

# Holographic Media Based on the Chalcogenide Glassy Semiconductors for Real Time Holography

Arcadi Chirita, Vladimir Prilepov, Nadejda Nasedchina  
Research and Innovation Institute, Moldova State University, Moldova Republic  
Email address: arc\_chirita@yahoo.com

**Abstract**—The investigation of the structures based on As-Se-S semiconductor thin layers were carry out. The studies of electro-physical and optical properties of the obtained structures showed the possibility of their emplementation in the systems of optical information inregistration. The prossesis of holograms recording in real time were studed.

**Keywords**— Chalcogenide glassy gemiconductors, real time holography.

## I. INTRODUCTION

Photothermoplastic (FTP) optical information carriers have high values of photosensitivity, resolution power, and short time of the optical information recording. At present, FTP carriers based on both organic [1-2] and inorganic semiconductors [3-4] are well known which do not differ in the principle of recording process, but only in the composition of the photosensitive layer. The great interest in the Chalcogenide Glassy Semiconductors (CGS) system As – Se – S is associated with the possibility of their use as photosensitve media for optical information recording [6]. High photosensitivity in combination with low dark conductivity allows use of CGS to create electrophotographic and photothermoplastic optical information carriers. Also, the ability of CGS to photo-structural transformations, manifested in the photo-darkening or photo-enlightenment of the layer under the action of irradiation, allows recording the optical information directly in the semiconductor layer [7]. These properties of CGS expand the range of capabilities of FTP carriers based on them compared to organic carriers, for example, in holographic interferometry, when the initial state of the object can be detected by photo-structural transformations in the CGS layer, and the change of its state is by photothermoplastic recording. Recording media based on CGS has selective spectral sensitivity. Therefore, to record holograms and interferograms in monochromatic laser radiation, it is necessary to obtain semiconductor layers with a maximum of spectral sensitivity near the wavelength of the using laser radiation [8]. Also, the main holographic parameters of the PTP carriers depend not only on the properties of CGS, but also on the physical parameters of the semiconductor-thermoplastic structure. An urgent task is to obtain a CGS structure-thermoplastic polymer with high values of sensitivity and resolution power for recording holograms and interferograms in real time with high values of diffraction efficiency [9]. Accomplishment of such task will allow not only to successfully apply PTP carriers in holographic microscopy, interferography and pulse holography, but also to develop new methods for their successful application in recording of optical information.

## II. MATERIALS AND METHODS

The PTP recording method belongs to methods of electrophotographic optical information recording. A typical PTP recording medium is a multi-layer structure [3-5]. The materials of each functional layer must possess either separately or simultaneously both the properties of photosensitivity and the properties of mechanical thermo-plasticity. This enables the relief-phase image formation via the photo-induced mechanical deformation of continuous thermoplastic medium in the electrical discharge field. In the PTP method of recording the discharge from high-voltage source generates homogenous distribution of positive charge on the surface of thermoplastic layer (Fig. 1.).

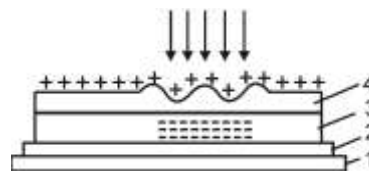


Fig. 1. Photo-thermoplastic carrier: 1) Flexible film, 2) Transparent metal electrode, 3) Photo-semiconductor, 4) Thermoplastic.

At hologram recording the PTP carrier is previously heated to the viscous state of the thermoplastic layer ( $T = 70-85^{\circ}C$ ). Simultaneously with the light exposing a high voltage (7-8 kV) charging unit is turned on and the thermoplastic surface is charged during 1-3 s by positive charges of the ionized air. In the illuminated regions of photo-semiconductor, an electric charge of the opposed sign is induced and under the influence of the electrostatic interaction a relief-phase image is formed on the surface of thermoplastic layer. Its notable peculiarity, determining our choice, is the effect of the photosensitivity amplification of the carrier due to the energy of the high-voltage source feeding the photocurrents. For suggested carriers on the CGS the sensitivity is well sufficient for holograms recording in real time.

