МАТЕРІАЛОЗНАВСТВО ТА МАШИНОБУДУВАННЯ

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THE FORMATION OF SURFACE NANOSTRUCTURES ON As-S-Ge CHALCOGENIDE FILM AFTER E-BEAM EXPOSURE

Background. Chalcogenide glasses comprise a unique materials platform and are attractive in view of various applications that make use their intriguing characteristic, the ability to form surface-relief patterns. 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.
Objective. The purpose of the paper is to study direct (without selective etching) surface relief formation of optical elements periodic nanostructures on thermal vacuum evaporated film $As_3S_{77}Ge_{20}$ of ~8.3 μm thickness using electron beam lithography, as well as investigate the changes in surface nanostructures height and shape depending on exposure.
Methods. The chemical composition was determined by energy dispersive analysis of X-rays. The film was irradiated by an electron beam using a scanning electron microscope. The influence of electron beam irradiation on $As_3S_{77}Ge_{20}$ amorphous chalcogenide thin film was investigated. Surface relief of the film was tapped by atomic force microscope.
Results. The exposure dose G varied from 12 mC·cm^{-2} to 12 C·cm^{-2}. The formation of cones with Gaussian profile on the surfaces of the films was detected after local electron irradiation. Exposition dependent evolution of height surface nanostructures has been detected. It can be seen that for $G < 2400$ mC·cm^{-2} the height of the surface relief gradually grows to 100–125 nm and for $G > 2400$ mC·cm^{-2}, relief height decreases. The initial and inversion doses of relief formation on this film have found. For 6,6 μm pitch is equal to $G_0 = 9{,}60$ mC·cm^{-2}, and the inversion dose of the surface relief shape $G_1 = 31.18$ C·cm^{-2}. At $d = 10$ μm, these parameters are $G_0 = 6{,}98$ mC·cm^{-2} and $G_1 = 36.19$ C·cm^{-2}. The dependences $h = F(G)$ at increasing interval (16 mC·cm^{-2} – 1200 mC·cm^{-2}) for $d = 6.6$ μm and $d = 10$ μm were fitted by exponential function.
Conclusions. The changing of shape and parameters of the obtained surface relief on $As_3S_{77}Ge_{20}$ film can be explained by the charge model. Our investigations have demonstrated that studied $As_3S_{77}Ge_{20}$ composition is suitable for e-beam recording. These results show that $As_3S_{77}Ge_{20}$ films can be used for fabrication of the optical elements.
Keywords: chalcogenide thin films; electron beam irradiation; surface nanostructures.

Introduction

Chalcogenide glasses formed from S, Se, Te with elements of IV and V groups are promising functional materials with attractive properties: high transparency in IR region, versatile photo-induced effects, high linear and non-linear optical properties, etc. Chalcogenide glasses comprise a unique materials platform and are attractive in view of various applications that make use their intriguing characteristic, the ability to form surface-relief patterns [1, 2]. Owing to these features, chalcogenide glasses possess significant application potential in view of photonic elements fabrication, such as diffraction gratings, microlens arrays, photonic crystals, nanostructured polarizers and waveplates, broad-band antireflection coatings, etc. Surface relief structures based on chalcogenide glasses can be used either directly as functional optical materials or indirectly, by using them on microstructure or nanostructure of other materials.

Numerous studies have concentrated 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 [3–6] as well and other compositions of chalcogenide glasses. Usually surface relief is created after films exposure by respective light intensity pattern using selective etching. Chalcogenide glasses and films are also sensitive to the electron or ion beams, X-rays [7–10] and perhaps photo-stimulated or stimulated by electron or ion beams; X-rays' change of their properties is the most interesting phenomena exhibited by these materials.

Investigations of electron beam exposure on Ge-As-Se systems showed the formation of different surface reliefs, mass transport or interaction between induced charges [11, 12]. Geometric parameters and shape of the reliefs depend on the chemical composition of the film. Recently, amorphous chalcogenides from the Ge-As-S system have been intensively studied [13—20], which are characterized by long-term stability as well as good transmission in the visible and near-infrared range. Photo-induced effects in thin films from Ge-As-S glasses were investigated in papers [21, 22]. Direct recording of surface reliefs does not require the step of selective etching for the formation of the surface relief, which is formed in this case directly during exposure process. Absence of the selective etching step is the advantage because often used etchants are toxic, and during selective etching process it is necessary to control many parameters (temperature, concentration of etchant, etc.). Thus, the development of one-step method for the fabrication of surface reliefs is considered perspective for the fabrication of planar optical elements.

