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Photoinduced structural changes in $\text{As}_{100-x}\text{S}_x$ layers

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Abstract. The present paper is concerned with investigations of photoinduced structural changes in $\text{As}_{100-x}\text{S}_x$ layers. Optical constants of variously treated (virgin, exposed, annealed) samples were determined from optical transmission measurements in the spectral region 400-2500 nm. The energy dependence of refractive index n for variously treated samples was fitted by the Wemple-DiDomenico dispersion relationship and used to estimate the single-oscillator model parameters. It was found, that exposure, as well as annealing leads to the increase in n values over the all investigated spectral region. Compositional dependencies of single-oscillator model parameter E_d (dispersion energy), optical dielectric constant $\epsilon(0)$ show maximum at stoichiometric composition $\text{As}_{40}\text{S}_{60}$ and, possibly, weak maximum at $\text{As}_{28.6}\text{S}_{71.4}$ composition. Changes of the parameters of the single-oscillator model induced by treatment are discussed on the base of photo- and thermally-induced structural changes, which were directly confirmed by Raman scattering measurements. Such photoinduced structural changes provide good etching selectivity of As-S layers in amine based solvents. Intensity dependence of the Raman bands corresponding to the As rich and S rich molecular fragments on exposure time is well described by the exponential decay, which correlates with exponential decay dependence of the etching rate of $\text{As}_{100-x}\text{S}_x$ layers on exposure.

Keywords: As-S layers, optical properties, Raman spectra.

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1. Introduction

The perspective imaging materials based on chalcogenide glasses and thin layers have attracted much attention and were extensively studied starting from the middle of 1960s. Their imaging properties were first shown in [1] and are connected with the wide variety of photoinduced phenomena observed in chalcogenide amorphous semiconductors [2]. Many publications were concerned with the photoinduced changes in thin films from As-S composition line [3-14]. As-S films were successfully applied in the field of diffractive optics as high resolution recording media [10,12]. But publications mostly were dealing with stoichiometric $\text{As}_{40}\text{S}_{60}$ composition for which high values of photoinduced changes of refractive index are characteristic. Only few papers have considered influence of composition [4, 5, 7]. Optical properties of As-S films in transparency region are well described by one-oscillator model [5, 7, 9-11]. Composition evolution of one-oscillator model parameters was studied for annealed As-S films in [5, 7]. Investigation and analysis of compositional trends can provide better insight on mechanisms of photo-induced transformations that is why in the pre-

sent paper we have studied imaging properties of As-S thin films as a function of composition. Present paper is concerned with the investigations of photo- and thermally induced changes of $\text{As}_{100-x}\text{S}_x$ films studied by optical techniques, Raman spectroscopy, dissolution rate. The results obtained (changes of the parameters of the single-oscillator model, Raman spectra, chemical properties induced by treatment) are discussed in terms of chemical ordering and polymerization of different molecular fragments incorporated into the films network.

2. Experiment

The bulk materials of $\text{As}_{100-x}\text{S}_x$ ($x = 71.4; 67; 62; 60; 58$) composition were prepared by the direct synthesis according to the conventional melt-quenched method from 5N purity elements. Arsenic and sulfur were weighed and placed in precleaned and outgassed (by heating under vacuum to 900 °C) quartz ampoules. The synthesis was performed in evacuated (up to a pressure 1×10^{-3} Pa) and sealed quartz ampoules using rocking furnace at 700 - 750 °C for 8-24 hrs. After synthesis the ampoules were

