

INFLUENCE OF THE ELECTRICAL FIELD ON THE FORMATION PROCESS OF HOLOGRAPHIC DIFFRACTION GRATINGS (HDG) IN VITREOUS CHALCOGENIDE SEMICONDUCTORS

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The influence of the electrical field on the process of formation of holographic diffraction lattices in vitreous chalcogenide semiconductor (ChVS) layers in the system $(As_2S_3)_x(As_2Se_3)_{1-x}$ has been studied. The thin film structures like metal -ChVS-metal, metal - ChVS-dielectric-metal, metal - ChVS-ion electrode, metal - ChVS-dielectric-ion electrode have been investigated. The ionic electrode was created by using a xerographic method. The processes of etching and metallization of holographic diffraction gratings have been also investigated. The surface of holographic gratings has been investigated by atom-force microscopy. It was established, that the electrical field essentially influences the optical and holographic parameters of ChVS structures. The application of the electrical field leads to the increase of regularity and depth of the relief by 25-30 %. In the same time the structure remains constant – quasi sinusoidal. It was shown, that the application of the electrical field to the studied structures leads, also, to the increase of the photosensitivity of ChVS by 1.5-2 times, and of the diffraction efficiency by 2.5-3.5 times. The dynamic range was expanded by 1.5 times, the time necessary for achievement of the diffraction efficiency was reduced by a factor of 2. It was established, that after etching and metallization, the diffraction efficiency of the samples, to which during the process of recording has been applied the electrical field, was higher by 50-200 %, depending on the exposition, in comparison with the case when the diffraction structure has been obtained in the absence of the electrical field. Possible mechanisms of the observed phenomena have been discussed.

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1. Introduction

The chalcogenide vitreous semiconductors have found wide applications in the systems of registration, storage and processing of the optical information [1-5]. They are also widely used in electronics as switches, gauges, etc. New phenomena have been discovered in vitreous chalcogenides and the use in applications became a challenging problem. Trunov and Bilanich discovered the photo-plastic effect and the polarization photo-plastic effect [6,7]. Influence of light on the interdiffusion in chalcogenide multilayers as well as in composite metal-chalcogenide layers has been investigated by Malyovanik et al. [8,9]. A survey of chalcogenide glass applications has been recently published by Lezal [10]. Recently, the chalcogenides were used for creation of holographic nanostructures by electronic lithography [11, 12]. Thin films of sulfides and arsenic

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selenium and hetero-junctions on their basis [5,11-18] are important as recording structures of analog and holographic images. First of all it is necessary to underline their advantages as media with very high resolution: $(8-10) \times 10^3 \text{ mm}^{-1}$, high signal/noise relation, and the opportunity of chemical amplification and transformation of the image in relief – phase due to selective etching [5] that allows for the creation of qualitative matrices for duplication of the holographic image.

Media for optical registration of information on the basis of photo-structural transformations alongside with a number of advantages possess also a number of basic shortcomings: low values of sensitivity ($10^{-1} - 10^1$) J/cm² and low values of diffraction efficiency [5].

The purpose of this work was to study the recording processes of the holographic interference lattices on chalcogenide vitreous semiconductor layers in condition of the application of an electrical field on samples, as well as the processes of etching and metallization of holographic diffraction lattices.

2. Samples and method

The samples for registration of holographic diffraction gratings were obtained by consecutive thermal evaporation in vacuum of Ni and As₂S₃, and of the solid solutions (As₂S₃)_x(As₂Se₃)_{1-x}. The thickness of the semi-transparent metal layer which served as one of electrodes at charging in an electrical field, was some tens angstroms. Thickness of semiconductor layers was 0.8 and 1 micrometer on the lavesan substrate, and in case of glass substrate: 1.2 micrometers.

In order to search for the influence of process of charging during recording of the holographic interference gratings, the semiconductor layer was used in the electrophotographic mode. The transmission spectra have been measured in the spectrophotometer Specord UV VIS. The sample thickness was measured with the interference microscope MII-4.

