Electron-beam recording of the diffraction gratings in the $(As_4S_3Se_3)_{1-x}Sn_x$ amorphous thin films

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Thin films of $(As_4S_3Se_3)_{1-x}Sn_x$ (x=0; 0.01; 0.03; 0.05) chalcogenide glasses have been used for the direct e-beam recording of the diffraction grating structures. The influences of the amorphous film composition on properties of the diffraction gratings were shown. The dependence of the diffraction efficiency of gratings with the period of Δ=1 µm and Δ=2 µm versus the radiation dose was investigated. An enhancement of the diffraction efficiency caused by the uniform laser irradiation was observed for gratings recorded in the $As_4S_3Se_3$:Sn thin films.

1. Introduction

Amorphous thin films of chalcogenide glasses (As_2S_3, As_2Se_3, As-S-Se, Ge-As-Se, etc.) have some advantages such as: are sensitive to light irradiation, e-beam, ion and X-ray exposure, are transparent in a spectral range up to 18 µm, etc. They are widely used in optoelectronics and in particular as registration media in holography and for fabrication different diffractive optical elements (DOE) with high resolution. For example, amorphous As_2S_3 and As-S-Se exhibit resolution higher up to 10^4 lines/mm, and can be used for fabrication of fine nanostructures and protective elements [1-5]. The nanostructuring capabilities of chalcogenide glass films using electron beam lithography were also established [6-8]. Actinic irradiation induces a structural transformation of amorphous chalcogenide films, which results in relatively high increasing of refractive index. Wide range of induced changes by irradiation both of refractive index and of the rate of chemical dissolution are decisive properties for forming of complex structures in amorphous chalcogenide films. Diffraction structures can also consist of up to ten superimposed crossed diffraction gratings which were recorded in As_2S_3 films by e-beam. [8, 9]. The relief structure composed by two superimposed gratings with same orientation, and gratings periods differed by 100 nm was formed in As-S film by e-beam and following chemical etching. The surface-relief grating structures formation by means of wet etching was studied in [10, 11]. Surface-relief structures with submicron-sizes were formed in a direct recording by light and ion beam on Se/As_2S_3 nanolayered films [12]. Formation of surface reliefs induced by electron beam on surface of Sb_2Se_3, Ge-Se and As-S-Se thin films has also been observed in [13-16].

The importance of possibility of the light- and thermo-induced amplification of diffraction efficiency of the holograms after their recording in chalcogenide films is emphasized in [14]. And an increase of diffraction efficiency of holographic gratings after their dark storage has been observed. A light-stimulated enhancement of holographic gratings recorded in As_2S_3 films has been studied as well.

Amorphous thin films of As-S-Se system are also attractive due to possibility of changing of optical properties by varying of amount of Se. For example, increasing amount of Se from 0 at.% to 60 at.% in $As_{40}S_{60-x}Se_x$ structure results in decreasing of energy gap value from 2.38 up to 1.82 eV [16]. Formation of complicated surface structures with different directions and dimensions in $As_{40}S_{15}Se_{45}$ films under He-Ne laser polarized wavelength are observed when hologram recording at opposite recording beam direction is carried out [17]. Recently it was demonstrated that the electron beam irradiation change also the dielectric parameters of the amorphous As_2S_3 film, the results of which could be significant to future implementation of reconfigurable photonic circuits, infrared telecommunications, photonic crystals, and all optical conversion and computing [18].

In the present paper we report some experimental results obtained in the amorphous $(As_4S_3Se_3)_{1-x}Sn_x$ thin films as registration media using the electron beam irradiation. The dependence of diffraction efficiency on radiation dose and amorphous film composition were studied. The electron beam patterning in amorphous films was realized using of the computer control of positioning of electron beam.

2. Experimental

Initially, amorphous thin films $(As_4S_3Se_3)_{1-x}Sn_x$ (x=0, 0.01, 0.03 and 0.05) with thicknesses ~ 2µm were prepared by thermal evaporation in vacuum onto glass substrates covered with conductive (Al or ITO) electrode necessary for charge leakage. E-beam recording of grating

structures was performed using scanning electron microscope (SEM) BS 300 Tesla. Diffraction gratings with grating period ($\varDelta$) of 1 µm and 2 µm were recorded. The dose of electron irradiation (q) was calculated using the formula [19]:

$$q = \frac{I \cdot \tau}{l \cdot d}, \qquad (1)$$

where τ is the scan time of one line, l is the length of this line, d is the electron spot diameter and I is the electron beam current or current density. The acceleration voltage of 25 kV has been applied during formation of diffraction gratings.