The photosensitive media for PTP carriers was synthesized on the basis of chalcogenide glassy semiconductors of the system As-S-Se, activated with the admixture of Sn. The content of the semiconductor materials was fitted so, that the

carriers should have maximum spectral photosensitivity for laser irradiation  $\lambda = 532$  nm.

Before the vacuum deposition of the semiconductor layer, the technology of semitransparent conductive layers deposition on flexible polyethyleneterephthalate (PET) films was developed. The semitransparent chrome electrode was superimposed onto the PET films by a method of electron-beam deposition in vacuum. The necessary technical equipment - a tape drive device of the PET film and monitoring system for uniform Cr stratum deposition on the PET films was developed and manufactured. The optimum regimes of velocity (0.21m/s) of PET film motion and optimum power of the electronic evaporator (1.1 kW) were established. The chrome metallized PET films for PTP-carrier production with optical transmission  $T \sim 63-68$  %, resistance of Cr layer 2-3 kohm/□ and film length not less than 2.5 m were obtained.

The technology of vacuum deposition of chalcogenide glassy semiconductors layers on PET films was improved by maintenance the selected evaporation temperatures [10-12]. This enabled to obtain the layers of photosensitive semiconductor  $As_2S_3$ ,  $As_4S_3Se_3$ ,  $As_2Se_3$ , and  $As_2S_3 - As_2Se_3 - Sn$  with constant physical parameters along the PET film base length. The homogenization of layers in the process of their getting leads to a shift of maximum of photoconductivity to the short-visible part of spectrum. There were identified eligibility criteria of application the concept of stoichiometric composition for chalcogenide semiconductors, both in simultaneous and separate ways of optical information recording. It was shown that the most important of them are their high photosensitivity and high dark resistance ( $\rho_{dark} \approx 10^{13} \div 10^{14}$  ohm·cm). An experimental installation was designed to determine these parameters for obtained layers of the As-S-Se-Sn system with various contents of components. In table 1 there are presented the obtained physical parameters for these layers, as well as their wavelength of maximal photosensitivity. Using vaporization of mechanical mixtures of  $As_2S_3$  and  $As_2Se_3$  at a specified ratio, it can be choose the composition with maximal photoconductivity in specified range of wave lengths.

TABLE 1. The electrophysical parameters for obtained CGS layers.

Source material	d, mkm	$\rho_{dark}$ , ohm·cm	$\lambda_{max}$ , nm	$S_s$ , lux <sup>-1</sup> ·s <sup>-1</sup>
$As_2Se_3$	1.6	$4 \cdot 10^{13}$	630	0.33
$As_4S_3Se_3$	1.6	$8 \cdot 10^{13}$	564	0.19
$As_2S_3$	1.6	$1.0 \cdot 10^{14}$	488	0.18

For a more consistent study of the spectral properties of the obtained thin films of  $As_2S_3(x)As_2Se_3(y)Sn(z)$  structures the installation was developed, which can be used to study the spectral characteristics of photoconductivity of the synthesized CGS semiconductors. For this study we used thin films of the following compositions:

- Nr.1:  $As_2Se_3 - 17$  at%;  $As_2S_3 - 82.3$  at%; Sn - 0.7 at%,
- Nr.2:  $As_2Se_3 - 10$  at%;  $As_2S_3 - 89.3$  at%; Sn - 0.7 at%,
- Nr.3:  $As_2Se_3 - 5$  at%;  $As_2S_3 - 94.3$  at%; Sn - 0.7 at%.

The solid solution of composition  $As_2S_3 - 82.3$  mol.%,  $As_2Se_3 - 17$  mol.%, Sn - 0.7 mol.% with the best photographic

properties was obtained. The study of optical and photoelectric properties of the developed compositions showed that the maximum of spectral photosensitivity is reached at  $\lambda_{max} = 532$  nm. The spectral dependence of photo current of the obtained composition is presented in Fig. 2.

