fig. 4 (curve 3) and in Fig. 5 (curve 2). This effect was not observed in the samples of amorphous  $\text{As}_2\text{Se}_3$  doped with rare-earth ions [6].

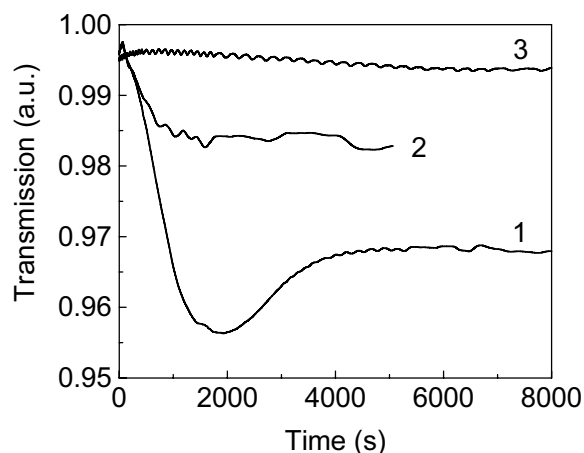


Fig. 3. The photodarkening relaxation (at  $\lambda=0.54\text{ }\mu\text{m}$ ) for the as-deposited amorphous  $\text{As}_2\text{S}_3$  (1),  $\text{As}_2\text{S}_3+0.1\text{ at. \% Dy}^{3+}$  (2), and  $\text{As}_2\text{S}_3+0.5\text{ at. \% Dy}^{3+}$  (3) thin films.

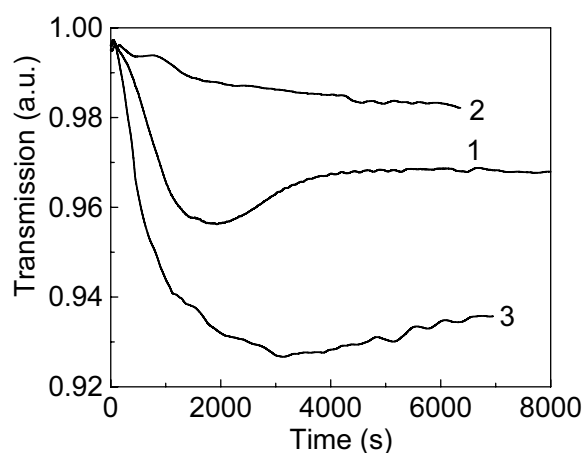


Fig. 4. The photodarkening relaxation (at  $\lambda=0.54\text{ }\mu\text{m}$ ) for the as-deposited amorphous  $\text{As}_2\text{S}_3$  (1),  $\text{As}_2\text{S}_3+0.15\text{ at. \% Pr}^{3+}$  (2), and  $\text{As}_2\text{S}_3+0.25\text{ at. \% Pr}^{3+}$  (3) thin films.

We can also observe that for some samples, especially, for the pure  $\text{As}_2\text{S}_3$ , the shapes of the relaxation curves are different. The maximum of the photodarkening takes place during about 2000 s, and then the transmittance increases (curve 1 in Fig. 3 and curve 3 in Fig. 4). This kind of dependence in measurements of the diffraction efficiency vs. recording time for amorphous  $\text{As}_2\text{S}_3$  thin films was observed in [16] and for  $\text{As}_2\text{Se}_3$  films in [17]. In order to stabilize the value of the diffraction efficiency, after reaching the maximum, the amorphous  $\text{As}_2\text{Se}_3$  films were doped with Sn impurities [17].

As a result, a stabilization of the maximum value of the diffraction efficiency was obtained. This effect was explained by the formation of new structural units like  $\text{SnSe}_{4/2}$ , which make the glass network more stable [17].

