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Amorphous Chalcogenide-Metal Multilayers

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Bi(Sb)/As₂S₃ nanomultilayers (NML) were developed and produced with different modulation periods in the 4-10 nm range using the computer-controlled cyclic vacuum evaporation technology. The influence of the thermo- and/or photo-induced interdiffusion on the optical parameters and electrical conductivity were investigated in such model nanostructured materials in order to establish the possibilities of surface pattern recording and to develop the method of solid phase synthesis which allows to create materials nanostructured at different scales.

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

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Introduction

A number of glassy or glassy-crystalline compositions in binary, ternary and more complex chalcogenide glass systems are known [1-2]. Bulk materials can be obtained by the method of direct synthesis from elemental components melted in an evacuated ampoule. Thin films of these materials usually are prepared by thermal evaporation in vacuum [3-4] but decomposition of the original multicomponent glass, changes of the parameters of layers obtained at different temperature conditions may occur during the thermal evaporation. At the same time the method of obtaining multicomponent layers via solid phase synthesis during the interdiffusion of different adjacent layers is known [5]. The similar process occurs in light-sensitive chalcogenide nanomultilayers (NML) during the light and/or heat stimulated interdiffusion [6-8]. These processes were described in our previous papers from the point of view of amplitude-phase optical recording, surface relief formation [8-9], but the mechanism of structural transformations, information about new phase formation during the interdiffusion are far from completeness.

One of the interesting problems is the dissolution of metals in chalcogenide glasses, since, for example, the enhanced light-stimulated diffusion of silver into the chalcogenide layers is a well known effect applied in optoelectronics, holography [10-11]. But the diffusion of silver is very fast, the nanostructures with Ag are not stable. We have extended investigations of photo- and thermo-stimulated interdiffusion effects in chalcogenide nanomultilayers towards the nanolayered structures

which contain alternating metal and chalcogenide layers. Namely the model Bi/As₂S₃ and Sb/As₂S₃ NML structures were investigated and the results are presented in this work.

I. Experimentals

We used high purity Bi or Sb, as well as As₂S₃ glass as initial materials for nanomultilayer fabrication. Bi/As₂S₃ or Sb/As₂S₃ nanomultilayers were prepared by computer-controlled cyclic vacuum evaporation of metal and glass from different sources onto the Si wafer or Corning glass substrata. The modulation period was 4 - 10 nm, the total thickness of the NML was 0,5 – 1,0 μm. Control layers of metal and As₂S₃ were deposited at the same time onto the separate substrata and used to check the composition and calculate the ratio of the sub-layer thicknesses in one modulation period.

The total thickness of the films was measured by AMBIOS XP-1 nanoprofilometer. The quality (periodicity, smoothness of the interfaces) of the multilayers was estimated by the standard Small Angle X-ray Diffraction (SAXRD) method (Siemens, CuKα, λ = 1,54 Å). Although the SAXRD spectra (see Fig. 1) do not showed very well defined, highly periodic structures like crystalline superlattices, the periodicity calculated from these experiments and from the data of thickness measurements for the given number of deposition cycles were in a good accordance.

Structural transformations, interdiffusion stimulated by heating or illumination were investigated at normal ambient conditions directly by SAXRD method and indirectly by optical transmission and electrical

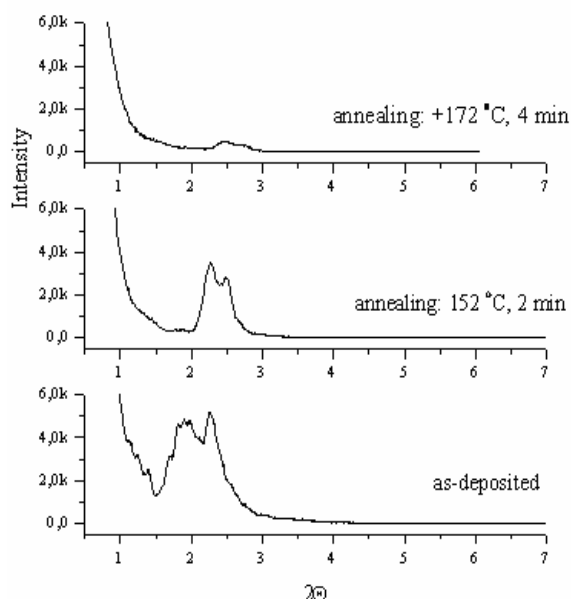


Fig. 1. SAXRD spectra of as-deposited and annealed Bi/As₂S₃ NML.

conduction measurements. Optical transmission spectra were measured by Shimadzu UV-3600 spectrophotometer in as-prepared and in the previously annealed or irradiated samples. Electrical conductivity was measured in plain, between two carbon electrodes placed in two parallel scratches what enabled to check the change of the conductivity after the intermixing of the parallel metal and chalcogenide glass sub-layers in the given NML. Measurements of the conductivity were performed in a vacuum cryostat in 150 - 400 K temperature range by Keithley 485 picoammeter. Annealing was usually performed in a normal atmosphere.

