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Relaxation of photodarkening in SiO-As₂(S,Se)₃ composite layers

I. Z. Indutnyi, P. E. Shepeliavyi, V. I. Indutnyi*

Institute of Semiconductor Physics of NASU, 45, prospect Nauki, 252028 Kiev, e-mail: indutn@dep14.semicond.kiev.ua

**Institute for Problems of Information Recording, National Academy of Sciences, ul. Shpaka, 2, Kyiv-113, 252113, Ukraine*

Abstract. Investigated in this work is the reversible photostimulated red absorption edge shift (photodarkening), ΔE_g , of As₂(S,Se)₃ nanoparticles embedded into the SiO matrix. As compared to continuous chalcogenide films, the remarkable ΔE_g increase (up to 4 times) with decreasing of chalcogenide particle sizes in composite SiO-As₂(S,Se)₃ layers was revealed. The exponential dependence of ΔE_g on storing time at different temperatures has been obtained. An activation energy of the transition of As₂S₃ nanoparticles structure from a metastable photoexposed state to a ground annealed state is equal to 0.78 ± 0.06 eV. The effects are related to a spatial confinement of a photoexcited carrier diffusion length and an influence of particle sizes on intermediate-range order scale structure relaxation in the chalcogenide nanoparticles.

Keywords: photodarkening, chalcogenide glasses, nanoparticles, SiO-As₂S₃, SiO-As₂Se₃

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1. Introduction

The photoinduced transformation of thin amorphous chalcogenide layers have attracted considerable attention owing to possibilities of developing basic principles of their physical mechanisms and exploring possible technical applications in optical recording, holography, microelectronics, optoelectronics. The most investigated chalcogenides are As₂S₃ and As₂Se₃ binary glasses. Illumination with the bandgap light induces structural changes of vacuum-evaporated chalcogenide layers, which results in changes of optical (shift of absorption edge, ΔE_g), chemical (change of solubility), mechanical and others properties [1-3]. In as-evaporated layers displayed are both irreversible photostimulated transformations caused by polymerization of breaking bonds and reversible ones which can be eliminated by thermal annealing just below the glass transition temperature. The annealed films exhibit only reversible photostimulated transformations which accompanied by the reversible red shift of absorption edge (i.e., photodarkening). A large number of scientific papers have been devoted to investigation of the mechanism of this phenomenon, a lot of models have been proposed [2-8], but there is no complete explanation of all experimental results as yet.

Recently, the effect of essential enhancement of photodarkening was revealed in composite SiO-As₂S₃ lay-

ers, when sizes of As₂S₃ particles, embedded in SiO matrix, are comparable with the scale of the medium-range order in the chalcogenide structure [9]. In this paper the results of further investigations of photodarkening in the composite films and peculiarities of ΔE_g relaxation are presented.

2. Experimental procedures

The samples were prepared by thermal vacuum evaporation and sequential deposition of a large number (from 48 to 130 couples) of ultrathin island-type SiO and As₂S₃ or As₂Se₃ layers onto polished silica substrates at room temperature. The effective thickness of each SiO layer was equal to 5 nm for all samples, and the effective thicknesses of the chalcogenide layers were changed for different samples from 2.5 to 0.7 nm in order to obtain a total chalcogenide thickness in multilayer samples from 90 to 130 nm. During SiO deposition some part of the substrate was screened to prepare a reference film of As₂S₃ or As₂Se₃ composition. The layers thickness being determined «in situ» by a quartz-crystal-oscillator monitoring system was also measured after deposition by microinterferometer both for the multilayer (composite) films and the reference ones. The deposited films were annealed at 450 K in the ambient atmosphere for two hours. Photodarkening was induced at 77 K by exposure to a high-pressure Hg lamp (light intensity 50 mW/cm²) for

one hour. The subsequent annealing-exposure circles were carried out in the same conditions. The storing of the samples at elevated temperatures were carried out in a thermostat with a temperature stability of 1 K.

The composite samples obtained form an effective SiO-As₂(S,Se)₃ media with a smaller fraction of chalcogenide. SiO layers are transparent in the spectral range of As₂S₃ and As₂Se₃ interband transitions which enables to study the photodarkening of chalcogenide nanoparticles in the SiO matrix by means of measuring their absorption coefficient (α) in annealed and exposed samples. For calculation of chalcogenide nanoparticles absorption from photometric measurements of the composite samples we used total chalcogenide layers thickness measured on the reference films. More detail experimental conditions on the sample preparations and optical measurements are described in [9].

