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Electron-Beam Recording of Surface Structures on As-S-Se Chalcogenide Thin Films

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The effect of electron beam irradiation on the amorphous chalcogenide film $As_{38}S_{36}Se_{26}$ was studied. The formation of cones with a Gaussian profile on the surfaces of the films was found after local electron irradiation. Exposition dependent evolution of height surface nanostructures has been detected. The dependence of the height of surface nanostructures on the dose of irradiation is analyzed. Charge accumulation model into interaction region between the film and the electron beam was used to explain the electron-induced phenomena of the surface structure of amorphous $As_{38}S_{36}Se_{26}$ films. Charges relaxation times, and electron beam penetration depth into film, and the initial and inverse doses are determined.

Keywords: chalcogenide thin films, electron beam irradiation, surface nanostructures.

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Introduction

Chalcogenides are promising materials with attractive properties, such as low losses and versatile photo-induced effect, which made them suitable candidates for production of gratings and other optical elements for visible (VIS), and infrared (IR) wavelengths [1, 2]. The interaction of these materials with the electron beam is of interest due to diversity of physical phenomena induced in chalcogenide films by laser irradiation in the region of their intrinsic absorption. Valuable efforts have been employed in research of photoinduced phenomena in amorphous chalcogenide films. Irradiation of chalcogenide film with an electron beam can be an effective method of charge generation inside the film.

Among them, a great attention has been paid to the As-Se-S glasses [3]. These systems are known by a large glass-formation region [4] as well as their excellent linear and nonlinear properties and the glasses are used in the holographic optical elements [5], optical memories [6], switching devices [7] and planar waveguides [8]. Several studies have focused on photo- and thermally induced changes and imaging properties of $As_{40}S_{60-x}Se_x$ layers (x = 0; 20; 30; 40; 60) with regard to their application for gratings fabrication [5, 9-15]. Investigations of electron beam exposure on Ge-As-Se systems showed the formation of different shaped surface reliefs, mass transport or interaction between induced charges [16-18]. Geometric parameters and shape of the reliefs depend on the chemical composition of the film.

In this study we systematically vary exposure time in order to find response of surface relief of $As_{38}S_{36}Se_{26}$ film for electron beam lithography using them for the production of periodic nanostructures.

I. Experimental

Thin film $As_{38}S_{36}Se_{26}$ of ~ 4.6 μm thickness was prepared by thermal vacuum evaporation of $As_{40}S_{30}Se_{30}$ bulk glass onto sapphire substrates. The chemical composition was determined by energy dispersive analysis of X-rays (EDAX) using scanning electron microscope (SEM) Tescan, model VEGA. The film was