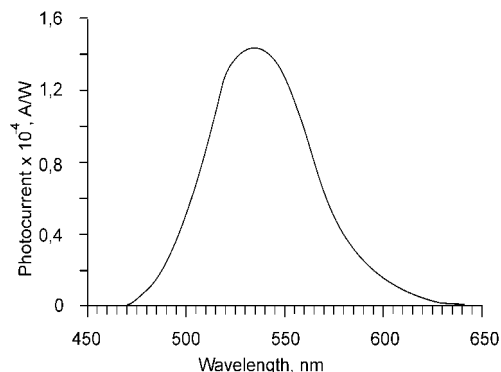


Fig. 2. Spectral dependence of the photosensitivity of the composition  $As_2S_3 - 82.3$  mol.%,  $As_2Se_3 - 17$  mol.%, Sn - 0.7 mol.%.

This composition differs by increased performance in the band gap and photoconductivity compared with the same composition without the admixture of tin, and, consequently, by increased photosensitivity of the media.

For a complete view of the possibility to use the studied CGS compositions in developing based on them media for photothermoplastic optical information recording methods the examination of their electrophotographic (EF) characteristics is needed [13]. The study of the EF characteristics was carried out by the conventional method, which is based on the measuring the surface potential decay dependences of the sample charged in the high voltage discharge field on time. The measured surface potential decay curves for the layers under study are shown in Fig. 3.

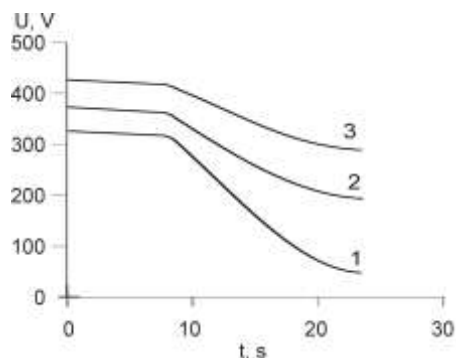


Fig. 3. The curves of potential decay of compositions: 1)  $As_2Se_3 - 5$  at%;  $As_2S_3 - 94.3$  at%; Sn - 0.7 at%; 2)  $As_2Se_3 - 10$  at%;  $As_2S_3 - 89.3$  at%; Sn - 0.7 at%; 3)  $As_2Se_3 - 17$  at%;  $As_2S_3 - 82.3$  at%; Sn - 0.7 at%.

From these dependences we can define the basic parameters of the EF characteristics, such as: the limiting charging potential  $V_0$ , dark and light resistivity  $\rho_{dark}$  and  $\rho_{light}$ , the value of the EF sensitivity, etc. The Fig.3 shows that the limiting charging potential varies with the increasing of the arsenic selenide concentrations (curves 1-3), which is associated with the decrease in resistivity. The main EF

characteristics of the studied compositions are presented in Table 2.

TABLE 2. Electrophotographic characteristics of three CGS compositions.

Composition of the layers, at%			Parameters of the layers	
As <sub>2</sub> S <sub>3</sub>	As <sub>2</sub> Se <sub>3</sub>	Sn	$\rho_{\text{dark}}$ , ohm·cm	$S$ , $\text{I} \times^{-1} \cdot \text{s}^{-1}$
82.3	17	0.7	$3.0 \cdot 10^{14}$	0.30
89.3	10	0.7	$3.7 \cdot 10^{14}$	0.19
94.3	5	0.7	$5.0 \cdot 10^{14}$	0.12

The most suitable coherent source for holograms recording on such carrier with composition As<sub>2</sub>S<sub>3</sub> - 82.3 mol.%, As<sub>2</sub>Se<sub>3</sub> - 17 mol.%, Sn - 0.7 mol.% is the laser with wavelength  $\lambda = 532$  nm.

