

Diffraction optical structures on the basis of chalcogenide glasses and polymers

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Thin films prepared from chalcogenide glasses and polymers were used in the fabrication of diffractive structures by holographic and electron recording technology.

(Received July 3, 2007; accepted October 1, 2007)

Keywords: diffractive optical structure, Chalcogenide glasses, Polymers, Electronoresist, Photoresist

1. Introduction

Diffraction optical structures are the main elements of diffraction optics that is important branch of modern optics. Diffraction optical elements (DOE) present the planar or fiberglass substrates with deposited on them of thin films of photo-resists or electron resists. Such structures work as phase plate which can be used in integrated photonic devices with good perspectives for application in the systems of filtering, multiplexing, routing, focusing, collimating of light [1-3] as well as for fabrication of photonic crystals [4] and sensors [5-7]. Some examples of functions of DOE are shown in the [2].

There are many requirements to materials which can be utilized as photo-resists or electron resists. In present the practice needs such materials which should provide high sensitivity, simple chemical development, good spatial-frequency response, high diffraction-efficiency level, high signal-to-noise ratio and high stability of the electronoresists and the holographic materials, the possibility to use the same films in the process of application of both methods of photo- and electron-beam lithography. Requirements for recording media are so high that it is necessary to continue the work for obtaining diffraction structures with programmed parameters. The key problem is related to elaboration of new materials for photoresists or electronoresists.

Among the large groups of materials which are utilized as photoresists and electronoresists are some compositions of chalcogenide glasses (ChG) and polymers which have high sensitivity to light or electron beam.

In this report results concerning the problems of fabrication and study of diffraction optical structures are discussed on the basis of the experience of the Center of Optoelectronics of the Institute of Applied Physics of Academy of Sciences of Moldova. The main attention is paid to registration media and diffraction gratings that can be utilized in fabrication of different diffraction optical structures for processing of optical information [13-14,18-20].

The holographic and electron lithography technologies were used for fabricating of the grating structures on thin films prepared from chalcogenide glasses and polymers. The electric field and other technological procedures have been used during

holographic writing process in order to obtain diffraction structures with high density and high quality.

2. Inorganic materials based on the chalcogenide glasses for fabrication of photoresists

For obtaining diffraction structures with designed parameters many authors pay their attention to chalcogenide glasses [see for example 8-12, 22-24]. All of them considered that this group of materials manifests many properties of holographic media. In the Center of Optoelectronics inorganic materials on the basis of chalcogenide glasses such as As_2S_3 , As_2Se_3 , $As-S-Se$, $As_2S_3-Sb_2S_3$, As_2S_3-Ge , $Ge-S$, $Ge-Se$, $As_2S_3:Sn$, $As_2Se_3:Sn$ were studied. Some compositions of ChG have been doped with following elements: Pr, Sm, Er, Dy, Mn, Sn.

It was shown that thin films prepared from studied undoped and doped chalcogenide glasses manifest excellent properties for fabrication of diffraction structures. Process of writing of diffraction structures carried out in the conditions when thin films of chalcogenide glasses were in contact with air. Especially such process also carried out when these films were in contact with liquid media, whose refracting index ranged from 1.3 to 1.8 [13].

As it is known the distance between interference lines d depends on wavelength (λ), refraction index of surrounding media (n_1), where the interference takes place and on the angle of interaction of laser beams ($\alpha=2\Theta$) according to formula (1):

$$d = \frac{\lambda}{2n_1 \sin \Theta} \quad (1)$$

The calculated dependences of resolution of diffraction structures on wavelength, refracting index and the angle of laser beam interaction are shown in Fig. 1. As it is seen in the case when $n_1=1$ even for high angle ($\alpha=150$ degrees) of laser beams interaction with $\lambda=370$ nm the maximum density of interference pattern can't exceed the value of 5400 lines/mm. At the same time in similar conditions of experiment the density of interference lines

can reach the value about 10000 lin/mm when the refractive index of surround media is equal to 1.9.

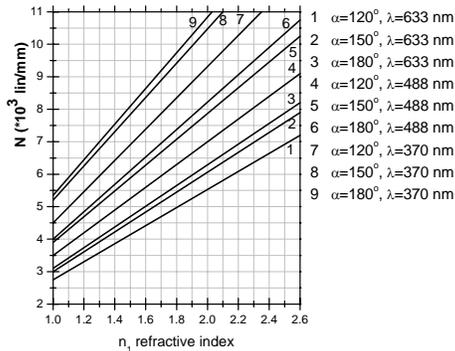


Fig. 1. The dependences of recording density on the refracting index of surrounding media calculated for the different wavelengths and the angles of laser beam interaction.

