EVIDENCE FOR SELF-ORGANIZATION PHENOMENON IN AS-EVAPORATED AMORPHOUS CHALCOGENIDE FILMS

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The inherent optical anisotropy and relaxation structure evolution in fresh As-S(Se) amorphous films have been interpreted as the results of self-organized nanonetworks of non-crystalline solids. To explain the appearance and characteristic features of the intrinsic anisotropy a phenomenological model based on the structural and chemical peculiarities (distinct structural sites) of as-evaporated amorphous films has been suggested. Conventional photo-induced anisotropy has also been considered. The role of $As_4S(Se)_4$ structural units relating to the appearance of optical anisotropies in the films which possess the properties of dissipative structures is being discussed.

1. Introduction

The isotropy of the structure and properties is considered to be one of the characteristic features of the amorphous materials. However, at present for the one very important and unusual class of materials, namely chalcogenides, the techniques for producing the optical anisotropy (birefringence) have been suggested. These techniques may be classified into two categories. The first category includes the preparation procedures of bulk glasses and special methods to obtain amorphous films (see [1] and references therein). As for the second one, chalcogenide glasses are known to exhibit a variety of photo-induced anisotropic phenomena (see [2,3] and references therein).

H. Fritzsche [4] has noted that initial prerequisites for anisotropic properties to be realized in amorphous chalcogenides lie in the fact that "on the molecular scale the structure of chalcogenide glasses is strongly anisotropic". The original macroscopic isotropy originates from the random orientation of the microscopic anisotropic structural units.

On the whole, the possibilities of producing amorphous structures with the inherent optical anisotropy are defined by self-organization processes in non-crystalline materials [5-7]. For today the self-organization has been manifested in many inorganic glasses. The self-organization phenomenon is considered to be one of ponderable reasons for suppressing crystallization processes when liquid melts are vitrified, especially with low cooling rates. As a result of self-organization processes the amorphous structure itself incorporates microscopic anisotropic features, achieving the free energy minimum and avoiding redundant mechanical stresses at a temperature of formation [5]. Such subtle structural peculiarities are difficult to be revealed in diffraction experiments. Only indirect manifestations of the self-organization in networks of chalcogenide glasses are known, for example, the so-called thermally reversing glass compositional windows [8]. The mechanisms which condition on probable manifestations of macroscopic-scale optical anisotropy in non-crystalline solids, as well as the nature of those microanisotropic separate fragments which produce this anisotropy has not been ascertained so far.

The films of amorphous chalcogenides condensed under non-equilibrium conditions of vacuum condensation with respect to manifestations of self-organization phenomena are of great

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interest for researchers. Such films may be related to the so-called dissipative structures whose formation is just conditioned by self-organization processes [6, 9].

The appearance of the anisotropic local structural arrangement in as-evaporated amorphous chalcogenide films is caused by the combined effect of two main factors.

The first one is the quantum-mechanical interaction of particles coming from vapour with a growing film. It ensures passing chemical "assemblage" processes of the amorphous matrix (network) from vapour fragments. The second factor is the presence of anisotropically distributed local internal stresses in the amorphous film matrix during its formation [10]. Both factors exhibit the interdependence of actions, however each of them conditions the appearance of corresponding nano-inhomogeneities: structural-chemical and "mechanical" individually [6, 10, 11].

The structural-chemical inhomogeneity is connected with the interactions in the electronic subsystem and finds itself due to co-existence of different structural units in the amorphous matrix [10]. A typical scale of its manifestation makes up $0.3 \div 0.6$ nm. The "mechanical" inhomogeneity finds itself in the variation of density and elastic constants of the amorphous matrix. The anisotropy of distributing attractive and repulsive forces in interatomic interactions which occurs in the process of amorphous film growth serves as the source of "mechanical" inhomogeneity, or rather, inhomogeneities in local elastic coefficients [12]. The scale of such inhomogeneity makes up $2 \div 5$ nm.

Clustering and nanoscale molecular phase separation are known to be important manifestations for structural-chemical inhomogeneity in amorphous chalcogenides [13-16].

