ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 9, № 1 (2008) С. 198-201

PHYSICS AND CHEMISTRY OF SOLID STATE
V. 9, № 1 (2008) P. 198-201

PACS: 78.66.JG ; 77.80.G

ISSN 1729-4428

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Amorphous Chalcogenide Nanomultilayers for Photonics

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We have developed a number of nanolayered structures from amorphous chalcogenide materials, which consists of stacks 1-10 nm thick sub-layers (Se, Te, AsSe, SeTe, As_2S_3, SiO_x, Sb, Bi) with alternating compositions, deposited by cyclic vacuum thermal evaporation on special glass, sapphire, silicon substrata. Efficient interdiffusion and composition or phase change in an acceptable time domains can be stimulated in these structures by laser irradiation, ion beams, current pulses, while the initial structures are stable at normal environment conditions. The main result of these stimulated solid state processes is the well localized change of optical and electrical parameters (transmittance, refractive index, conductivity, permittivity) which in turn can be used for optical recording, surface pattern formation, memory devices.

Key words: nanostructures, multilayers, interdiffusion, optical characteristics.

Стаття поступила до редакції 06.05.2007; прийнята до друку 15.12.2007

Introduction

Chalcogenide glasses are versatile functional materials for photonics due to the number of peculiar characteristics and effects like wide range of optical transparency, high refractive index n and specific electrical resistance, which can be smoothly changed, predicted by changing the composition in Ge(As, Sb)-S(Se,Te) and more complex systems or switched by external influences due to the stimulated transformations between more or less stable structures [1-3]. Amorphous-amorphous or amorphous-crystalline structural transformations are the basis of optical recording, formation of amplitude ($\Delta\alpha$) and phase (Δn) optical reliefs [1, 3, 4]. The phase relief may be complemented by the change of the thickness (Δd), i.e. by the geometrical surface relief formation directly during the optical recording or afterwards due to the selective chemical etching. The last process is widely used nowadays for fabrication of molds, holographic gratings, integrated optical elements [5,6],. The direct relief formation without etching is possible due to the known effect of light-stimulated volume expansion or contraction in chalcogenides [7-9], but usually the $\Delta d/d \approx$ 1% and the spatial resolution is limited by the diffraction. Essentially larger expansion effects were observed due to the light- and ion-stimulated interdiffusion in chalcogenide nanolayered films (NLF) [10-12].

The diffraction limit in optical recording may be overcame by optical near-field lithography in chalcogenide films [13] or by using high energy radiation, electron beams for recording since structural transformations in chalcogenide glasses can be stimulated also this way [14,15]. In this paper we review our results on the possibilities of direct, one-step surface relief formation by laser beam or accelerated ions (H^+,D^+) on a-Se layers or a-Se/As_2S_3 nanolayered films with the purpose of estimation of the efficiency and practical applicability of the NLF in photonics.

I. Experimental

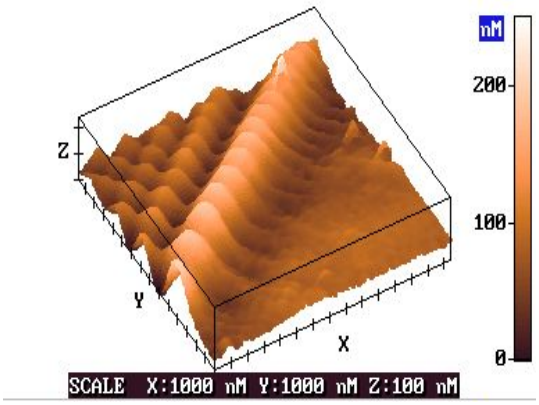
We have selected for examples, as model materials α-Se and As_2S_3 layers as well as α-Se/As_2S_3 NLF because of the most known parameters and rather simple technology, although a number of similar structures, like Se_xTe_{1-x}/As_2S_3 ($0 \le x \le 1$), As_xSe_{1-x}/As_2S_3 ($0 \le x \le 0.4$), GeS/GeSe were investigated, sometime with better recording parameters. First 0.5-1.0 μm thick films were fabricated by vacuum evaporation of crushed high purity bulk materials to determine the evaporation parameters. High quality α-Se/As_2S_3 nanolayered films (NLF) were prepared by computer-controlled cyclic vacuum evaporation onto the Si wafer or Corning 7059 glass substrata. The modulation period was 6 nm, the total thickness of the NLF was 0.5-1.0 μm. To study the surface modification induced by light or ion beams, samples were irradiated with He-Ne laser (output power P=25 mW), red diode laser (P=100 mW) green diode

