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# Relaxation of photodarkening in a-As<sub>2</sub>S<sub>3</sub> films doped with Pr<sup>3+</sup>, Dy<sup>3+</sup> and Nd<sup>3+</sup>

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In the present paper we have focus our study on relaxation of photodarkening in a-As<sub>2</sub>S<sub>3</sub> doped with rare-earth ions (Dy<sup>3+</sup>, Pr<sup>3+</sup>, Nd<sup>3+</sup>). 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.

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*Keywords:* Amorphous chalcogenide films, optical absorption, photoinduced phenomena

## 1. Introduction

The illumination of amorphous chalcogenide films with photon energy from the region of fundamental optical absorption ( $h\nu \geq E_g$ ) cause 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, in special of a new class of inorganic photoresists [1,2]. Special interest for the applications of chalcogenide glassy films is connected with doping of the glass by optically active rare-earth ions, which alter optical, photoelectrical and transport properties of the host material. The choice of rare-earth ions (Nd<sup>3+</sup>, Dy<sup>3+</sup>, Pr<sup>3+</sup>) 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 a little attention has been devoted 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 As<sub>2</sub>Se<sub>3</sub> amorphous chalcogenide films with Sn and rare-earth ions (Er<sup>3+</sup>, Sm<sup>3+</sup>, Dy<sup>3+</sup>, Ho<sup>3+</sup>, Nd<sup>3+</sup> and Pr<sup>3+</sup>) [5-7]. It was established that doping of amorphous chalcogenide films doped by metals assists in stabilizing the glassy matrix with respect to light exposure and thermal treatment.

From X-ray diffraction measurements it was shown, that the rare-earth ions (Dy<sup>3+</sup> and Sm<sup>3+</sup>) being introduced in glassy matrix decrease the interlayer distance in structural clusters [8]. According to the new "slip-motion" model [9] the metal impurities, which influence the structure of the glass matrix must be manifested in the photodarkening process. In the present paper, we have focus our study on relaxation of photodarkening in  $\alpha$ -As<sub>2</sub>S<sub>3</sub> doped with rare-earth ions (Dy<sup>3+</sup>, Pr<sup>3+</sup>, and Nd<sup>3+</sup>). In order to initiate the photostructural transformations in the thin film samples a red ( $\lambda=0.63 \mu\text{m}$ ,  $P=0.6 \text{ mW}$ ) and a green ( $\lambda=0.54 \mu\text{m}$ ,  $P=0.75 \text{ mW}$ ) continuous He-Ne lasers were used simultaneously as a sources of light exposure.

Some experiments were performed with nanosecond pulsed N<sub>2</sub> 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 As<sub>2</sub>S<sub>3</sub> 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.

## 2. Experimental 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 a quadratic function

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

and when plotted in the Tauc co-ordinates  $(\alpha \cdot h\nu)^{1/2}$  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 As<sub>2</sub>S<sub>3</sub> 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 As<sub>2</sub>S<sub>3</sub> (curve 1) and doped with Dy (curve 2) thin films are presented in Fig. 1a. As in the case of bulk glasses, doping the evaporated As<sub>2</sub>S<sub>3</sub> thin films affects strongly the optical absorption edge spectra, as 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 As<sub>2</sub>S<sub>3</sub>. This value is in good agreement with previously

reported data [12]. Doping of As<sub>2</sub>S<sub>3</sub> glass with rare-earth ions shift the absorption edge in the red region of the spectra, and was found to decrease E<sub>g</sub>, with the new optical gap value being dependent on the nature and concentration of the metal ion dopant [13].

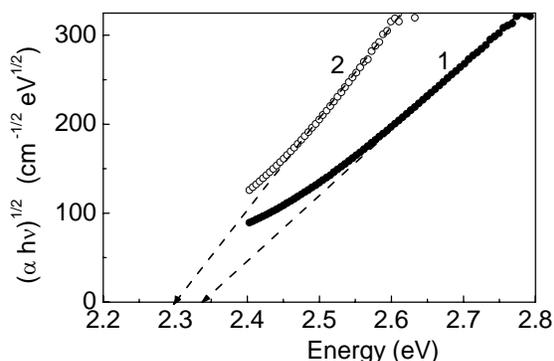


Fig. 1a. The absorption coefficient for as-deposited amorphous As<sub>2</sub>S<sub>3</sub> (1) and As<sub>2</sub>S<sub>3</sub> + 0.1 at. % Dy (2) thin films.