quenched in cold water (temperature $\sim 15^\circ\text{C}$, which is equivalent to a cooling rate of the order of 10Ks^{-1}). Thin films ($d = 0.4 - 5\ \mu\text{m}$) were deposited by the vacuum thermal evaporation ($p \approx 10^{-3}\ \text{Pa}$) from the resistance heated quartz crucible onto clean glass substrates (microscopic slides) kept under room temperature. During the deposition process the substrates were rotated by means of a planetary rotation system, which provided the uniformity of the samples thickness. Deposition rate was continuously measured using the quartz microbalance technique and in the present study was within $1 - 6.0\ \text{nm/s}$. Care was taken during sample preparation to minimize exposure to light sources. Thin film samples were kept in complete darkness until required. The samples were illuminated either by the halogen lamp ($I = 10 - 30\ \text{mW/cm}^2$, IR cut off filter), Hg lamp, Ar laser or by natural light. Some samples were annealed in Ar atmosphere at $T_g - 20^\circ\text{C}$ for 1-4 hours. The optical transmission of $\text{As}_{100-x}\text{S}_x$ films was measured in the spectral region of 0.3 to $2.5\ \mu\text{m}$ using an UV-VIS-NIR spectrophotometer (JASCO-570). The Raman spectroscopy investigations were carried out by using Fourier Transformation (FT) BRUKER IFS55 IR spectrophotometer with FRA-106 accessory. Raman spectra were excited using a laser beam with $\lambda = 1064\ \text{nm}$ having an output power $90\ \text{mW}$ during measurements of glasses and $15\ \text{mW}$ for measurements of the films. The wavelength of the laser beam was critical to avoid any photostructural changes in chalcogenide glasses and films within the time scale of 100 scans for glasses and 1000 scans for films. The resolution of the Raman spectrometer was $1\ \text{cm}^{-1}$. All measurements were performed at room temperature. Measurements of selective etching in the amine based etching solutions were carried out by interferometric method [13] and using MII-4 microinterferometer as described in [15].

3. Results

The optical constants were calculated from transmission spectra data using the method suggested by Swanepoel [16]. This method assumes use of films with uniform thickness, which, when absent, produces a shrinking in the transmission spectrum, leading to less accurate results and even serious errors. The use, as was said above, of planetary rotation system during vacuum evaporation provided excellent uniformity of the samples. For all studied $\text{As}_{100-x}\text{S}_x$ compositions exposure to the band gap light lead to the shift to higher wavelengths (photo-darkening). Energy dependencies of the refractive index $n(E)$ were well fitted by the Wemple - Di Domenico dispersion relationship [17].

$$\varepsilon_1 = n^2 = 1 + \frac{E_d E_0}{E_0^2 - E^2} \quad (1)$$

where $E = h\nu$ is the photon energy, E_0 is the single-oscillator energy and E_d is the dispersion energy. Position of the energy of the effective dispersion oscillator E_0 is typi-

cally near the mean peak of the ε_2 spectrum, which is identified by the mean transition energy from the valence band of the lone pair states to the conduction band state. Here it is necessary to note, that in amorphous As-S substances the valence-band edge involves transitions between lone-pair states and anti-bonding conduction band states [17]. By plotting $(n^2 - 1)^{-1}$ against E^2 , and fitting a straight line, E_0 and E_d were determined from the slope $(E_d E_0)^{-1}$ and the intercept on the vertical axis, E_0/E_d .

The dependencies of $n(\lambda)$, values of single oscillator energy E_0 , dispersion energy E_d were obtained for the as-evaporated, annealed and exposed samples. Exposure and annealing lead to the increase of E_d and optical dielectric constant (Fig. 1-2) and to the decrease of E_0 value. Dependence of E_d for annealed samples is similar to the presented in [5], also n values were somewhat lower. Such differences in n values are connected with different conditions of films fabrication, which, as was shown in [8], can lead to the changes in n .

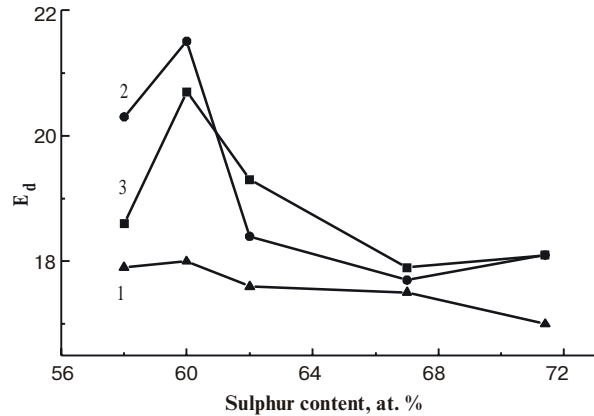


Fig. 1. Dependence of dispersion energy E_d on sulphur content for $\text{As}_{100-x}\text{S}_x$ layers: 1 – as-evaporated layers, 2 – exposed, 3 – annealed.