Beside that the high values of refracting index of surround media also lead to the decreasing of reflected light according to the formula (2):

$$R = \left(\frac{n_2 - n_1}{n_2 + n_1} \right)^2 \quad (2)$$

where n_1 is the refractive index of surround media and n_2 is refractive index of chalcogenide thin film. The kinetics curves of diffraction efficiency of grating structures with density of 3000 lines/mm written in As_2S_3 at $\lambda=488$ nm for two different kinds of surround media are shown in Fig. 2.

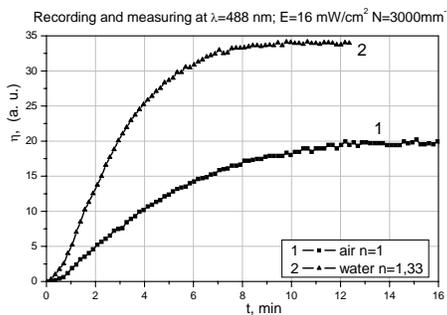


Fig. 2. The kinetics of diffraction efficiency growth for diffraction gratings with density 3000 lines/mm written in As_2S_3 at $\lambda=488$ nm for two different kinds of surround medium (water with $n=1,33$ and air with $n=1$).

The advantage of utilizing of immersion liquids with higher refractive index in comparison with air is evident. As a result microstructures in the form of diffraction gratings have been obtained with high density of registered lines such as 5650 lines/mm with period $0.18 \mu\text{m}$ (Fig. 3).

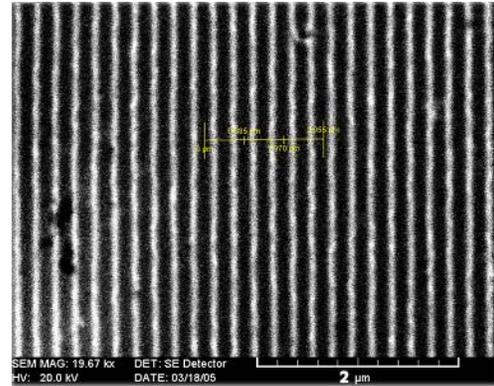
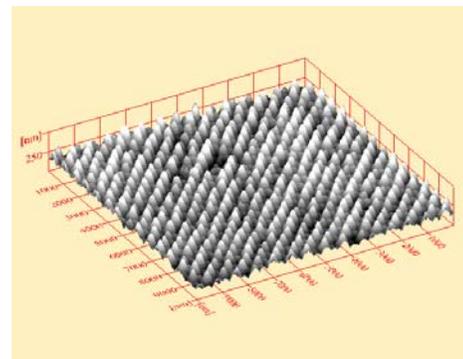
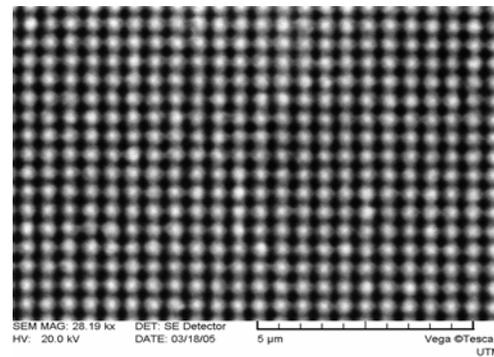


Fig. 3. Diffraction structures.

The last result was achieved due to special method of exposition by laser and electron beam and by selection of special condition of etching elaborated in our collective [13,14, 20].



Superimposed gratings, observed by scanning electron microscope (a) and atomic-force microscope (b).

For the improvement of the quality of gratings the electric field was applied to thin films in the process of their exposing by laser beam. It was shown, that applying the electric field to the studied structures leads to the increase of: the photosensitivity of ChG by 1.5-2 times, the diffraction efficiency by 2.5-3.5 times, the dynamic range is expanded by 1.5 times, the time necessary for achievement of present value of diffraction efficiency is reduced by 2 [14].