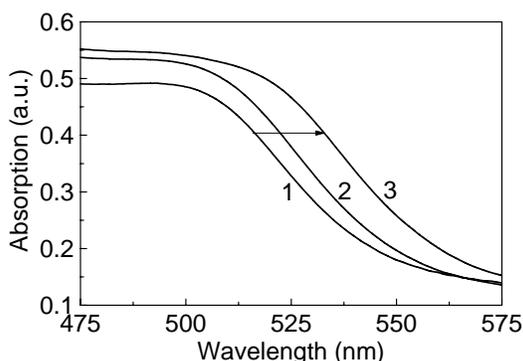


Fig. 1b. The absorption spectra of as-deposited As<sub>2</sub>S<sub>3</sub> thin films (L=8.55 μm) (1), irradiated during 20 min (2), and irradiated during 3600 min (3).

Irradiation of As<sub>2</sub>S<sub>3</sub> thin films prepared by thermal evaporation was found to cause a photodarkening effect, as manifested by measurements of the absorption edge of thin films (L=8.85 μm) before and after irradiation (Fig.1b). It was found that irradiation causes a shift of the absorption edge in the Urbach region to lower energies. This shift is equal to Δλ=6.3 nm when the film is irradiated for 20 min, and increases to Δλ=16.8 nm when the film is irradiated for 6 hours. From Raman measurements was established that irradiation treatment for 20 and 40 min causes the decrease in the intensity of bands at 364 and 495 cm<sup>-1</sup> and those in the frequency region 100 to 250 cm<sup>-1</sup> [13]. When the irradiation time was increased to 6 hours the glass exhibited a broad Raman

spectrum with a pronounced feature at 231 cm<sup>-1</sup>, which may be associated with As clustering in the glass [14]. Such changes may be interpreted in terms of optical polymerization of As<sub>4</sub>S<sub>4</sub> structural units into the glassy network, as reported previously in a study of photoinduced changes in the infrared spectrum of amorphous As<sub>2</sub>S<sub>3</sub> films [15].

The experimental data shows that the metal impurities influence the photodarkening, and 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. Fig.2a and 2b show the relaxation curves for amorphous As<sub>2</sub>S<sub>3</sub> films doped with Dy<sup>3+</sup> and Pr<sup>3+</sup> ions. For the amorphous As<sub>2</sub>S<sub>3</sub>:Dy samples, as in the case of As<sub>2</sub>Se<sub>3</sub> samples, the small concentrations of rare-earth ions essentially reduce the photodarkening effect. At the same time, high concentrations of rare-earth ions (0.25 at.% Pr<sup>3+</sup> and 1.5 at. % Nd) increase the sensitivity of photostructural transformations. This is illustrated in Fig.2b (curve 3) and in Fig.3a (curve 2). This effect was not observed in the samples of amorphous As<sub>2</sub>S<sub>3</sub> doped with rare-earth ions [6]. We also can observe, that for some samples, especially for the pure As<sub>2</sub>S<sub>3</sub>, the shape of the relaxation curves are different: the maximum of the photodarkening take place during of about 2000 s, and than the transmittance increased (curve 1 on the Fig.2a and curve 3 on the Fig.2b). Such kind of dependence in measurements of the diffraction efficiency vs. recording time for amorphous As<sub>2</sub>S<sub>3</sub> thin films was observed in [16] and for As<sub>2</sub>Se<sub>3</sub> films in [17]. For reducing the decrease part of the diffraction efficiency after reaching the maximum, in [17] the amorphous As<sub>2</sub>Se<sub>3</sub> films were doped with Sn impurities. As result, a stabilization of the maximal value of the diffraction efficiency was obtained. The authors explain this effect by the formation of new structural units like SnSe<sub>4/2</sub>, which make the glass network more stable.

