Studies of Ag Diffusion Processes into Thin-Film As$_2$S$_3$ Structures Doped With Sn under the Exposure of X-Ray Radiation

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**ABSTRACT:** The processes of silver diffusion into thin-film structures (As$_2$S$_3$)$_{0.995}$Sn$_{0.005}$ under the X-ray radiation were studied. Thin-film layers of silver, about 12 nm thick, were deposited by vacuum thermal evaporation on the (As$_2$S$_3$)$_{0.995}$Sn$_{0.005}$ surface. The thin layer structures were irradiated with X-ray radiation in the range of absorbed doses of 0.3-0.6 Gy using the X-ray tube with a copper anode (voltage 45 kV, current 40 mA) as an X-ray source without any filters (the continuous spectrum of X-ray, or “white” spectrum). The possibility of X-ray images recording with their subsequent visualization using the chemical etching in a 5% solution of NaOH is shown.

**KEYWORDS:** Chalcogenide Glassy Semiconductors, Diffusion Of Metals, X-Ray Imaging

**INTRODUCTION**

Chalcogenide glassy semiconductors of As-Se-S system are widely used for recording of optical information. Photothermoplastic carriers based on As-Se-S have high values of holographic sensitivity - up to $10^6$ cm$^2$/J [1], resolution power - up to 4000 mm$^{-1}$ [2], and diffraction efficiency - up to 40% [3-4]. Chalcogenide glassy semiconductors are sensitive materials to electron-beam recording [5-7], as photoresist materials sensitive in UV-visible regions with a resolution up to 7000 ln/mm [8], and photoinduced transformation (photodarkening, photorefraction) [9-11]. The investigations of As$_2$S$_3$ thin films as photoresists for X-ray photolithography were studied in work [12]. The aim of this work was to study the photodiffusion effects of Ag in As$_2$S$_3$ thin films doped by Sn under X-ray radiation. Chalcogenide glassy semiconductors of the As-Se-S system are widely used for recording of optical information. Photothermoplastic carriers based on As-Se-S have high values of holographic sensitivity - up to $10^6$ cm$^2$/J [1], resolution power - up to 4000 mm$^{-1}$ [2], and diffraction efficiency - up to 40% [3-4]. Chalcogenide glassy semiconductors are sensitive materials to electron-beam recording [5-7] and can be used as photoresist materials sensitive in UV-visible regions with a resolution up to 7000 ln/mm [8], and photoinduced transformation (photodarkening, photorefraction) [9-11]. The investigations of As$_2$S$_3$ thin films as photoresists for X-ray photolithography were studied in work [12]. This work aimed to study the photodiffusion effects of Ag in As$_2$S$_3$ thin films doped by Sn under X-ray radiation.

**EXPERIMENTAL RESULTS AND DISSCUSION**

Thin films of (As$_2$S$_3$)$_{0.995}$Sn$_{0.005}$ with a thickness of 1.6 µm were obtained by vacuum thermal evaporation on sapphire substrates (Fig.1). A thin Ag layer about 12 nm thick was deposited on the (As$_2$S$_3$)$_{0.995}$Sn$_{0.005}$ surface.

**Fig.1** Experimental setup: 1) Sapphire substrate, 2) (As$_2$S$_3$)$_{0.995}$Sn$_{0.005}$, 3) Ag thin layer 4) Mask, 5) X-ray

To study the optical transmittance of the Ag layer, a sapphire substrate was placed next to the (As$_2$S$_3$)$_{0.995}$Sn$_{0.005}$ sample [13]. The process of silver deposition was carried out in a simultaneous mode, both on a clean substrate and the surface of the semiconductor layer. A principal scheme of the experimental X-ray setup is shown in Fig.2. An X-ray tube with a copper anode (voltage 45 kV,
current 40 mA was used as an X-ray source (1, Fig.2) without any filters (the continuous spectrum of X-ray, or “white” spectrum). The X-ray beam passed through the slit diaphragms (2) is projected through the mask (3) onto the sample (4). The absorbed dose rate measured after the mask (3) was 0.65 Gy/h.

Fig.2 Experimental setup: 1) X-ray tube 2) Slits, 3) Mask, 4) Sample

Fig.3 shows the spectral dependences of the transmittance of Ag thin film with a thickness of about 12 nm on a sapphire substrate (curve 1) and an Ag/\((\text{As}_2\text{S}_3)_{0.995}\text{Sn}_{0.005}\) thin film structure (curve 2). The transmittance of the Ag/\((\text{As}_2\text{S}_3)_{0.995}\text{Sn}_{0.005}\) structure in the spectral range of 550–1000 nm is higher than the Ag layer on a sapphire substrate due to the partial diffusion of Ag into the \((\text{As}_2\text{S}_3)_{0.995}\text{Sn}_{0.005}\) layer during silver thermal deposition.

Fig.3 Spectral dependences of the transmittance spectra: 1) Ag thin layer, 2) Ag/\((\text{As}_2\text{S}_3)_{0.995}\text{Sn}_{0.005}\), 3) Ag/\((\text{As}_2\text{S}_3)_{0.995}\text{Sn}_{0.005}\) after radiation dose of 0.52 Gy