Using the synthesized semiconductor the photothermoplastic carrier for real time holography was obtained. A flexible polyethylentereftalat film (1, Fig. 1) was covered with the transparent chrome electrode (2). The photo-semiconductor layer based on chalcogenide glassy semiconductors of As<sub>2</sub>S<sub>3</sub> - 82.3 mol.%, As<sub>2</sub>Se<sub>3</sub> - 17 mol.%, Sn - 0.7 mol.% system (3) with a thickness of 1,7  $\mu\text{m}$  was deposited onto the metal electrode. The thermoplastic layer (4) based on poly-N-epoxypropylcarbazole was deposited with the thickness of 0,6  $\mu\text{m}$  was deposited onto the semiconductor layer. The carrier was heated up to a viscous state of the thermo-plastic layer ( $T=79^{\circ}\text{C}$ ). At the same time, the beginning of the exposure was accompanied by high-voltage charging. The surface of the thermo-plastic is charged for 2, 8 s with positive charge of ionized air. On the light exposed area of the semiconductor, the opposite charge is induced, due to the effect of electro-static interaction and a phase relief image is formed on the surface of the thermoplastic layer. Relief – phase diffraction gratings were recorded by the use of an optical system based on DPSS laser with  $\lambda = 532$  nm wavelength. The PTP carrier was illuminated by equal intensity plane-parallel laser beams, which were forming in the photosensitive semiconductor layer an interference pattern with spatial frequency  $\nu = 1000 \text{ mm}^{-1}$ . The diffraction efficiency (DE) of recorded diffraction grating was close to 30%. The AFM image of the obtained relief-phase diffraction grating is presented in Fig.4.

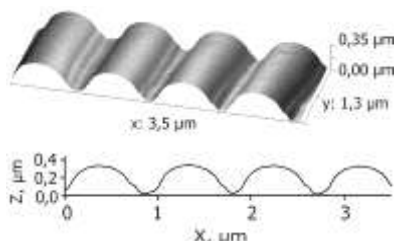


Fig. 4. The AFM image of diffraction grating surface with spatial frequency  $\nu = 1000 \text{ mm}^{-1}$  and diffraction efficiency 30%.

The obtained carriers can be successfully used for real time holography.

### III. RESULTS AND DISCUSSION

The holographic characteristics of obtained PTP carriers were studied using the holographic set up, the schematic

diagram of which is shown in Fig. 5. A specific feature of the experiment is the spatial separation of a plane-parallel laser beam using a set of prisms (Fig. 5, a, b, c).

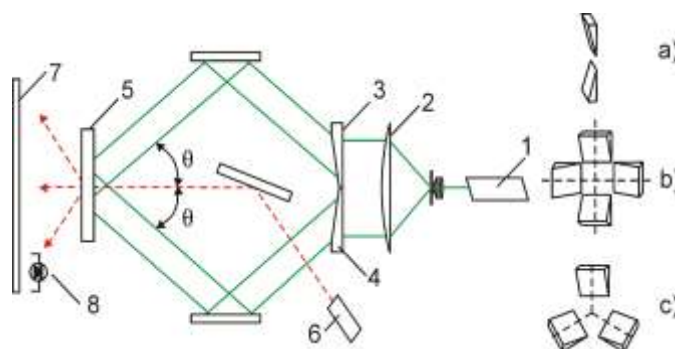


Fig. 5. 1) Nd:Yag laser ( $\lambda=532\text{nm}$ ), 2) Collimator, 3-4) Prisms, 5) PTP carrier, 6) He-Ne laser  $\lambda=632,8 \text{ nm}$ , 7) Screen, 8) Photodetector.

Using two prisms in optical scheme (Fig.5a) the interference pattern is formed on the PTP carrier surface (Fig.6).

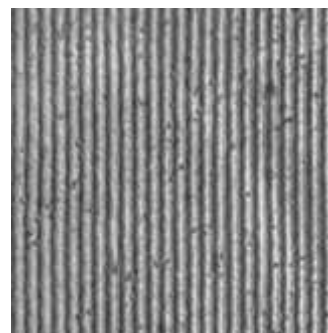


Fig. 6. PTP carrier surface with a registered relief-phase diffraction grating.