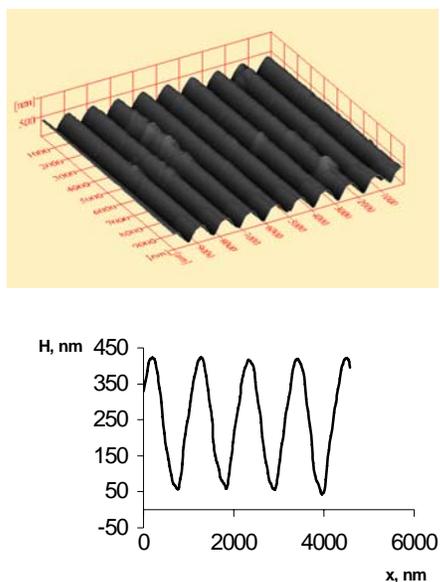


Fig. 4. Profile image of gratings obtained under application of electric field.

The high quality of grating profile can be seen at the Fig.4, where image of gratings obtained through Atomic-Force Microscope in Technical University of Moldova is shown. For such behavior there are some reasons that have been commented at the previous workshop in the paper [14].

4. New polymers for fabrication of resists

For registration of information by optical or e-beam methods a great interest present polymer compositions for their optical properties, low cost and easy fabrication [15-17]. This class of materials was used for e-beam recording of diffraction gratings. The following polymer layers were used:

PEPC – polyepoxypropylcarbazole

CAM:OMA – copolymer carbazolylalkylmethacrylate with octylmethacrylate

CEM:MMA – copolymer carbazolylethylmethacrylate with methylmethacrylate

The 5 μm thick layers from these materials were deposited onto lavsan substrates covered with a semitransparent electrode for electric charge leakage.

The diffraction gratings with constant period (Λ) of 1 μm and 2 μm were recorded in polymer layers by electron beam of scanning electron microscope BS-300. The beam current determining the electron irradiation dose was varied in the range 0.1 to 15 nA.

The mentioned polymers manifest different sensitivity to the electron-beam irradiation.

In Fig. 5 the $\eta(I)$ dependencies for the gratings recorded in the layers of CAM:OMA co-polymers of the composition 80:20 mol.% (solid line) and PEPC (dashed line) are presented. A distinguishing feature for the CAM:OMA is the increase of η with increasing of

recording current at $I > 1$ nA resulting in rather high values of η .

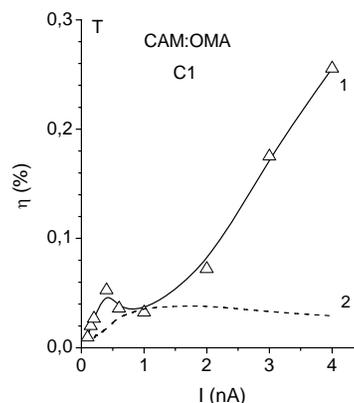


Fig. 5. Dependences $\eta(I)$ for gratings recorded in CAM:OMA layer of 80:20 mol % composition (1) and in PEPC layer (2).

For CEM:MMA layers dependences $\eta(I)$ are similar to ones for CAM:OMA layers. In this case nontrivial sharp growth of efficiency with beam current occurred at the range of high beam currents ($I > 5$ nA). (Fig.6.). Reproducibility of this effect has been established.

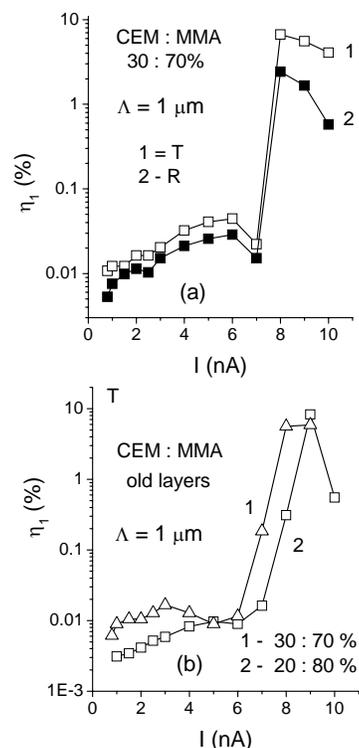


Fig. 6. Dependences of efficiency on beam current for grating of 1 μm period layers recorded in fresh samples (a) and in samples stored during 1 year (former sample parties) (b).

In the case of utilizing polymers for registration of information it is very important to be sure that these materials are stable. For studying this problem the e-beam writing was made both in the fresh and in the dark stored layers. The properties of layers remain stable even after 1 year of storage that is confirmed by Fig. 6b. Really as it is seen the gratings, recorded in these two cases, are practically the same.

It is important to note that in the process of caring out of experiments with electron-beam lithography technology the threshold behavior of e-beam writing in CEM:MMA layers was observed. It can permit the significant improvement of parameters of investigated resists [15] that can be important for forming of submicron structures. The sharp efficiency rising with beam current can be observed from the Fig.7.