To study the processes of Ag diffusion in \((\text{As}_2\text{S}_3)_{0.995}\text{Sn}_{0.005}\), the obtained samples were irradiated with X-ray radiation in the range of absorbed doses of 0.3–0.6 Gy. A lead plate 3 mm thick with a hole of 4 mm in diameter was used as a mask (3, Fig.2). The spectral dependence of transmittance was measured before and after irradiation at the same point of the sample. Fig.3 shows the spectral dependences of the transmittance of the Ag/\((\text{As}_2\text{S}_3)_{0.995}\text{Sn}_{0.005}\) structure before (curve 2) and after irradiation at an absorbed dose of 0.52 Gy (curve 3). As can be seen from the dependence in Fig.3, the optical transmittance increased due to the diffusion of Ag from the near-surface layer into the depth of the semiconductor layer \((\text{As}_2\text{S}_3)_{0.995}\text{Sn}_{0.005}\). Fig.4 shows the \(T-T_0\) dependence (\(T_0\) - transmittance before irradiation, \(T\) - transmittance after irradiation at an absorbed dose of 0.52 Gy) in the spectral range of 400-550 nm, where there are no interference processes in thin films (Fig.3).
As can be seen from Fig.4, the maximum enlightenment of the Ag/ (As$_2$S$_3$)$_{0.995}$Sn$_{0.005}$ layer, due to the diffusion of Ag under X-ray radiation, does not exceed 0.8% at a wavelength of 520 nm. For comparison, the processes of Ag photodiffusion under the visible irradiation in the obtained Ag/ (As$_2$S$_3$)$_{0.995}$Sn$_{0.005}$ thin films were studied. The sample was irradiated with 447-nm laser radiation at a beam intensity of 180 mW/cm$^2$ until the maximum values of transmittance. Fig.5 shows the T-T$_0$ dependence in the spectral range of 400-550 nm.

As can be seen from Fig.5, the maximum transmittance of the Ag/ (As$_2$S$_3$)$_{0.995}$Sn$_{0.005}$ layer, due to the diffusion of Ag under visible radiation, is about 3.5% at a wavelength of 520 nm. The processes of diffusion of Ag into chalcogenide glassy semiconductors under the action of visible radiation have been studied in sufficient detail and make it possible to record optical information and high-resolution holograms [14]. Unlike visible light (Fig.5), X-ray does not have the same significant effect on Ag diffusion into the (As$_2$S$_3$)$_{0.995}$Sn$_{0.005}$ layer (Fig.4). The studies in work [15] showed the negligible effect of X-ray irradiation on the atomic or electronic structure of simple chalcogenide glass films and the negligible effect of X-ray irradiation on silver diffusion in Ag/As$_2$S$_3$ films. As was shown in work [15] the X-ray induced diffusion of silver is relatively slower than under bandgap light illumination which is confirmed by investigations of this work (Fig.4 and Fig.5). However, the effect of silver diffusion in (As$_2$S$_3$)$_{0.995}$Sn$_{0.005}$ under the action of X-rays is clearly pronounced (Fig.4), which, unlike [15], can be explained by doping with tin in a small percentage (0.5%). In the work [16] was shown that for the composition (As$_2$S$_3$)$_{0.3}$(As$_2$Se$_3$)$_{0.7}$, doped with Sn in the range of 0.015–0.030 at.%, the maximum of photoconductivity in visible spectra was at 0.02 at.% of tin. Photothermoplastic carriers based on the As-Se-S system doped with Sn have high values of sensitivity (10$^6$ cm$^2$/J) for holograms recording in real-time [1].

The effect of silver diffusion under X-ray irradiation (As$_2$S$_3$)$_{0.995}$Sn$_{0.005}$ thin films can be used for recording X-ray images. A brass mesh (4, Fig.1) was used as a mask for X-ray image recording using the contact method. After X-ray radiation with an absorbed dose of 0.52 Gy, the sample was chemically treated in a 5% solution of NaOH. Fig. 6 (left image) shows the brass mesh zoomed by microscope and the image of the mesh recorded in X-ray radiation after chemical treatment (right image).
Fig. 6 Zoomed by microscope images of a brass mesh (left image) used as a mask and obtained by chemically treatment of Ag/(As$_2$S$_3$)$_{0.995}$Sn$_{0.005}$ after X-ray radiation.

As can be seen from Fig. 6, the rate of chemical etching of the semiconductor layer is irradiated places is greater than in non-irradiated places. This can be explained by the diffusion of copper under the action of X-rays, which makes the (As$_2$S$_3$)$_{0.995}$Sn$_{0.005}$ layer less resistant to chemical etching in irradiated areas.

CONCLUSION

The (As$_2$S$_3$)$_{0.995}$Sn$_{0.005}$ multilayer structure is sensitive not only in the visible region of the spectrum but also to X-rays. Diffusion of silver in (As$_2$S$_3$)$_{0.995}$Sn$_{0.005}$ under X-ray irradiation changes the rate of chemical etching in the irradiated areas with respect to the non-irradiated areas of the semiconductor. This effect allows the recording of X-ray images with subsequent visualization of images using chemical etching.

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BIBLIOGRAPHY

2. A. Chirita, et.al, Recording holograms of micro-scale objects in real time, Laser Physics, 23 2013, pp.036002-036006
5. M. Iovu, et.al, Electron-beam recording of diffraction gratings in (As$_3$S$_3$Se$_3$)$_{1-x}$Sn$_x$ amorphous thin films, Journal of Optoelectronics And Advanced Materials Rapid Communications, 12, 7-8, 2018, pp. 377 - 380
7. S. Sergeev, et.al, Superimposed equally oriented diffraction gratings formed in As$_2$S$_3$ films. Chalcogenide Letters, 17, 1, 2020, pp.25 - 31
13. A. Aparimita, et.al. Photo - and thermally induced property change in Ag diffusion into Ag/As$_2$Se$_3$ thin films, Applied Physics A, 124, 2018, pp.267
16. I. Burdiyan, I. Feshchenco, Photocurrent and Optical Transmission Spectra of Sn- and Pb-Doped (As$_2$S$_3$)$_{0.3}$(As$_2$Se$_3$)$_{0.7}$(Sn) Glass Films, Inorganic Materials, 41, 9, 2005, pp.1013–1015