The diffraction efficiency for the first order of diffraction (η_1) was measured by He-Ne laser (λ=633 nm, 0.65 W/cm^2) in the transmission mode at normal incidence using neutral filters. The absolute value of the diffraction efficiency η_1 was determined by the well known formula:

$$\eta_1 = \frac{I_1}{I_0} \cdot 100\,\% \qquad (2)$$

Here I_1 is the intensity in the first order diffraction maximum; I_0 is the intensity of the incident laser beam.

3. Results and discussion

The dependence of the diffraction efficiency η_1 of gratings with the periods $\varDelta$=1 µm (1) and $\varDelta$=2 µm (2) on the e-beam dose value (q) for the amorphous $As_4S_3Se_3$ thin films is illustrated in Fig. 1. The curves $\eta_1(q)$ for both grating periods rise with an e-beam current density. It was observed that at a high value of q the efficiency value of gratings η_1 with $\varDelta$=1 µm (curve 1) saturated and then slowly decreased with increasing the dose, which is associated with the erasure of these gratings. For gratings with $\varDelta$=2 µm there was a jump of η_1 with an increase of q. The highest efficiency values exhibited by gratings were recorded at the highest radiation doses; they are about 0.4 % and 3.5 % for the grating periods of $\varDelta$=1 µm and $\varDelta$=2 µm, respectively.

The effect of enhancement of the diffraction efficiency of gratings recorded by e-beam at low radiation doses was observed by laser light exposure. The intensity of the diffracted beam increased under uniform illumination with the He-Ne laser beam just during the measuring of the diffraction efficiency. As a result, the diffraction efficiency became 1.5-2 times higher than the initial one. These experimental results show that more pronouncedly manifest the gratings with the period $\varDelta$=2 µm. Fig. 2 presents the dependence of efficiency on the exposure time for gratings recorded at doses q=0.9 mCcm^{-2} (1), q=1.4 mCcm^{-2} (2) and q=1.7 mCcm^{-2} (3). The diffraction efficiency increased firstly during 80-100 s after starting of the light illumination but then decreased slowly during the light illumination.

Figs. 3a (in the a.u. units) and 3b (in the absolute units) illustrate the dependence of the diffraction efficiency of gratings with the period of $\varDelta$=2 µm on the radiation dose η_1 (q), for amorphous $(As_4S_3Se_3)_{1-x}Sn_x$ (x=0; 0.03; 0.01; 0.05) thin films. As can be seen from the graph, with the addition of tin to the host material, there is a jump in the diffraction efficiency at high irradiation doses. And with increasing of the irradiation dose, the diffraction efficiency continues to rise in difference from the host material $As_4S_3Se_3$.

The gratings corresponding to a jump of the diffraction efficiency η_1 were additionally investigated with an atomic force microscopy (AFM) (Fig.4). As a result, it was established that in these gratings, besides the modulation of the amplitude phase characteristics, the relief formation occurs, which corresponds to the amplitude and relief-phase changes. Using special software (Gwyddion), the depth profile for this pattern was determined (Fig. 5, 6).
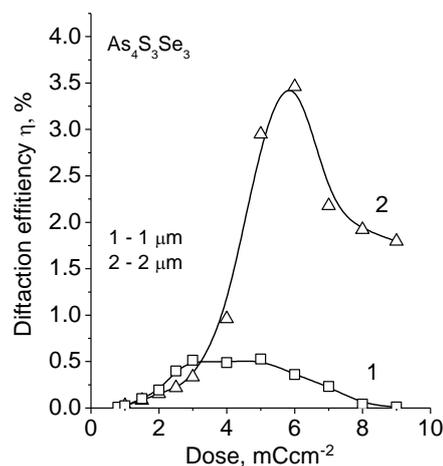
Fig. 1. Dependence of the diffraction efficiency η_1 of gratings with the period $\varDelta$=1 µm (1) and $\varDelta$=2 µm (2) on the e-beam current for the amorphous $As_4S_3Se_3$ thin films
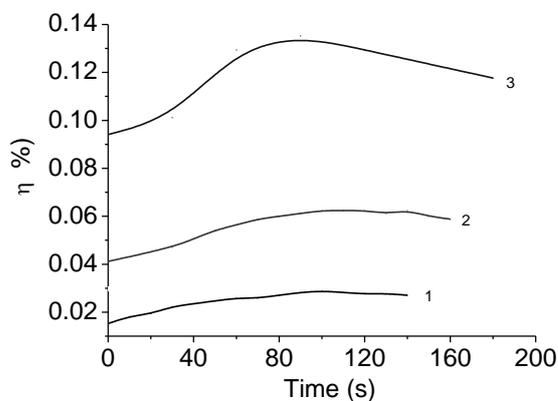
Fig. 2. Dependences of the diffraction efficiency η_1 on the light exposure time (λ=633 nm, 0.65 W/cm^2) for gratings with the period $\varDelta$=1 µm for amorphous $(As_4S_3Se_3)_{0.99}Sn_{0.01}$ thin films. Approximately values of the radiation dose q, mCcm^{-2}: 0.9(1), 1.4(2) 1.7(3)

