

# Electro-optical properties of As-Se-S—dielectric structure for optical information recording in real time

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The results of electro-optical properties studies of chalcogenide glassy semiconductors thin film structures based on  $X\text{at.}\% \text{As}_2\text{S}_3:(100-X)\text{at.}\% \text{As}_2\text{Se}_3$  system for holographic information recording on to photo-thermoplastic carriers in stationary and pulsed modes.

(Received April 6, 2015; accepted June 24, 2015)

**Keywords:** Chalcogenide glassy semiconductors, Photothermoplastic media

## 1. Introduction

The hologram recording in real time scale is one of the most perspective directions of practical using of photo-thermoplastic carriers based on chalcogenide glassy semiconductors of As-Se-S system. Such carriers possess high holographic sensitivity (порядка  $10^6 \text{ cm}^2 \cdot \text{J}^{-1}$ ), (of the order of  $10^6 \text{ cm}^2 \cdot \text{J}^{-1}$ ), high resolution power (up to  $4000 \text{ mm}^{-1}$ ) and high rate of optical information recording ( $\sim 3\text{s}$ ) [1-2]. Also on As-Se-S system based photo-thermoplastic carriers the pulse holograms were recorded in a laser radiation of  $\lambda=694\text{nm}$  and light pulse duration of 40ns [3].

The studies of electro+phzysical properties of thin film structures of  $X\text{at.}\% \text{As}_2\text{S}_3:(100-X)\text{at.}\% \text{As}_2\text{Se}_3$  system for thermoplastic recording of stationary and pulse holograms were the objective of this work.

## 2. Experiment

Photo-thermoplastic (PTP) carrier consists of photo-sensitive semiconductor of As-Se-S system and thermoplastic layers successively deposited on to transparent basis. In this case during the heating, charging and exposition process, the non-equilibrium charge carriers in the illuminated spots migrate to the semiconductor - thermoplastic interface. Due to the Coulomb interaction of electrical charges on to the thermoplastic surface and those at semiconductor-thermoplastic interface a surface deformation of the thermoplastic layer heated to the plastic state occurs [4]. As a result the relief-phase hologram is recorded on the surface of the thermoplastic layer. Schematic diagram of such carrier is shown in Fig. 1.

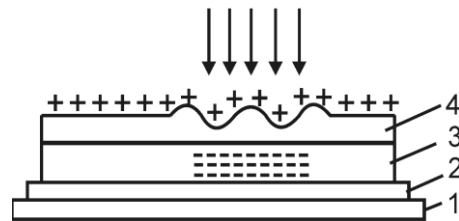


Fig. 1. Photo-thermoplastic carrier: 1) substrate; 2) conducting electrode; 3) photosensitive semiconductor; 4) thermoplastic.

Thin films of chalcogenide glassy semiconductors were fabricated by thermal evaporation in vacuum. During the evaporation of  $X\text{at.}\% \text{As}_2\text{S}_3:(100-X)\text{at.}\% \text{As}_2\text{Se}_3$  mechanical mixture a continuous series of solid solutions is formed, according to Vegard's law a linear dependence of the band gap on the percentage of mixed components [5]. Thus, the selection of a ratio value of X in a ratio  $X\text{at.}\% \text{As}_2\text{S}_3:(100-X)\text{at.}\% \text{As}_2\text{Se}_3$  allows to obtain a CGS layer with the maximum of spectral photo-sensitivity for the given wavelength of the optical radiation. Upon subsequent deposition on a semiconductor surface of thermoplastic layer on the basis of poly-N-epoxypropylcarbazole one can obtain the carrier with the maximum photosensitivity for the given laser radiation wavelength.

For to obtain the maximum of spectral photo-sensitivity close to  $\lambda=532 \text{ nm}$  the compositions obtained at the evaporation of  $(X)\text{at.}\% \text{As}_2\text{S}_3:(100-X)\text{at.}\% \text{As}_2\text{Se}_3$  mixture were studied. The investigation of photocurrent spectral dependence determined as the ratio of light and dark current intensity to the power of the incident radiation  $P$  had shown that the maximum of spectral sensitivity at  $\lambda=532 \text{ nm}$  is for thin layer (thickness of  $1,5 \mu\text{m}$ ) having the composition of  $67\text{at.}\% \text{As}_2\text{S}_3:33\text{at.}\% \text{As}_2\text{Se}_3$  (curve1, Fig. 2).