3. Results

Absorption spectra, α vs photon energy, $h\nu$, are shown in Fig. 1 for two cases: (a) the reference As₂Se₃ layer of 127 nm thickness and (b) the composite (SiO - As₂Se₃)₉₀ film (90 - number of SiO - As₂Se₃ layer-couples in the sample), with effective thickness of each As₂Se₃ layer in the composite of 1.36 nm. The open circles are the absorption after annealing of the films, while the solid circles are the same ones after illumination. As seen from Fig. 1, both samples exhibit photodarkening, and photostimulated effect in-

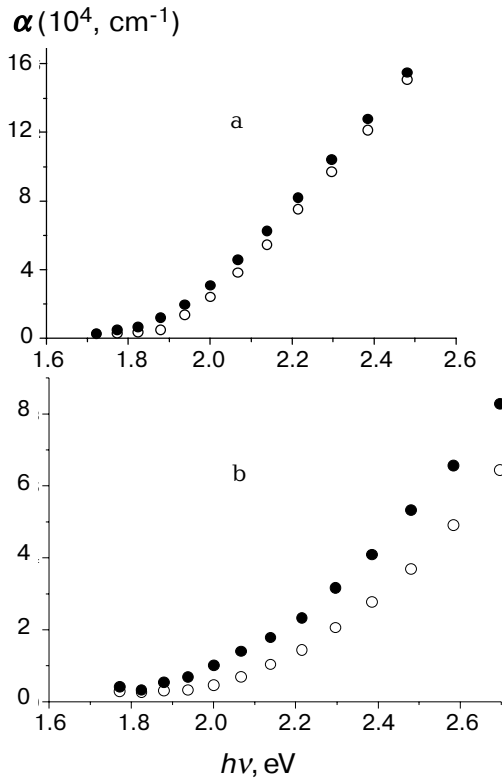


Fig. 1. Spectral dependence of absorption coefficient, α , of As₂Se₃ layer with thickness 127 nm (a), and multilayers (SiO - As₂Se₃)₉₀ sample with effective thickness of each As₂Se₃ layer in composite of 1.36 nm (b). O - annealed, ● - exposed samples.

creases in composite samples. In this work the photostimulated optical gap changes, ΔE_g , were obtained as the absorption edge shifts at $\alpha = 2.5 \cdot 10^4 \text{ cm}^{-1}$ level.

Fig. 2 shows the dependence of ΔE_g on effective thickness of As₂Se₃ and As₂S₃ layers in composite samples. Dots denoted by figures 1 and 1' correspond to reference As₂Se₃ and As₂S₃ layers. The results show essential increasing of photodarkening when the chalcogenide layer effective thickness (and dimensions of chalcogenide island in SiO matrix) decreases. For composite SiO - As₂S₃ sample with effective As₂S₃ layer thicknesses of 0.7 nm ΔE_g increases more than 4 times in comparison with reference «thick» film; for selenide based composite sample with effective As₂Se₃ layer thickness of 1.36 nm the ΔE_g increases approximately by 2.5 times. It should be mentioned that maximum values of photodarkening obtained so far for chalcogenide films (to our knowledge) corresponds to $\Delta E_g = 0.15 \text{ eV}$ for As₂S₃ and 0.66 eV for As₂Se₃ [2] that are by 2 - 2.5 time less than maximum ΔE_g revealed in our composite samples. The second feature of composite layers is smaller absorptivity of chalcogenide inclusions than that of continuous reference films.

Fig. 3 shows, as an example, the dependence of photostimulated ΔE_g on the time of exposure (kinetics of photodarkening) of composite (SiO - As₂Se₃)₉₀ sample. We can see that after fifteen minutes of exposure the photostimulated absorption edge shift is saturated. That is why we used one hour exposure to ensure the saturation of photostimulated transformation.

The exposed state of chalcogenide is metastable and relaxes towards the ground annealed state. Such relaxation occurs also at smaller temperatures than the glass transition ones, for example at room temperature, but more slowly. To investigate the relaxation peculiarities, the kinetics of ΔE_g decreasing with storing time at different temperatures were measured. Fig. 4 shows the dependencies of $-\ln(\Delta E_g)$ on the storing time for the SiO-As₂S₃ composite samples with effective As₂S₃ thicknesses of 0.7 nm. Numbers on the plots indicate the storing temperatures, the dots are experimental

