"INTRINSIC" AND PHOTOINDUCED ANISOTROPIES IN AS-DEPOSITED AMORPHOUS As_xS_{1-x} FILMS

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Optical anisotropy of amorphous As_xS_{1-x} films making use of wave-guide technique has been investigated. Fresh amorphous films obtained by a standard method of thermal evaporation in vacuum have been shown to possess a significant (about 10^{-2}) "intrinsic" optical anisotropy (the birefringence) between the in-plane and normal directions in the film. This anisotropy is characterized by a relaxational behavior, which is enhanced by thermal annealing. A simple phenomenological model, taking into account structural and chemical properties of the fresh-deposited films, has been proposed to explain the appearance and characteristic features of the anisotropy. Namely, the latter has been connected to the existence of layered formations involving quasicrystalline clusters with relevant polarization.

Introduction

Non-crystalline solids are typically isotropic objects because the isotropy of the structure is an essence of the amorphous material determination. That is why a possibility of creating an anisotropic state in substances, for which the isotropic one is natural, in particular, in such an important class of compounds as chalcogenides, attracts an active interest. The methods of producing amorphous materials can be schematically divided into two groups (see Table). The first one includes the procedures of fabricating vitreous-like materials under the temperature gradient [1], and thin amorphous layers by using special fabrication techniques [2]. Methods, involving the treatment of the already fabricated materials [3–8], are classified to the second group, which is characterized by a temporary resulting anisotropy. The study of whether the formation of amorphous anisotropic structures is possible, is a challenging problem beyond doubt.

Chalcogenide glasses are known to manifest a variety of photoinduced phenomena [9–13]. The photoinduced anisotropy phenomenon, which was demonstrated in chalcogenide films for the first time in [12], is distinguished among them. One of its manifestations is an optical birefringence under the irradiation of amorphous chalcogenides by linearly polarized light. To explain the results of experimental investigations, various models were proposed, in particular, those considering the native U-charged defects [14], the orientations of normal bonding orbitals [15], or certain structural formations [16]. Nevertheless, the actual physical mechanism of this phenomenon remains obscured.

In this article, it is shown for the first time that even the amorphous films, prepared by conventional thermal sputtering method, possess a well-pronounced "intrinsic" (in contrast to the photoinduced) optical anisotropy, subjected to an essential dark relaxation after the specimen fabrication. The "intrinsic" optical anisotropy can be irreversibly destroyed by either the thermal annealing or the nonpolarized light irradiation of the specimen in the absorption range of the film substance. We used the method of resonance excitation of directed optical modes in a waveguide. Note that the "intrinsic" optical anisotropy under consideration substantially differs in amplitude and relaxation kinetics from both the photoinduced one [12,13,16—18] and the anisotropy resulting from the photoinduced anisotropic crystallization [19]. Although the considered materials belong to the As–S system, the phenomena described can be observed in other systems as well.

Methods of fabricating chalcogenide and oxide anisotropic non-crystalline solids

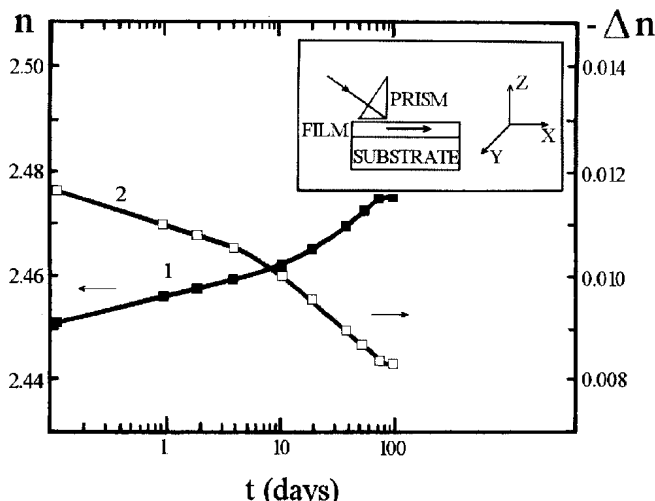| Method of production	Technology	Anisotropy	Ref.
Fabrication	cooling under the temperature gradient (bulk glasses)	quasistable	[1]
	oblique deposition		[2]
	stretching		[3]
Treatment	elastic deformation	temporary	[4]
	electrical field		[5]
	magnetic field		[6]

Fig. 1. Dependences of the refractive index n_y, measured along the polarization direction in the film plane (*1*), and the birefringence parameter $\Delta n = n_z - n_y$ (*2*) on the storage time after the deposition for the $As_{0.4}S_{0.6}$ film. The experimental setup is shown in the inset

Specimen Fabrication and Experimental Procedure

Experimental measurements were conducted using the as-prepared As_xS_{1-x} films ($0.20 \leq x \leq 0.43$). The deposition was carried out making use of a standard vacuum evaporation technique at a pressure of 5×10^{-5} mm Hg. As_xS_{1-x} glasses were used as the initial material for evaporation.