Modulation of the relief depth of the gratings pattern registered in the $(As_4S_3Se_3)_{0.95}Sn_{0.05}$ amorphous films is illustrated in Fig. 6.

The depth profile data that are the results of processing of the diffraction pattern are given in Table 1.
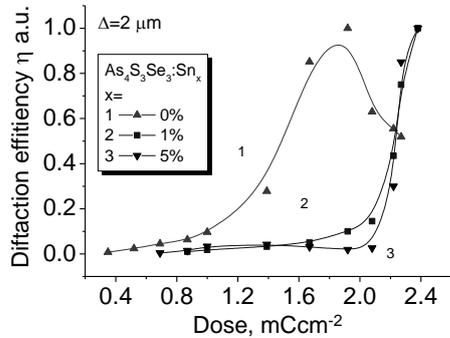
Fig. 3a. Dependence of the diffraction efficiency η of gratings with the period Δ=2 μm on e-beam dose for the amorphous $(As_4S_3Se_3)_{1-x}Sn_x$ thin films (x=0 (1); x=0.01 (2); x=0.05 (3)).
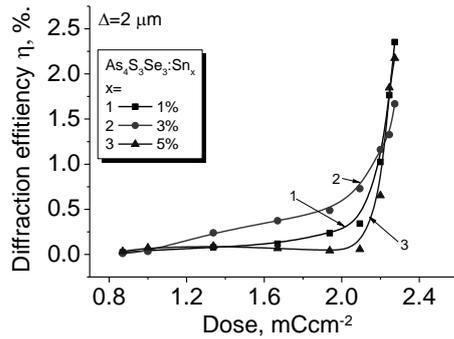
Fig. 3b. Dependence of the diffraction efficiency η of gratings with the period Δ=2 μm on e-beam dose for the amorphous $(As_4S_3Se_3)_{1-x}Sn_x$ thin films (x = 0.01 (1); x=0.03 (2); x=0.05 (3)).

Table 1. Dependence of the depth relief h of grating patterns with the period Δ=2 μm, registered in the $(As_4S_3Se_3)_{0.95}Sn_{0.05}$ amorphous film for different doses of the e-beam

Dose, $mCcm^{-2}$	2.22	2.27	2.38
$h_{average}$, nm	3	3.3	4.5

The experimental results show that with an increase of the intensity of the e-beam dose the thickness modulation of the amorphous film occur and the relief depth increases. It can be concluded that a jump of the diffraction efficiency with an increase of the e-beam dose and is the result of the modulation of the thickness and of the amplitude and phase characteristics of the amorphous film induced by the e-beam exposure.