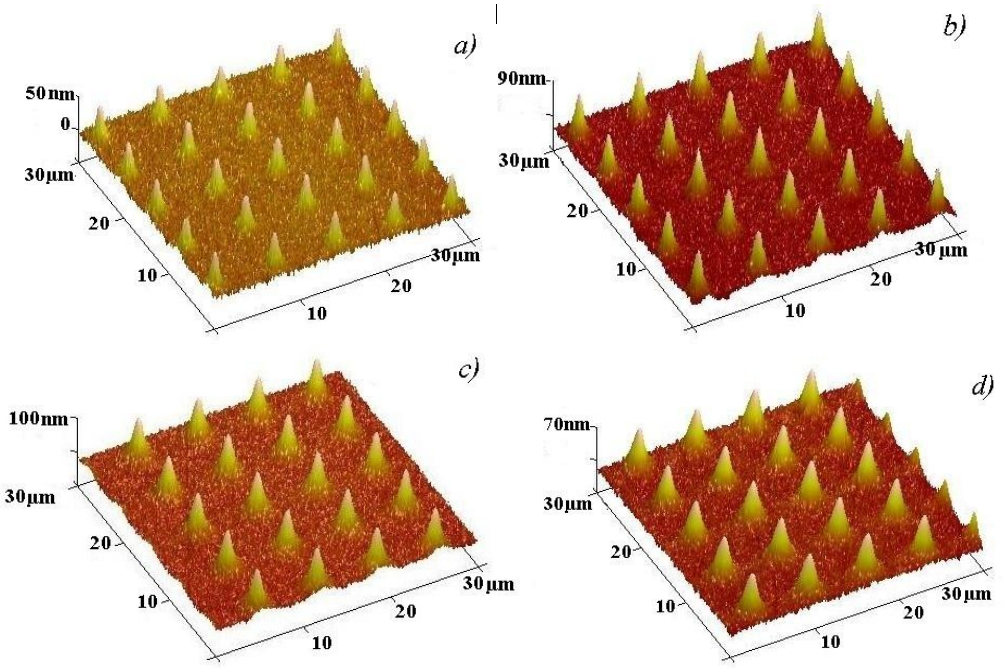

Fig. 1. AFM images of surface relief on $As_{38}S_{36}Se_{26}$ film after e-beam exposure: *a* – 60 mC·cm^{-2}; *b* – 240 mC·cm^{-2}; *c* – 2400 mC·cm^{-2}; *d* – 12 C·cm^{-2}. Distance between dots – 6.6 µm.

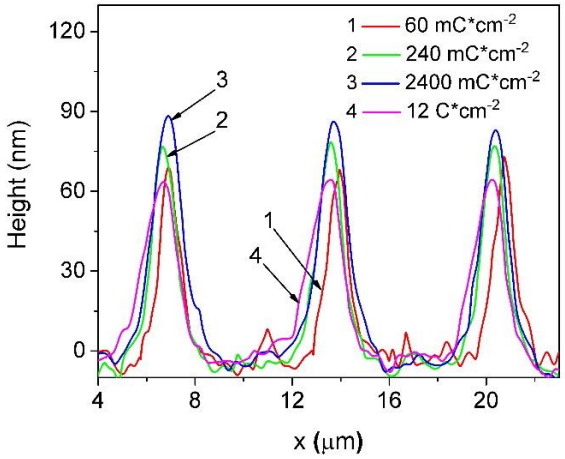

Fig. 2. Profile of recorded surface relief on $As_{38}S_{36}Se_{26}$ film after e-beam exposure. Distance between dots – 6.6 µm.

irradiated by an electron beam using a scanning electron microscope (SEM, Tescan, model VEGA). The accelerating voltage V = 30 kV, spot size B = 640 nm, and the electron beam current I = 19 nA. The exposure dose *G* varied from 12 mC·cm^{-2} to 12 C·cm^{-2}. The surface relief of the film was studied by atomic force microscope (AFM, Bruker, model ICON). Exposure dose was determined by expression: $G = I \cdot t/S\ (\mu C \cdot cm^{-2})$, where *S* is the irradiated area (cross-sectional area of the electron beam focused on the surface of the film). All exposures were performed in a low vacuum mode under nitrogen at a pressure of 10 Pa. Square matrices of 100 microns in size were made of a certain number of points. The distance between the points was 6.6 µm and 10 µm.

II. Results and discussion

Nanostructures with a height of approximately 100 nm were formed on $As_{38}S_{36}Se_{26}$ film after e-beam exposure. The formed cones on the surfaces of the films have Gaussian profiles. The examples of surface reliefs that occur when the surface is irradiated as square matrix of dots with distance 6.6 µm between the irradiated dots are shown in Fig. 1. The images of the experimentally obtained atomic force microscope (AFM) relief profiles are shown in Fig. 2.

The results show that $As_{38}S_{36}Se_{26}$ is quite sensitive to electron beam irradiation. The height of the surface relief using logarithmic scale is plotted in Fig. 3. It can be seen from Fig. 3 that for $G < 2400$ mC·cm^{-2} the height of the

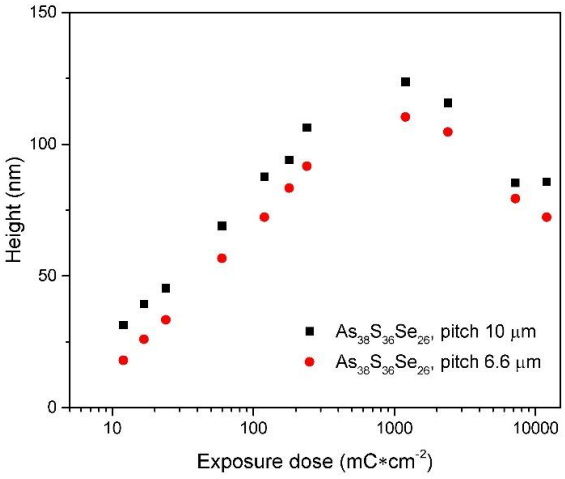

Fig. 3. Dependence of surface reliefs height which were formed by electron beam on the exposure dose.

