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Image formation properties of $As_{40}S_{20}Se_{40}$ thin layers in application for gratings fabrication

A. V. Stronski [a], M. Vlček [b], P. E. Shepeliavyi [a] , A. Sklenař [b], S. A. Kostyukevich[a]

[a] *Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, Kyiv, 252028, Ukraine*

[b] *University of Pardubice, 532 10 Pardubice, Czech Republic*

Abstract. The present paper is concerned with investigations of image formation properties of $As_{40}S_{20}Se_{40}$ thin layers. Spectral dependence of the refraction index, n, of variously treated (virgin, exposed, annealed) samples was estimated from optical transmission in the spectral region 400 - 2500 nm. The n energy dependence of 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. 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 $As_{40}S_{20}Se_{40}$ layers in nonaqueous amine based solvents. The sensitivity values obtained on 488 nm wavelength consisted ~ 9 cm^2/J. Surface relief patterns that were fabricated have good surface quality. Diffraction efficiency values of holographic diffraction gratings (HDG) obtained on the base of $As_{40}S_{20}Se_{40}$ layers consisted 60-70 %. Relief profile of HDG was close to sinusoidal one. High quality polymer HDG copies were obtained. AFM profiles of the initial replica copies were practically identical to the profile of the master grating.

Keywords: $As_{40}S_{20}Se_{40}$ layers, optical properties, Raman spectra, surface relief formation, diffraction gratings.

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1. Introduction

Among major areas of research in modern optical technology there are fiber-optic communications, optical imaging, diffractive optics. The development of novel materials is the key aspect of the above mentioned areas. The chalcogenide glasses and systems on their base have attracted much attention and were extensively studied starting from the middle of 1960s. Glasses from As-S-Se line were successfully applied in the field of diffractive (as high resolution thin film inorganic resists) [1-2] and fiber optics [3]. In the present paper we have studied optical and chemical properties of $As_{40}S_{20}Se_{40}$ thin films using mainly various optical techniques and applied such media for gratings fabrication.

2. Experiment

The bulk materials of $As_{40}S_{20}Se_{40}$ composition were prepared by the direct synthesis according to the conventional melt-quenched method from 5N purity elements. The synthesis was performed in evacuated quartz ampoules using rocking furnace at 700 - 750 ^oC for 8 - 24 hrs. After synthesis, the ampoules were quenched in cold water. Thin films (d = 0,4 - 5 μm) were deposited by the vacuum thermal evaporation ($P = 1 * 10^{-3}$ Pa) from the resistance heated quartz cruicible 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 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 Xe-lamp (I = =10 - 30 mW/cm^2 , IR – cut-off filter) or by natural light. Some samples were annealed in Ar atmosphere at 150 °C during 4 hours. The optical transmittance of $As_{40}S_{20}Se_{40}$ films was measured in the spectral region of 0,3 to 2,5 μm using an UV-VIS-NIR spectrophotometer (JASCO-570). The Raman spectroscopy investigations were carried out by using BRUKER IFS55 IR spectrophotometer with FRA-106 accessory. All measurements were performed at room temperature. Measurements of selective etching in the amine based etching solutions were carried out by using the high sensitive quartz resonance method and with the help of MII-4 microinterferometer as described in [2] . The holographic diffraction gratings were recorded in the setup close to the described in [1, 2] using the argon laser radiation. For the production of HDG copies the "Yantar-3" photopolymer material was used. Profiles of the master HDG and polymer copies were measured using of scanning probe microscope "Dimension 3000" and electron microscope JSM-35.

3. Results

3.1. Optical properties

The optical constants were calculated from transmittance data using the method suggested by Swanepoel. Typical transmission curve of $As_{40}S_{20}Se_{40}$ film is shown in Fig.1. Dependence n(λ) is presented in Fig. 2 as an example of the unexposed sample. The energy dependencies of the refractive index n(E) were well fitted by the Wemple - Di Domenico dispersion relationship (Fig. 3). The dependencies of $n(\lambda)$, values of single oscillator energy E_o , dispersion energy E_d were obtained for the as-evaporated, annealed and exposed samples. Exposure and annealing lead to the increase of dielectric constant and to the decrease of E_o value. It is known, that the correspondence between E_o and optical band gap energy E_g for chalcogenide glasses can be expressed as $E_o \approx 2 E_g$ [4]. Using this expression we obtain E_g values 1.94; 1.91 and 1.85 eV for as evaporated, exposed and annealed films, correspondingly. As shown in [5] , dispersion energy E_d obeys a simple empirical relationship : $E_d = \beta N_c Z_a N_e$, where β = 0,37 ± 0,04 eV in covalent crystalline and amorphous materials, N_c is coordination number of cation nearest neighbour to the anion, Z_a is the formal chemical valency of the anion, and N_e is total number of valence electrons (cores excluded) per anion. If we assume that $Z_a = 2$, $N_e = 9.33$, than for as-evaporated films, where $E_d = 18.0$ we find $N_c \sim 2.61$ (that is lower than usually taken for calculations value of $N_c = 3$). This can be understood if we take into account that 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 such bonds can exceed 7 %