The deposition was performed in vacuum on previously decontaminated plates of quartz glass at a temperature of 300 K. The rate of film condensation was 3—4 nm/s. The film chemical content was monitored by local X-ray analysis. The thickness of the studied films was maintained within the interval of 0.9—1.2 μm.

The refractive index (and, correspondingly, the birefringence parameter) as well as the film thickness was measured making use of the method of resonance excitation of the film optical modes in a waveguide and a prism coupler made up of a gallium phosphide crystal. The discrete optical modes with TE and TM polarizations were excited in turns in the film through the prism coupler at a certain radiation wavelength of a He—Ne laser ($\lambda = 633$ or 1150 nm). A high accuracy of monitoring the resonance angle of input at the optical mode excitation was ensured by the use of a G-5M goniometer.

The absorption of optical waves in the film is relatively weak and can be neglected when calculating the effective refractive indices of excited optical modes. The intensity of the testing beam was selected to be minimal to prevent photostructural transformations.

An irrefutable advantage of this method, in comparison with other conventional ones, e.g., with ellipsometric one, is its capability to immediately determine the refractive indices along each of two selected directions, one of them being in the plane of the film and the other one normal to the film. The relative accuracies of the refractive index and film thickness measurements were $\delta n/n = 10^{-4}$ and $\delta d/d = 10^{-3}$, respectively. The chemical content of the films was monitored with an accuracy of 0.5 at. %. The photoinduced anisotropy in the films was created by an Ar-laser beam ($\lambda = 514.5$ nm) incident normally to the film surface.

Experimental Results

The as-deposited As_xS_{1-x} films are characterized by relatively large (10^{-2}) values of the "intrinsic" birefringence. The optical anisotropy of the films was determined by a parameter $\Delta n = n_z - n_y$, where n_z and n_y are the refractive indices measured along polarization directions when the E-vector of the optical wave was perpendicular or parallel to the film plane, respectively. Note that this parameter was independent of the testing beam wavelength ($\lambda = 633$ or 1150 nm).

Fig. 1 exhibits the dark relaxation of the "intrinsic" birefringence in $As_{0.4}S_{0.6}$ films. The process is accompanied by an increase of the refractive indices n_y and n_z, with n_z varying faster than n_y. The variations of Δn, n_z, and n_y are the most significant just after condensation.

Such a behavior of the dark relaxation changes of the parameters concerned is typical of the As_xS_{1-x} specimens in the whole investigated range of the parameter x.

The maximal attainable absolute values of the "intrinsic" birefringence $\Delta n < 0$ as a function of the As content in the as-deposited specimens are depicted in Fig. 2. It is seen that the maximal values of $|\Delta n|$ were reached for the films with the content being in the neighborhood of $As_{0.3}S_{0.7}$.

The refractive indices of the films, as well as the birefringence parameter, vary substantially if the thermal annealing is applied. Fig.3 illustrates the changes in n_y and Δn for the $As_{0.3}S_{0.7}$ films after 1 h of their thermal annealing at various temperatures T_a. For the annealing temperature approaching the softening
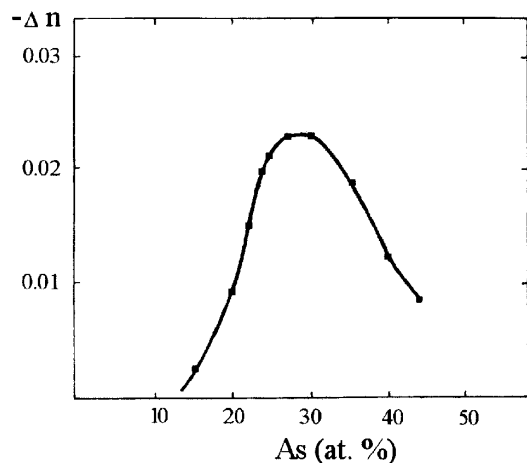
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Fig. 2. Composition dependence of the birefringence parameter $\Delta n = n_z - n_y$ for the as-deposited $As_x S_{1-x}$ amorphous films

Fig. 3. The refractive index n_y (1) and the birefringence parameter Δn (2) of the $As_{0.3}S_{0.7}$ film for the light with the wavelength $\lambda = 633$ nm after 1 h of annealing at various temperatures T_a

value T_g, the quantity Δn tends to values typical of the bulk glass. Accordingly, the birefringence parameter decreases. The film becomes practically isotropic at the annealing temperature of about 430 K. The maximal attainable changes of the birefringence parameter $|\Delta n|$ for $As_x S_{1-x}$ films are equal to 0.020–0.023.