Problem statement

In present work we studied direct (without selective etching) surface relief formation of optical elements periodic nanostructures on $As_3S_{77}Ge_{20}$ films using electron beam lithography, evolution of surface nanostructures height and shape depending on exposure keeping in mind that direct one step grating recording simplifies greatly the fabrication processes of the optical elements.

Experimental

Thin film $As_3S_{77}Ge_{20}$ of ~8.3 μm thickness was prepared by thermal vacuum evaporation of $As_4S_{66}Ge_{30}$ 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 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). The irradiation dose was determined by formula: $G = I \cdot t / S$ (μC·cm^{-2}), where S is the exposure 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.

Results and discussion

Formed nanostructures with a height of approximately 100 nm were detected in $As_3S_{77}Ge_{20}$ film after e-beam irradiation. The 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 and 10 μm between the irradiated dots are shown in Table 1. The images of the experimentally obtained atomic force microscope (AFM) relief profiles are shown in Fig. 1.

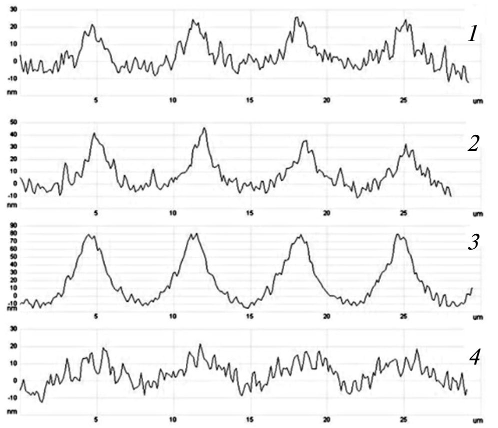
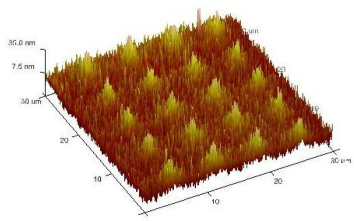
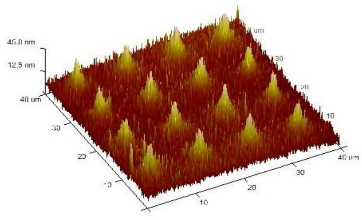
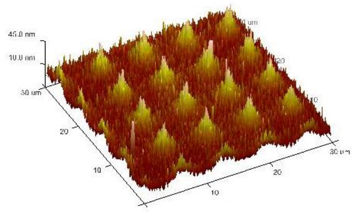
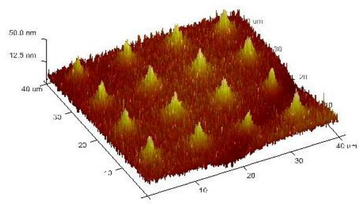
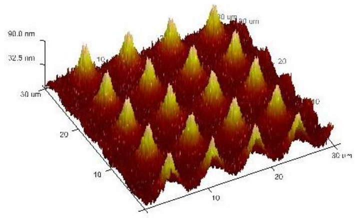
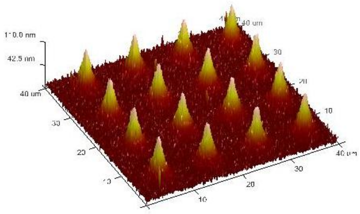
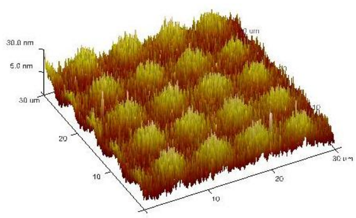
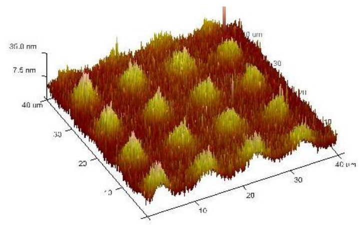


