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PHOTOSENSITIVE PROPERTIES OF CHALCOGENIDE VITREOUS SEMICONDUCTORS IN DIFFRACTIVE AND HOLOGRAPHIC TECHNOLOGIES APPLICATIONS

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The basical problems related to the application of chalcogenide vitreous semiconductor layers (mainly of As-S-Se compositions) for holography and technology of the production of different holographic optical elements are considered. The mechanisms of light sensitivity and characteristics of such media were studied. Complex investigations of the HOE relief formation was carried out and the factors which influence the relief characteristics were evidenced. Close to theoretical limit, the operational characteristics of optical elements make possible to consider layers of chalcogenide vitreous semiconductors as prospective registering media for holography, diffractive optics, optoelectronics, information recording, etc.

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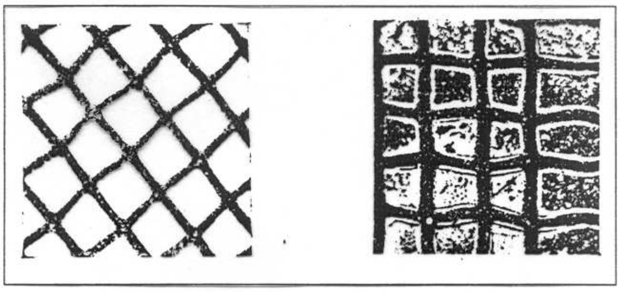
1. Introduction

Chalcogenide vitreous semiconductors (ChVS) as one of the most prospective materials were intensively studied during several decades. Perhaps the most interesting phenomena exhibited by these materials are photo-stimulated changes of their properties. They have complex nature, including various effects such as photodarkening (redshift in absorption edge), volume photoexpansion, photoinduced anisotropy, etc. First reports of the image recording with the use of thin ChVS layers (Fig. 1), were made by the group from Institute for Physics of Semiconductors, NAS Ukraine, Kiev [1, 2]. Two discovered effects ”photographic sensitivity of thin semiconductor layers” [1] and ”photographic sensitivity of the system of thin semiconductor and metal layers ” – “photodoping effect” [2] served as a basis in the development of the two groups of registering media on the base of ChVS layers and ChVS-metal (or metal containing substance). ChVS layers have amorphous structure, and due to the inherent for them wide spectrum of the photoinduced phenomena they have wide range of practical applications. The amorphous structure determines their extremely high resolution capability up to the level of several nanometers [3-4], which corresponds to the density of information recording ~ 1Tbyte/cm^2 [3].

Photoinduced changes in ChVS layers have two components: reversible and irreversible [5]. In binary ChVS the irreversible changes are rather significant and overpass the reversible component. The use of the ChVS layers as a media for the recording of phase-relief holograms mainly is connected with the irreversible changes, which were considered in present work. ChVS layers are easily dissolved in different etching solutions. After exposure the etching rates of the ChVS layers are changed, which effect enables the fabrication of various surface reliefs.

Light sensitivity of the thin film ChVS-metal (mainly silver) structures is determined by the photostimulated diffusion of metal into semiconductor layer [6-7]. During exposure process and as a result of exposure of such structures the silver from the exposed sites penetrates into ChVS layer, thus creating a photodoped layer. Much work has been carried out to explain the mechanism of photodoping.

The most detailed description of the photodoping mechanism is presented in [6]. The properties of photodoped ChVS layers are essentially different from those of the initial ChVS and metal layers. In particular, photodoped layers have high chemical resistance to the alkaline etchants, which easily dissolve the initial ChVS layers. This makes possible to produce relief images, which depict distribution of the actinic radiation. Application possibilities of the photodoping effect (this phenomenon is promising, in particular, for ultrahigh resolution photolithographic processes and for fabrication of optical elements) are considered in detail in [7].