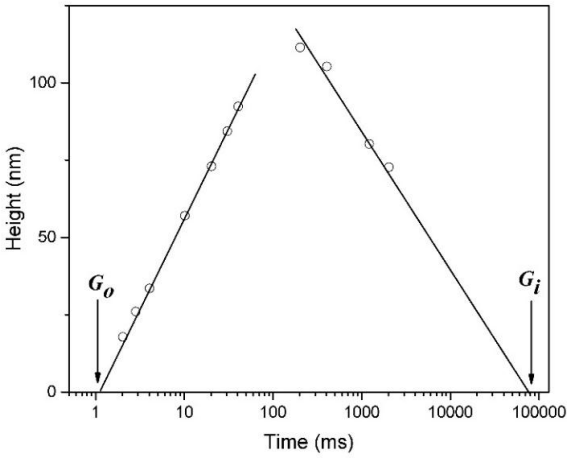

Fig. 4. Linear approximation of the dependence of the surface relief height of the $As_{38}S_{36}Se_{26}$ film on the irradiation time for a matrix period 6.6 μm.

surface relief gradually grows to 120 nm and for $G > 2400$ mC·cm^{-2}, relief height decreases. The changing of shape and parameters of the obtained surface relief on $As_{38}S_{36}Se_{26}$ film can be explained by the charge model, which was used earlier for the relief formation processes in Ge-As-Se chalcogenide films [16-18]. According to this model, at the initial stage of irradiation (in the low-dose region), the increase in the height of the surface relief in the cone form is due to the rapid increase in the magnitude and density of the positive charge near the film surface. Moreover, the formation of a relief of this shape is due to the electrostatic expansion of the structure in the region of this charge. The initial dose at which a surface relief appears characterizes a sensitivity of the film to electron irradiation and determines its effectiveness for use as an electronic resist for one-stage (dry) electron lithography.

It can be seen from Fig. 4 that dependences $h=F(t)$ both in the region 2 ms – 40 ms (12 mC·cm^{-2} – 240 mC·cm^{-2}), and in the region 200 ms - 2000 ms (1200 mC·cm^{-2} – 12 C·cm^{-2}) can be well approximated by straight sections. The intersection points of these lines with the abscissa axis have found. They have the following values: t_0= 1.1 ms and t_i = 76,42 s. Accordingly, the initial dose of relief formation on this film at d = 6.6 μm is equal to G_0 = 6,5 mC·cm^{-2}, and the inversion dose of the surface relief shape G_i = 451,6 C·cm^{-2}. At d = 10 μm, these parameters are G_0= 3,13 mC·cm^{-2} and G_i = 1751 C·cm^{-2}.

According to the two-layer charge model [18], the process of formation of the space charge region inside the irradiated film region is non-equilibrium. Relaxation times of processes of charge formation Q_- and Q_+ were determined from exponentially increasing (2 ms – 40 ms) and exponentially decreasing (200 ms - 2000 ms) sections. Fig. 5a, 5b show the results of an exponential approximation of the dependences $h = F(t)$ for d = 6.6 μm using the corresponding formulas. It can be seen that the approximation curves correlate well with the measurement results (points). Relaxation times that determined as a result of this approximation are τ_1 = (12.82 ± 2.09) ms and τ_2 = (961.54 ± 400.46) ms, respectively. Relaxation times have similar values for the matrix of irradiated regions with d = 10 μm. It can be seen that τ_1 and τ_2 are very different from each other. As well as for films of the Ge–As–Se system [18], Q_+ charge relaxation occurs much faster than Q_- in the As-S-Se film. It should be noted also that exponential relaxation was observed during storage of films [12] and exponential decreasing of concentration of non-stoichiometric structural units during light exposure of