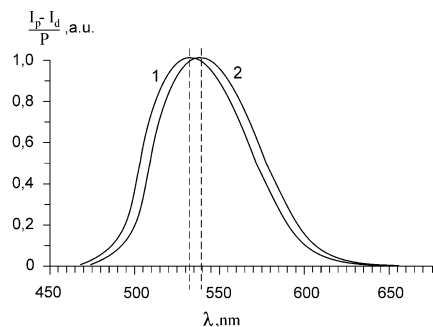


Fig. 2. Photocurrent spectral dependence of thin layers of 67at.%As<sub>2</sub>S<sub>3</sub>:33at.%As<sub>2</sub>Se<sub>3</sub> system : 1) T=22°C 2) T=79°C.

For to use the obtained layers in PTP process one can take into account the temperature shift of the spectral photo-sensitivity maximum at the CGS heating from room temperature to the temperature of recording. For the thermoplastic on the basis of poly-N-epoxypropylcarbazole the recording temperature at PTP process is of 79°C. The photocurrent spectral dependence at 79°C is given in Fig. 2 (curve2). The maximum of the relative spectral sensitivity at T=79°C for the layers of 67at.%As<sub>2</sub>S<sub>3</sub>:33at.%As<sub>2</sub>Se<sub>3</sub> composition is at  $\lambda=540$  nm (Fig. 2, curve2). Thin CGS layers with the maximum of spectral sensitivity close to  $\lambda=532$  nm at the temperature of 79°C were obtained for the composition of 72at.%As<sub>2</sub>S<sub>3</sub>:28at.%As<sub>2</sub>Se<sub>3</sub>. For the given composition the maximum of spectral sensitivity at T=22°C is close to  $\lambda=526$  nm (curve1, Fig. 3), and at T=79°C is shifted in a long wavelength region to  $\lambda=532$  nm (curve2, Fig. 3).

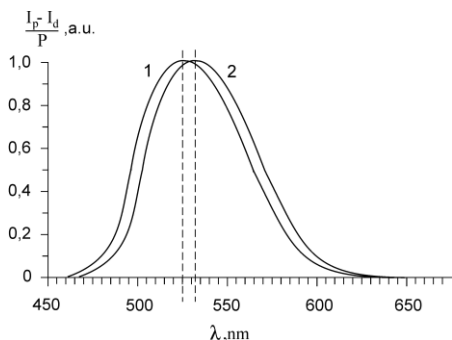


Fig. 3. Photocurrent spectral dependence of 72 at.%As<sub>2</sub>S<sub>3</sub>:28 at.%As<sub>2</sub>Se<sub>3</sub> system thin layers: T=22°C 2) T=79°C T=22°C 2) T=79°C.

Thus a semiconductor layer of 72at. %As<sub>2</sub>S<sub>3</sub>: 28at.%As<sub>2</sub>Se<sub>3</sub> system was obtained having the thickness of 1,5  $\mu\text{m}$  and a maximum of photocurrent spectral dependence close to  $\lambda=532$  nm at the temperature of T=79°C. A thermoplastic poly-N-epoxypropylcarbazole layer of a thickness of 0,5  $\mu\text{m}$  was deposited on to the semiconductor surface and the PTP carrier for hologram recording in a laser radiation of  $\lambda=532$  nm was obtained. On the obtained PTP carriers the holographic gratings on the spatial frequency  $\nu=1000$  mm<sup>-1</sup> and recording time of 1,4s were recorded. The holographic sensitivity of the PTP carriers on the basis of 72at.%As<sub>2</sub>S<sub>3</sub>:28at.%As<sub>2</sub>Se<sub>3</sub> system was  $6 \cdot 10^6$  cm<sup>2</sup>·J<sup>-1</sup> for laser radiation  $\lambda=532$  nm.