laser (max output power 20 mW), 180 keV H^+, D^+ ions. The laser irradiation of the samples was done in normal atmosphere. The irradiations with H^+ and D^+ were done at the 200 keV linear accelerator of the Department of Experimental Physics of the University of Debrecen [16]. Irradiation usually was performed via a metal microgrid with mesh size 40x40 μm which was placed in front of the sample. Surface reliefs were investigated by atomic force microscope (NT-MTD type AFM). Optical spectra were measured by Shimadzu 3600 spectrophotometer.

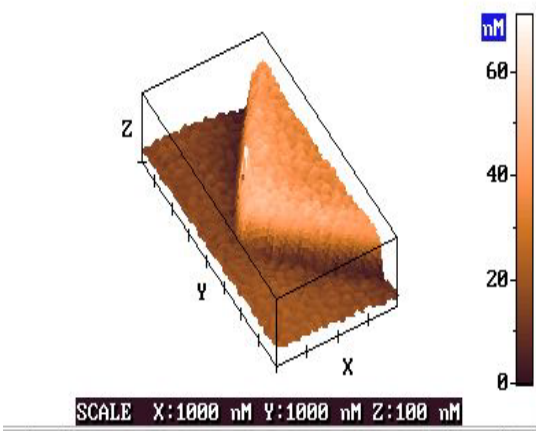
II. Results and discussion

AFM measurements directly confirmed the known effects of photoinduced expansion with $\Delta d/d \leq 1$ % in separate As_2S_3 film under the green laser irradiation with total exposure up to 600 J/cm^2 and the contraction of a-Se layer with $\Delta d/d \approx 1$ % in the regime of diffraction pattern recording with red laser light and total exposures up to 10^3 J/cm^2. It was established, that such large exposures do not cause any crystallization in As_2S_3, while in a-Se the mentioned illumination with low intensity, non-heating He-Ne laser beam resulted in sporadic crystallite growth on the surface. It was essential to take into account these results for explanation of induced expansion in NLF as well as of ion-Se interaction. Almost the same values of thickness change were obtained with deuteron irradiation, although the magnitude of the effect was lower (or the kinetics slower) for ions relative to the laser light at the same, integrated energy which reached the surface. It may be caused by slightly different amount of energy, absorbed in the irradiated volume and by the differences in the pathways of energy transformation to the transforming glass network as it was mentioned in [16,17]. Since this way of direct surface relief formation is not really efficient we do not touch the problem of the spatial resolution, although replacing the diffraction-limited visible laser illumination by accelerated ion irradiation may lead to the improvement of the quality of the surface reliefs on amorphous chalcogenide films.

According to our expectations the stimulated local expansion in NLF was much more efficient for surface relief formation in a one-step, direct process. The efficiency of the thickness change was essentially higher in the case of contact mask application in comparison with previous data [10] on holographic recording: $\Delta d/d \approx 14$ %, as it was estimated from surface profile measurements by AFM (see Fig.1a). The total exposure during 30 min was near 600 J/cm^2. The possible small expansion of As_2S_3 sub-layers in this NLF, as well as the contraction of Se sub-layers compensate each over and may be neglected, as well as the photoinduced crystallization of Se sub-layers, since the interdiffusion process dominates the recording with expansion, based on the lower specific volume of the amorphous As-S-Se mixture in comparison with a sum of the separate sub-layers [10]. In Fig.1a one can see a surface pattern caused by the interference of the light diffracted on the mesh corner. The depth modulation is quite enough for fabrication of high efficiency surface gratings, elements



a)



b)