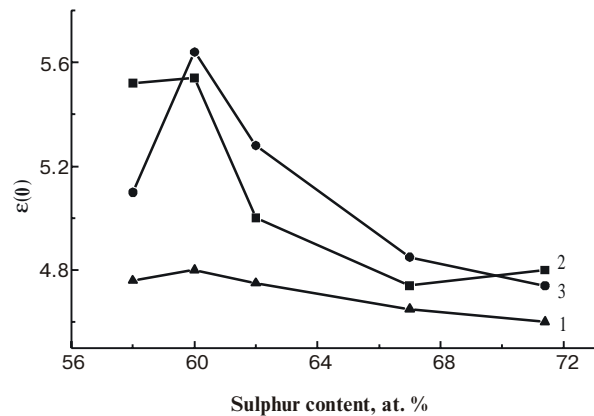


Fig. 2. Dependence of optical dielectric constant $\varepsilon(0)$ on sulphur content for $\text{As}_{100-x}\text{S}_x$ layers: 1 – as-evaporated layers, 2 – exposed, 3 – annealed.

Raman spectra of fresh evaporated $\text{As}_{100-x}\text{S}_x$ layers (Fig. 3) show the presence of numerous weak bands (136; 146; 169; 191; 213; 223; 234; 275; 476; 495 cm^{-1} , etc.) that correspond to As rich and S rich fragments [3, 18-20]. Dominant features of this spectra are bands 345 cm^{-1} (symmetrical vibrations of $\text{AsS}_{3/2}$ pyramids and vibrations of As_4S_4 molecular fragments) and 363 cm^{-1} (As_4S_4 molecular fragments). Spectra were reduced according to the Shuker-Gammon procedure [21]. Reduced Raman spectra exhibit general features of one-phonon density of states if matrix element terms are slowly varying with frequency. The profile of the Raman spectra of $\text{As}_{40}\text{S}_{60}$ layers in the 280-450 cm^{-1} range suggest the existence of the main five component bands at 311, 331, 346, 363, 382 cm^{-1} . Tentative deconvolution of the Raman spectra of $\text{As}_{40}\text{S}_{60}$ layers into constituent bands is shown in Fig. 4. It can be seen that the structure of the evaporated $\text{As}_{100-x}\text{S}_x$ film can be represented in the form of matrix that consists of pyramidal units $\text{AsS}_{3/2}$. This matrix contain considerable amounts of As_4S_4 , S_2 and S_n fragments, that contain As-As and S-S «wrong» bonds other defects can be present in the structure as well. The presence of such defects, fragments is essential for polymerization processes of the molecular groups in the main glass matrix under annealing or exposure. The amplitude of changes in n , E_d , optical dielectric constant must be proportional to the initial concentration of such molecular groups. Indeed that can be seen in composition evolution of the intensity of bands in Raman spectra corresponding to the As rich and S rich molecular fragments (Fig. 5), and its comparison with compositional changes of E_d , optical dielectric under exposure or annealing. Decrease in amplitude of changes for $x \leq 60$ to some extent can be connected with increased presence of As_4S_3 molecular fragments (275 cm^{-1} band,

