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Study of $As_{50}Se_{50}$ thin film photodarkening induced by multiple wavelength beams

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This paper deals with study of photodarkening induced in chalcogenide glass thin films of composition $As_{50}Se_{50}$. The kinetics of photoinduced changes under the exposures to a band gap monochromatic beam of LED diode, as well as to beams with energy higher and lower than band gap value, were measured and discussed. Mathematical expression describing the time dependences of photodarkening was established. Related structural changes were studied using Raman spectroscopy as well.

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*Keywords:*As-Se, Thin Films, Photodarkening

1. Introduction

Chalcogenide glasses exhibit plethora of photoinduced changes in their physical and chemical properties [1,2] in dependence on the exposure wavelength and intensity. The changed properties can be e.g. optical properties, proportions of the sample [3], chemical resistance etc. Thin films are usually much more sensitive to exposure than bulk samples. The depth in which the photoinduced changes occur depends on absorption coefficient of the sample for the particular wavelength. The absorption coefficient usually increases with decreasing exposure wavelength which results in stronger absorption within the material and thereby the irradiation is fully absorbed in thinner surface layer of the material.

Glasses of As-Se system, especially their thin films, exhibit photodarkening being exposed to a beam covering visible part of spectra. In this paper we study photodarkening induced in thin $As_{50}Se_{50}$ films by exposure to narrow spectral ranges (beams of LED diodes) which either correspond to the band gap or are above/below this energy value.

2. Experimental

The bulk sample of amorphous $As_{50}Se_{50}$ was prepared by melt-quenching method in quartz ampoule from 5N purity arsenic and selenium. The thin films were deposited by thermal evaporation method (Tesla Corporation, model UP-858) from bulk glass placed in molybdenum boat in a vacuum of 2.10^{-4} Pa by evaporation rate 1-2 $nm.s^{-1}$. Thickness of the thin films was about 1000 nm. These samples were exposed to LED diodes Roither Lasertechnik (Austria) emitting beams with maximum outputs at wavelengths 375, 405, 450, 525, 630 and 690 nm. Exposure times were 90 minutes for each sample. Transmission spectra were measured ex situ on fiber spectrometer EPP2000 (StellarNet Inc.) in times from 1 second to 90 minutes of exposure. Raman spectra were measured using FTIR spectrometer IFS 55 (Bruker) with Raman spectroscopy module FRA 106 working with excitation source Nd:YAG laser (1064 nm). SEM images and thin film composition analysis were obtained on scanning electron microscope JEOL JSM-5500LV with energy-dispersive X-ray (EDAX) microanalyzer. Ellipsometer VASE (J.A. Woollam Co. Inc.) was used to record change of light beam polarization under its reflection from as-prepared $As_{50}Se_{50}$ film in spectral range 0.7 - 6.5 eV (190 nm-1800 nm). Angle of incidence (AOI) was set close to the Brewster angle (three AOI were selected: 70, 75 and 80°). Optical reflectance (AOI of 18°) and transmittance measurements were also carried out using the same instrument. In the case of reflection configurations (ellipsometry and optical reflectance) back side of glass substrates were stuck with Scotch tape to eliminate substrate back side reflections. Sample model structure was considered as a slightly rough single layer deposited on a glass substrate. Dielectric function of the layer was modeled by Tauc-Lorentz parameterization. Recorded ellipsometric, reflectance and transmittance spectra were then simultaneously numerically treated in a fitting procedure (WVASE software) to adjust free parameters of the layer dielectric function, its thickness and roughness.

3. Results

It was found using ellipsometry technique that as-prepared $As_{50}Se_{50}$ thin films have their optical band gap 1.91 eV. This value corresponds to wavelength 649 nm which is close to peak wavelength of used 630 nm LED. Exposure to beam of narrow spectral range emitted by this

LED as well as to beams emitted by sub-band gap LED (690 nm) and over-band gap LEDs (375 nm, 405 nm, 450 nm, 525 nm) resulted in photodarkening of thin films. For illustration the used LEDs spectral characteristics so as transmission spectra of as-prepared $As_{50}Se_{50}$ thin film are given in Fig. 1.