When such diffraction grating is illuminated by the He-Ne laser beam (6, Fig. 5), diffraction maxims of zero, first and higher orders are formed on the screen. Diffraction efficiency (DE) of recorded gratings was defined as the ratio of light intensity in the first diffraction maximum to the light intensity passing through the unexposed area of the studied sample. This method of DE determination allows excluding the influence of light absorption in the metal electrode - semiconductor structure. The diffraction efficiency of the registered grating was  $\eta = 30\%$ .

When the plane-parallel laser beam is divided into four components (Fig. 5b), an interference pattern of mutually perpendicular dark and light stripes will be formed in the photosensitive layer of the PTP carrier (Fig. 7a).

The surface relief of the obtained image consists of depressions in the illuminated areas of the interference pattern and protuberances in the places of the dark stripes of the raster. The diffraction efficiency of each of the four first diffraction orders (Fig. 7b) reaches a value of  $\eta = 24\%$ . It should be noted that doubling the density of the recorded information, as compared with the two-beam scheme, reduced the value of the diffraction efficiency from  $\eta = 30\%$  to  $\eta = 24\%$ . The latter suggests that the information capacity of the carrier under study makes it possible to register multiplex

holograms without a significant loss of the values of the diffraction efficiency.

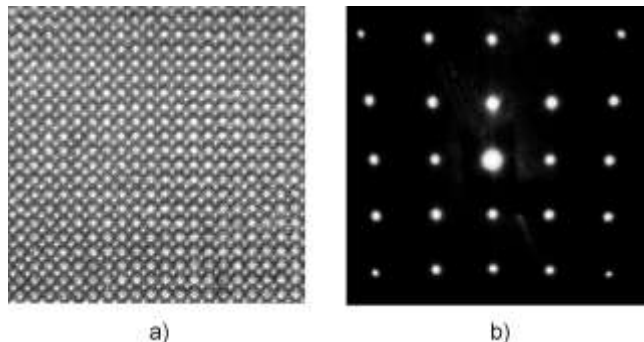


Fig. 7 a) Image of the surface of the PTP carrier, b) the arrangement of the diffraction orders when the hologram is illuminated by the laser beam  $\lambda = 632.8$  nm.

When the plane-parallel laser beam is divided with the help of three prisms (Fig. 5c), the nature of the interference pattern changes. In this case, each of the beams will interfere with another two beams, creating a system of successively alternating light and dark bands on the surface of the PTP carrier, forming an angle of  $120^\circ$  between them. Fig. 8a shows an image of a diffraction grating registered on the surface of a PTP carrier.

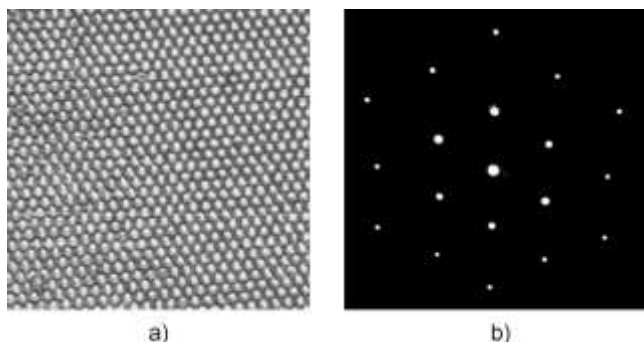


Fig. 8 a) Image of the surface of the PTP carrier, b) the arrangement of the diffraction orders when the hologram is illuminated by the laser beam  $\lambda = 632.8$  nm.

The diffraction efficiency of each of the first maxima reaches a value of  $\eta = 22\%$ . A transparent Z symbol on an opaque background was used as a test object for hologram recording using this optical scheme. In this case, the other two laser beams are considered as reference beams of the holographic recording scheme. When the recorded hologram is illuminated with one of the beams, the image of the initial test object is reconstructed in the first diffraction orders (Fig. 9).