The samples have been subjected to selective etching in a water solution of KOH in alkali which allowed for getting positive etching. Research of the surface formed phase diffraction gratings (of constant equal to 0.5 and 1 micrometer) has been carried out in the Atomic-Force Microscope. Last work cycle consisted in the metallization of the samples by thermal evaporation of aluminium.

3. Results and discussion

The kinetic characteristics of the formation of diffraction gratings in the system (As₂S₃)_x(As₂Se₃)_{1-x} are shown in Fig. 1. The curves drawn by continuous lines correspond to holographic diffraction gratings, which were formed as a result of photostructural transformations in ChVS to whom an electric field was applied, whereas the curves illustrated by dashed lines correspond to the lattices generated without the application of the field. The values of diffraction efficiency obtained on the samples when an electrical field is applied are higher (by 2-3.5 times). In such situation the character of kinetic curve changes too: it does not look anymore like a curve with a strongly pronounced maximum and exhibits a saturation character.

Without applying the electrical field the maximal values of the diffraction efficiency (η), which were observed on the samples prepared on lavesan substrates, were about 1.5 % and on glass substrates 12 %. The application of the electrical field allows to increase these values up to 5.5 % and 40 %, the spatial frequency of lattices being 2000 mm^{-1} . Similar results have been obtained in all studied structures: : metal - ChVS-ionic electrode, metal –ChVS- dielectric-ionic electrode, metal - ChVS-dielectric-metal. At the same time in the samples metal - ChVS-metal the interaction of metal electrode with ChVS was observed and this confirms our previous results.

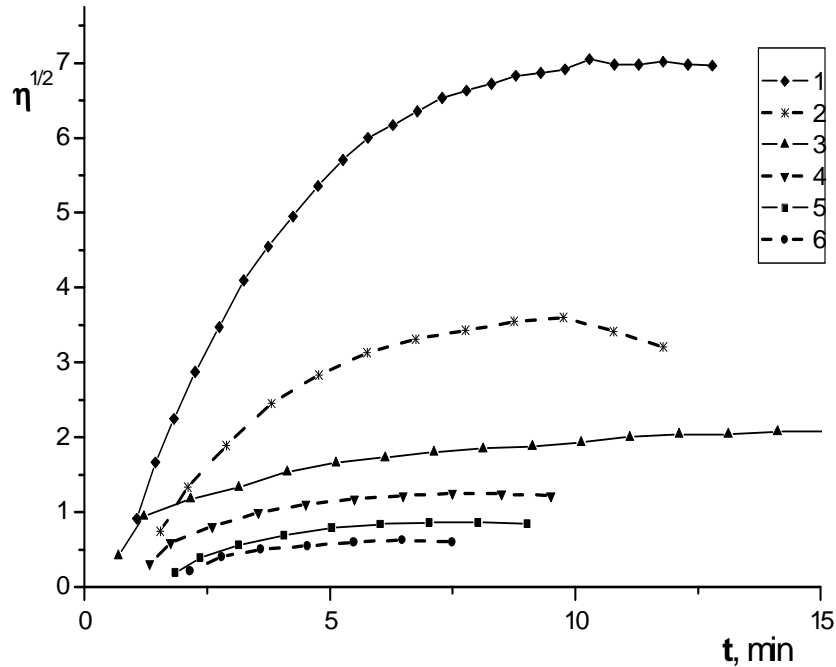


Fig. 1. The diffraction efficiency versus recording time. 1,2-As₂S₃ (on glass); 3,4-(As₂S₃)_{0.7} (As₂Se₃)_{0.3} (on lavsan); 5,6-As₂S₃ (on lavsan). 1, 3 and 5 in an electric field.

The same structures were used for measuring of the kinetic formations of HDG at various recording temperatures (from 20 °C up to 60 °C). It was shown that the increase of temperature leads to the reduction of η in both cases: in the presence of a field, and without it. One can assume, that the dominating role in determining the effect of increase of η (Fig. 1) is not due to heating processes by electric current but to the presence of electrical field.