The amorphous  $\text{As}_2\text{S}_3$  thin films under study are not sensitive to the light irradiation with  $\lambda=0.63 \mu\text{m}$ . This can be explained by very small value of the absorption coefficient at this wavelength (Fig. 2). At the same time, there have been reported [18] the experimental data on holographic grating recording with focused sub-bandgap light of 633 nm He-Ne laser in amorphous  $\text{As}_2\text{S}_3$  films. The focused light recording is explained by the photostimulated relaxational structural changes accompanied by the photoinduced generation and recharging of the existing D-centers in amorphous semiconductors. The photostructural changes under subband gap irradiation with both continuous and pulsed light were also observed in amorphous Ge-Se films [19]. Figure 6 illustrates the dependence of the transmittance decrement to different rare-earth ion concentrations in amorphous  $\text{As}_2\text{S}_3$  thin films, being excited with green light ( $\lambda=0.54 \mu\text{m}$ ). One can see from Fig. 6 that the actions on the photodarkening effect of different rare-earth species are different.  $\text{Dy}^{3+}$  ions always decrease the photodarkening, while  $\text{Nd}^{3+}$  ones increase the process.  $\text{Pr}^{3+}$  ions initially decrease the photodarkening. For concentrations higher than 0.1 at. % they decrease it. The behavior of rare-earth ions in amorphous  $\text{As}_2\text{S}_3$  films is different from that observed earlier in amorphous  $\text{As}_2\text{Se}_3$  films, where the rare-earth ions suppressed the photodarkening in all cases [6].

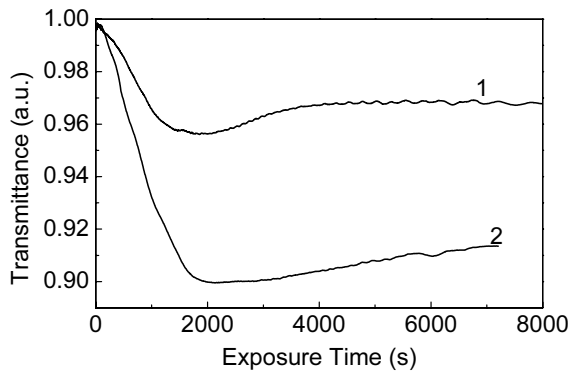


Fig. 5. The photodarkening relaxation (at  $\lambda=0.54 \mu\text{m}$ ) for the as-deposited amorphous  $\text{As}_2\text{S}_3$  (1) and  $\text{As}_2\text{S}_3+1.5 \text{ at. \% Nd}^{3+}$  (2) thin films.

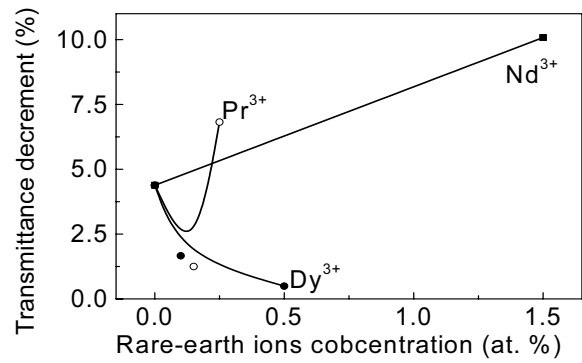


Fig. 6. The dependence of transmittance decrement on rare-earth ion concentration ( $\text{Dy}^{3+}$ ,  $\text{Pr}^{3+}$ , and  $\text{Nd}^{3+}$ ) in amorphous  $\text{As}_2\text{S}_3$  films at  $0.54 \mu\text{m}$ .

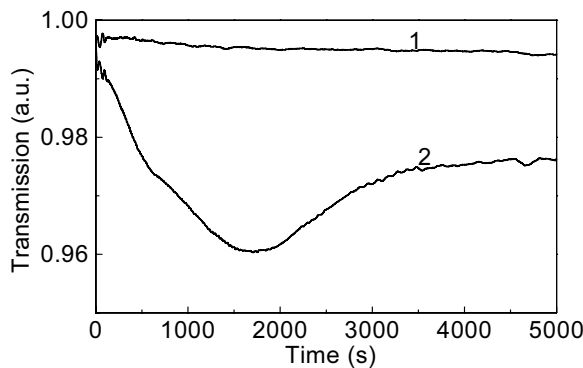


Fig. 7. The photodarkening relaxation in as-deposited  $\text{As}_2\text{S}_3$  thin films during the excitation with pulsed  $\text{N}_2$  laser: (1) measured at  $\lambda=0.63 \mu\text{m}$  and (2) measured at  $\lambda=0.54 \mu\text{m}$ .