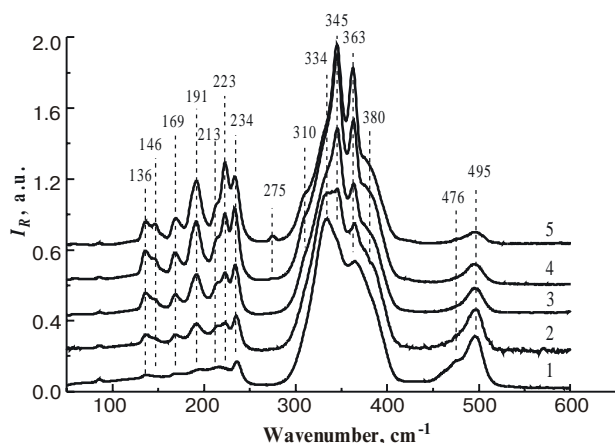


Fig. 3. Raman spectra of as-evaporated $\text{As}_{100-x}\text{S}_x$ layers. Spectra were reduced according to the Shuker-Gammon procedure, normalized by an area and shifted by 0.2 in relation to each other. 1 – $\text{As}_{28.6}\text{S}_{71.4}$; 2 – $\text{As}_{33}\text{S}_{67}$; 3 – $\text{As}_{38}\text{S}_{62}$; 4 – $\text{As}_{40}\text{S}_{60}$; 5 – $\text{As}_{42}\text{S}_{58}$ layers.

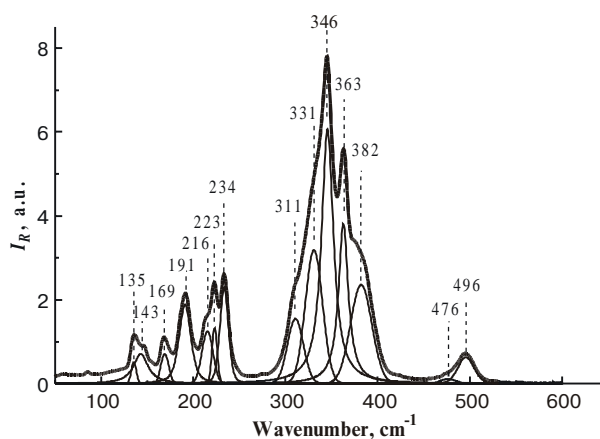


Fig. 4. Tentative deconvolution of Raman spectra for as-evaporated $\text{As}_{40}\text{S}_{60}$ layers into constituent bands.

Fig. 3). Under exposure or annealing, concentration of such As rich and S rich molecular fragments as well as corresponding Raman bands are decreased. Intensity dependence of the respective bands on exposure time is well described by the exponential decay (Fig. 6). Intensity change under exposure for 136; 146; 169; 191, 213, 223, 234 cm^{-1} bands ascribed to the As rich fragments is different (Fig. 6).

Such photoinduced structural changes provide good etching selectivity of $\text{As}_{100-x}\text{S}_x$ layers in various nonaqueous amine based solvents. Dependence of the etching rate V_e on exposure time is well described by the exponential decay (Fig.7). Type of such dependence is not influenced by the spectral composition of exposing light [14].

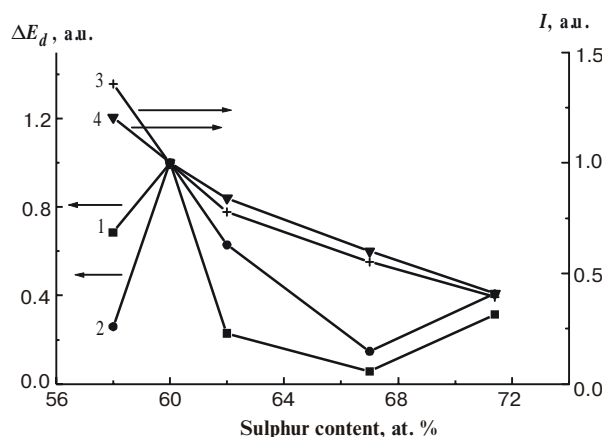


Fig. 5. Composition dependence of ΔE_d for annealed (curve 1) and exposed (curve 2) $\text{As}_{100-x}\text{S}_x$ layers. Here ΔE_d is E_d difference between values characteristic for the respectively treated layers and as-evaporated layers. ΔE_d values were normalized for that ones which are characteristic for $\text{As}_{40}\text{S}_{60}$ layers. Composition dependence for the reduced Raman spectra bands of $\text{As}_{100-x}\text{S}_x$ layers: curve 3 – 191 cm^{-1} ; curve 4 – 223 cm^{-1} . Intensities were normalized to the ones characteristic for $\text{As}_{40}\text{S}_{60}$ layers.