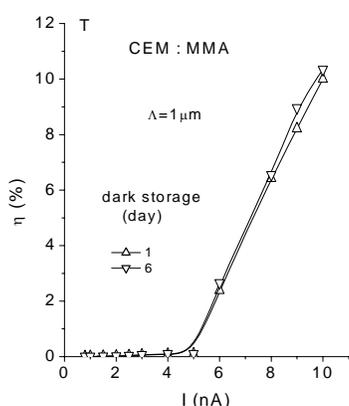


Fig. 7. Dependences of efficiency on beam current for fresh and 6 days dark stored layers.

So it was shown that copolymers CEM: MMA hold much promise for e-beam writing. As large as 10 % efficiency has been obtained for gratings formed by direct electron beam writing in layers from CEM:MMA copolymers [17]. It has been shown by SEM investigations that the relief gratings (Fig. 8) have been formed at high beam currents.

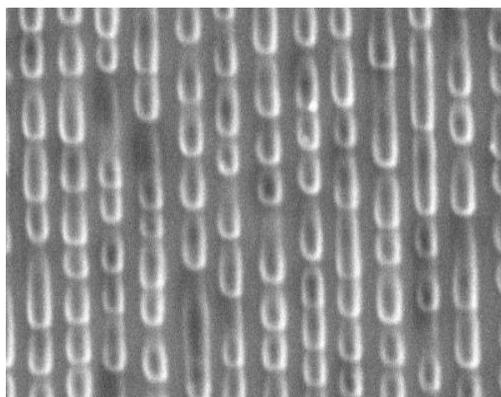


Fig. 8. Micrograph of the relief grating with period of 1 μm, formed by direct e-beam writing.

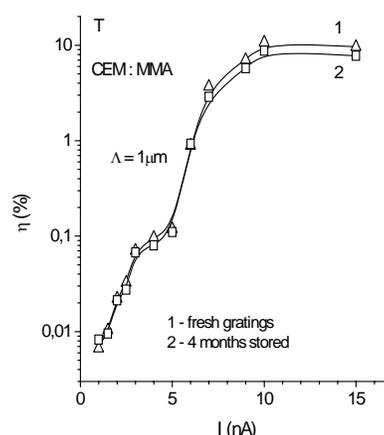


Fig. 9. Effect of 4 month dark storage on efficiency of gratings of 1 μm period, formed in CEM:MMA layer.

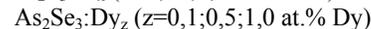
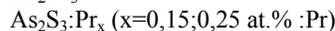
The important role of carbazole rings in process of surface modulation can be assumed. Gratings exhibited stability upon dark storage (Fig. 9.) and white light illumination as well. After chemical etching the value of diffraction efficiency is as much as 30-35%.

5. New composite materials on the basis of polymers and chalcogenide glasses for fabrication of resists

The composites on the base of chalcogenide glasses (ChG) and polymer materials represent an important and growing class of hybrid materials with promising physical and optical characteristics. For application in optoelectronics it is very important that both chalcogenides and polymer materials exhibit high photoinduced changes. The combination of these properties by creation of new composites based on chalcogenide glasses and polymers can allow obtaining new materials with new multifunctional properties. The composites obtained by this method have many advantages, such as low cost, simplicity of making, and good optical properties. This is why these composite materials have a promising perspective for fabrication of fiber optics amplifiers, recording media for high-resolution diffraction gratings, planar-integrated optical elements, all-optical switches, luminescent screens, laser light amplifiers, and etc.

For fabrication of resists new composite materials on the basis of polymers and chalcogenide glasses the following materials for investigation were utilized [16]:

Chalcogenide glasses:



-Polymers: polyvinyl alcohol (PVA) with structure $[-\text{CH}_2\text{CH}(\text{OH})-]_n$

polyvinylpyrrolidone (PVP) with structure $[-C_6H_9NO-]_n$

Typical absorption spectra of polymer-chalcogenide layers are shown in Fig.10 before illumination (1) and after illumination (2).