Fig. 1. Profile of recorded surface relief on $As_3S_{77}Ge_{20}$ film after e-beam exposure: *1* — 120 mC·cm^{-2}; *2* — 240 mC·cm^{-2}; *3* — 2400 mC·cm^{-2}; *4* — 12 C·cm^{-2}. Distance between dots — 6.6 μm

The results show that $As_3S_{77}Ge_{20}$ is quite sensitive to electron beam irradiation. The height of the surface relief using logarithmic scale is plotted in Fig. 2. It can be seen that for $G <$ 2400 mC·cm^{-2} the height of the surface relief gradually grows to 100—125 nm and for $G >$ 2400 mC·cm^{-2}, relief height decreases. The changing of shape and parameters of the obtained surface relief on $As_3S_{77}Ge_{20}$ film can be explained by the charge model, which was used earlier for the relief formation processes in Ge-As-Se chalcogenide films [5, 6, 11]. 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

***Table* 1.** AFM images of surface relief on $As_3S_{77}Ge_{20}$ film after e-beam exposure

$As_3S_{77}Ge_{20}$	6.6 μm	10 μm
120 mC·cm^{-2}		
240 mC·cm^{-2}		
2400 mC·cm^{-2}		
12 C·cm^{-2}		

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 [6].

It can be seen from Fig. 3 that dependences $h = F(G)$ both in the region 16 mC·cm^{-2} – 1200 mC·cm^{-2}, and in the region 2400 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 been found. Accordingly, the initial dose of relief formation on this film at $d = 6.6$ μm is equal to G_0 = 9.60 mC·cm^{-2}, and the inversion dose of the surface relief shape G_i = 31.18 C·cm^{-2}. At d = 10 μm, these parameters are G_0 = = 6.98 mC·cm^{-2} and G_i = 36.19 C·cm^{-2}.

According to the two-layer charge model [6], the process of formation of the space charge region inside the irradiated film region is non-equilibrium. The creation of surface relief is due to structural

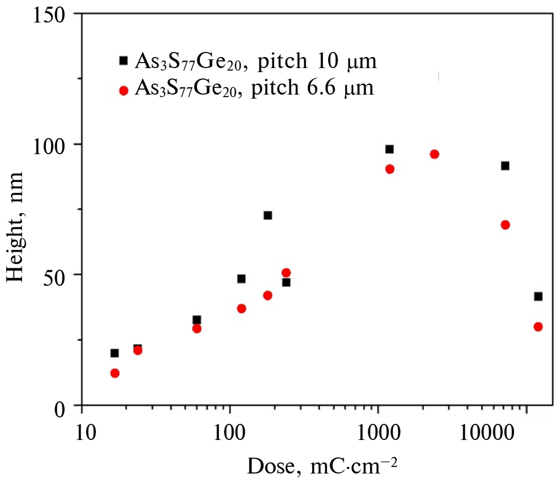


Fig. 2. Dependence of height of surface reliefs formed by electron beam on the exposure time

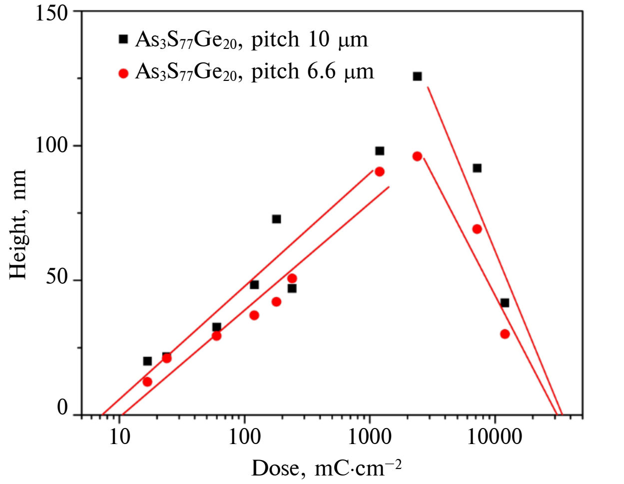


Fig. 3. Linear approximation of the dependence of the surface relief height of the $As_3S_{77}Ge_{20}$ film on the irradiation dose for matrix periods 6.6 μm and 10 μm