The diffraction efficiency of the reconstructed image of each of the Z symbols reaches  $\eta = 18\%$ . The decrease in diffraction efficiency, as compared with the diffraction grating (Fig. 6), is due to an increase of the spectrum of spatial frequencies recorded at each point of the hologram. The investigated PTP carrier allows recording successfully the rasterized images with simultaneous interference of both three and four laser beams.

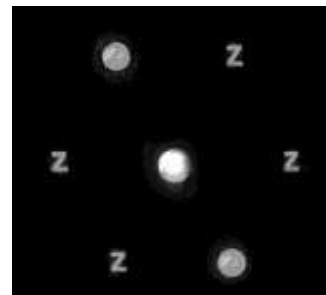


Fig. 9. Reconstructed holographic image of the test-object.

The study of holographic recording of micro-objects on the obtained PTP carriers were carried out. The optical scheme of the unit for hologram recording is shown in Fig. 10.

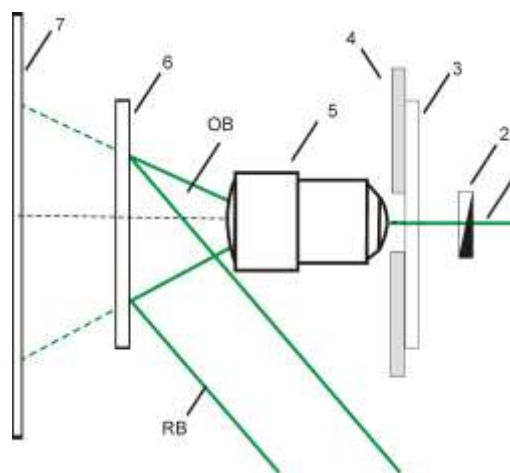


Fig. 10. Holographic set up: 1) Laser beam 532 nm, 2) Optical shutter, 3) Glass plate, 4) Cooling device, 5) One-tube microscope, 6) PTP carrier, 7) Screen.

The laser beam with a wavelength  $\lambda = 532$  nm (1, Fig. 5) passes through the optical shutter (2) and the glass plate (3) with a thickness of 10 mm. The glass plate is attached to the cooling device (4), which allows lowering the plate temperature up to  $-5^\circ\text{C}$ . The heat-conducting portion of the cooling element (4) is attached to the front surface of the glass plate, which is located in the focal plane of the one-tube microscope (5). The large thickness of the glass plate, and the low thermal conductivity of the glass, makes it possible to eliminate the process of condensation of the water vapor from the air on the opposite side of the glass plate. The one-tube microscope (5) focuses on the surface of the PTP carrier (6) the image of the condensed water droplets. The hologram is recorded as a result of the interference of the object beam OB and the reference beam RB. Registration of holographic images began with the appearance of the first signs of condensation of water vapor from the air on the cooled surface of the glass plate. Fig. 6a shows the reconstructed image of the initial phase of the process of condensation of water vapor. On the reconstructed holographic image, single droplets with the regular spherical shape and the size of 8-10 microns are observed (Fig. 11a). On the next hologram, recorded after 10 s, the phase of formation of condensation centers is completed and the condensed droplets with the size of 15–20  $\mu\text{m}$  are

observed. As can be seen in the reconstructed image, at this phase of the condensation process, along with an increase in the size of the droplets, there is a deviation from the spherical shape (Fig. 11b). On the next hologram, registered through the same time interval, condensed droplets with a size of 20–25  $\mu\text{m}$  were fixed, which makes it possible to note a decrease in the rate of vapor condensation (Fig. 11c). All the drops on the selected surface have clear contours and three-dimensional holographic image of each drop can be restored. Fig. 11d shows the final process of the water droplets condensation.