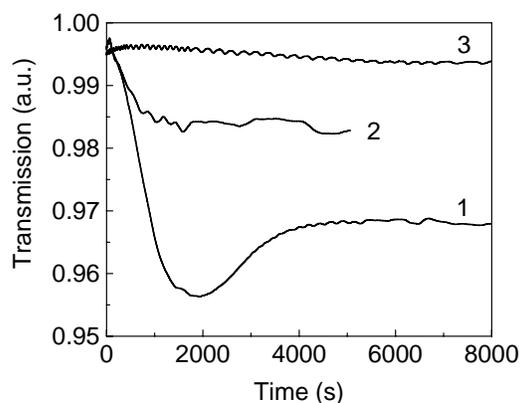


Fig. 2a. The photodarkening relaxation (at λ=0.54 μm) for the as-deposited amorphous As<sub>2</sub>S<sub>3</sub> (1), As<sub>2</sub>S<sub>3</sub>+0.1 at.% Dy<sup>3+</sup> (2), and As<sub>2</sub>S<sub>3</sub> + 0.5 at. % Dy<sup>3+</sup> (3) thin films.

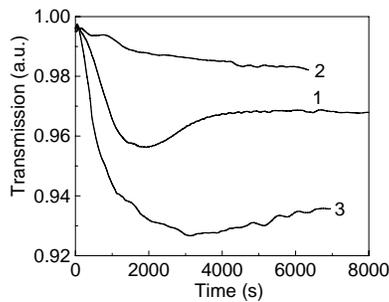


Fig. 2b. The photodarkening relaxation (at  $\lambda=0,54 \mu\text{m}$ ) for the as-deposited amorphous  $\text{As}_2\text{S}_3$  (1),  $\text{As}_2\text{S}_3+0.15$  at.%  $\text{Pr}^{3+}$  (2), and  $\text{As}_2\text{S}_3+0.25$  at.%  $\text{Pr}^{3+}$  (3) thin films.

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.1b). At the same time, the authors [18] have been reported the experimental data on holographic grating recording with focused sub-bandgap light of  $0.63 \mu\text{m}$  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 sub-bandgap irradiation with both continuous and pulsed light also were observed in amorphous Ge-Se films [19].

Reversible photodarkening induced in Ge-As-S-Se film by illumination with sub-band gap photons has been recently observed by Kincl et al. [20].

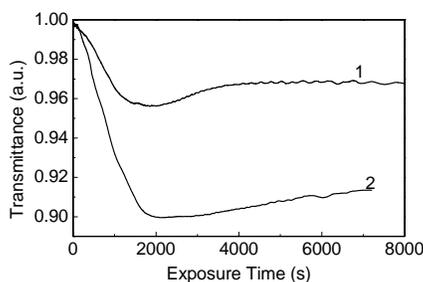


Fig. 3a. The photodarkening relaxation (at  $\lambda=0,54 \mu\text{m}$ ) for the as-deposited amorphous  $\text{As}_2\text{S}_3$  (1) and  $\text{As}_2\text{S}_3+1.5$  at.%  $\text{Nd}^{3+}$  (2) thin films.

Fig. 3b illustrates the dependence of the transmittance decrement on different species of rare-earth ions concentration in amorphous  $\text{As}_2\text{S}_3$  thin films, when excited with green light ( $\lambda=0,54 \mu\text{m}$ ). From the Fig.3b it is seen, that the action on the photodarkening effect of different rare-earth species is different.  $\text{Dy}^{3+}$  ions always decrease the photodarkening, while  $\text{Nd}^{3+}$  increase the process.  $\text{Pr}^{3+}$  ions initially decrease the photodarkening, than at more concentrations decrease it. The behavior of rare-earth ions in amorphous  $\text{As}_2\text{S}_3$  films is different than observed earlier

in amorphous  $\text{As}_2\text{S}_3$  films, where the rare-earth ions in all cases suppressed the photodarkening [6].