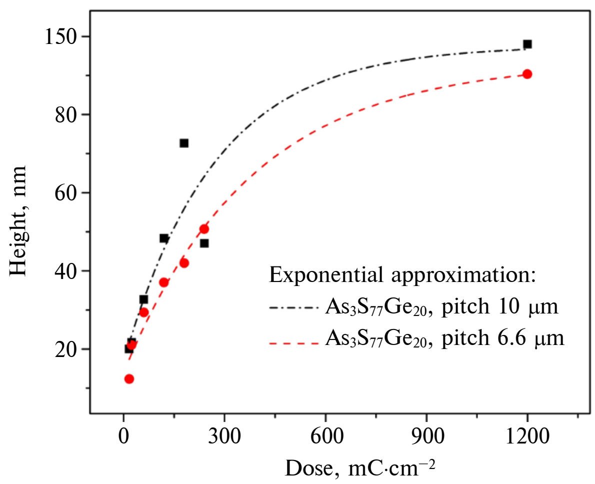


Fig. 4. Exponential approximation of the dependences $h = F(G)$ for the interval 16–1200 mC·cm^{-2}

changes in the film and the appearance 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 [6]. Fig. 4 shows the results of an exponential approximation of the dependences $h = F(G)$ at increasing interval (16 mC·cm^{-2} – 1200 mC·cm^{-2}) for d = 6.6 μm and d = 10 μm. Relaxation times that determined as a result of this approximation are τ_1 = (641.35 ± 110.42) ms for d = 6,6 μm and τ_1 = = (458.95 ± 210.71) ms for d = 10 μm.

It can be seen that the approximation curves correlate quite well with the measurement results (points). It can be concluded there is exponential dependence of height of surface nanostructures that have been previously shown by researchers [5, 6]. It should also be noted that exponential relaxation was observed during storage of films [4] and exponential decreasing of concentration of non-stoichiometric structural units during light exposure of chalcogenide films was observed in [23].

Conclusions

Our investigations have demonstrated that studied $As_3S_{77}Ge_{20}$ 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 height evolution of surface nanostructures has been detected. These results show that $As_3S_{77}Ge_{20}$ films can be used for fabrication of the optical elements.

Acknowledgments

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ФОРМУВАННЯ ПОВЕРХНЕВИХ НАНОСТРУКТУР НА ХАЛЬКОГЕНІДНІЙ ПЛІВЦІ As-S-Ge ПІСЛЯ ОПРОМІНЕННЯ ЕЛЕКТРОННИМ ПУЧКОМ

Проблематика. Халькогенідні стекла формують унікальний клас матеріалів та є привабливими з точки зору їх різноманітних застосувань, що обумовлені їхніми неперерсічними властивостями та можливістю утворювати поверхневий рельєф. Взаємодія цих матеріалів з електронним променем становить інтерес через різноманітність фізичних явищ, спричинених у халькогенідних плівках лазерним опроміненням.

Мета дослідження. Дослідження прямого (без селективного травлення) формування поверхневого рельєфу періодичних наноструктур на плівці $As_3S_{77}Ge_{20}$ товщиною ~8,3 мкм, виготовленій вакуумним термічним випаровуванням, із використанням електронно-променевої літографії. Вивчення зміни висоти і форми поверхневих наноструктур залежно від дози опромінення.

Методика реалізації. Хімічний склад плівки визначали за допомогою енергетично-дисперсійного аналізу рентгенівських променів. Плівку опромінювали електронним променем за допомогою скануючого електронного мікроскопа. Було досліджено вплив опромінення електронним пучком на аморфну халькогенідну тонку плівку $As_3S_{77}Ge_{20}$. Поверхневий рельєф плівки сканували атомно-силовим мікроскопом.