As one should expect, the refractive indices and the birefringence parameter occurred to be markedly sensitive to the substrate temperature T_s. Note that when T_s increases, the value of n_y grows linearly and has a tendency to reach values typical of the bulk glasses ($n = 2.6$ for $As_{0.4}S_{0.6}$). This is quite natural since more homogeneous (from the chemical and structural points of view) and thermodynamically more stable films are formed just when being deposited on the heated substrates. An essential decreasing of $|\Delta n|$ for $T_s > 300$ K was also found.

Several comments concerning the properties of the specimens under investigation should be made. First, the phenomenon of "intrinsic" optical anisotropy was observed in the as-deposited $As_x S_{1-x}$ films only. The "intrinsic" birefringence is absent from the thermally annealed, at $T_a \leq T_g$, films of $As_x S_{1-x}$. Second, the "intrinsic" optical anisotropy is unstable, i.e. relaxes in time, if the specimens are hold in the dark at ambient temperature. Third, the anisotropy decreases if the films are irradiated by circularly polarized or unpolarized light. At last, all film specimens became amorphous after the treatment of any kind: annealing, irradiation, etc. This is confirmed by the results of electron diffraction and Raman scattering studies.

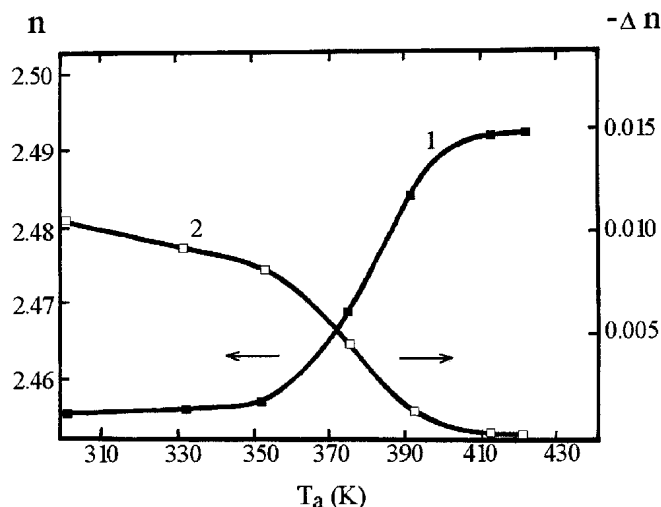In addition to the discovered "intrinsic" optical anisotropy, the appearance of the well-known
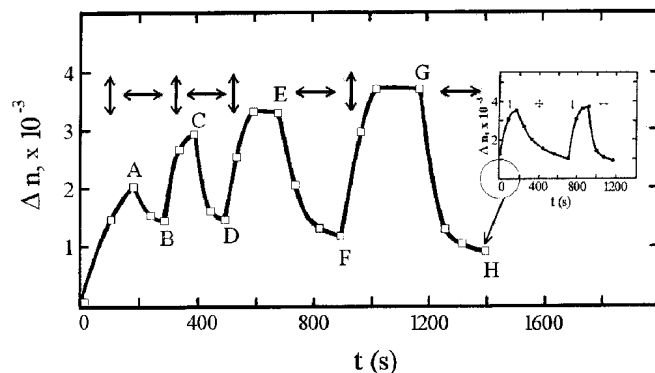

Fig. 4. Inducing and destroying the photoinduced birefringence $\Delta n = n_z - n_y$ in the amorphous $As_{0.4}S_{0.6}$ film by changing the polarization state of the linearly polarized light. Vertical and horizontal double-head arrows correspond to a polarization state of the laser beam ($\lambda = 514$ nm, $I = 60$ mW/cm^2). The inducing of the birefringence by the linearly polarized light and its destroying by a circularly polarized one is shown in the inset

photoinduced optical anisotropy is possible, in both the as-prepared and annealed film specimens, if linearly polarized light in the range of characteristic absorption irradiates them. The change of the incident light polarization results in inducing, destroying, or reproducing the birefringence along this or that orthogonal polarization direction in the film plane (Fig. 4). To destroy the birefringence, a circularly polarized light may be also applied (see the inset in Fig. 4). The cycles of the birefringence inducing/destroying are reproduced repeatedly.