Samples were irradiated by focused diode laser beams with $\lambda = 532$ or 635 nm. The power densities at the surface of the samples were in 0,1 - 80,0 W/cm² range. HITACHI S4300-CFE scanning electron microscope was used to study the surface and cross-sections of the samples.

II. Experimental results and discussion

It was established, that the NMLs with thicker (3 nm) Bi(Sb) sub-layers (sample #1) 467) had a better defined structure, but for optical and electrical investigations only samples with smaller Bi (Sb) thicknesses ($d \approx 1$ nm) were suitable because of the proper optical and electrical characteristics. The structure of the optimum investigated NMLs (samples #2 and #3 for Bi/As₂S₃ and Sb/As₂S₃ accordingly) was: modulation period $\Lambda = 4 - 5$ nm, thickness of the metal sub-layers 1,0 - 1,5 nm. Since the interfaces and the periodicity in such structures are not very perfect the surface roughness of the as-prepared NML also is about 1 nm (measured by AFM). Therefore it may be concluded that probably our NMLs consists of layer-arranged metal clusters separated by As₂S₃ layers. Additional transition layers may appear at interfaces or the period may change a little during the

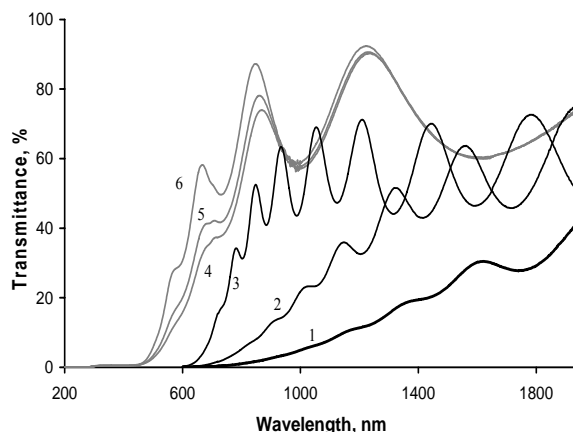


Fig. 2. Spectral dependences of the transmittance for Bi/As₂S₃ NML samples as-deposited (1), annealed at 120 °C (2) and at 160 °C (3) and for the Sb/As₂S₃ sample as-deposited (4), after 10 min annealing at 90 °C (5) and at 100 °C (6).

deposition. This may be the reason of the double-maximum diffraction peak, presented in Fig. 1. If the estimated thickness of metal sub-layers is smaller ($\sim 0,6$ nm, sample #4 in our experiments), there is no significant difference in optical spectra between the NML and thick As₂S₃ layer and the stimulated changes of optical parameters in such NML were not essential.

Optical transmission spectra of the selected NML samples are presented in Fig. 2. These spectra reflect the characteristics of a quasi-homogeneous wide band gap amorphous semiconductor layer: the optical gap and the index of refraction can be calculated according to the known methods of analysis of the absorption edge and interference pattern [12-13]. It was established that Bi/As₂S₃ samples #4 are almost transparent at $\lambda = 635$ nm where irradiation occurs. The efficiency of stimulated diffusion processes must be low in this case the more so that the thickness of metal layer is very small and no significant amount of three-component material with changed optical parameters can be created due to the intermixing. Samples #1 consist of thick Bi layer, so the optical transmission is low and do not changes essentially after treatments in an acceptable time scale.

Thermally- or light-induced bleaching was observed in the selected NMLs with optimum parameters (thickness of metal sub-layer equals to 1 - 1,5 nm, samples 2 and 3). It is evident from Fig. 2 that large changes of optical transmission and corresponding changes in refraction and reflection can be induced in a wide spectral range. The question is: does it is light- or thermally-induced effect? It seems that the thermal effects of the focused laser beam are important for stimulation of interdiffusion in these type of NLFs because the total energy E , which is necessary for obtaining the same degree of bleaching on the power density P decreases with increasing P (see. Fig. 3), i.e. the diffusion increases with increasing temperature. At the same time, since the efficiency of the changes is better for Sb/As₂S₃ NML in comparison with Bi/Sb/As₂S₃ NML with the same initial structure (see Fig. 4) it may be assumed that besides the higher diffusion