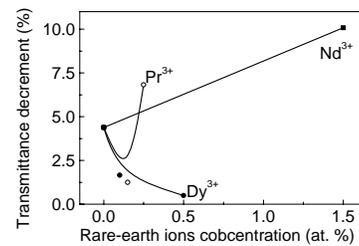


Fig.3b. The dependence of transmittance decrement on rare-earth ions concentration ( $\text{Dy}^{3+}$ ,  $\text{Pr}^{3+}$ , and  $\text{Nd}^{3+}$ ) in amorphous  $\text{As}_2\text{S}_3$  films at  $0,54 \mu\text{m}$ .

The relaxation of photodarkening in amorphous  $\text{As}_2\text{S}_3$  also was 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  $0,54 \mu\text{m}$ . Fig.4a 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 for that obtained when the sample was irradiated with continuous light at  $\lambda=0,54 \mu\text{m}$  (Fig.4a, curve 2 and Fig. 2a, curve 1). In both cases the maximum value of photodarkening is reached during the time exposure 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.4b). A small effect of photodarkening we can observe 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.4b, curve 2), also differ 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 associated with the structural changes in the network of chalcogenide glass, induced by doping with rare-earth ions (of acceptor-like D-centres present in a- $\text{As}_2\text{S}_3$  films [21]).

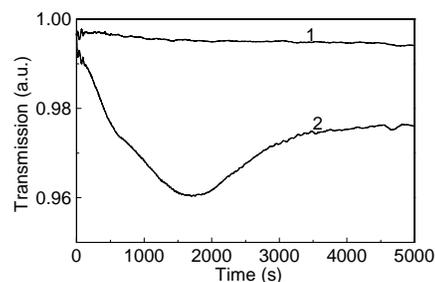


Fig.4a. The photodarkening relaxation in as-deposited  $\text{As}_2\text{S}_3$  thin films during the excitation with pulsed  $\text{N}_2$  laser. (1) – measured at  $\lambda=0,63 \mu\text{m}$  and (2) – measured at  $\lambda=0,54 \mu\text{m}$ .

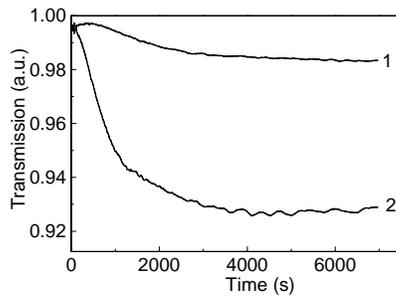


Fig.4b. The photodarkening relaxation in as-deposited As<sub>2</sub>S<sub>3</sub>+0.25 at.% Pr<sup>3+</sup> thin films during the excitation with pulsed N<sub>2</sub> laser. (1) – measured at  $\lambda=0,63 \mu\text{m}$  and (2) – measured at  $\lambda=0,54 \mu\text{m}$ .

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 ( $0<\alpha<1$ ). Stretched exponential relaxation fits many relaxation processes in disordered and quenched electronic and molecular systems [22]. Such dependence was used for interpretation of the experimental results on photodarkening relaxation in amorphous AsSe and As<sub>2</sub>Se<sub>3</sub> doped with Sn and rare-earth ions [5-7].

### 3. Summary

It was shown that the illumination of amorphous chalcogenide films with photon energy from the region of fundamental optical absorption cause changes in optical transmission and refractive index. The relaxation of photodarkening in  $\alpha$ -As<sub>2</sub>S<sub>3</sub> doped with rare-earth ions (Dy<sup>3+</sup>, Pr<sup>3+</sup>, and Nd<sup>3+</sup>) was investigated. In order to initiate the photostructural transformations samples, the excitation was performed with continuous He-Ne lasers at  $\lambda=0.63 \mu\text{m}$ ,  $\lambda=0.54 \mu\text{m}$ , and N<sub>2</sub> 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 the concentration and species of rare-earth ions. The small concentrations of rare-earth ions essentially reduce the photodarkening, while the high concentrations (0.25 at.% Dy<sup>3+</sup> 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:  $T(t)/T(0)=A_0+A\exp[-(t-t_0)/\tau]^{(1-\alpha)}$ .

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