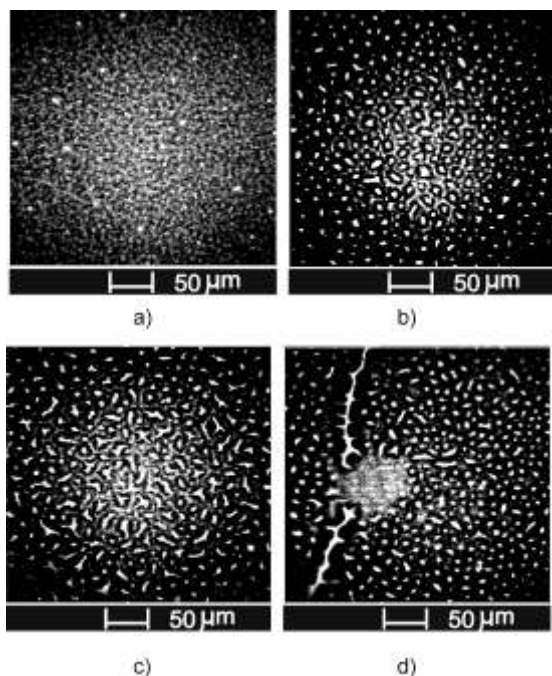


Fig. 11. The reconstructed images of holograms of condensed water droplets: a) the initial moment of condensation, b) after 10 s, c) after 20 s, d) after 90 s.

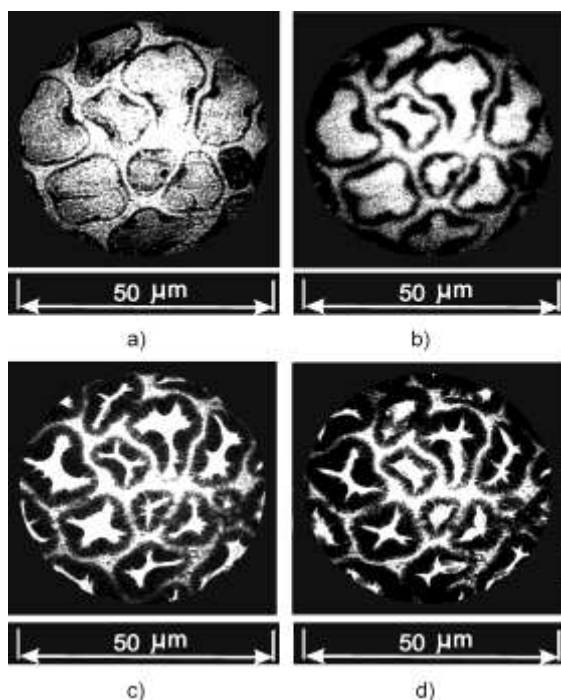


Fig. 12 Reconstructed holograms of the water droplets.

The three-dimensional characteristics of the recorded objects can be restored. Figure 12 shows images of sequential scanning of water droplets along the depth of the reconstructed hologram. When the hologram is reconstructed in the reference beam RB, the geometric shape of the base of each drop condensed on the surface of the glass substrate is clearly visible (Fig.12a).

Further scanning in the depth of the image allowed to trace the change in the shape of the droplets from the base to the top (Fig. 12b-12d). The obtained images clearly show that the formed droplets differ from each other in their size and geometry. Thus, the technique of photothermoplastic recording can be successfully applied for real time holography of micro-objects.

#### IV. CONCLUSION

Elaboration of optoelectronic structures on the basis of As-Se-S-Sn system for optical information recording should take into account the features of holographic information recording in real time. The maximum of holographic sensitivity coincides with the maximum of photocurrent spectral dependence for the chosen chalcogenide glassy semiconductors system. The method of real time holograms recording will be useful for the study of some micro-objects in microelectronics, biology, and medicine.