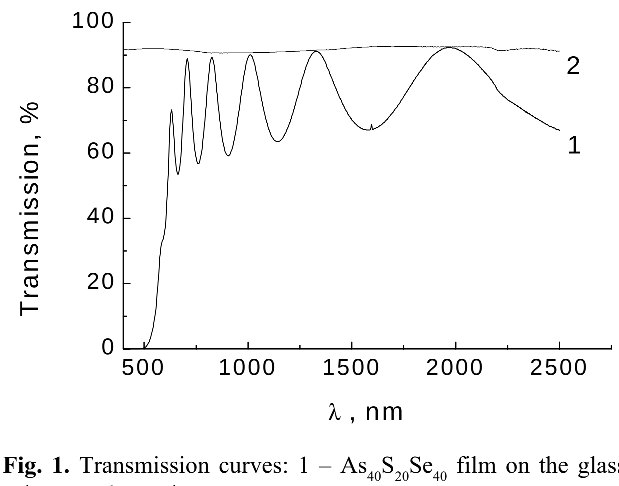

Fig. 1. Transmission curves: 1 – $As_{40}S_{20}Se_{40}$ film on the glass substrate, 2 – substrate.

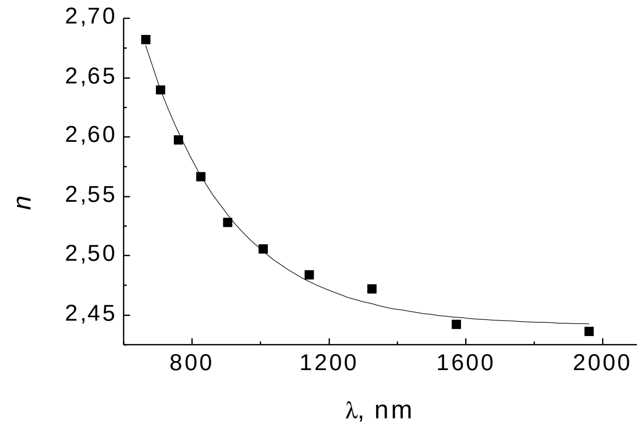

Fig. 2. Dependence of the refractive index vs wavelength, unexposed film.

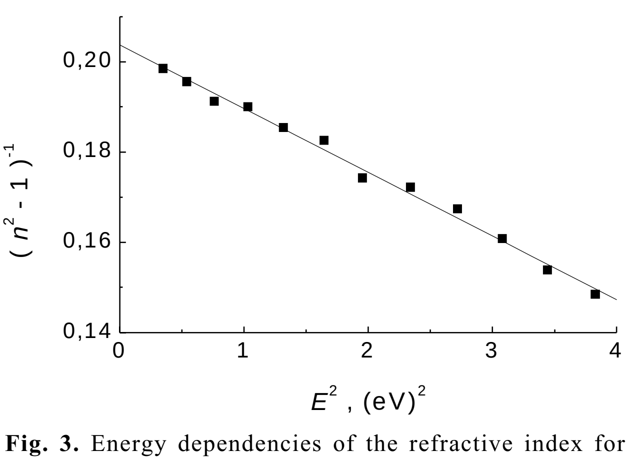

Fig. 3. Energy dependencies of the refractive index for $As_{40}S_{20}Se_{40}$ film.

[6]. The structure of the evaporated $As_{40}S_{20}Se_{40}$ film can be represented in the form of matrix, which consists of pyramidal units $AsS(Se)_{3/2}$. This matrix contain considerable amounts of $As_4S(Se)_4$ and $S(Se)_2$ fragments that contain As-As and S(Se)-S(Se) «wrong» bonds.

Other defects, pores and hollows can be present in the structure as well.