While the "fresh-prepared" As_xS_{1-x} specimens are irradiated by a linearly polarized light, with the E-vector of the latter being successively orthogonally changed in the film plane, a reverse birefringence will arise and grow tending to the maximum. The value for the parameter of the reverse photoinduced birefringence ($\Delta n = n_y - n_x$) can be estimated (see Fig. 4) as a distance between points A and B, C and D, E and F, etc. The more the luminous flux density the faster the birefringence induction. But, in the intervals of saturation, the amplitude values of $|\Delta n| = |n_y - n_x|$ are almost independent of the exposition time. The similar kinetics of the creating or destroying of the photoinduced optical anisotropy is observed as well for the films previously annealed at T_g.

Discussion

First of all, it should be noted that we deal, most probably, with two independent phenomena. These are the "intrinsic" optical anisotropy of the thermally deposited films and the photoinduced one. Each of them is due to a certain external reason: the fabrication technology for the former and the polarized light irradiation for the latter.

The following plausible simple model can serve to explain the experimental results given above. It is of reason to suggest that the phenomenon of optical anisotropy in the as-deposited amorphous films is connected to the existence of optically active structural units. The latter are formed during the whole procedure of film fabrication from generally passive structural units, composed of the initial substance of glass. The optical anisotropy can reveal itself in a bulk specimen only above a certain concentration relation between those active and nonactive structural units. In the bulk glass, even anisotropic structural units, due to their relative orientation disordering, do not form anisotropic properties at the macrolevel. In contrast to this, amorphous materials, which are structurally more unstable, have the properties essentially dependent on the fabrication technology and further thermal treatment. We believe that, in the process of the amorphous film deposition, the anisotropic structural units are prone to orient themselves according to a certain preferential spatial orientation with respect to the condensation plane. The composed anisotropic structure is made "frozen" when condensating on a cooled substrate. The structural anisotropy manifests itself with respect to the directions, which lie in the film plane or are normal to it. In this case, the structural and physical properties of the material remain isotropic in the film plane.

An obvious experimental fact is a high instability of optically active structural units with respect to the thermal treatment or prolonged specimen storage after the deposition. Irreversible changes of the optically anisotropic properties are due to spontaneous dark relaxation transformations in the films at ambient temperature. Structural reconstructions and relaxation transformations, aimed at attaining the relatively more equilibrium state with a minimization of the free energy, cause the variations of the physical properties of the films, in particular, its refractive indices and birefringence parameter.

The characteristic features of the considered "intrinsic" optical anisotropy in "fresh" films allow us to suggest that the optically active structural units are capable to appear during the film deposition in vacuum and are "destroyed" by the following thermal treatment.

Let us consider probable structural units. The initial microstructure of the investigated thin films differs essentially from that for bulk glass and irreversibly changes after the annealing or irradiation by light from the absorption range of the film material. The availability of the molecular structural units As_4S_4 and As_4S_3 was confirmed by the Raman spectra measurements of the as-deposited $As_{0.4}S_{0.6}$ films [20–22]. Therefore, the as-deposited As_xS_{1-x} films (we take into account compositions in the vicinity of $As_{0.4}S_{0.6}$) contain the pyramidal AsS_3 units and the admixture of molecular units such as As_4S_4 (of the realgar type) and S_n. The presence of the so-called "irregular" homopolar bonds, as we think, is crucially important for the manifestation and further relaxational instability of the discovered "intrinsic" birefringence. Those units probably bear relation to the formation of the structural anisotropy. The processes of annealing or irradiation diminish the manifestations of the vibration modes of the bonds As–As in Raman spectra of the films concerned, which evidences for a remarkable decreasing of the molecule As_4S_4 concentration. Bond breaking and bond redistribution between atoms take place at those processes, which results in a structural polymerization. Such a film stands by its structure nearer to glass, being more isotropic.

The fact [23, 24] that the molecular nanoscale phase separation, where the crucial role belongs also to the structural units of the As_4S_4 type [24], is more pronounced in the amorphous As_xS_{1-x} films than in the vitreous-like specimens, may serve as an additional argument in favor of the suggestions made above.