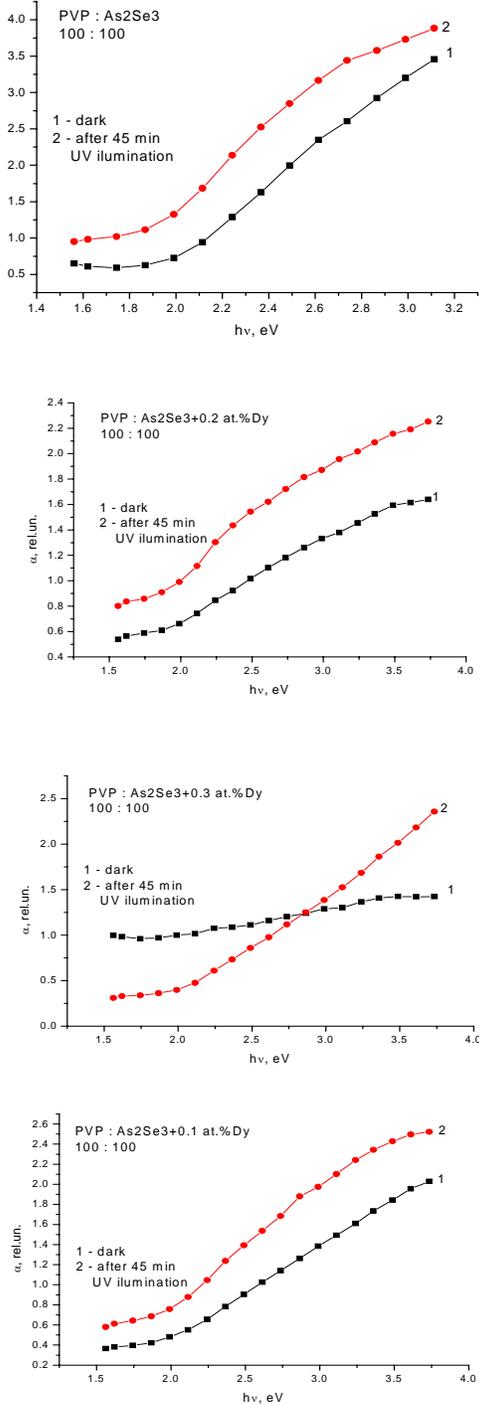


Fig.10. The absorption edges of undoped and doped As₂Se₃/PVP composite before and after UV illumination.

The analogical results were obtained for composites PVA-As₂S₃ and PVP-As₂S₃.

On the base of studied optical properties of investigated composites one can come to the conclusion that these materials can be applied as recording media for fabrication of different diffractive elements for optoelectronics.

To investigate the holographic characteristics the recording setup was mounted by traditional scheme for recording of transmitted diffraction gratings.

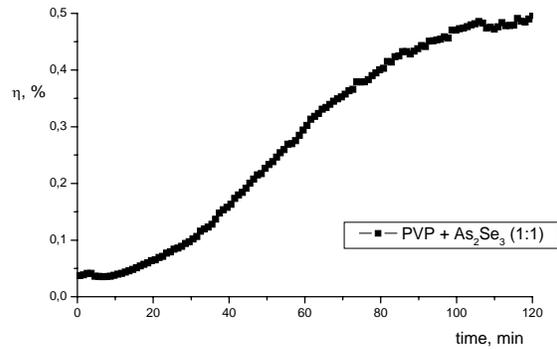


Fig.11. Diffraction efficiency kinetics of the As₂Se₃/PVP composite film (film thickness $d=3\mu\text{m}$).

The kinetics of diffraction efficiency of one of studied composites is shown in Fig. 11. The data presented in Fig.11 confirm that the values of diffraction efficiency of the composite materials are the same as in the case of many polymer materials. Studying the diffraction efficiency dependence on concentration of As₂S₃ in polymer and on spatial frequency of recording gratings it was shown that with increasing of As₂S₃ concentration from 50% to 100% by weight of polymer the diffraction efficiency increasing twice. Maximum achieved diffraction efficiency turns to be 0,5% that as it was mentioned above is of order of diffraction efficiency in polymer films [21].

6. Conclusions

On the basis of chalcogenide glasses and polymers diffraction optical structures can be obtained for using in integrated photonic devices. Thin films prepared from chalcogenide glasses and polymers were used for fabricating of diffraction structures by the both holographic and electron recording technology. The electric field and other technological procedures have been used during holographic writing process in order to obtain diffraction structures with high density and high quality.

The studied materials have a good perspective for application for fabrication of optical structures for spectral filtering, multiplexing, routing, focusing, collimating, photonic crystals and sensors.

Acknowledgements

Authors would like to thank S.Buzurniuc, A.Nastas, A.Prisacari, S.Robu, V.Verlan for participating in carrying out of experiments. The work was supported by grants from SNC of Academy of Sciences of Moldova. Study of morphology of diffraction structures have been done on Scanning Electron Microscope and Atomic-Force Microscope in Technical University of Moldova.

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