The qualitative explanation of the mentioned results can be given within the framework of the electronic model [14]. As a result of illumination of ChVS samples non-equilibrium charge carriers are generated. Thereafter they diffuse away from the positions of high concentration, where have been generated. Part of non-equilibrium carriers is trapped by the localization levels. As it is known, their concentration in ChVS is very high, thus resulting in the formation of inhomogeneous space-charge distribution that can remain in place for a period of time after the light is removed. This residual spatial charge creates an internal electrical field pattern that modulates the local refractive index of the material by virtue of the electro-optical effect. The application of an external electric field changes the optical properties of the samples due to the distortion of the distribution of trapped charge and in such a way promotes the increase of extent of separation of an internal spatial charge that should be manifested in the increase of the refraction index. In such conditions selective etching leads to formation of more relief structures and to corresponding growth of the diffraction efficiency of the grating structures.

Thus, there is an increase in depth of the modulation of the optical parameters of ChVS layers that has been established experimentally.

By applying a strong electrical field to the investigated structures, the Franz-Keldysh effect could appear. It should lead to displacement of absorption edge toward the long-wave part of a spectrum that is equivalent to the increase of absorption at the given wavelength and to the corresponding increase in concentration of non-equilibrium carriers of a charge contributing in such a way to the increase of the index of refraction. It is not known yet how the Franz-Keldysh effect influences the position of absorption edge in the process of photo-restructuring of samples.

In connection with above mentioned facts the spectrum of optical transparency of ChVS layers in the cases of applying to them an electrical field and without it was investigated. In both cases the identical capacity of a laser beam has been used. The analysis of these curves has allowed for the determination of the degree of change of the index of refraction and the transparency of layers under laser radiation action (Fig. 2). As it is seen from the figure the absorption edge of the illuminated samples is shifted towards the long-wavelength part of the spectrum. The extent of displacement is the same if the samples were illuminated in a field or in its absence. Thus, as one would expect, from the point of view of position of absorption edge of restructured samples it does not exist a reaction caused by the Franz-Keldysh effect.

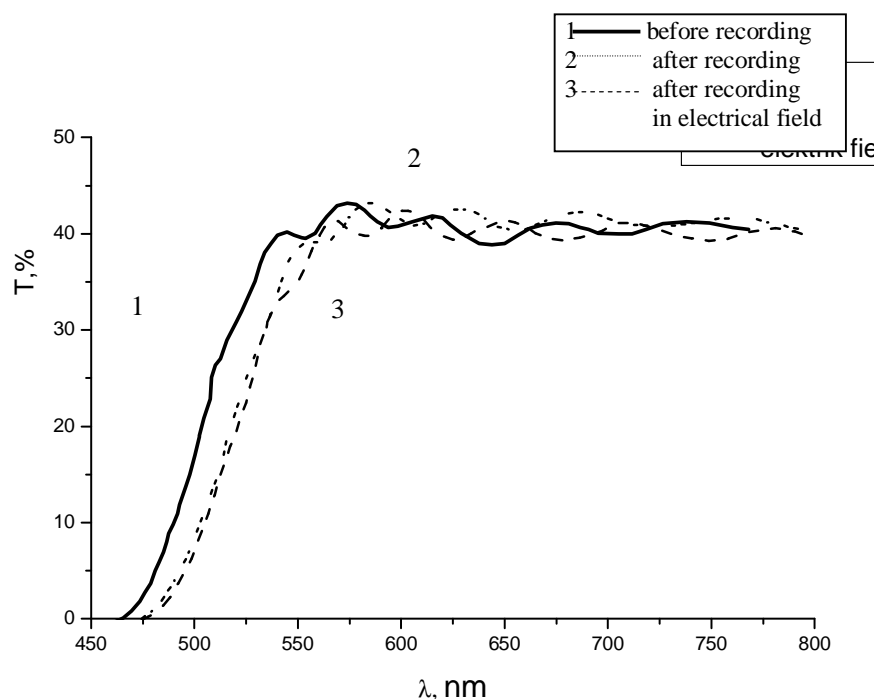


Fig. 2. The transmission spectrum of As_2S_3 , 1 - before recording; 2 - after recording (dotted line), 3 - after recording in the electrical field.