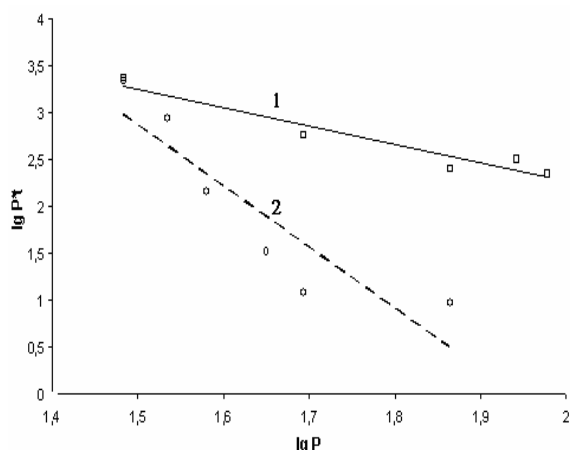


Fig. 3. The dependence of the exposition $E = P.t$ (t in seconds) which is necessary to obtain the same ($I/I_0 = 6$) bleaching on the power density P , W/cm^2 of laser illumination ($\lambda = 635$ nm) for the Bi/As_2S_3 sample #2 (2) and Sb/As_2S_3 sample #3 (1).

coefficients and lower activation energies of the diffusion and new phase formation, photo-electron processes, changes in conductivity also contribute to the stimulation of the interdiffusion at the same conditions of excitation. These problems need separate investigations.

The change of the refractive index due to the annealing or irradiation-induced effects was calculated from the interference pattern in optical transmission spectra assuming that the nano-heterogeneous NML may be described as an effective media. The initial value of the refractive index measured at $1.0 \mu m$ for a number of investigated NML was in the 2,6 - 2,7 range and the maximum decrease of the refractive index n after the recording (annealing) was $\approx 0,1$ that means near 5% changes due to the intermixing in the NML. The changes of optical transmission and of the refractive index are extremely large in comparison with known photo-induced changes in homogeneous chalcogenide layers [14] and even in comparison with a model Se/As_2S_3 NML [8], where the change of transmission at the given wavelength relative to the initial one $I/I_0 \approx 1,3 - 1,5$.

It seems that we deal with amorphous structures, since no significant sign of crystalline phase was detected by XRD neither in as-deposited nor in the annealed samples although NMLs may contain some nanocrystalline phase and be X-ray amorphous. To check this possibility we modeled the intermixing process in a

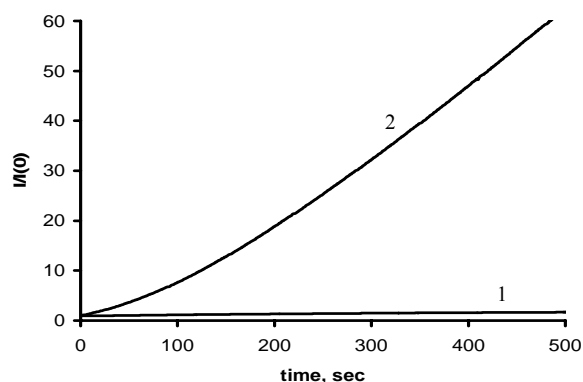


Fig. 4. Time dependence of the bleaching during irradiation of the Bi/As_2S_3 NML (sample #2) (1) and the Sb/As_2S_3 NML (sample #3) (2) by the laser with $\lambda = 635$ nm, $P = 30 W/cm^2$.

double Bi/As_2S_3 heterostructure with thicker (up to 1 - 2 μm) metal and chalcogenide sub-layers (see Fig. 5). It was concluded that first of all S component of the chalcogenide sub-layers diffused to the Bi during the annealing and created Bi_2S_3 phase (darkened regions in the Bi layers in Fig. 5.b). Three-component $Bi(Sb)_x(As_2S_3)_{1-x}$ glasses are created on the other side with decreasing width of the optical band gap E_{gopt} (in comparison with homogeneous amorphous As_2S_3 layer) in the NML during the interdiffusion. At the same time the total transmission of the NML increases, since the non-transparent metal layer disappears. The last process determines the bleaching and the recording of the amplitude optical relief, although the refractive index change due to the creation of a multicomponent layer instead of compositionally modulated nanostructure also contributes to the formation of optical phase-changed relief. As far as the maximum amount of Bi or Sb which can be introduced to As_2S_3 without phase separation (appearance of Bi_2S_3 , Sb_2S_3 crystalline phase) is less than 5 at % similarly to the analogous metal- As_2S_3 systems [2], the process of stimulated intermixing at certain ratio of metal/chalcogenide sub-layer thicknesses may terminate in a quasi-homogeneous three-component amorphous material or in a layered nanocomposite with thin sub-layers of the matrix (As_2S_3), $Bi(Sb)_x(As_2S_3)_{1-x}$ solid solution and $Bi(Sb)_2S_3$ crystalline phase up to the homogeneous multicomponent material. Solid phase synthesis of a multicomponent film with a composition predicted by the parameters of initial NML and interdiffusion conditions can be performed this way.