#### ACKNOWLEDGMENTS

This research was supported by the institutional project 15.817.02.34A

#### REFERENCES

- [1] N. Davidenko, I. Davidenko, V. Pavlov, N. Chuprina, V. Kravchenko, N. Kuranda, E. Mokrinskaya, S. Studzinsky. "Photothermoplastic recording media and its application in the holographic method of determination of the refractive index of liquid objects", *Applied Optics*, vol. 57, issue 8, pp. 1832-1837, 2018
- [2] N. Davidenko, I. Davidenko, S. Studzinsky, V. Pavlov, E. Mokrinskaya, N. Chuprina, V. Kravchenko. "Some features of information properties of holographic recording media based on a photoconducting carbazolyl-containing oligomer doped with an organic electron acceptor", *Applied Optics*, vol. 55, issue 12, pp. B31-B35, 2016
- [3] A. Chirita, F. Dimov, S. Pradhan, P. Bumacod, O. Korshak. "Real-time nano-seconds pulse holograms recording on photo-thermoplastic media", *Journal of Nanoelectronics and Optoelectronics*, vol. 7, issue 5, pp. 415-418, 2012
- [4] A. Chirita, N. Kukhtarev, T. Kukhtareva, O. Korshak, V. Prilepov. "Holographic imaging and interferometry with non-Bragg diffraction orders on volume and surface-relief gratings in lithium niobate and photo-thermoplastic media", *Journal of Modern Optics*, vol. 59, issue 16, pp. 1428-1433, 2012
- [5] Chirita A., Kukhtarev N., Kukhtareva T., Korshak O., Prilepov V. Jidcov I. "Recording holograms of micro-scale objects in real time", *Laser Physics*, vol. 23, pp. 036002-036006, 2013
- [6] A. Chirita, T. Galstean, M. Caraman, O. Korshak, V. Prilepov. "Photo-thermo-plastic recording on chalcogenide glassy semiconductors for real-time holography", *Journal of Optoelectronics and Advanced Materials Rapid Communications*, vol. 7, issue 3-4, pp. 293-295, 2013
- [7] A. Chirita. "Real-time scaling of micro-objects by multiplexed holographic recording on photo-thermoplastic structure", *Journal of Modern Optics*, vol. 57, issue 10, pp. 854-858, 2010
- [8] A. Chirita, V. Prilepov, M. Popescu, I. Andries, M. Caraman, Iu. Jidcov. "Effect of optical coating in the thin-film system of chalcogenide glassy semiconductor-dielectric when recording the holographic optical information", *Journal of Optoelectronics and Advanced Materials*, vol. 17, issue 7-8, pp. 925-929, 2015

- [9] I. Andries, T. Galstian, A. Chirita. "Approximate analysis of the diffraction efficiency of transmission phase holographic gratings with smooth non-sinusoidal relief", *Journal of Optoelectronics and Advanced Materials*, vol. 18, issue 1-2, pp.56-64, 2016
- [10] V. Prilepov, M. Popescu, A. Chirita, O. Korshak, P. Ketrush, N. Nasedchina. "Technology of fabrication of chalcogenide glassy semiconducting films", *Journal of Optoelectronics and Advanced Materials Rapid Communication*, vol. 15, issue12, pp.1362 – 1368, 2013
- [11] V. Prilepov, P. Gasin, A. Chirita, D. Spoiala. "Influence of fine- grained vanadium-based layers on the photo response multiplicity in structures with amorphous As<sub>2</sub>Se<sub>3</sub> films", *Technical Physics*, vol. 55, issue 5, pp.747-749, 2010
- [12] V. Prilepov, M. Popescu, A. Chirita, O.Korshak, P. Ketrush, N. Nasedchina. "Technology of chalcogenide glassy semiconductor layers fabrication", *Chalcogenide Letters*, vol. 10, issue 7, pp.249 – 257, 2013
- [13] A. Chirita, V. Prilepov, M. Popescu, O. Corsac, P. Chetrus, N. Nasedchina. "Electro-optical properties of As-Se-S - dielectric structure for optical information recording in real time", *Optoelectronics and Advanced Materials - Rapid Communications*, vol. 9, issue 7-8, pp.919-923, 2015