It should be born in mind that the films of amorphous chalcogenides are formed under noticeably non-equilibrium conditions. Therefore their structural state, whose formation is defined by spontaneous self-organization processes, exhibits the distinct internal metastability. The latter is a driving motive for various structural transformations and relaxation processes which take place both under the action of extremal influencing factors and spontaneously [13]. To our mind, the behaviour and intensity of such structural changes are to a great extent defined by the presence of structural-chemical and "mechanical" inhomogeneities in the films of amorphous chalcogenides. The peculiarities of changes in physical (macroscopic) parameters of films during structural transformations allow one to make certain conclusions as to the nature of spatial and spatial-temporal (dynamic) inhomogeneities of their structure. At the same time such data make self-organization mechanisms of amorphous chalcogenides clear.

A determining peculiarity of structural transformations in dissipative structures considered in the present work is their stochastic character. In other words, the relaxation or stimulated transition of some structural fragment (fragments) into a new topologic-energy state is not strictly determined but it finds itself as the probabilistic process. Therefore, while analyzing structural transformations in such objects it is expedient to make use of the ideology of the so-called geometrical frustration [6,17].

In this paper we have reported about significant intrinsic optical anisotropy (contrary to the photo-induced one) of the as-evaporated chalcogenide films. Our results suggest the appearance of the intrinsic optical anisotropy in these thin films be stipulated by the self-organization process during their formation and growth.

The intrinsic optical anisotropy examined in this article essentially differs in magnitude and relaxation kinetics both from the conventional photo-induced anisotropy [2, 3] and the photo-induced anisotropic crystallization [18].

2. Experimental

The experiments were carried out on as-evaporated (fresh) As_xS_{1-x} ($0.20 \leq x \leq 0.43$) and As_ySe_{1-y} ($0.15 \leq y \leq 0.50$) film samples. As_xS_{1-x} films were prepared by the standard vacuum evaporation. As_ySe_{1-y} samples were prepared by the flash thermal evaporation method in vacuum ($p = 5 \cdot 10^{-3}$ Pa). The film composition is relatively uniform over the film thickness, as can be seen from electron probe microanalysis data. A typical evaporation rate was $3-4$ nm·s^{-1}. The film thickness ranged from 0.9 to 1.5 μm.

A prism-coupling technique was used to measure the refractive index, birefringence and thickness of the amorphous films. The experimental arrangement is as follows. A guided wave of $\lambda=633$ nm (or 1150 nm) was generated with a GaP prism. To avoid possible photostructural changes in case the 633-nm wavelength was used, the probing light intensity was reduced to sufficiently low values. The wave-guiding technique ensures significant and distinct advantages over traditional techniques, e.g. ellipsometric method, namely the ability of the refractive index to be determined independently in the film plane and perpendicularly to it [19]. The accuracy of the refractive index and the film thickness measurements is $\delta n/n=10^{-4}$ and $\delta d/d=10^{-3}$, respectively. The photo-induced anisotropy was stimulated by an Ar-ion laser ($\lambda=514.5$ nm), its beam propagating normally to the film surface. All experiments were carried out at room temperature.

3. Results and discussion

A relatively high (10^{-2}) intrinsic birefringence is observed in As_xS_{1-x} [20,21] and As_ySe_{1-y} [22] films immediately after their deposition. The optical anisotropy of as-evaporated amorphous films was determined as $\Delta n = n_z - n_y < 0$, where n_z and n_y are refractive indices measured with the light for which the electric field vector runs perpendicularly to the film plane and in the film plane, respectively. It should be mentioned that the refractive index in the film plane is uniform, i.e. $n_x=n_y$.

Fig.1 shows compositional dependencies of the maximal values of the **intrinsic** birefringence Δn for As_xS_{1-x} amorphous films as a function of As content in samples. It was found that the maximum of $|\Delta n|$ in fresh films (curve 1) is located around $As_{0.3}S_{0.7}$ composition. The intrinsic birefringence diminished during storage of the samples in the dark (approximately three months) or about one-month storage under conventional laboratory illumination (curve 2) [20, 21]. Both in the first and second cases, the magnitude $|\Delta n|$ reaches a certain level of its own metastable saturation. After reaching this state the birefringence reduces in three times and corresponding refractive indices n_x, n_y and n_z increase greatly.