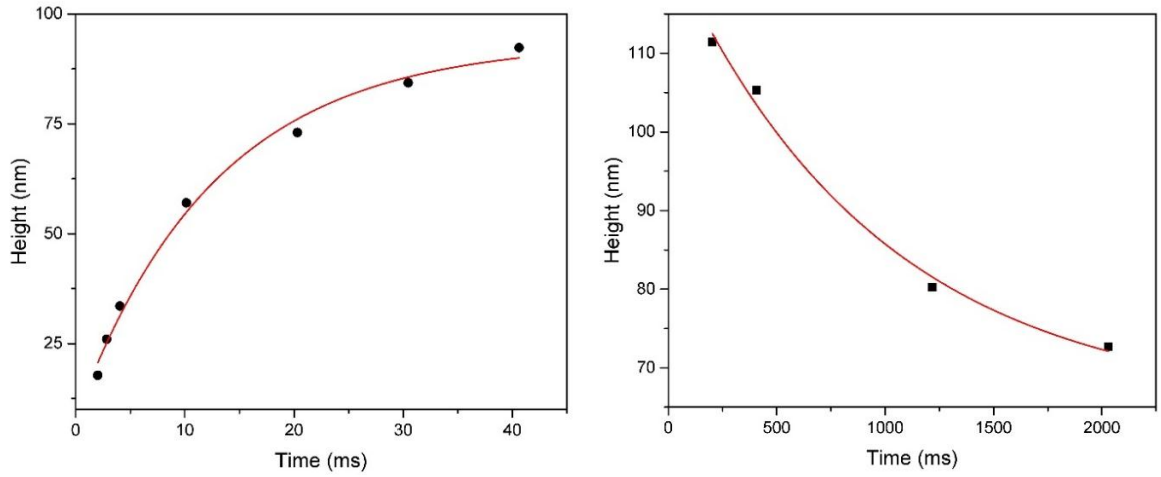

Fig. 5. Exponential approximation of the dependences $h = F(t)$ using formulas $h = h_{01} + h_1 \cdot \left(1 - \exp\left(-\frac{t}{\tau_1}\right)\right)$ for the interval: a – 2 ms - 40 ms; b – $h = h_{02} + h_2 \cdot \exp\left(-\frac{t}{\tau_2}\right)$ for the interval 200 ms – 2000.

chalcogenide films was observed in [9].

The formation of surface relief is due to structural changes in the film and the emergence of a space charge region (SCR) during the interaction of the film and the electron beam. The penetration of primary electrons into the film leads to the accumulation of charge in the film and on its surface, as well as the emission of electrons from the film back into the vacuum [17].

The interaction region value between of $As_{38}S_{36}Se_{26}$ film and electron beam was calculated by the formula [19]:

$$R = 0.0276 \cdot \frac{A \cdot E_0^{\frac{5}{3}}}{\rho \cdot Z^{\frac{8}{9}}},$$

where A is average atomic weight, Z is average nuclear charge, ρ is the density of irradiated material (the density of the initial glasses used to obtain the films was taken for calculations) and E_o is the energy of incident electrons. Following parameter values were used to determine the numerical value of R for the $As_{38}S_{36}Se_{26}$ film: $\rho \approx 3.69$ g·cm^{-3} [20], A = 60.54 g·mol^{-1}, Z = 27.14 (A and Z were determined similarly [16]). Value of $R \approx$ 7.0 μm was obtained for the $As_{38}S_{36}Se_{26}$ film.

Conclusions

Our investigations have demonstrated that studied $As_{38}S_{36}Se_{26}$ composition is suitable for e-beam recording. The formation of cones with Gaussian profile on the surfaces of the films was detected after electron irradiation. Exposition dependent evolution of height surface nanostructures has been detected. Charge relaxation times, and initial and inverse doses, and size of interaction region have been determined: $\tau_1 = (12.82 \pm 2.09)$ ms and $\tau_2 = (961.54 \pm 400.46)$ ms, $G_0 = 6{,}5$ mC·cm^{-2}, $G_i = 451.6$ C·cm^{-2}, $R \approx 7.0$ μm. These results show that $As_{38}S_{36}Se_{26}$ films can be used for fabrication of the optical elements by local electron irradiation method.

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Електронно-променевий запис поверхневих структур на халькогенідних плівках As-S-Se

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Досліджено вплив опромінення електронним пучком на аморфну халькогенідну плівку $As_{38}S_{36}Se_{26}$. Було виявлено утворення конусів з гауссовим профілем на поверхнях плівок після локального опромінення електронами. Проаналізовано залежність висоти поверхневих наноструктур від дози опромінення. Для пояснення електронно-індукованих явищ поверхневої структуризації аморфних плівок $As_{38}S_{36}Se_{26}$ використана модель акумулювання заряду в області взаємодії плівки та електронного пучка. Визначені часи релаксації зарядів, глибина проникнення електронного пучка в плівку, початкова та інверсна дози.

Ключові слова: халькогенідні тонкі плівки, опромінення електронним пучком, поверхневі наноструктури.