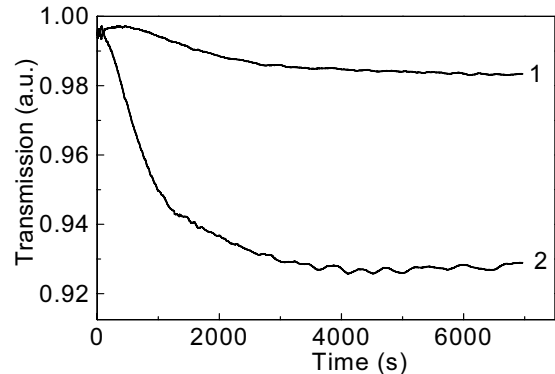


Fig. 8. The photodarkening relaxation in as-deposited  $\text{As}_2\text{S}_3+0.25 \text{ at. \% Pr}^{3+}$  thin films during the excitation with pulsed  $\text{N}_2$  laser: (1) measured at  $\lambda=0.63 \mu\text{m}$  and (2) measured at  $\lambda=0.54 \mu\text{m}$ .

The relaxation of photodarkening in amorphous  $\text{As}_2\text{S}_3$  was also measured during irradiation with pulsed  $\text{N}_2$  laser ( $\lambda=0.34 \mu\text{m}$ ). The transmittance during the irradiation with pulsed light was measured both at  $0.63 \mu\text{m}$  and at  $0.54 \mu\text{m}$ . Figure 7 represents the experimental results for undoped amorphous  $\text{As}_2\text{S}_3$  films. No photodarkening effect was observed at  $\lambda=0.63 \mu\text{m}$ , while at  $\lambda=0.54 \mu\text{m}$  the shape of the relaxation curve is similar to that obtained when the sample was irradiated with continuous light at  $\lambda=0.54 \mu\text{m}$  (Fig. 7, curve 2 and Fig. 3, curve 1). In both cases the maximum values of photodarkening are obtained during the exposure time of about 2000 s.

The picture is quite different for the amorphous  $\text{As}_2\text{S}_3$  films doped with  $\text{Pr}^{3+}$  ions (Fig. 8). Insignificant effect of photodarkening can be observed in sub-bandgap region, at  $\lambda=0.63 \mu\text{m}$ . In the region of the fundamental absorption edge ( $\lambda=0.54 \mu\text{m}$ ), the relaxation of photodarkening (Fig. 8, curve 2), also differs from that obtained at irradiation with the continuous light with  $\lambda=0.54 \mu\text{m}$ . The minimum in the relaxation curve is absent. In this case the presence of the photodarkening in the Urbach absorption region ( $\lambda=0.63 \mu\text{m}$ ) can be attributed to the structural changes in the network of chalcogenide glass induced by doping with rare-earth ions (of acceptor-like D-centers present in a- $\text{As}_2\text{S}_3$  films [20]).

The transmission relaxation  $T(t)$  curves in the initial time interval (up to the minimum of transmission) can be described by the so called stretched exponential function  $T(t)/T(0)=A_0+A\exp[-(t-t_0)/\tau]^{(1-\alpha)}$ , where  $t$  is the exposure time,  $\tau$  is the apparent time constant,  $A$  characterizes the exponent amplitude,  $t_0$  and  $A_0$  are the initial coordinates, and  $\alpha$  is the dispersion parameter ( $0<\alpha<1$ ). The parameter  $\alpha$  determined from Fig. 8 (curve 2) gives a value of  $\alpha=0.38$ . Stretched exponential relaxation fits many relaxation processes in disordered and quenched electronic and molecular systems [21]. This dependence was used for interpretation of the experimental results on photodarkening relaxation in amorphous  $\text{AsSe}$  and  $\text{As}_2\text{Se}_3$  doped with Sn and rare-earth ions [5-7].

#### 4. Conclusions

It was shown that the illumination of amorphous chalcogenide films with photon energy from the region of fundamental optical absorption causes changes in optical transmission and refractive index. The relaxation of photodarkening in  $\alpha\text{-As}_2\text{S}_3$  doped with rare-earth ions ( $\text{Dy}^{3+}$ ,  $\text{Pr}^{3+}$ , and  $\text{Nd}^{3+}$ ) was investigated. In order to initiate the photostructural transformations in samples, the excitation was performed with continuous He-Ne lasers at  $\lambda=0.63 \mu\text{m}$ ,  $\lambda=0.54 \mu\text{m}$ , and  $\text{N}_2$  pulsed laser at  $\lambda=0.34 \mu\text{m}$ . It was established that the impurities influence the photodarkening, and the degree of reduction or increasing of the process depends on wavelength of the light excitation and on concentration and species of rare-earth ions. Low concentrations of rare-earth ions significantly reduce the photodarkening, while the high concentrations (0.25 at. %  $\text{Dy}^{3+}$  and 1.5 at. % Nd) increase the sensitivity of photostructural transformations. The relaxation curves of photodarkening in the investigated materials can be described by the exponential function.

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