At the same time it was revealed, that under the action of laser radiation in the case when the electrical field has been applied to ChVS layers an increase of the index of refraction occurs, which is higher than in the absence of the electrical field. As it is known, the index of refraction depends on the magnitude of dielectric permittivity determining dielectric properties of materials which in turn depends on the shift of the charged particles inside atoms, molecules or other structural units. The large change of the parameter of refraction in samples taking place during illumination of samples in

the electrical field proves that in such conditions the samples are polarized by external electrical field.

As well-known, the photo induced dichroism and photo induced double-refraction phenomena were observed in vitreous semiconductors by many researchers. These phenomena were explained by the fact that during the illumination of vitreous semiconductors an interaction of the polarized radiation of the laser with optical anisotropic structural elements, whose optical axes are randomly oriented, takes place. The application of an electrical field leads to the orientation of structural elements along the field. Thus, in our case, most likely, there is a simultaneous influence on the orientation of the mentioned structural elements of two factors: the electromagnetic field of the polarized laser radiation and the external electrical field. After the removal of an electrical field the spatially focused optical anisotropic structural elements come back to equilibrium during a long interval of time that should be manifested in the increased value of the parameter of refraction and in residual polarization of a sample, not only during illumination, but also after its switching. Thus, after switching off the illumination and removal of electrical field an increased refraction should be observed for a long period of time. This fact was observed experimentally. When the electrical field is applied the parameter of refraction reaches a value, which is by 2.6 times higher, than for samples to which the electrical field has not been applied. The optical transparency in both cases differs only by some percents. These facts cause the observable increase on Fig. 1 of the diffraction efficiency of the HDG in an electrical field.

The comparison of kinetic of selective etchings in the two cases allows to conclude that, qualitatively, the character of etching does not change, but the optimum time of etching of HDG formed in the electrical field increases, fact that speaks in favour of getting larger amplitude of modulation of thickness of the samples. This fact proved to be true also because the diffraction efficiency measured in samples when the electrical field was applied, becomes higher by 50-200%. The etching leads to the amplification of diffraction efficiency.

In Fig. 3 it is shown the surface of a lattice (1000 nm^{-1}) formed in a field (b) and without it (a). The structures in both cases are shown. Research of a surface of HDG in a atom-force microscope allows to conclude, that the structure of lattices with a high degree of accuracy can be approximated by a cycloid (on samples with $\sim 2000 \text{ nm}^{-1}$). Figure shows that the presence of the electrical field results in increase of the degree of regularity and depth of a relief by 25-30 %. The structure thus becomes quasi sinusoidal. These facts allow for asserting, that the matrix for duplicating the holographic information obtained with diffraction structures formed in a field, will be of higher quality.

We must remark that recently, Beev et al. [19] investigated the Bragg gratings recorded in polymer dispersed liquid crystals and observed that in the case of electrical field applied during recording, a significant increase of the diffraction efficiency occurred. It is interesting to observe that two years ago, Jain [20] has shown that visible and UV light can cause photoinduced atom displacements in inorganic glasses as well as in polymers, and one may observe similar photoinduced scalar and vectoral phenomena. Nevertheless, the magnitude of the displacements in glasses is much smaller than in polymers and, therefore, the photo-induced phenomena in chalcogenides are less developed than in polymers.