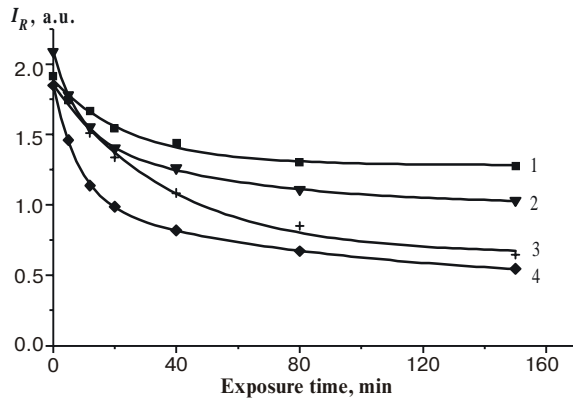


Fig. 6. Intensity dependences on exposure (halogen lamp) of Raman spectra bands for $\text{As}_{40}\text{S}_{60}$ layers: 1 – 136; 2 – 192; 3 – 223; 4 – 233 cm^{-1} .

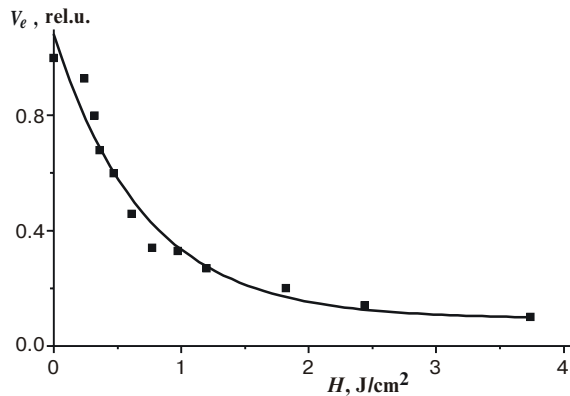


Fig. 7. Dependence of dissolution rate V_e of $\text{As}_{40}\text{S}_{60}$ layers on exposure H (Hg lamp).

4. Discussion

It can be seen from data in Figs 1-2 that maximal changes in E_d occur at the stoichiometric $\text{As}_{40}\text{S}_{60}$ composition. This is in accordance with data presented in [5]. Maximal changes in $\epsilon(0)$ also occur at $\text{As}_{40}\text{S}_{60}$ composition. Here it is necessary to note that in glasses of $\text{As}_{100-x}\text{S}_x$ system major extrema are observed in compositional dependencies of such structurally determined parameters as glass transition temperature T_g , relaxation enthalpy ΔH , specific heat capacity C_p , etc., when the stoichiometric $\text{As}_{40}\text{S}_{60}$ composition is reached [22-23]. At this composition average coordination of Z in the glass network reaches 2.4 and according to the topological models has the optimal network topology [24]. Some small peculiarity in composition dependence of one-oscillator model parameters (Figs 1-2) also possibly is present at 28.5at.% As ($\text{As}_{28.6}\text{S}_{71.4}$), similar feature was observed in [22, 23] for As-S glasses composition dependencies of glass transition temperature, relaxation enthalpy, specific heat ca-