3.2. Raman spectra

Raman spectra of fresh evaporated $As_{40}S_{20}Se_{40}$ layers (Fig. 4 , curve 1) show the presence of numerous weak bands (118; 155,7; 171,6; 190,7 cm^{-1}, etc.) that correspond to As rich and S(Se) rich fragments . The presence of such defects, fragments leads to the lower value of N_c . Annealing or exposure results in polymerization of the molecular groups in the main glass matrix, thus the number of homopolar bonds, defects and hollows is diminished. That is clearly seen in Raman spectra (Fig. 4, where with the increase of exposure dose the peaks corresponding to the homopolar bonds are decreased and the spectra are nearing towards the bulk ones (Fig. 4, curve 5), where the two intensive and broad peaks near 239 and 354 cm^{-1} are the dominant features.This results in the increase of the relative density of main structural units $AsS(Se)_{3/2}$, that provides higher values of E_d – 21.0 and 20.75, correspondingly, and thus higher values of N_c – 3.04 and 3.0.

3.3. Selective etching

Such photoinduced structural changes provide good etching selectivity of $As_{40}S_{20}Se_{40}$ layers in various non-aqueous amine based solvents. The best obtained sensitivity values attained ~ 40 cm^2/J [7]. The characteristic curve of the $As_{40}S_{20}Se_{40}$ layers (dependence of the h/h_0 ratio on exposure value H, where h_0 – initial thickness of $As_{40}S_{20}Se_{40}$ layer, h – thickness of the exposed film after the etching process) is presented in Fig. 5. The lightsensitivity, S, was determined as reciprocal value to the H at which the $h/h_0 = 0.5$. For $As_{40}S_{20}Se_{40}$ layers, $S_{0,5}$ value (for the 488 nm wavelength) reached 8.8 cm^2/J , the value of a contrast coefficient was 0.92.

3.4 . Holographic diffraction gratings

Holographic diffraction gratings with spacial frequency 1600 mm^{-1} were fabricated by layers exposure with an interference pattern using the scheme described in [1,2]. After exposure the selective etching was carried out and after that the reflective layer (Al) was deposited. Surface relief patterns that were fabricated have good surface quality, that can be seen from their AFM images (Fig. 6a) Diffraction efficiency values of holographic diffraction gratings obtained on the base of $As_{40}S_{20}Se_{40}$ layers were equal to 60-70 %.

3.5. HDG replicating

The $As_{40}S_{20}Se_{40}$ layers are good media for HDG replicating processes. Such layers have higher mechanical and thermal hardness that the organic resists which are traditionally used for gratings fabricating. For the fabrication of gratings copies the photopolymer material "Yantar-3" was used. In Figs. 6-7 the AFM image of initial master grating obtained on the base of $As_{40}S_{20}Se_{40}$ layers (Fig. 6a) and its polymer copy (Fig. 7a) are shown. From comparison of the AFM profiles of the master grating and its polymer copy (Fig. 6b and Fig. 7b, respectively) it can be concluded that they are practically identical and close to the sinusoidal one.

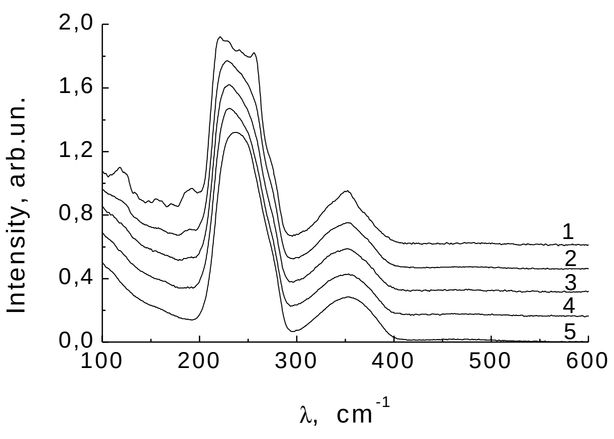

Fig. 4. Raman spectra of $As_{40}S_{20}Se_{40}$ films: 1 – as-evaporated film, 2 – 4 exposure by natural light, 2 – 0.5, 3 – 1, 4 – 4 hours, respectively, 5 – bulk glass.