Some indirect information about the structural

Table. 1.

Activation energy $E_{a\sigma}$ of DC electrical conductivity and the optical band gap E_g^{opt} for Bi/As_2S_3 and Sb/As_2S_3 NML

NLF	$E_{a\sigma}, E_g^{opt}, eV$ (as-deposited)	$E_{a\sigma}, E_g^{opt}, eV$ (annealed 80°C)	$E_{a\sigma}, E_g^{opt}, eV$ (annealed 100°C)	$E_{a\sigma}, E_g^{opt}, eV$ (annealed 135°C)	$E_{a\sigma}, E_g^{opt}, eV$ (annealed 160°C)
$Bi/As_2S_3 (\sigma)$	0,26	0,27	0,28	0,65	0,78
$Bi/As_2S_3 (opt)$	0.59	0.49	0.67	1.28	1.38
$Sb/As_2S_3 (\sigma)$	0,27	0,30	0,44	0,71	0,80
$Sb/As_2S_3 (opt)$	0,68	0,68	0,70	0,87	-

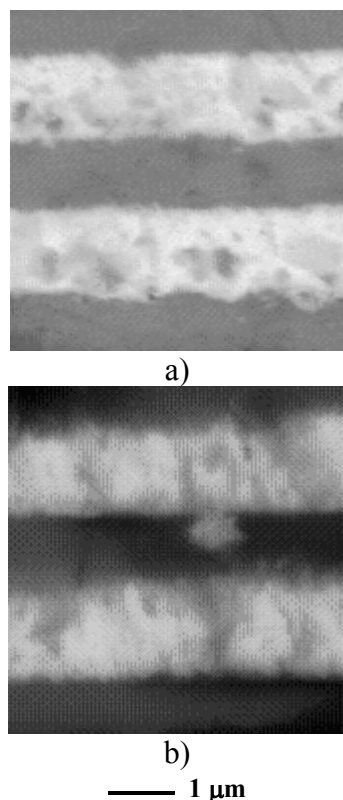


Fig. 5. Scanning electron microscope picture of the cross-section of a double Bi/As₂S₃ heterostructure with thick metal and chalcogenide sub-layers before (a) and after (b) the annealing.

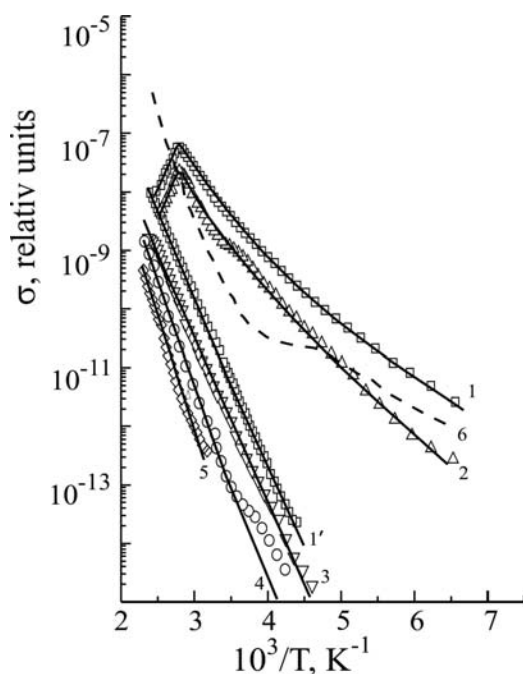


Fig. 6. Temperature dependence of electrical conductivity σ for Bi/As₂S₃ NML: 1- first heating of the as-deposited sample, 1'- cooling after the first heating, 2, 3, 4 and 5- heating after annealing during 10 min at 353 K, 373 K, 408 K and 433 K respectively. 6- temperature dependence of electrical conductivity for Bi₂S₃ polycrystalline layer.

changes in NML due to the interdiffusion may be obtained from the temperature dependences of electrical conductivity. With aim to supplement the data about the mechanism of these changes the measurements of the DC conductivity were performed in initial and annealed or illuminated samples. Results are presented in Fig. 6 and Fig. 7, as well as in the Table. 1.