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On the other hand, the extrema in physical properties are also observed in bulk specimens with the similar chemical contents [24, 25]. For example, the structure of glasses was found to become, in general, more stable and equilibrium if certain molecular units are available [24, 26]. Analogously, we explain the extremal value of $|\Delta n|$ in the films that include about 30 at. % of As by the influence of the structural units $S=AsS_{3/2}$, whose role is to optimize the process of partial polymerization of "separated" structural units. It was their presence that was connected with the anomalous and threshold manifestations of the structural properties of glasses in the vicinity of the As_2S_5 content [24].

Furthermore, we take into account that the as-deposited As_xS_{1-x} films may be characterized as those being made up of definite formations, i.e. peculiar quasicrystalline clusters. The evidence for this is as follows. The relation $n_\parallel^c > n_\perp^c$ between the refractive indices for the polarization directions parallel or normal to the layer, respectively, is typical of the As_2S_3 crystal. The cluster stratification may therefore be reflected in the "intrinsic" optical anisotropy of the as-deposited films. But here, additional experiments, including those with a structure-sensitive technique, would be necessary for more unambiguous analysis.

It is of interest to compare the values of Δn, shown in Fig. 2, and the parameters of natural birefringence in relevant crystals. In particular, for the amorphous As_2S_3 films, $\Delta n = -0.02$, while the crystal birefringence parameter is equal to -0.5 [27]. Moreover, for the photoinduced birefringence in an amorphous film, we have the value which is of about $1/10$ as much of the former and of about $1/100$ as much of the latter.

Fig. 5 schematically illustrates the process of photoinduced optical anisotropy in an As_2S_3 film. Here, the values of the refractive indices and the orientation of the supposed quasicrystalline clusters are shown depending on the E-vector orientation of the linearly polarized incident light.

Fig. 5. Schematic illustration of the clusters oriented by light with the horizontally (panel a) and vertically (panel b) polarized E-vector. Only several oriented clusters are shown for simplification. The values of the refractive indices and the transitions between mutually orthogonal states (a hatched region) for the $As_{0.4}S_{0.6}$ amorphous film are depicted on the top

formation of a film anisotropic microstructure, which reveals itself at the nanoscale level. Molecular units As_4S_4 and S_n are candidates for such structural elements.

In addition, a photoinduced birefringence in the amorphous films is considered. The model, which is based on the existence of optically active microstructural units, mainly in the form of layered clusters, is proposed to interpret the results.

Conclusions

An "intrinsic" optical anisotropy in the as-deposited As_xS_{1-x} films, whose optical axis is directed normally to the film plane, has been discovered. The optical anisotropy is unstable. The birefringence relaxationally diminishes while the specimens are being held in the dark, and disappears after the thermal annealing of the specimens or their irradiation by unpolarized light in the range of the film material absorption. The optical anisotropy of the "fresh" specimens are explained by the
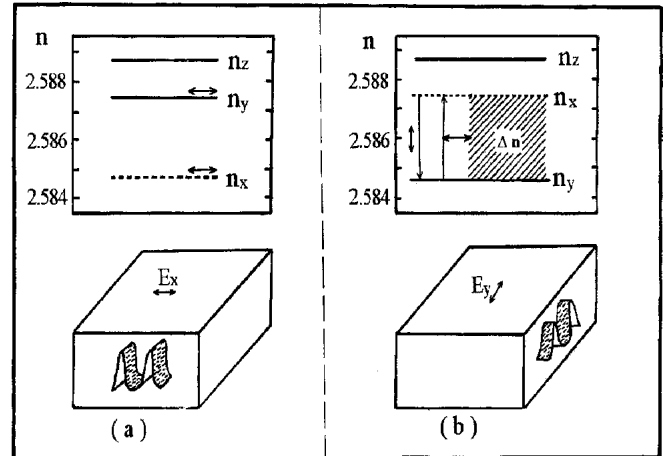
1. *Papel V.N., Edmond J.T.* // J. Opt. Soc. Amer.— 1982.— **72**.— P.644—647.

2. *Rajgopalan S., Horshavardhan K.S., Malhotra L.K., Chopra K.L.* // J. Non-Cryst. Solids.— 1982.— **50**.— P.29—34.

3. *Tanaka K.* // Jpn. J. Appl. Phys.— 1989.— **28**.— P.679—683.

4. *Yu P.Y., Cardona M.* // Phys. status solidi (b).— 1971.— **47**.— P.251—256.