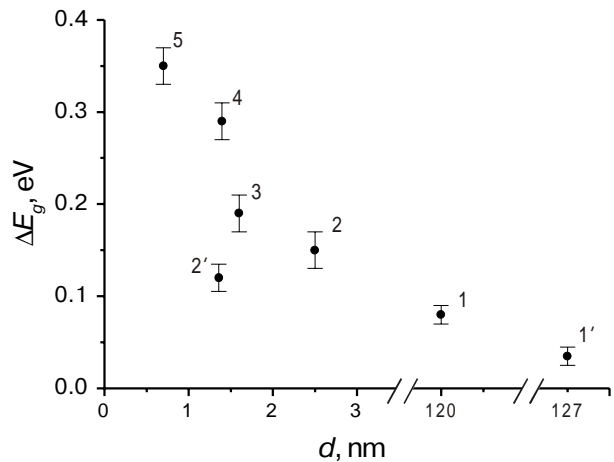


Fig. 2. Magnitude of the light-induced edge shift, ΔE_g , as a function of chalcogenide layer effective thickness. Dots 2-5 correspond to composite SiO - As₂S₃ samples, 2' - SiO - As₂Se₃, 1 and 1' - reference As₂S₃ and As₂Se₃ films.

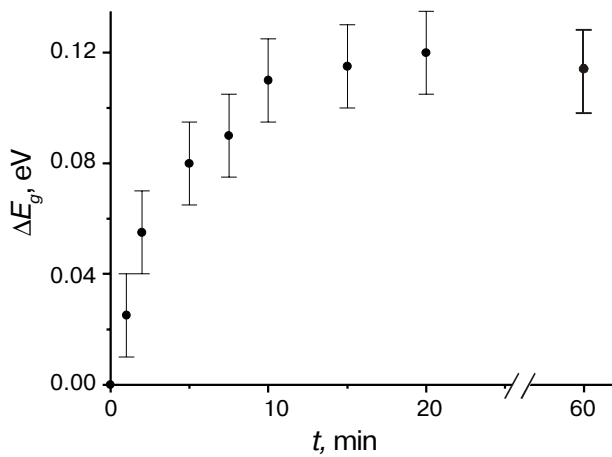


Fig. 3. Dependence of ΔE_g on the time of exposure. SiO-As₂Se₃ composite samples with effective As₂Se₃ thicknesses of 1.36 nm.

values, solid lines are linear approximations. The kinetics of relaxation at all investigated temperatures can be expressed by the exponential dependence:

$$\Delta E_g = A + B \cdot \exp(-t/\tau), \quad (1)$$

where A, B are the constants, ($A+B=\Delta E_g^0$ is initial value of ΔE_g immediately after exposure), τ is the characteristic time of relaxation, that decreases with growing the storing temperature. Using the formula (1) for fitting the experimental dots in Fig. 4 (solid line) we obtained τ values for different storing temperatures. The dependence of $\ln(\tau)$ on inverse temperature is shown in Fig. 5 and has the Arrhenius-type behavior.

4. Discussion

The reversible photodarkening in As₂S₃ layers is caused by two-stage process: photoexcitation of the electron system of chalcogenide followed by relaxation of the amorphous structure into the new metastable state. Numerous investigations involving optical (Raman, IR-spectra) measurements [7], polarized X-ray and other measurements [4-6] have led to the conclusion that photodarkening are connected with structural changes in the chalcogenide medium-range order, the appearance of photoinduced homopolar bonds were also admitted. Most of the researchers considered the electron stage of photoinduced transformations as including formation of some localized exciton-like state by a photoexcited electron-hole pair with the respective rearrangement of bonds. Such a self-trapped exciton (STE) can relax to the initial state, became metastable as intimate valence-alternation pair, or relax to other bonding configuration, some of them may contain more homopolar bonds. As suggested by Fritzsche [2], these recombination-induced bond rearrangements accumulate during exposure to produce a more disordered structure on the medium-range scale. The top of the As₂(S,Se)₃ valence band is formed by the interactions between the lone-pair p -orbitals of the chalcogens. As it follows from Fritzsche's model, the optical gap narrowing is mainly caused by stronger lone-pair in the ex-