At the elaboration of PTP carriers for pulse hologram recording in a nanosecond range at laser radiation  $\lambda=532$  nm some problems appear related to the features of DPSS lasers, namely, a fixed value of pulse duration (5 ns), which does not allow to study interchangeability of exposure parameters such as  $E$  and  $t$  in the range of seconds to a nanosecond. For the recoding of the pulse holograms the composition of CGS system (X) at.%As<sub>2</sub>S<sub>3</sub>:(100-X)at.%As<sub>2</sub>Se<sub>3</sub> was matched experimentally. Unlike previous studies, the maximum sensitivity of the holographic recording pulse 5 ns pulse duration was obtained for the composition of 62 at.% As<sub>2</sub>S<sub>3</sub>: 38at.% As<sub>2</sub>Se<sub>3</sub>. Maximum spectral dependence of the photocurrent at T = 79°C for these layers is close to  $\lambda = 545$  nm (Fig. 4).

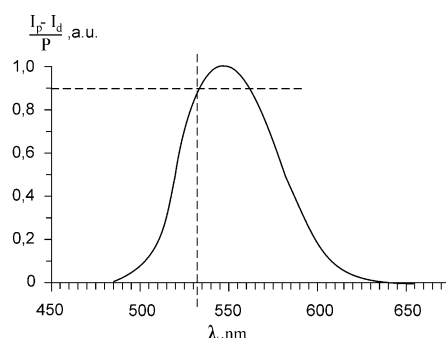


Fig. 4. Photocurrent spectral dependence at T=79°C for thin layers having the composition of 62at.%As<sub>2</sub>S<sub>3</sub>:38at.%As<sub>2</sub>Se<sub>3</sub>.

At the stationary recording process the maximum holographic sensitivity for  $\lambda=532$  nm coincides with the photocurrent maximum at the same wavelength for the composition of 72at.%As<sub>2</sub>S<sub>3</sub>:28at.%As<sub>2</sub>Se<sub>3</sub> (Fig. 3, curve 2). For to interpret the shift of the holographic sensitivity maximum at the pulse recording to higher energies of the photons the investigations were carried out of the pulse hologram recording (pulse duration of 5ns) at the PTP carrier illumination both from the thermoplastic layer side as well as from the substrate side (Fig. 5).

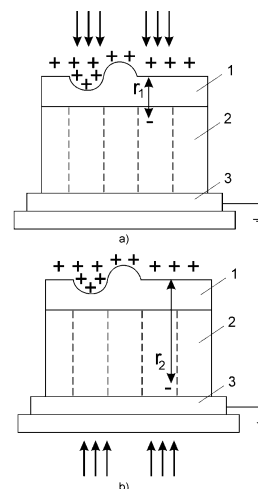


Fig. 5. PTP carrier: 1-thermoplastic, 2-CGS, 3- semitransparent conducting electrode; a) – illumination from the thermoplastic layer side, b)- illumination from the substrate side.

At the PTP carrier illumination from the thermoplastic layer side the signal on his way to the CGS is attenuated only by the absorption in the thermoplastic layer and by the processes of light reflection at air-thermoplastic and thermoplastic – CGS interfaces. At the illumination from the substrate side the processes of the light absorption and reflection occur in a more complex structure – heating element, substrate, conducting electrode, CGS. For to keep identical recording conditions, the same value of the CGS layer exposing were picked up for each recording process—both at the illumination from the thermoplastic layer side (Fig. 5a), as well as from the substrate side (Fig. 5b). The recording conditions (temperature, the corona discharge potential, time of the light pulse delay, the pulse duration and the time of recording) were the same for both experiments. As a result the Diffraction gratings have been recorded with a spatial frequency of 1000 mm<sup>-1</sup> at the value of the diffraction efficiency (7%) under illumination of PTP carrier according to Fig.5. Recording of holograms with equal values of the diffraction efficiency suggests that the processes of carriers photo-generation in the layer CGS are identical for both recording methods. The experiment essence was to reduce the exposure to reach the threshold sensitivity of PTP carrier (when the diffraction efficiency is of 1%) for both recording methods. The exposure is reduced by reducing the intensity of the laser radiation with the help of neutral filters at constant pulse duration of 5 ns. The ratio of light intensity decrease for both recording methods was similar. Fig. 6 shows the dependence of the diffraction efficiency on the exposure at pulse holograms recording on PTP carrier based on 62at.% As<sub>2</sub>S<sub>3</sub>: 38at.% As<sub>2</sub>Se<sub>3</sub> CGS system.