The thermal annealing of the films under study at $T_a \leq T_g$ gave $|\Delta n|=0$. The refractive index of films takes the values close to typical ones for corresponding bulk glasses (for example, $n \approx 2.60$ for bulk As_2S_3 [23]). Compositional dependences Δn obtained for virgin As_ySe_{1-y} amorphous films are quite similar in behaviour [22]. The intrinsic birefringence $|\Delta n|$ achieves maximal magnitudes in the vicinity of As_2Se_5 composition.
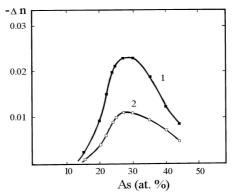

Fig.1. Compositional dependencies of the birefringence $\Delta n = n_z - n_x$ for As_xS_{1-x} amorphous films taken immediately after the sample deposition (1) and after a month storage under conventional laboratory illumination (2) (after [21]).

These isostructural correlations indicate to the fact that the effect of intrinsic optical anisotropy is conditioned by common peculiarities of the structure of fresh amorphous films. Taking into consideration the physical essence of the birefringence phenomenon one may consider that anisotropic microstructural fragments exist in the amorphous matrix of such films. As refractive indices $n_x = n_y \neq n_z$, these fragments do not have to disturb the isotropic character of amorphous

network macrostructure in the film plane. The As-S(Se) system comprises the well-known objects whose structure is completely formed from fragments of similar kind . For example, here belong c-As$_2$S$_3$ crystals (orpiment) and c-As$_2$Se$_3$ crystals, which have a layered structure. These crystals possess the natural birefringence. For example, for c-As$_2$S$_3$, $\Delta n_n = n(s) - n(l) < 0$; $n(s)$=2.5 (on the average) and $n(l)$=3.0, which are in-plane and out-of-plane refractive indices, respectively. Moreover, from the point of qualitative aspect the refractive indices $n(s)$ and $n(l)$ in crystals somehow agree with the relation $n_z < n_y$, and $n_x = n_y$ found for as-evaporated films. That's why we believe that it can be logically assumed that the structural base for the appearance of birefringence in c-As$_2$S(Se)$_3$ crystals and intrinsic optical anisotropy in a-As$_x$S(Se)$_{1-x}$ amorphous films with $0.20 \leq x \leq 0.40$ is one and the same: i.e. the availability of layered structural fragments. It is clear that the structure and spatial topography of layered fragments are essentially different in crystals and films. For crystals these are flat layers with strict crystallographic ordering in the arrangement of atoms. And what can layered fragments represent in amorphous films? To answer this question one should analyze some important moments.

Firstly, when crystals, bulk glasses and films in As-S(Se) systems are formed one and the same driving forces act which are related to self-organization processes in them. First of all, this is quantum-mechanical (chemical) interactions between As and S(Se) atoms. However, their action is observed under drastically different conditions. Optically active crystals grow under equilibrium crystallization conditions, whereas the films with inherent optical anisotropy are formed from deposited vapours on cold substrates in vacuum. Optically isotropic glasses are formed with fast cooling of the melt. Thus, when the objects under study being thermodynamically open and far from thermodynamic equilibrium system are formed, external conditions influence their terminal structure actively.

Secondly, certain condensation conditions ensure the formation of self-organized structures with optical anisotropy for a relatively wide interval of chemical composition for films of As-S(Se) system. Though these anisotropic materials are mainly produced at the certain control parameter values (for example, condensation rate or substrate temperature), however the action of the self-organization factor ensures the formation of layered structural fragments in the films of mentioned systems under the conditions of a wide change in correlative concentrations of arsenic and sulphur (selenium) atoms.

Thirdly, peculiarities of birefringence manifestation in c-As$_2$S(Se)$_3$ crystals and the inherent optical anisotropy in As-S(Se) films give a possibility to make a logical supposition: layered structural fragments in the amorphous matrix of films are formed with greater probability in the orientation of their own plane parallel to the substrate plane.

To our mind, consideration of mentioned peculiarities in their inseparable unity testifies to the fact that the reasons for the formation of layered structural fragments with appropriate topological and orientation parameters are completely defined by combining the definite technological conditions of vacuum condensation process and the self-organization ones in As-S(Se) films. As it is known [24], the main structure-forming factors of these processes are as follows:

1. chemical composition and energy state of vapour phase particles;
2. sharp anisotropic conditions of condensation processes with respect to parallel or perpendicular directions to the substrate plane;
3. energy activity of particles adsorbed from vapour phase on the growing film surface.