Fig. 1. a) 3D AFM picture of the pattern recorded on Se/As_2S_3 nanolayered film with total thickness d=900nm, illuminated through a microgrid with 17mW, 532 nm diode laser for 30 min. b) 3D AFM picture of the pattern recorded on the same NLF due to the irradiation through a microgrid with 180 keV D^+ ions, fluence 1.6 10^{16} ion/cm^2.

which can be read out by visible light or mechanically. The distance between the edge and the first maximum equals near 2 μm, that corresponds to the diffraction conditions in our experiment with green laser (λ=532 nm), but the real form, half width of the "bumps" may be smaller, below 1 μm. It is evident that in the case of direct, one-step surface relief formation on the basis of light-stimulated interdiffusion in NLF the resolution is limited by the diffraction.

Experiments with light ion irradiation were more promising and similar for H^+ and D^+. In Fig.1b the surface pattern produced on a-Se/As_2S_3 NLF of 900 nm total thickness by 180 keV D^+ irradiation is shown. The maximum ion fluence was $3.2 \cdot 10^{16}$ ions/cm^2 in this experiment. The maximum depth modulation is almost equal to the modulation obtained at laser illumination with the same integrated energy (exposure) calculated for the $3.2 \cdot 10^{16}$ ions/cm^2 with 180 keV energy. The average $\Delta d/d \approx 6$ %, which is two times smaller than the maximum relief height obtained in laser irradiation experiments on this sample. This value probably could be increased by applying higher fluences, but it was not possible within a real time domain, as far the ion current density had to be kept ≤ 170 nA/cm^2 to prevent the

undesirable heating of the sample. Nevertheless, the depth profile is also sufficient for nano-pattern formation. In the case of light ions, which do not initiate large recoil cascades, the resolution is limited by the scattering of ions on the target atoms. In these scattering events the direction of the motion of the ions changes and the ions move along a complex trajectory in the matter. The higher the ion energy, the less these collisions can change the trajectory of the ions. Thus, the resolution limit critically depends on the ion mass, energy and on the total thickness of the "resist" layer. It can be improved by increasing the ion energy or decreasing the thickness. However, the decrease of the thickness leads to the decrease of the resulting relief height in our case. The use of multilayers instead of single layers can substantially decrease the resist thickness needed to obtain patterns of a given height. The resolution limit in our experiments could be estimated from the relief edge steepness. It is about 250 nm (see the Fig.1b), that approximately coincides with the lateral straggling calculated with the SRIM/TRIM 2003 code [18]. It means that the minimal spacing between two surface nano-elements to be completely resolved is about 400-500 nm.

The efficient phase modulation of the light by the Δn and Δd proifile can be reduced by the opposite direction of this changes. The amplitude relief of the recording may add to the efficiency, but it is rather small in Se/As_2S_3 NML (see the changes of the absorption edge in Fig.2), so the relative change of the initial optical transmission τ_0 should be increased. It was achieved by the insertion of S, Bi sub-layers to the NML with As_2S_3. The interdiffusion of the metal and chalcodenide is first of all heat-stimulated (i.e thermal annealing or heating by the laser beam is the driving force) . It results in three-component glass formation in the case of dissolution without phase separation and the transmission of the irradiated (annealed) changes essentially in wide spectral range (see Fig.3). The n decreases in this case irreversibly: $\Delta n \geq -0.02$ and the thickness is not changing essentially. Therefore this type of media is also applicable for amplitude-phase optical recording of gratings, for example. Moreother, the change of the non-linear optical characteristics of the NML under focused laser illumination allows the creation of the patterned element for non-linear optical elements. Further applications of such nanostructured materials in nanophotonics are predictable if the technics of e-beam or focused ion beam recording will be developed, or the SPM recording will be realised. First steps in this direction are promising but the results will be the matter of other publication.