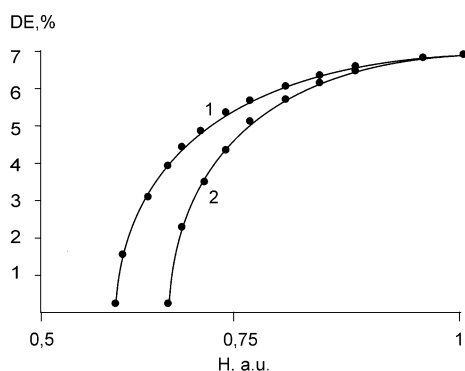


Fig. 6. Diffraction efficiency dependence on the exposure at pulse hologram recording: 1 - illumination from thermoplastic layer side; 2 - illumination from the substrate side.

As one can see from Fig. 6, at PTP carrier illumination from the substrate side (curve 2) the holographic sensitivity threshold is less than at the illumination of the same carrier from thermoplastic layer side (curve 1). At PTP carrier illumination from the substrate side by short light pulse (5ns) the generated charge carriers in the initial moment are located at a greater distance from the interface between the thermoplastic – CGS (r2, Fig. 5b) in comparison with the

case when illumination is from a thermoplastic layer side (r1, Fig. 5a). The strength of the Coulomb interaction between the charges on the surface and in the semiconductor volume is inversely proportional to the square of the distance, and one can assume that the charges generated near the conductive electrode, do not manage to reach the thermoplastic - CGS interface. For comparison of PTP carriers based on 72at.% As<sub>2</sub>S<sub>3</sub>:28at.% As<sub>2</sub>Se<sub>3</sub>, having the maximum value of the photocurrent at  $\lambda = 532$  nm ( $T = 79^{\circ}\text{C}$ ) and a maximum holographic sensitivity at the pulse recording at a wavelength of  $\lambda = 532$  nm, the dependencies of light absorption on layer thickness for both compositions at a light wavelength of  $\lambda = 532$  nm were drawn calculated from of the Bouguer - Lambert absorption law (Fig. 7a). The absorption coefficients  $\alpha = 1,6 \cdot 10^4 \text{ cm}^{-1}$  at a wavelength  $\lambda = 532$  for the composition of 72at.% As<sub>2</sub>S<sub>3</sub>:28at.% As<sub>2</sub>Se<sub>3</sub> and  $\alpha = 1,9 \cdot 10^4 \text{ cm}^{-1}$  for the composition of 62at.% As<sub>2</sub>S<sub>3</sub>:38at.% As<sub>2</sub>Se<sub>3</sub> were derived from the transmission spectral dependence of the layers of studied compositions.

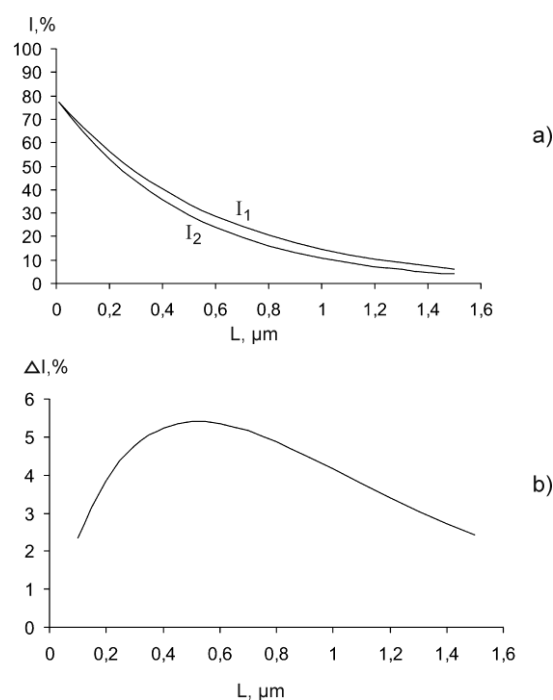


Fig. 7.a) The dependence optical transmission on CGS layer thickness on the wavelength  $\lambda = 532$  nm for different CGS compositions: 72at.% As<sub>2</sub>S<sub>3</sub>:28at.% As<sub>2</sub>Se<sub>3</sub> (curve I<sub>1</sub>) and 62at.% As<sub>2</sub>S<sub>3</sub>:38at.% As<sub>2</sub>Se<sub>3</sub> (curve I<sub>2</sub>).