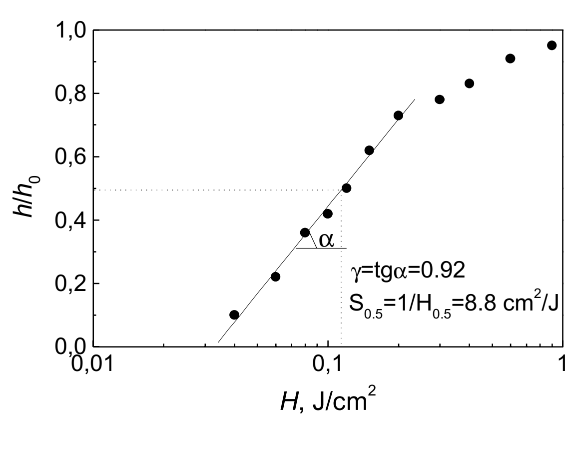

Fig. 5. Dependence of the h/h_0 ratio vs exposure value. Exposure on 488 nm wavelength.

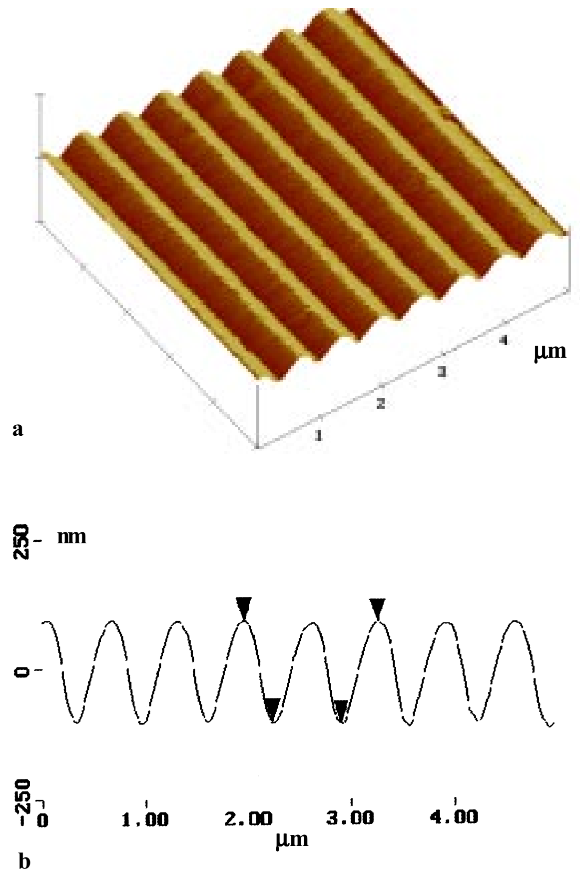

Fig. 6. Atomic force microscope image of holographic grating obtained on the base of $As_{40}S_{20}Se_{40}$ films: a – 3D image, b – grating profile.

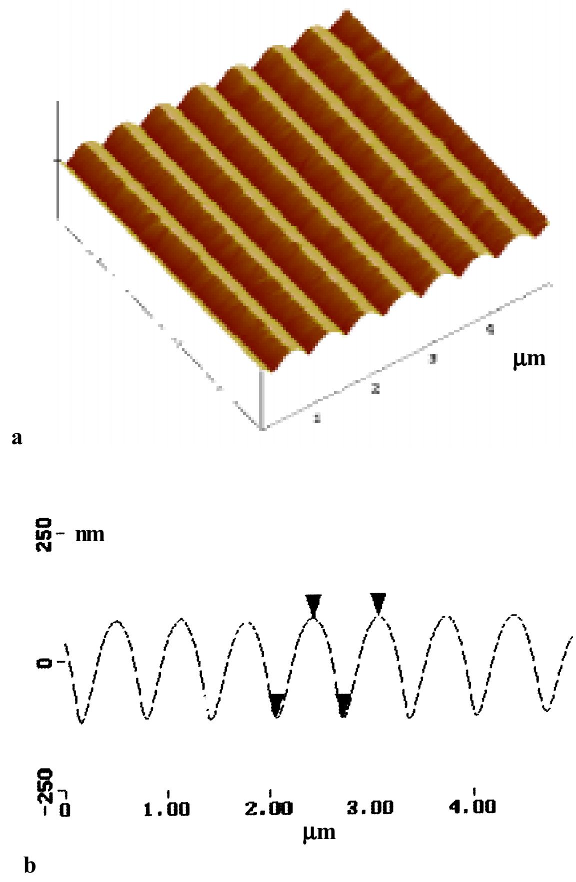

Fig. 7. Atomic force microscope image of polymer copy of master grating presented in Fig. 6: a – 3D image, b – grating profile.

4. Conclusion

The investigations carried out show that registering media based on $As_{40}S_{20}Se_{40}$ layers are rather promising for the fabrication of diffractive optical elements and other optical applications.

5. Acknowledgements

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