How can these factors direct self-organization processes to the formation of anisotropic structural fragments? The analysis of mass-spectra for vapour phase during evaporation of crystals and glasses of different chemical composition in As-S and As-Se systems [25] gives the following results. Complex mass-spectra were obtained in all articles without any exception. For substances of similar compositions they were close not only by a qualitative set of vapour components but by a quantitative ratio of them. By averaging the results in [25], all vapour particles can be divided into three main groups: chain-like (X$_n$, де n=2, 3, 4, 5, 6, 7); "two-dimensional" (AsX, As, As$_2$X, As$_2$X$_2$, As$_2$X$_3$, As$_2$X$_4$, As$_3$X$_2$ та As$_3$X$_3$); molecule-like: (X$_8$, As$_3$X$_4$, As$_4$, As$_4$X$_4$, As$_4$X$_3$), where X=S, Se. In Table 1 the quantitative estimate of relative parts of the atoms from each group of vapour particles depending on the substance composition is given.

First of all, we will stress that structure-forming processes in films are stochastic-agglomeration ones to a great extent. Vapour phase particles from each group (see Table 1) will take part in the formation of self-organized nanonetworks of the film during its growth differently. Their

geometric parameters should agree to the topology of the growing film surface. For two-dimensional particles their connectivity into separate layers with prevailing orientation parallel to the film plane will be energetically more favourable. Just these vapour particles condition the formation of structural fragments responsible for the appearance of optical anisotropy. The correlation in compositional dependences of $|\Delta n|$ parameter (Fig. 1) and relative part of atoms belonging to two-dimensional components confirms this fact. Molecule-like vapour components are mainly implanted into the growing amorphous matrix of the film forming "isolated" molecular (zero-dimensional) structural fragments. For their transition into an "open" planar-like configuration certain magnitudes of the activation energy (denoted by ΔE) are necessary. To our mind, the magnitudes of this energy for the majority of molecular-like structural fragments correspond to the level at which the time of their probable "opening" $\tau \sim \exp(-\Delta E/k \cdot T_S)$ (here k-Boltzmann constant, T_S – the substrate temperature) will be much larger than that of nanonetwork "freezing" in the film. Probably, during condensation a minor part of molecular-like structural fragments manages to "be open" and connected into two-dimensional or three-dimensional structural fragments of the amorphous matrix. Chain-like vapour fragments as the most mobile are able to form separate one-dimensional fragments of the amorphous network and incorporate into two- and three-dimensional structural fragments of the film matrix.

Table 1. Compositional dependences of vapour fragments with different topological and oriented structure in percentage.

Composition	Percentage part of atoms in chain-like vapour components,	Percentage parts of atoms in "two-dimensional" vapour components, %	Percentage part of atoms in molecule-like vapour components, %
$As_{10}X_{90}$	65	20	15
$As_{20}X_{80}$	25	60	15
$As_{30}X_{70}$	15	70	15
$As_{40}X_{60}$	10	60	30
$As_{44}X_{56}$	5	55	40

Taking into account correlative parts of three different types of particles and their noticeably different role in the formation of the amorphous atomic network we consider that the structure of films in As-S(Se) systems may conventionally be related to one of three hypothetic models. With As content less than 20 at. % in the films the atomic chains of different length bound between themselves are the main structural fragment of films. In separate sites small "pieces" of two-dimensional layered formations are incorporated into these chains. Just in such sites the "knots" are formed where some separate one-dimensional chains are branched. In other local sites of the amorphous matrix between chains some molecule-like fragments may be wedged.

For fresh films with 20-40 at. % As the amorphous matrix is modeled by corrugated and bent layers of different size in three-dimensional space. In some sites these layers can be connected by "bridges" between themselves. Molecule-like structural fragments are concentrated between such layers. With increasing the concentration of arsenic atoms more than 40 at. % the sizes of typical layered sites will decrease up to the magnitudes ratable to those ones of molecular fragments. Therefore, in a reasonable structural model the layers and separate molecules can be considered as chaotically "mixed" and partially connected by short bridges between themselves.