The activation energy $E_a\sigma$ at temperatures below the glass softening temperature T_g in the case of chalcogenide glasses is usually comparable with optical band gap ($E_{\text{gopt}} \geq 2 E_a\sigma$), except of the formation of a peculiar sub-band in the gap due to the presence of great amount of Bi₂S₃ in Ge-Se glasses [15]. The change of the type of the conductivity from “p” to “n” is possible in this case. No data is available on such a change in Bi(Sb)-As₂S₃ systems: our results support on the whole the formation of three-component amorphous (nanocrystalline) layer after the intermixing. The differences in $E_a\sigma$ and E_{gopt} in Sb/As₂S₃ NML may be related just to the formation of a separate phase, but there are not enough data to support it. Interdiffusion is thermally stimulated, therefore the results on the optical changes in annealed or irradiated NMLs with metals may be explained by the same model of thermally activated diffusion.

It is necessary to mention that the activation energy of conductivity for a separate Bi₂S₃ polycrystalline layer at temperatures above 100°C equals 1,15 eV. So in the case of thick metal sub-layers in the NML the creation of Bi₂S₃ or Sb₂S₃ transition layers at the interfaces after the interdiffusion is possible, the conductivity will be

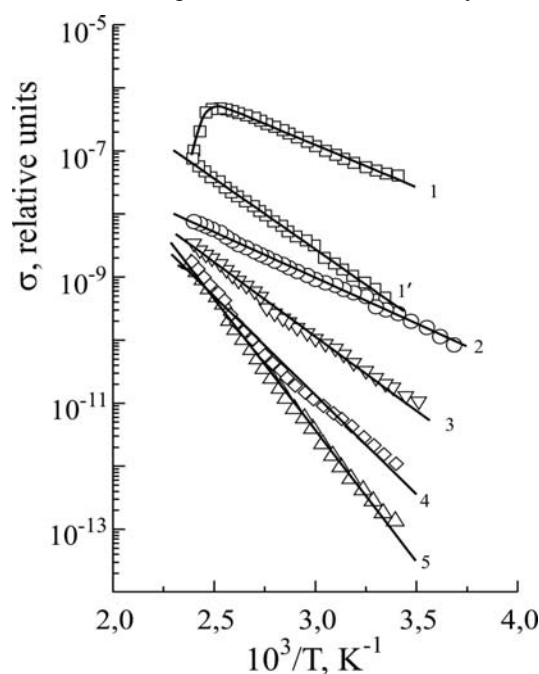


Fig. 7. Temperature dependence of electrical conductivity σ for Sb/As₂S₃ NML: 1- first heating of the as-deposited sample, 1'- cooling after the first heating, 2, 3, 4 and 5- heating after annealing during 10 min at 353 K (2), 373 K (3), 408 K (4), 433 K (5) respectively.

determined by this layers, i.e. solid phase synthesis of a crystalline phase can be realized but the recorded optical relief in this case may be not better because of the large absorption by the residual metal film in a non-homogeneous composite layer.

All investigated changes in optical parameters are irreversible, so these type of materials can be used for archival memory, or for creation of optical, integrated-optical elements, which need high local changes of optical parameters (and electrical, if necessary). These changes are comparatively slow due to the mass transport through the interfaces in an amorphous media but stable at the same time in respect of low intensity (up to $0,5 \text{ W/cm}^2$) read out light in a wide spectral range, including infrared.

Conclusions

We conclude that $\text{Bi(Sb)/As}_2\text{S}_3$ nanolayered composite films may be used for modeling solid state synthesis, optical recording, one-step fabrication of optical relief with high intensity laser beams in the spectral range of high optical absorption. Amplitude-phase relief can be created with high modulation parameters and stability in respect of low intensity $P < 0,5 \text{ W/cm}^2$ read out in the same spectral range or in the IR spectral range.

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Аморфні мультишари халькогенід-метал

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Наномультишари $\text{Bi(Sb)/As}_2\text{S}_3$ були розроблені і виготовлені з різними періодами модуляції з шарами 4 - 10 нм, використовуючи циклічну технологію випаровування в вакуумі, з комп'ютерним керуванням. В цих зразках досліджувався вплив термо- та/або індукованої фото- самоїфузії на оптичні параметри і електричну провідність для того, щоб встановити можливість застосування зразків для запису на їх поверхні і розробити метод твердого фазового синтезу, який дозволить створювати різні наноструктурні матеріали.

Ключові слова: наноструктури, мультишари, interdiffusion, оптичні і електричні характеристики.