For the single diffraction gratings of the amorphous

$As_4S_3Se_3$-Sn thin films registered at a low exposure doze (current intensity 0.88 – 1.75 $mCcm^{-2}$), a new effect was detected (Fig. 2). It appeared during the read out process of the diffraction efficiency with the He-Ne laser (λ=633 nm). In the course of the perpendicular illumination by the uniformly distributed laser light the sample surface in the place with the registered diffraction grating, an increase of the diffraction efficiency up to some maximum value with its subsequent decrease to some minimal value was observed in the real time. It is evident that a further rise of the diffraction efficiency occurs due to the interaction of the actinic radiation with the amorphous material and, as a result of it, photostructural transformations and modulation of the amplitude-phase characteristics, such as refractive index and transmission take place.
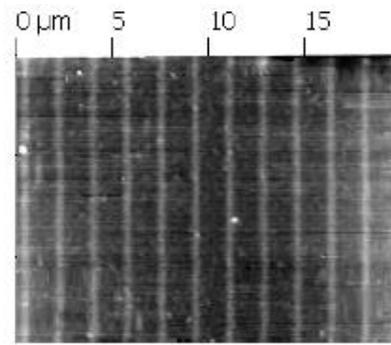
Fig. 4. The AFM diffraction pattern registered in the $(As_4S_3Se_3)_{0.95}Sn_{0.05}$ amorphous film
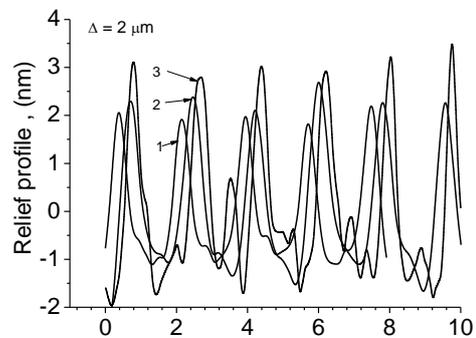
Fig. 5. The relief profile of grating patterns registered in the $(As_4S_3Se_3)_{0.95}Sn_{0.05}$ amorphous film, obtained at doses q ($mCcm^{-2}$): 1 – 2.22; 2 – 2.27; 3 – 2.38
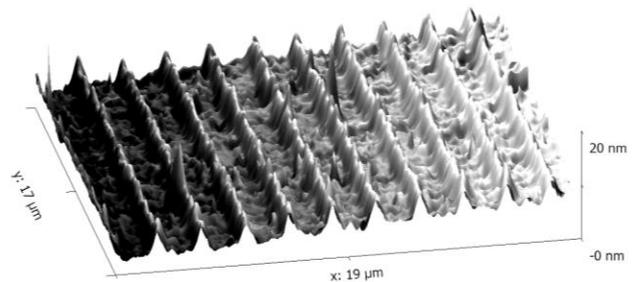
Fig. 6. Modulation of the grating relief registered in the $(As_4S_3Se_3)_{0.95}Sn_{0.05}$ amorphous films

It is well known that the exposed (dark) portions of the grating react more intensively to the actinic radiation than the unexposed (light) ones. This is due to the fact that the photostructural transformation in the exposed portions is more intensive by reason of a strong absorption of the photons with the same energy, as was demonstrated resulting from the shift of the absorption edge in the red region of the spectra for the investigated materials. This can be explained by the fact that in the light portions of the sample the velocity of photostructural changes is not essential for the respective wavelength, while the dark portions react very rapidly. After some time (of about ~1 min) of the uniformly exposure of the actinic light, the photostructural transformation reaches a maximum value but then the diffraction efficiency begins to decrease (after about ~3 min). The diffraction efficiency decrease can also be interpreted in the terms of the reversibility of photostructural transformations in the investigated material, which leads to the easement of the registered information.

The band gap energy of the studied amorphous $(As_4S_3Se_3)_{1-x}Sn_x$ thin films is about E_g=1.85-2.1 eV as was estimated via optical (spectroscopic) measurements. Thus, the wavelength of He-Ne laser irradiation λ=633 nm ($h\nu$=1.97 eV) corresponds to spectral range of the optical absorption edge. It is important that the absorption is weak during diffraction efficiency measurement. Nevertheless the optical recording can also be realized by the He-Ne laser in amorphous $(As_4S_3Se_3)_{0.99}Sn_{0.01}$ films using the holographic interferometry method. The electron irradiation of the studied material results in some increase of the absorption of the He-Ne laser irradiation. Therefore the increase of the diffraction efficiency of gratings can be explained by the continuation of the optical parameters modulation and/or an increase of the modulation of the surface relief depth, caused by the non-uniform light absorption which is evidently stronger in the e-beam irradiated areas of the recorded gratings than in non-irradiated ones. In general, different levels of the incident uniform light irradiation can improve the diffraction efficiency of grating. As it turned out, additional irradiation of the diffraction gratings to the uniform actinic light can improve its characteristics.

4. Summary

The influence of material composition on properties of the diffraction gratings registered by e-beam was demonstrated. The surface relief modulation induced by the direct e-beam record at the high dose of the radiation was revealed in the amorphous $(As_4S_3Se_3)_{1-x}Sn_x$ thin films. The enhancement of the diffraction efficiency under uniform illumination with the He-Ne laser beam was observed for gratings recorded by e-beam in the studied thin films. This effect can be attributed to non-uniform light absorption in the irradiated and non-irradiated thin film portions due to its different optical properties.

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