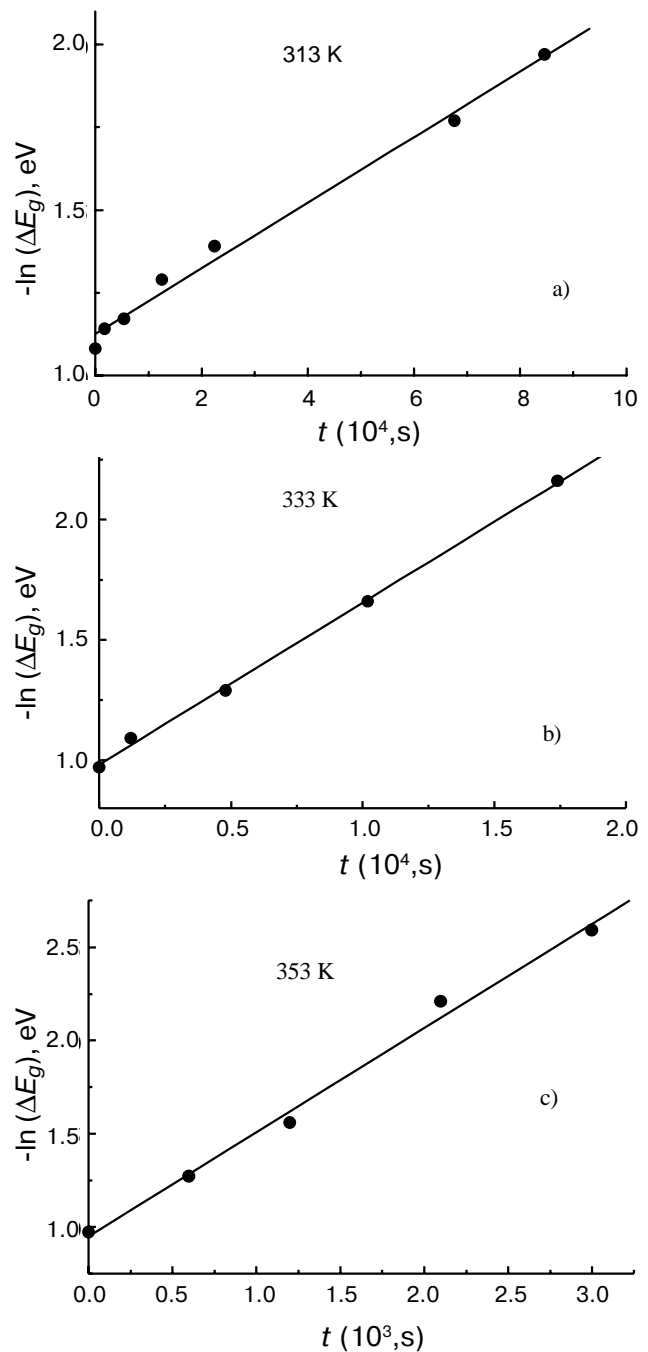


Fig. 4. ΔE_g relaxation at different temperatures: a) - 313 K, b) - 333 K, c) - 353 K. SiO-As₂S₃ composite samples with effective As₂S₃ thicknesses of 0.7 nm.

posed state relative to the annealed state and to a lesser extent by local defects - an increase in the concentration of metastable valence-alternating pairs (VAP), or homopolar bonds.

The models which include a recombination stage through STE consistently explain the known temperature dependence of photodarkening [3]: with decreasing temperature the electrons are localized near the sites of excitation, the probability of STE formation increases, and the effect is enhanced. By using such models, we can explain the obtained dependence of ΔE_g on effective layer thickness (which is related to

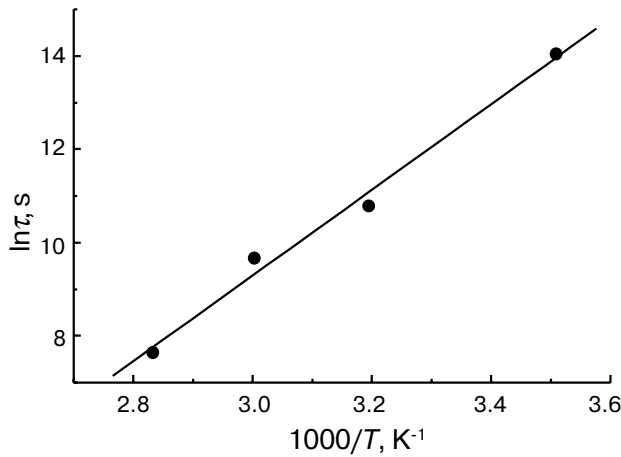


Fig. 5. The temperature dependence of decay time, τ (the same sample as at Fig. 4). Points are experimental values, solid line is linear approximation.

the chalcogenide particle dimensions). When the size of the As₂(S,Se)₃ particles embedded into the dielectric SiO matrix is decreased, the diffusion length of the photoexcited electrons is confined, resulting in an enhancement of the STE formation rate, photostructural transformations and photodarkening. The increase of ΔE_g may be also related to the effect of mechanical strain in nanoparticles, but our estimation showed [9] that this effect was negligible.

The decrease of α in composite sample in comparison with continuous chalcogenide films may be caused by two reasons. The first one is creation of As - O bonds at SiO-As₂(S,Se)₃ interface. Such local regions may be considered as microinclusions of phase with smaller absorptivity (the optical gap of As₂O₃ is 5 eV [10]). The second one is a quantum-dimensional effect that can be revealed in absorption spectra when the nanoparticle size becomes close to the Bohr radius of an exciton a_B . For As₂(S,Se)₃ the estimated values of a_B is equal to several angstroms [11].