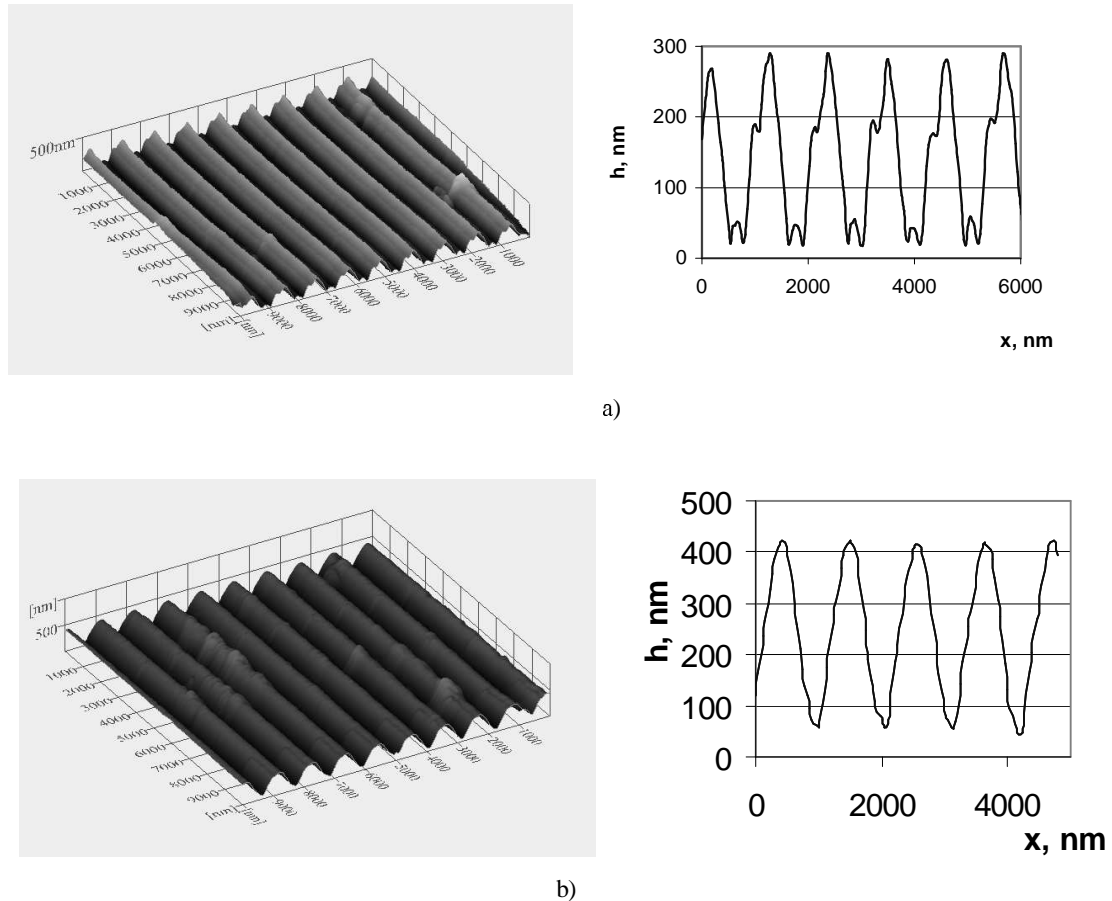


Fig. 3. Topography and the structure of strokes HDG: a) recorded without electrical field; b) recorded under electrical field.

Apparently, it is necessary to expect the best results due to optimization of processes of etching, metallization that are very important for creation of holographic nanostructures by optical method.

4. Conclusions

The process of registration of holographic interference lattices on chalcogenide vitreous semiconductor films in electrical field has been investigated. It is shown, that there is an increase in amplitude of modulation of permitting factor and of index of refraction by 2-3 % and 270 %, accordingly.

The formation of HDG on ChVS in a field results in the increase of diffraction efficiency by 2.5-3.5 times and holographic sensitivity in 2-3 times. There is an increase by 1.5 times of a dynamic range. Thus, the necessary time for the achievement of a given value for diffraction efficiency decreases by a factor of 2.

It is shown that after the process of selective etching the diffraction efficiency in the samples illuminated when a field is applied increases by 50-200 % in dependence of exposition.

The maximum of achieved value of diffraction efficiency without a field is 13 %, after etching, is 30 %. Using the illuminated samples in the presence of a field the maximal value of

diffraction efficiency reaches 40 %, and after etching 45%. These parameters result in HDG of 2000 mm⁻¹.

Research of a HDG surface in atom-force microscope allows to conclude, that the structure of a lattice with a high degree of accuracy can be approximated by a sinusoid at expositions up to 400 mW/cm² and a trapeze at expositions of equal 1300 mW/cm². However, the samples got in an electrical field have quasi-sinusoidal structure. The adding of field leads to the increase of the degree of regularity and depth of the relief by 25-30 %.

The investigations carried out in this work show convincingly the advantages of sample illumination in an electrical field and allows for asserting, that the matrix for duplicating the holographic image got with these samples will be better than in the case of preparation outside electrical field.

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