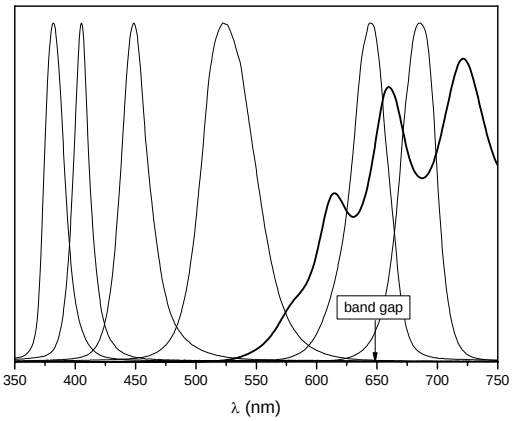

Fig.1. Characteristics of the diodes used for exposure and transmission spectra of as-prepared $As_{50}Se_{50}$ thin film (d~1000nm).

The depth dependences of beam transmissions for particular wavelengths used for exposure (Fig. 2) were calculated using absorption coefficients in accordance with equation:

$$I = I_0 \cdot \exp(-\alpha d) \tag{1}$$

where I is the intensity of the beam in particular depth of a thin film, I_0 is the intensity of the beam before penetrating into the thin film, α is the absorption coefficient for particular wavelength and d is the depth of penetration into a thin film. Fig. 2 gives evidence that over-band gap beams emitting diodes can induce photostructural changes only in the vicinity of thin film surface. Contrary more than 80% of (sub)band gap beams pass through thin films so one can expect lower efficiency of photostructural changes which should proceed within the whole volume of the film.

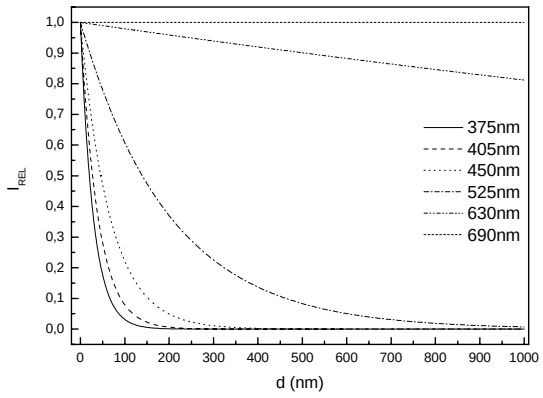

Fig. 2. Depth dependences of beam transmission in as-prepared $As_{50}Se_{50}$ thin film.

The wavelengths λ_t where T=10% were deducted from transmission spectra of thin films collected ex situ during their exposures. These wavelengths λ_t (T=10%) were plotted as a functions of exposure time for particular exposure wavelengths (Fig. 3). Time dependences were fitted by function:

$$\Delta\lambda_t = \Delta\lambda^{MAX} \frac{t^q}{k^q + t^q} \tag{2}$$

where t is time of exposure (s), $\Delta\lambda_t$ is the difference between wavelengths λ (T=10%) in exposed and as-prepared thin film's spectra (nm) at time t, $\Delta\lambda^{MAX}$ is the limit value of the difference Δλ (T=10%) between as-prepared and fully exposed[1] thin film (nm), k is time when $\Delta\lambda_t=\Delta\lambda^{MAX}/2$ (s) thus it represents the rate of photodarkening and q is cooperativity coefficient.

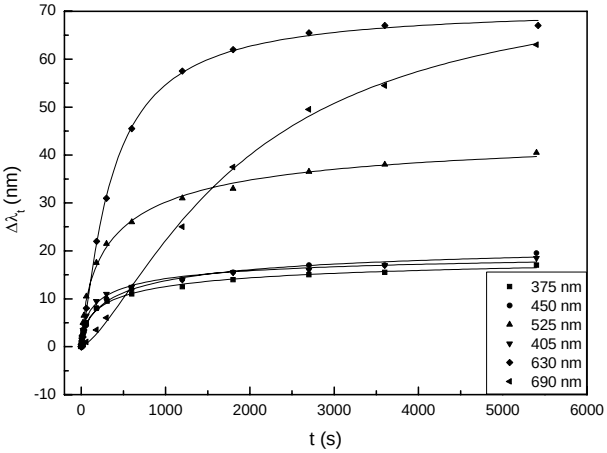

Fig. 3. Time of exposure dependences of $\Delta\lambda_t$(T=10%) for particular exposure wavelengths. Experimental data (points) interlarded by fit according to equation (2) (lines).