For the interpretation of the absorption signal distribution in CGS layer, the dependence of the absorption difference  $I_1 - I_2$  in the layers of different 72at.% As<sub>2</sub>S<sub>3</sub>:28at.% As<sub>2</sub>Se<sub>3</sub> and 62at.% As<sub>2</sub>S<sub>3</sub>:38at.% As<sub>2</sub>Se<sub>3</sub> composition is brought in Fig. 7b, from which one can see that the greatest difference in the absorption is observed for composition 62at.% As<sub>2</sub>S<sub>3</sub>:38at.% As<sub>2</sub>Se<sub>3</sub> close to 0,6 μm from the thermoplastic - CGS interface. Low value of charge carrier mobility is characteristic for chalcogenide

glass semiconductors of As-Se-S system. According to the literature sources the drift mobility of charge carriers in  $\text{As}_2\text{Se}_3$  is of the order of  $\mu=5\cdot 10^{-7} \text{ cm}^2/\text{V}\cdot\text{s}$  [5]. For comparison of the recording mechanisms the studies of the DE kinetics on charging time have been carried out close to the threshold sensitivity of PTP carrier (at DE = 1%). The kinetics of DE growth at the pulse recording was measured in a laser radiation  $\lambda = 1064 \text{ nm}$ , which does not affect the recording process. The DE kinetics growth in time for the PTP on the basis of the composition of 72at.%  $\text{As}_2\text{S}_3$ :28at.%  $\text{As}_2\text{Se}_3$  with the sensitivity maximum at the stationary recording process and for the composition of 62at.%  $\text{As}_2\text{S}_3$ :38at.%  $\text{As}_2\text{Se}_3$  with the sensitivity maximum at the pulse recording process is brought in Fig. 8a.

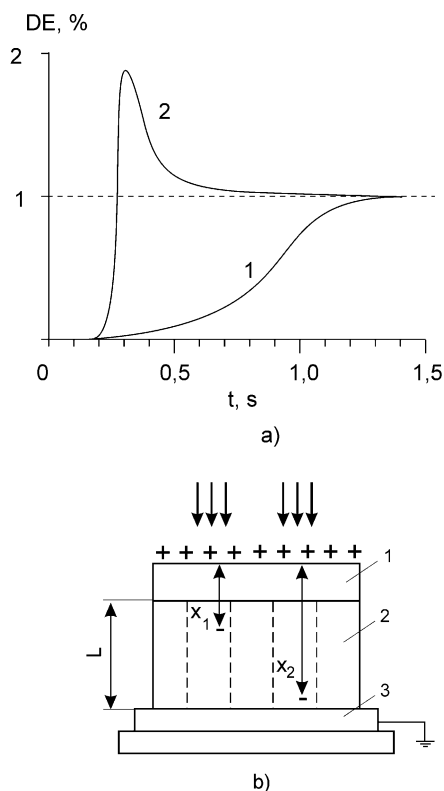


Fig. 8. a) DE growth kinetics during stationary (1) and pulse (2) recording process, b) PTP carrier: 1) thermoplastic layer, 2) CGS, 3) conductive electrode.