The films possessing the birefringence are related to the second structural model. That is why the amorphous network can be described in the form of large corrugated and bent layered clusters built, mainly, from $AsS(Se)_{3/2}$ pyramidal units [26]. Between them some $As_4S(Se)_4$, $As_4S(Se)_3$ and, to a lesser extent, S_8 and As_4 molecule-monomers are implanted, their presence in As-rich as-deposited films being strongly supported by Raman scattering measurements [27-29]. The layered clusters themselves possess prevailing orientation of their own plane parallel to the film plane. Such orientation reflects a combined structure-forming effect of anisotropy elements from both main two-dimensional vapour components and orienting plane – the surface of the growing film.

The concentration of molecular fragments in As-rich films can reach 10-35 at. % [15,26], that agrees qualitatively with the data of Table 1. Hence, under suitable preparation conditions of films with 20-40 at. % As self-organization processes result in specific nanostructures with simultaneous manifestations of clustering and molecular phase separation. Similar self-organization processes at synthesis of appropriate glasses from melts result in the formation of analogue clustered structures with much less molecular phase separation. In the glass matrix part of molecular fragments is considerably less and layered fragments possess equally-probable orientation of their own planes.

The "separated" structural layers (large layered clusters) in virgin films are connected between themselves under the action of weak Van der Waals bonds only. Large layered clusters themselves consist of pyramidal structural units and a small concentration of connected atomic chains. In the formed amorphous network heteropolar As-S(Se) bonds prevail. Alongside some homopolar bonds are present. This is important for the appearance and subsequent relaxation instability of the inherent birefringence. Meanwhile, a two-dimensional property of the structure helps to realize minimal local stresses within such large clusters.

The orienting influence of the growing film surface and initially weak Van der Waals interaction between large layered clusters define their prevailing mutual orientation in the film plane. Molecular monomers, "wedging in" between layers, increase the effect of their relative "separation". They are able to cause the local deformation of layered clusters, disturbing their mutual plane orientation. The respective peculiarities of the structure will be more distinct in the vicinity of those sites of large layered clusters, where the latter are connected by "bridge" atoms or short chains between themselves. As a result a pronounced anisotropy of the structure will be observed in the amorphous matrix of as-evaporated films. Due to its existence we have the birefringence effect.

The films with self-organized nanostructures are noticeably unstable. Intense relaxation structural changes under natural storage, annealing and band-gap illumination take place in them [20-22]. The nature of these changes lies in breaking and switching of the chemical bonds between different atoms. These structural transformations are of stochastic character, i.e. the time evolution of this system depends on the reasons unpredicted with absolute accuracy [6]. Weak homopolar bonds of molecular fragments are considered to play a dominant role in these changes. In particular, when As-As bonds are broken, partial (one broken bond) or full (two broken bonds) opening of realgar-type of $As_4S(Se)_4$ molecules with the change of their cage-like configuration by a planar-like one takes place.

Newly-formed planar-like structural fragments in two possible configurations are connected with neighboring large layered clusters. New chemical bonds noticeably change the structure of large layered clusters. Firstly, their prevailing orientation parallel to the film plane is lost when mutual "sewing together" of these clusters occurs. The anisotropy of the refractive index decreases, respectively. Secondly, in the sites of the connection of large layered clusters with planar-like structural fragments the appearance of additional mechanical stresses is possible. Similarly to [16] this can be considered as achieving the features of stressed rigid state by the initial local-stress-free amorphous network.

Wholly, in the relaxation process the cross-linked structure of films noticeably approaches the structure of corresponding glasses, which is described by the stacked distorted layer model [30]. The refractive index of films becomes close to that of bulk glasses, respectively [20]. The results of studying the Raman scattering measurements testify to this fact [27-29]. After annealing or band-gap illumination the Raman spectrum of the film becomes close to that of the bulk glass except for some remaining bonds of As-S(Se) bending bond vibration, indicating to the presence of a small amount (a few per cent) of $As_4S(Se)_4$ molecules. The essence of such irreversible relaxation structural changes in as-deposited films quite corresponds to the model of polymerization transformations [26]. The results of electron-diffraction studies of relaxation evolutions in As-Se films confirm this conclusion [31-32]. The changes in the intensity and position of FSDP and maxima of RDF indicate to the fact that main changes in these transformations take place outside the first coordination sphere.