Результати дослідження. Доза експозиції *G* варіювалась від 12 мКл·см$^{-2}$ до 12 Кл·см$^{-2}$. Було виявлено формування конусів із гаусовим профілем на поверхнях плівок після локального опромінення електронами. Встановлено залежність висоти одержаних поверхневих наноструктур від дози експозиції. Видно, що для $G < 2400$ мКл·см$^{-2}$ висота поверхневого рельєфу поступово зростає до 100–125 нм, а для $G > 2400$ мКл·см$^{-2}$ вона зменшується. Було знайдено початкову та інверсійну дози формування

поверхневого рельєфу. Для матриць із відстанню між точками опромінення d = 6,6 мкм початкова доза становила G_0 = = 9,60 мКл·см$^{-2}$, а інверсійна – G_i = 31,18 Кл·см$^{-2}$. Для d = 10 мкм ці параметри дорівнювали G_0 = 6,98 мКл·см$^{-2}$ і G_i = 36,19 Кл·см$^{-2}$. Залежності $h = F(G)$ у зростаючому інтервалі дози (від 16 до 1200 мКл·см$^{-2}$) для d = 6,6 мкм і d = 10 мкм було апроксимовано експоненційними функціями.

Висновки. Зміну форми та параметрів отриманого рельєфу поверхні на плівці $As_3S_{77}Ge_{20}$ можна пояснити моделлю акумулювання заряду. Наші дослідження показали, що вивчена композиція $As_3S_{77}Ge_{20}$ придатна для запису електронним променем та може бути використана для виготовлення оптичних елементів.

Ключові слова: халькогенідні тонкі плівки; електронно-променевий запис; поверхневі наноструктури.

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ФОРМИРОВАНИЕ ПОВЕРХНОСТНЫХ НАНОСТРУКТУР НА ХАЛЬКОГЕНИДНОЙ ПЛЕНКЕ As-S-Ge ПОСЛЕ ОБЛУЧЕНИЯ ЭЛЕКТРОННЫМ ПУЧКОМ

Проблематика. Халькогенидные стекла формируют уникальный класс материалов и являются привлекательными с точки зрения их различных применений, обусловленных их незаурядными свойствами и возможностью образовывать поверхностный рельеф. Взаимодействие этих материалов с электронным пучком представляет интерес в связи с разнообразием физических явлений, индуцированных в халькогенидных пленках лазерным облучением.

Цель исследования. Изучение прямого (без селективного травления) формирования поверхностных наноструктур на пленке $As_3S_{77}Ge_{20}$ толщиной ~8,3 мкм, изготовленной термическим вакуумным испарением, с использованием электронно-лучевой литографии. Изучение изменения высоты и формы поверхностных наноструктур в зависимости от дозы облучения.

Методы реализации. Химический состав пленки определяли с помощью энергодисперсионного анализа рентгеновских лучей. Пленку облучали электронным пучком с использованием сканирующего электронного микроскопа. Было исследовано влияние облучения электронным пучком тонкой аморфной халькогенидной пленки $As_3S_{77}Ge_{20}$. Рельеф поверхности пленки был сканирован с помощью атомно-силового микроскопа.

Результаты исследования. Доза облучения G варьировалась от 12 мКл·см$^{-2}$ до 12 Кл·см$^{-2}$. Было обнаружено образование конусов с гауссовым профилем на поверхностях пленок после локального электронного облучения. Определена зависимость высоты полученных поверхностных наноструктур от дозы облучения. Видно, что для $G < 2400$ мКл·см$^{-2}$ высота рельефа поверхности постепенно увеличивается до 100–125 нм, а для $G > 2400$ мКл·см$^{-2}$ она уменьшается. Были найдены начальная и инверсионная дозы формирования поверхностного рельефа. Для матриц с расстоянием между точками облучения d = 6,6 мкм начальная доза составляла G_0 = 9,60 мКл·см$^{-2}$, а инверсионная – G_i = 31,18 Кл·см$^{-2}$. Для d = 10 мкм эти параметры равнялись G_0 = 6,98 мКл·см$^{-2}$ и G_i = 36,19 Кл·см$^{-2}$. Зависимости $h = F(G)$ в интервале возрастания дозы (16 мКл·см$^{-2}$ – 1200 мКл·см$^{-2}$) для d = 6,6 мкм и d = 10 мкм были аппроксимированы экспоненциальными функциями.

Выводы. Изменение формы и параметров полученного поверхностного рельефа пленки $As_3S_{77}Ge_{20}$ можно объяснить моделью аккумуляции заряда. Наши исследования показали, что изученная композиция $As_3S_{77}Ge_{20}$ пригодна для регистрации электронного луча и может быть использована для изготовления оптических элементов.

Ключевые слова: тонкие халькогенидные пленки; электронно-лучевая запись; поверхностные наноструктуры.

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