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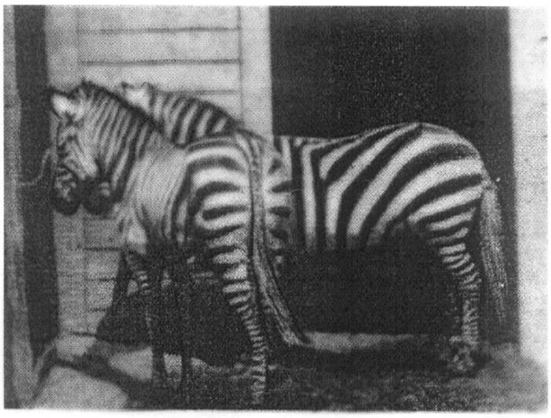

b

Fig. 1. First in the world images obtained on ChVS layers (left- Sb_2S_3 layers, right- As_2S_3 layers)-a [1] and ChVS-metal structures-b [2].

In present work are considered the peculiarities of the photostimulated processes in thin layers of the chalcogenide vitreous semiconductors, physical and technological bases of their use as registering media in holography, including fabrication of the holographic optical elements.

2. Peculiarities of the photostructural transformations in ChVS layers

The illumination of ChVS with light having energy close or even lower then that of the bandgap of the material after absorption, which results in the creation of the electron-hole pairs, whose subsequent recombination brings bond reforming processes, that is microscopic network change, brings structural, mechanical, optical, etc. changes in these materials. The optical changes involve photo-increased refractive index and absorption edge shift to the longer wavelength side. Photo-irradiation causes increase in refractive index value in the whole considered region (0.4-2.5 μm).

Spectral dependencies of the refractive index of considered ChVS layers (mainly of As-S-Se composition) in the absorption edge and transparency regions are well described within the frame of the single oscillator model [8-10]. Compositional dependencies of the optical properties in the transparency region and their evolution under the action of the external factors (exposure or annealing) were analyzed within the frame of the single-oscillator and Penn models. The character of the irreversible photostructural transformations according to the results of optical properties and Raman spectra investigations is determined by the ordering of the local structure as the main reason of the photoinduced changes. The analysis within the frame of Penn model has shown the increase of the number of the heteropolar bonds under the exposure or annealing of the $As_{40}S_{60-X}Se_X$ films. Along the $As_{100-X}S_X$ compositional crossection maximal structural changes under exposure or annealing are characteristic for the compositions near stoichiometric $As_{40}S_{60}$. At the same time, for the $As_{40}S_{60-X}Se_X$ cross section is characteristic approximately the same level of the structural changes under the influence of the external factors. The presence of the photostructural changes was directly confirmed by the investigation of Raman scattering [10-11]. As-evaporated As-S-Se films contain substantial amounts of the non-stoichiometrical molecular fragments, which contain homopolar bonds, pores, voids. Exposure or annealing leads to the polymerization of the molecular groups in the main matrix and thus, the quantity of the homopolar bonds is decreased.

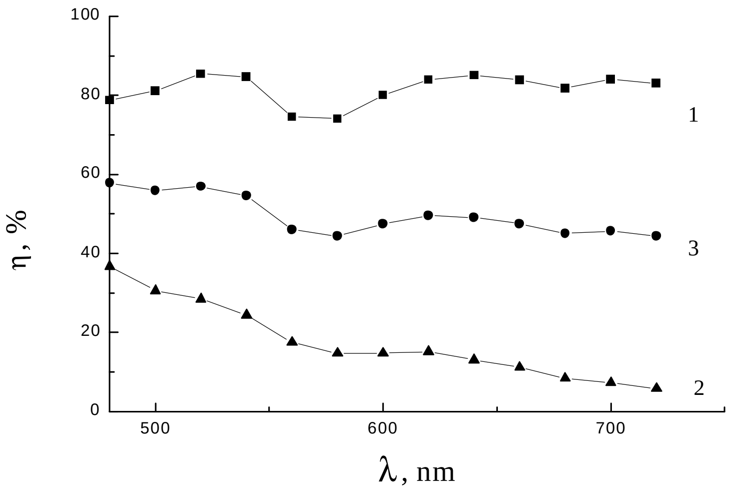

Fig. 2. Spectral distribution of the diffraction efficiency (relative units) for the grating with spatial frequency 2400 mm^{-1} obtained on the base of $As_{40}Se_{60}$ layers. 1 - S - polarization, 2 – P - polarization, 3- non-polarized light [21].