5. *Gladkievicz R.K., Tuac J.* // Solid State Communs.— 1972.— **10**.— P.1261—1264.

6. *Weiser G., Dersh U., Thomas P.* // Phil. Mag. B.— 1988.— **57**.— P.721—723.

7. *Tanaka K.* // J. Non-Cryst. Solids.— 1990.— **119**.— P.243—252.

8. *Mazets T.F., Smirnova N.N., Smorgonskaya E.A., Tikhomirov V.K.* // Pis'ma Zh. Tekhn. Fiz.— 1992.— **18**.— P.46—49.

9. *Lyubin V.M., Tikhomirov V.K.* // J. Non-Cryst. Solids.— 1991.— **137-138**.— P.993—996.

10. *Tanaka K.* // The Encyclopedia of Materials: Science and Technology.– Oxford: Pergamon, 2001.

11. *Shimakawa K., Kolobov A., Elliott S.R.* // Adv. Phys.— 1995.— **44**.— P.475—588.

12. *Zhdanov V.G., Malinovskii V.K.* // Pis'ma Zh. Tekhn. Fiz.— 1977.— **3**.— P.943—946.

13. *Elliott S.R., Tikhomirov V.K.* // J. Non-Cryst. Solids.— 1996.— **198-200**.— P.669—674.

14. *Tikhomirov V.K., Adriaenssens G.J., Elliott S.R.* // Phys. Rev. B.— 1977.— **55**, N 2.— P.660.

15. *Krecmer P., Moulin., Stephenson R.J. et al.* // Science.– 1997.— **277**.— P.1799—1802.

16. *Tanaka K., Ishida K., Yoshida N.* // Phys. Rev. B.— 1996.— **54**.— P.9190—9195.

17. *Fritzsche H.* // Ibid.— 1995.— **52**.— P.15854—15861.

18. *Adriaenssens G.J., Tikhomirov V.K., Elliott S.R.* // J. Non-Cryst. Solids.— 1998.— **227-230**.— P.688—693.

19. *Ishida K., Tanaka K.* // Phys. Rev. B.— 1997.— **56**.— P.206—209.

20. *Nemanich R.J., Connell G.A., Hayes T.M., Street R.A.* // Ibid.— 1978.— **12**.— P.6900—6914.

21. *Mikla V.I., Vysochanskii Yu.M., Kikineshi A.A. et al.* // Izv. Vyssh. Ucheb. Zaved., Fiz.— 1983.— N 11.— P.73—77.

22. *Frumar M., Firth A.P., Owen A.E.* // J. Non-Cryst. Solids.— 1983.— **59-60**.— P.921—924.

23. *Grothaus J., Boolchand P.* // Ibid.— 1985.— **72**.— P.1—7.

24. *Boolchand P., Georgiev D.G., Qu Tao et al.* // Compte Rend. Chimie.— 2002.— **5**.— P.713—724.

25. *Wagner T., Kasap S.O., Vlcek M., Sklenar A.* // J. Mater. Sci.— 1998.— **33**.— P.5581—5597.

26. *Thorpe M.F., Jacobs D.J., Chubynsky M.V., Phillips J.P.* // J. Non-Cryst. Solids.— 2000.— **266-269**.— P.859—866.

27. *Zallen R., Blossey D.F.* Physics and Chemistry of Materials with Layered Structures.— Dordrecht: Reidel, 1976.

“ВЛАСНА” ТА ФОТОІНДУКОВАНА АНІЗОТРОПІЯ У СВІЖОВИГОТОВЛЕНИХ АМОРФНИХ ПЛІВКАХ As_xS_{1-x}

В.І. Мікла, В.М. Кришеник

Р е з ю м е

Досліджено оптичну анізотропію аморфних плівок As_xS_{1-x} у хвилеводному режимі. Показано, що свіжовиготовлені аморфні плівки, одержані традиційним способом, проявляють “власну” оптичну анізотропію (величиною порядку 10^{-2}) в напрямках, розміщених в площині плівки й перпендикулярних до неї. Для цієї анізотропії характерна релаксаційна поведінка, яка підсилюється термічним відпалом. Появу й характерні риси “власної” анізотропії аморфних плівок ми пояснюємо в рамках феноменологічної моделі з урахуванням структурних і хімічних особливостей свіжоосаджених плівок. Анізотропію плівок пов'язано з наявністю шаруватих утворень, які містять квазікристалічні кластери відповідного поляризаційного стану.