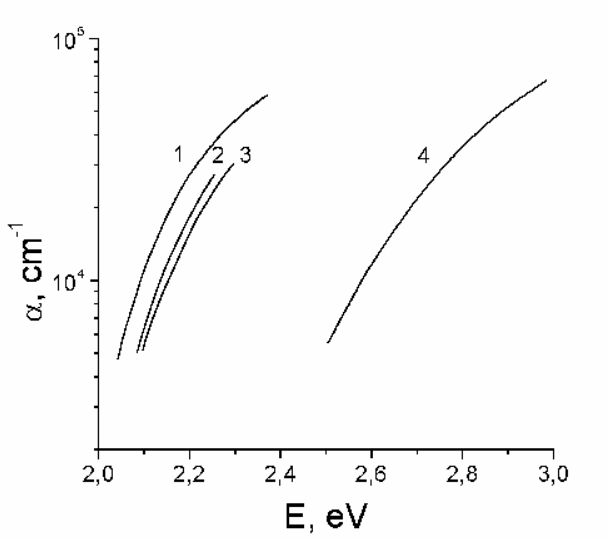


Fig. 2. Optical absorption spectra: 1– for homogeneous, 500 nm thick Se layer; 2– for 900 nm thick Se/As_2S_3 NML as deposited; 3– Se/As_2S_3 NML irradiated; 4– homogeneous 500 nm thick As_2S_3 layer.

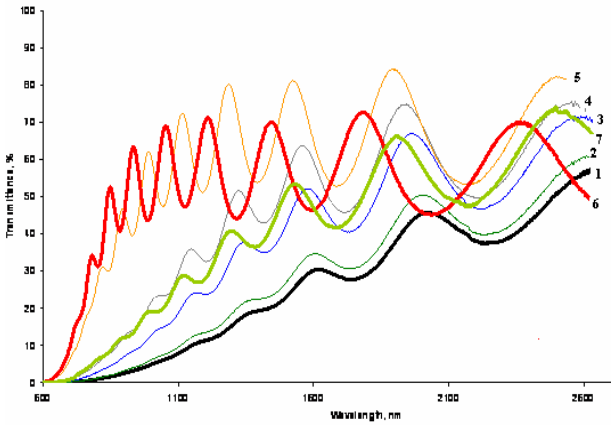


Fig. 3. Spectral dependences of the transmittance for as-deposited Bi/As_2S_3 NML sample after 10 min annealing at 60 C (1), 80 C (2), 100 C (3), 120 C (4), 140 C (5) and 160 C (6) and for the same sample after laser irradiation with λ=635 nm, P=30 W/cm^2 (7).

Conclusions

Surface or amplitude-phase optical relief structures were fabricated in a direct, one-step process of recording by light or ion beam on $Se(Sb,Bi)/As_2S_3$-type nanolayered films. The most efficient geometrical relief formation with a depth profile up to few hundred nanometers and submicron spatial resolution can be performed on nanolayered Se/As_2S_3 films due to the stimulated interdiffusion under the irradiation by relatively low energy H^+ or D^+ ions. NML structures with Sb,Bi sub-layers are efficient for amplitude-phase recording without essential thickness variations.

This work was supported by Hungarian OTKA Grant T046758 as well as by the Indian-Ukrainian and Indian-Hungarian bi-lateral R&D cooperation grants.

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Аморфний наномультишаровий халькогенід для фотоніки

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Вивчено цілий ряд наношарових структур з аморфних халькогенідних матеріалів, які складаються з стопки 1-10 нм товстих підшарів (Se, Te, AsSe, SeTe, As_2S_3, SiO_x, Sb, Bi), вирощені циклічним вакуумним тепловим напиленням з парової фази на підкладках із спеціального скла, сапфіру, кремнію. Ефективна взаємна дифузія і композиційна або фазова зміна в прийнятних інтервалах часу може стимулюватися в цих структурах лазерним випромінюванням, іонними пучками, імпульсами струму, тоді як початкові структури стійкі в нормальних умовах навколишнього середовища. Головний результат цих стимулювальних технологій, – добре локалізована зміна оптичних і електричних параметрів (коефіцієнт пропускання, коефіцієнт заломлення, провідність, питома провідність), які у свою чергу можуть використовуватися для оптичного запису, поверхневого формування рисунка, пристроїв пам'яті.