The correlation of the compositional dependencies of the dispersion energy, optical dielectric constant and structurally dependent parameters such as relaxation enthalphy and heat capacity was shown in [10-12]. Slight deviation from linear of the mole volume compositional dependence for glasses of $As_{40}S_{60-X}Se_X$ composition [13] correlates with the slight peculiarities on the compositional dependencies of the dispersion energy, optical dielectric constant, thermodynamical parameters. This is explained by the following: under substitution of the sulfur to selenium due to small deviation from the statistical substitution the quantity of the sulfur-deficient structural units is somewhat increased. This leads to the presence of some amount of the Se_n chains in the structure of $As_{40}S_{60-X}Se_X$ glasses, which is confirmed by the analysis of the Raman spectra. The presence of the slightly increased number of Se chain structures leads to the deviation of the mole volume concentration dependence from the linear [14-15]. The consideration of peculiarities of the photostructural changes mechanism show absence of the essential influence of the diffusion processes due to initial high concentration of the non-stoichiometric molecular fragments. Consideration of the evolution of such molecular fragments determines an exponential decay with the increase of exposure, which is experimentally confirmed by the decay of the Raman bands, which correspond to the non-stoichiometric molecular fragments containing homopolar bonds [15].

3. Fabrication of the optical elements with the use of ChVS layers and their characteristics

The basic principles and approaches of application of the registering media on the base of As-S-Se layers for holography and technologies of fabrication of the holographic optical elements with the use of such registering media were developed in [16-23]. Photoinduced structural changes in ChVS layers provide the selectivity of etching processes. Spectral distribution of light sensitivity correlates with the absorption spectra of chalcogenide layers. Differences in etching rates for exposed and unexposed parts of ChVS layers provide means for the surface relief formation. The use of non-aqueous amine (diethylamine, triethyeamine, ethylenediamine, etc) based etching solutions enabled to provide necessary etching selectivity and relief quality. The dependence of layer etching rate on exposure time for such types of solvents is well described by the exponential decay. Prediction and simulation of the relief formation processes can be done from etching curves of variously treated layers. Complex investigations of the main stages of diffractive elements relief formation (mainly for holographic diffraction gratings) were performed. The simulation and experimental study of the surface relief formation under transfer of an intensity pattern to a surface relief profile during development is important because the properties of the obtained relief (on the example of gratings) depend on the form and depth of the obtained groove relief. Factors were established, which provide optimal characteristics for the fabrication of the relief. There was the possibility to change the spectral dependencies of the diffraction efficiency and to provide the necessary dependence of the reflection coefficient in the operational region by means of changing conditions of the relief formation in the layers of the chalcogenide vitreous semiconductors. The possibilities to obtain blazed gratings with help of the additional treatment of the initial relief, ion etching through chromium mask, were also shown.

With the use of C4HVS based registering media the lenses and matrices of binary Fresnel lenses formed in the substrate material (mainly glass) were fabricated. They have values of diffraction efficiency ~33%, that is ~ 80% from theoretical limit [16]. The transmission diffraction gratings with 6-12 μm periods and maximal values of the diffraction efficiency 20-28% in the 0.6-2.0 μm spectral range were produced with the use of the contact printing and binary masks. With the use of the halftone masks and contact printing the matrices of the refractive microlenses (with the lens diameter ~ 12 μm) were obtained [23].