The dependence of parameter $\Delta\lambda^{MAX}$ on the exposure wavelengths (Fig. 4) gives evidence that the most significant shifts are caused by gap and sub-band gap exposure beams (630 and 690 nm). Contrary the significantly smaller changes take place in exposures by over-band gap beams (375-525 nm). Explanation could be found in the different penetration depth dependences for particular wavelengths (Fig. 2) due to various absorption coefficients' values. Over-band gap beams are fully absorbed in several tens or hundreds of nanometers, thus only surface thin layer of the whole thin film is changed by exposure and the rest is (theoretically) unexposed. During exposure the samples are getting darker (photodarkening) which makes the layer influenced by the exposure even thinner. The band gap and sub-band gap wavelength beams are not fully absorbed even in the whole thickness of the thin film. Thereby the optical

[1] Term 'fully exposed' means optical parameters of the sample are not influenced by extended exposure time.

parameters of the sample are changed in the whole thickness.

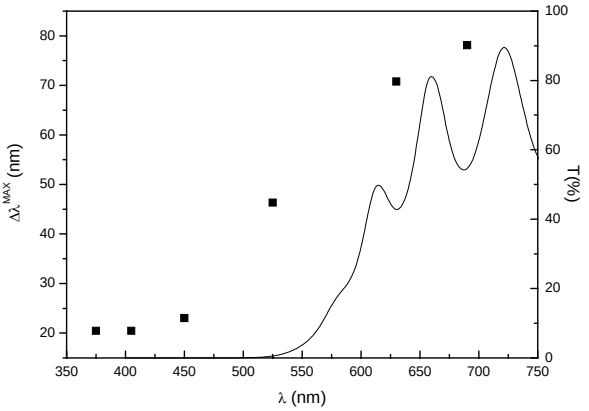

Fig. 4.The exposure wavelengths dependence of $\Delta\lambda^{MAX}$ and transmission spectra of as-prepared $As_{50}Se_{50}$ thin film.

It could be surprising that even sub-band gap beam can induce structural changes. Fig. 1 gives evidence that a small part of 690 nm LED's irradiance spectral distribution infringes to the over band gap region. We assume that this small part of 690 nm LED's beam is responsible for the photoinduced changes observed (sub-band gap part of the beam passes through the sample without absorption as is indicated in Fig. 2).

The dependence of *k* parameter on the exposure wavelengths (Fig. 5) proves that exposures done by band gap and over band gap beams (375-630 nm) run by nearly equal rate of photoinduced changes. The only one exception is the exposure to 690nm beam which exhibit several times higher value of *k* parameter. As mentioned above, there is a part of the sub-band gap beam's spectral distribution (690 nm LED) which infringes to over-band gap wavelength and causes the changes. As the sample is getting darker during the exposure the band gap value moves toward lower energies (higher wavelengths), which results in absorption of larger part of the beam. Thus the rate of photoinduced changes increases during the exposure. The final rate of photoinduced changes caused by 690 nm LED's beam is still significantly lower (higher value of *k* parameter) in comparison with the other used diodes.

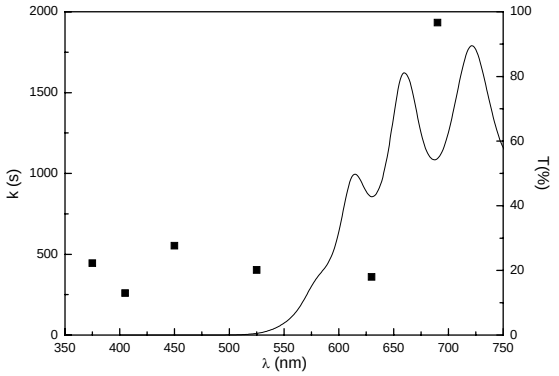

Fig. 5. The exposure wavelengths dependence of k parameter and transmission spectra of as-prepared $As_{50}Se_{50}$ thin film.