At the stationary process of recording the PTP carrier is illuminated during entire process of charging (from  $t=0$  to  $t=1,4\text{s}$ ) at the laser radiation intensity  $I=1,2\cdot 10^{-7} \text{ W}/\text{cm}^2$  (exposure power  $H=1,68\cdot 10^{-7} \text{ J}/\text{cm}^2$ ), and DE increases from 0 to 1% during the time interval from  $t=0,15$  to  $t=1,4\text{s}$  (curve 1, Fig. 8a). At the stationary illumination the process of non-equilibrium charge carrier photo-generation and recombination has a stationary feature and the concentration of the photo-induced carriers per unit of time does not change during the entire recording process. During such process the force of Coulomb interaction between electric charges increases with the increase of the superficial potential increase, and also due to the thermoplastic layer thickness decrease at the development of the recesses on the thermoplastic surface. At the pulse

illumination the concentration of non-equilibrium charge carriers is determined only by the rate of their recombination on the traps and the space charge in CGS layer during the total charging time  $\tau$  is preserved in a time range of  $\tau=10^{-5}\div 10^{-6} \text{ s}$ . The duration of the Coulomb interaction force between electric charges on the thermoplastic surface and semiconductor volume is limited only by this time range. As one can see from DE kinetics growth on time (curve 2, Fig. 8a) at the pulse illumination a sharp increase of DE occur in a time of  $\sim 0,1\text{s}$ , after which a sharp decrease during  $\sim 0,2\text{s}$  begins up to the final establishing of the diffraction efficiency of 1% during the total charging time of  $t=1,4\text{s}$ .

On the basis of the obtained results one can make a conclusion that at the pulse illumination in the moment of the maximum value of Coulomb force an “impact” deformation occurs on the surface of viscous liquid, which is heated up to plastic state thermoplastic. Due to the inertia of the thermoplastic mass transfer the deformation process is stretched in time to  $\sim 0,1 \text{ s}$ . After the expiration of photo-induced charge carrier lifetime the coulomb interaction is gone and under the influence of elastic forces and superficial tension the thermoplastic surface tends to align, which leads to a sharp decline of diffraction efficiency (curve 2, Fig. 8a). The PTP carrier heating is terminated when a charging unit is turned on and the thermoplastic layer temperature is continuously decreasing during recording process, which is reducing the thermoplastic fluidity and increases its viscosity. Due to this reason the process of surface relief erasing slows and the DE value is preserved at a level of 1% (curve 2, Fig. 8a). One should notice that the minimum energy exposure at the pulse recording makes a value of  $H=5\cdot 10^{-5} \text{ J}/\text{cm}^2$  which by two orders of magnitude exceeds the exposure at the stationary recording process and, correspondingly, decreases the PTP holographic sensitivity at the pulse recording to  $S=2\cdot 10^4 \text{ cm}^2/\text{J}$ .

Based on the above one can conclude that at the pulse illumination is essential area of formation of photo-induced charges in the CGS volume. As one can see from Fig. 8b the maximum photons absorption in semiconductor layer for 62at.%  $\text{As}_2\text{S}_3$ :38at.%  $\text{As}_2\text{Se}_3$  composition is situated closer to the CGS-thermoplastic interface than for 72at.%  $\text{As}_2\text{S}_3$ :28at.%  $\text{As}_2\text{Se}_3$  composition and the force of Coulomb interaction, inversely proportional to the square distance between the electric charges on to the surface and in the volume (Fig. 8b), is higher for the composition with higher value of the absorption coefficient for the used laser radiation wavelength. As a result of experiments it was established that such composition is CGS of 62at.%  $\text{As}_2\text{S}_3$ :38at.%  $\text{As}_2\text{Se}_3$ .

### 3. Conclusion

At the elaboration of optoelectronic structures on the basis of  $X\text{at.}\% \text{As}_2\text{S}_3:(100-X)\text{at.}\% \text{As}_2\text{Se}_3$  system for optical information recording one should take into account the features of holographic information recording. At a stationary recording process the maximum of holographic

sensitivity coincides with the maximum of photocurrent spectral dependence for the chosen CGS composition of  $X\text{at.}\% \text{As}_2\text{S}_3:(100-X)\text{at.}\% \text{As}_2\text{Se}_3$  system. At the pulse PTP illumination in the nanosecond range an essential importance has the region of photo-induced charge carrier formation in the CGS volume and the maximum of holographic sensitivity shifts to the shorter wavelength region of spectrum relative to the maximum of photocurrent spectral dependence.

### Acknowledgments

The investigations performed in this work were supported by STCU Grant # 5808.

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