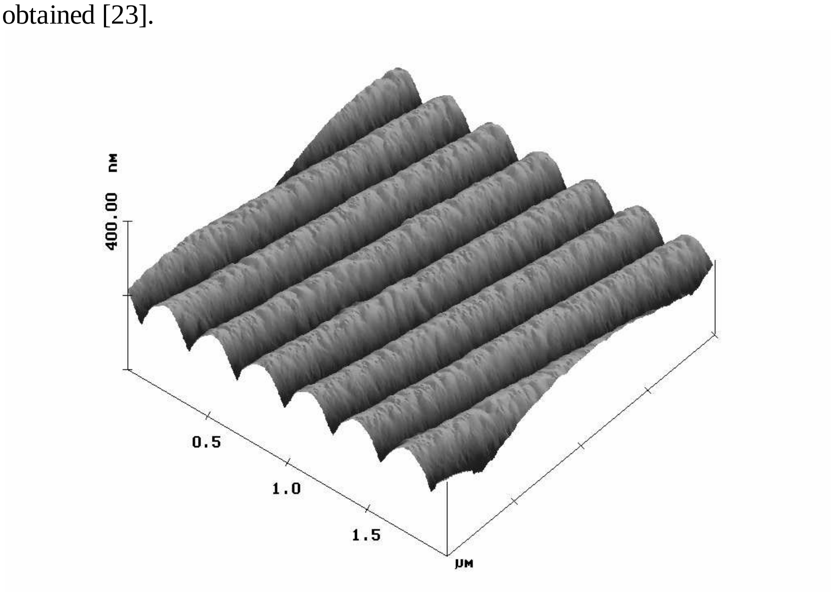

Fig. 3. AFM image of the grating with the spatial frequency 3600 mm^{-1} obtained on the basis of $As_{40}Se_{60}$ layers [21].

The values of the diffraction efficiency (measured in Littrov scheme, 60-78% in non-polarized light, 80-95% in polarized light, see Fig. 2) obtained for the phase-relief gratings, which were fabricated on the base of the As-S-Se layers are close to the theoretical limit [16-22]. The ratio of the resolution capability of the gratings to the theoretical values was not less than 0.9, and high quality of the gratings surface relief (see Fig. 3) provided low level of the scattered light (~10^{-6}). ChVS layers have better mechanical properties than traditional organic photoresists. This provides opportunities to get high-quality polymer copies of the initial master gratings obtained on the base of ChVS layers (Fig. 4) [17,20]. The gratings replicated into polymer have diffraction efficiencies close to the initial master copies. The characteristics of the gratings obtained on the base of As-S-Se layers are on the level of modern requirements for such optical elements [21-22].

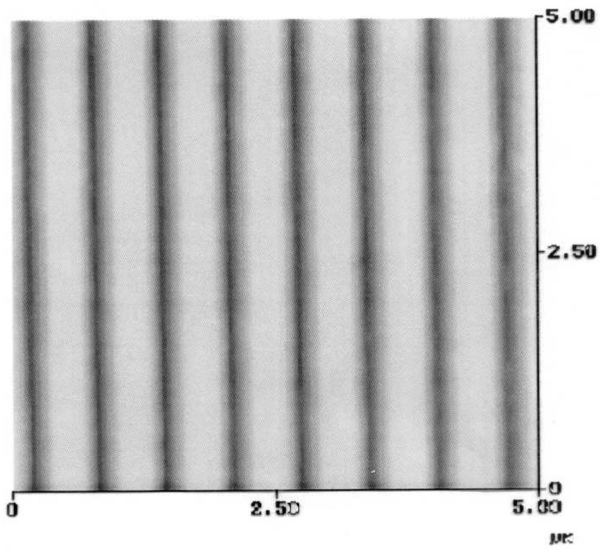

Fig. 4. AFM image of polymer copy of grating obtained from ChVS gratings relief [19].

4. Conclusions

The photostimulated transformations in the investigated compositions of ChVS layers offer possibilities for the preparation of vacuum-deposited inorganic photosensitive high-resolution media for fabrication of microrelief structures. The sensitivity range and the chemical properties of such media can be changed with the aim of optimization or adjustment to the existing recording conditions, by changing the initial glass composition and respective amine based solvents. The wide range of the possible compositions provides some control in variation of recording media parameters, and enables choosing the proper sensitivity on the given wavelength, if necessary.

High values of the operational parameters obtained for the optical elements on the base of ChVS layers allows to consider these materials as prospective for applications, in optics, optoelectronics, information recording, etc.

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