capacity. But this peculiarity at 28.5 at.% As is not so clear and needs further experimental confirmation, additional films compositions must be investigated. As was shown in [17], dispersion energy E_d obeys a simple empirical relationship: $E_d = \beta N_c Z_a N_e$, where $\beta = 0.37 \pm 0.04$ eV in covalent crystalline and amorphous materials, N_c is coordination number of cation nearest neighbor to the anion, Z_a is the formal chemical valence of the anion, and N_e is a total number of valence electrons (cores excluded) per anion. Thus, the changes in E_d indicate photoinduced structural changes in nearest neighbor atomic configuration. The structure of evaporated thin films is somewhat different from the glass one, for example, as-deposited As_2S_3 layers contain significant number of defects, including dangling bonds of S atoms, the concentration of As-As bonds is estimated as $\sim 32\%$ [25]. Illumination and annealing decrease the concentration of As-As bonds up to 16 and 10%, respectively [25]. Therefore the atomic density contributing to the irreversible photoinduced structural changes is roughly $\sim 10^{22} \text{ cm}^{-3}$.

Assignment of the bands for the vibrational spectra of $\text{As}_{100-x}\text{S}_x$ glasses in first approximation usually is made on the base of the molecular model [18]. As-deposited $\text{As}_{100-x}\text{S}_x$ films represent partially polymerized mixture of AsS_3 pyramidal units and As_4S_4 , S_2 and S_n non-stoichiometric molecular units [3, 20, 25-26]. For $x \leq 60$ appears weak feature at 275 cm^{-1} , which arise from the presence of As_4S_3 molecular fragments [20, 26]. For $x \geq 60$ bands at about 331-345 cm^{-1} appear which can be connected with extra sulfur atoms incorporated into (-S-S-) chains linking $\text{AsS}_{3/2}$ together [22,23]. As we have seen in Fig. 5 there is rough correspondence between the composition dependence of the initial intensity of Raman bands corresponding to the homopolar molecular fragments and composition dependence of the evolution of one-oscillator model parameters under exposure or annealing if $x \geq 60$.

Molecular fragments observed in as-evaporated $\text{As}_{100-x}\text{S}_x$ films are related to the molecular composition of vapor, which is partially frozen during condensation onto substrate. It is known that in $\text{As}_{100-x}\text{S}_x$ vapor various As_mS_n , S_n clusters are present [27]. During condensation these molecular fragments recombine with each other to form network with bond distribution close to a random one. The exposure or annealing of the films leads to the stabilization of the structure through redistribution of the chemical bonds of nearest environment. Under exposure the interaction between As-As and S rich molecular fragments takes place with the increase of the number of $\text{AsS}_{3/2}$ structural units. There is no significant influence of the diffusion processes, because due to high concentration of As-As and S rich molecular fragments (as was said above $\geq 30\%$) in initial as-evaporated films they are in the nearest environment to each other (in a cube with a side length of ~ 2 atoms). It was also noted that in amorphous chalcogenides photo-excited carriers are rapidly localized to a range of a few Angstroms with resulting recombination-induced bond rearrangements [28]. Such bonds rearrangements with decrease of homopolar bonds are favored thermodynamically. Thus, the change of the

number of As-As and S rich molecular fragments N_H and, respectively, the number of homopolar bonds at light exposure can be written as:

$$dN_H/dt = -CaI N_H \quad (2)$$

where a is absorption coefficient, I – light intensity, C – constant.

Solution of the equation (2) gives

$$N_H = N_{H0} \exp(-CaH) \quad (3)$$

where N_{H0} is the number of As-As and S rich molecular fragments (and number of respective homopolar bonds) in the initial as-evaporated film, $H=It$ - exposure value. Exponential decay dependence of the etching rate V_e on exposure may be considered connected with similar dependence (3) of the number of molecular fragments on exposure, but here it is necessary to note that during dissolution of $As_{100-x}S_x$ layers etching of stoichiometric molecular fragments $AsS_{3/2}$ and non-stoichiometric As-As and S rich molecular fragments can proceed in several stages [29], different mechanisms are possible and thus interconnection of V_e and N_{H0} can be more complex.

Conclusion

The investigations carried out show that registering media based on $As_{100-x}S_x$ layers are rather promising for the various imaging and other optical applications.

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