The peculiarities of photodarkening relaxation result mainly from the mechanism of appearing the metastable state with lower optical gap. Exponential kinetics of relaxation are connected with thermostimulated transitions from the metastable state (medium order structural changes - twisting of the adjacent As(S,Se)_{3/2} pyramids about their shared chalcogene atom, other changes of the spatial arrangement of neighboring structural units, or local defects - VAP, homopolar bonds) into the ground state and, as a consequence, with the decrease of their concentration, $N(t)$, when growing the time of storing. When $\Delta E_g \ll E_g$ we can suppose with reasonable accuracy that $\Delta E_g(t) \propto N(t)$ [8], and $N(t) = N_0 \exp(-t/\tau)$, where N_0 is an initial concentration of the photoinduced changes immediately after exposure. It results in exponential dependence of ΔE_g vs time that was revealed in the experiments (see Eq. (1)). The characteristic time of relaxation, τ , from the metastable to the initial annealed state is described by expression:

$$1/\tau = \Omega \exp(-E_a/kT), \quad (2)$$

where Ω is an oscillation frequency in the metastable state,

E_a is an activation energy of the transition. This expression reasonably fits the experimental data in Fig. 5, and from such fitting one can obtain the E_a value. For a composite SiO - As₂S₃ with effective chalcogenide layers thicknesses of 0.7 nm we obtained $E_a = 0.78 \pm 0.06$ eV.

Values of E_a for evaporated As₂S₃ films have been estimated from the above experimental study of the annealing kinetics and the dependencies of photodarkening on the light intensity [8]. It was obtained that E_a varies from site to site, and the number distribution of the photogenerated defects having an energy barrier E_a can be approximated with a gaussian function, $\exp[-(E_a - E_0)^2/\sigma^2]$, where E_0 and σ^2 denote the central barrier height and the variance. For As₂S₃ films $E_0 = 1$ eV, and $\sigma = 0.5$ eV [8]. In our composite samples E_a variations are less pronounced and central barrier height is lower than that of continuous layers. This result can be explained, possibly, by a more homogeneous structure of chalcogenide nanoparticles embedded into the dielectric matrix and spatial confinement of structure relaxation.

References

1. V. M. Lyubin, Photostructural transformations in chalcogenide vitreous semiconductors, *Avtometrija (Russia)* **4**, 18-27(1988).
2. H. Fritzsche, The origin of reversible and irreversible photostructural changes in chalcogenide glasses, *Philos. Magazine B* **68**(4), 561-572(1993).
3. S. R. Elliott, A unified model for reversible photostructural effects in chalcogenide glasses, *Journ. Non-Cryst. Solids* **81**(1-2), 71-98(1986).
4. C. Y. Yang, M. A. Paesler, and D. E. Sayers, Measurement of local structural configurations associated with reversible photostructural changes in arsenic trisulfide films, *Phys. Rev. B* **36**(17), 9160-9167(1987).
5. L. F. Gladden, S. R. Elliott, G. N. Greaves, Photostructural changes in bulk chalcogenide glasses: an EXAFS study, *Journ. Non-Cryst. Solids* **106**(1-3), 189-192(1988).
6. J. M. Lee, M. A. Paesler, and D. E. Sayers, Kinetic X-ray absorption studies and computer structural modeling of photo-darkening in amorphous arsenic sulfide, *Journ. Non-Cryst. Solids* **123**(1-3), 295-309(1990).
7. O. I. Shpotyuk, Coordination defects formation model for reversible photostructural transformations in amorphous As₂S(Se)₃, *Physics and applications of non-crystalline semiconductors in optoelectronics*, A. Andriesh and M. Bertolotti, 123-129, Kluwer Academic Publishers, Netherlands, 1997.
8. K. Tanaka, Light intensity dependence of photodarkening in amorphous As₂S₃ films, *Thin Solid Films* **157**(1), 35-41(1988).
9. I. Z. Indutnyi, P. E. Shepeljavi, Reversible photodarkening in As₂S₃ nanolayers, *Journ. Non-Cryst. Solids*, **227-230**, 700-704(1998).
10. W. M. Pontuschka, P. C. Taylor, ESR in X-irradiated As₂O₃ glass, *Sol. State Commun.* **38**(7), 573-577(1981).
11. N. F. Mott, F. A. Davis, *Electron Processes in Non-Crystalline Materials*, Clarendon Press, Oxford, 1979.