Raman spectra of studied samples (Fig. 6) were used for study of structural changes of the samples responsible for changes in their optical properties. Time of exposure for all exposed samples was 90 minutes, which corresponds to the state of the samples after measuring the kinetics of photodarkening.

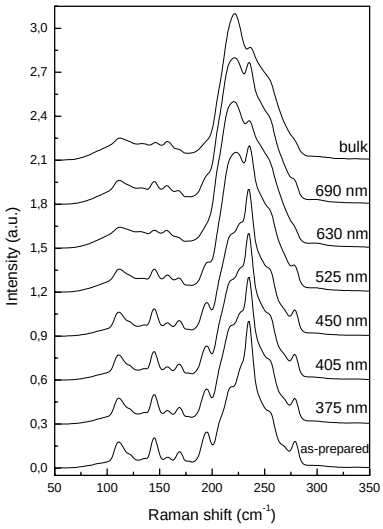

Fig. 6. Raman spectra of $As_{50}Se_{50}$ samples. Numbers specify the peak wavelength of exposure beams.

The spectra of $As_{50}Se_{50}$ thin films exhibit presence of As_4Se_3 clusters presented by bands at 168, 195, 236, 254 and 279 cm^{-1} [4,5], $AsSe_3$ pyramids (222cm^{-1}) [6] and homopolar bond As-As (111 and 144 cm^{-1}). The bands of As_4Se_3 cluster presence are significantly dominant in the spectrum of as-prepared (unexposed) thin film. Contrary the bulk sample spectrum exhibits major presence of $AsSe_3$ pyramids. By exposure to all wavelength beams the structures advance from virgin structure toward the bulk one. The progress of structural changes in dependence on exposure beam's wavelength exhibits similar trends as values of $\Delta\lambda^{MAX}$ in optical properties. Therefore the over-band gap beams (375-525 nm) caused very small changes in Raman spectra because only a thin layer of the thin film was changed by exposure due to strong absorption. Band gap and sub-band gap beams with deeper penetration depth (630 and 690 nm) evoke more significant shifts in samples structures.

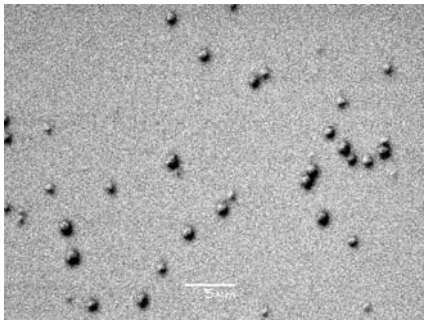

Fig. 7. SEM image of a sample exposed to LED with peak wavelength 375 nm for 90 minutes.

All exposures were done in the air. We found that partial surface photooxidation of samples took place after 90 minutes exposures for all used diodes. SEM gave evidence of small inhomogeneous structures on the surface (Fig. 7) which were identified by EDAX analysis as As_2O_3. It means partial oxidation of As-As bonds occurs during long exposures which is in good agreement with data given in [7].

4. Conclusions

It was found that the degree of photoinduced changes in optical properties of $As_{50}Se_{50}$ thin film strongly depends on the exposure beam's wavelength. We assume that the cause of this phenomenon consists in differences in penetration depths of particular wavelengths. The rates of photoinduced changes caused by band gap and over-band gap beams are nearly equal.

It was observed that even sub-band gap beam exposure (690 nm LED) induced measurable changes in optical properties, but the kinetic was significantly lower than in case of band gap and over-band gap beams (375 – 630 nm diodes). We assume that the reason is the non-ideality of the 690 nm diode's beam (part of the beam's spectral distribution of this diode infringes to over-band gap region of $As_{50}Se_{50}$ thin film).

According to Raman spectroscopy the structure of $As_{50}Se_{50}$ glass consists mainly of $AsSe_3$ pyramids and As_4Se_3 cages. Band of $AsSe_3$ pyramids is significantly more intensive in the structure of bulks. Contrary the as-prepared thin films contain mostly As_4Se_3 clusters. Thin films' structures move by exposure toward the bulk material structure. The degree of the changes in the Raman spectra is proportional to the penetration depths for particular exposure beams.

Acknowledgements

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