The additional information as to the self-organization nature of inherent optical anisotropy in fresh chalcogenide films is given by the change in $|\Delta n|$ and refractive index in the film plane with varying the substrate temperature T_S at condensation (Fig. 2). The linear growth in n_x (n_y) with

increasing T_S reflects the same structural transformations when the film structure in relaxation transformations approaches more isotropic and stable structure of the glass. Thus, at higher temperatures T_S in the films during condensation those relaxation processes are able to take place whereas at ambient temperature they last for tens of days. The non-monotonic dependence $|\Delta n|$ vs. T_S is more interesting. The decrease in $|\Delta n|$ at $T_S > 300$ K is also explained by the intensification of relaxation processes. The decrease in $|\Delta n|$ with decreasing the substrate temperature below 300 K is unexpected. We believe that this fact is first of all due to the decrease in the activity of vapour components under such conditions.

Based on the above data it follows that the self-organization processes in As-(S,Se) as-evaporated films greatly depend on external factors. In particular, the formation of large layered clusters is possible at sufficient energy and migration activity of vapour particles only. Such activity allows them during their stay on the growing film surface to move and reorient for the most stable connectivity in the amorphous film matrix, more precisely in large layered clusters. The decrease in T_S suppresses this activity. As a result the vapour components are connected in the film matrix more chaotically and disorderly, forming greatly deformed corrugated layered structural fragments with noticeably smaller sizes. That is why the latter can't be related to large layered clusters. With such shape of layered fragments any prevailing orientation parallel to the surface disappears. Consequently, the optical anisotropy decreases.

So, with decreasing the condensation temperature of the film the self-organization processes related to the formation of optically anisotropic structure are suppressed. The similar strong influence on self-organization processes was observed by us through other technological parameters at condensation of As-(S,Se) films [20-22]. Such threshold behaviour as to external factors is typical for synergetic systems. It reflects stochasticity and a threshold character over the dynamic displacement amplitudes and the fraction of atoms in the soft configurations [6].
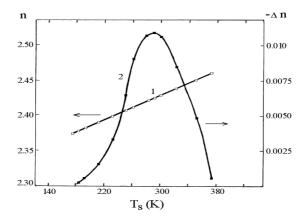

Fig. 2. Refractive index n (1) measured at $\lambda = 633$ nm for the polarization direction lying in the film plane and the birefringence Δn (2) for amorphous $As_{0.4}S_{0.6}$ film as a function of the substrate temperature T_S (after [20]).

As we consider, taking these peculiarities into account can allow one to prepare the films with optical anisotropy for other materials and systems as well. It will require the choice of proper condensation conditions with the activation of the processes for forming large layered clusters in the amorphous matrix of the films. The peculiarity of As-S(Se) films is the fact that the preparation conditions of specific anisotropic structures coincided with conventional vacuum condensation ones.

At first sight, it seemed possible to expect a noticeable increase in $|\Delta n|$ for the films prepared at low T_S at their warming-up to ambient temperatures in the post-condensation period. Such behaviour was not observed in reality. This is due to the fact that the conditions favourable for self-organization processes of films during their preparation can't be practically realized in the amorphous matrix being already formed. Spontaneous reorientation and diffusive displacement for quite large-scale sites of the atomic network with the formation of large layered clusters having a certain spatial orientation become impossible. Besides, the system itself stops being

thermodynamically open, and for suitable stochastic transformations a very important external orienting factor – two-dimensionality of the growing film surface – is lost.

Meanwhile, for the materials of As-S(Se) systems with 20-40 at. % As an "intrinsic" orienting motive – the anisotropy of two-dimensional structural units is constantly present. The possibilities of manifesting this orienting factor in macro-parameters of the substance may be created only when the additional external orienting (anisotropically directed) factor – for example, the electric field is involved.

Indeed, in addition to the above-mentioned intrinsic anisotropy, the conventional photo-induced anisotropy can be independently produced when As_xS_{1-x} "fresh" or annealed samples ($0.20 \leq x \leq 0.40$) were subjected to the linearly polarized band-gap light (Fig.3). By alternating the polarization states of the light the birefringence can be induced and erased. The erasure can also be produced by the circularly polarized light (see the insert in Fig. 3). The inducing/erasing cycles for the birefringence can be run repeatedly. The amplitudes of a quasi-reversible birefringence are the distance between points A-B, C-D, E-F, etc. (Fig.3). Almost the same behavior of the inducing and erasing photo-induced birefringence is typical for the annealed films.
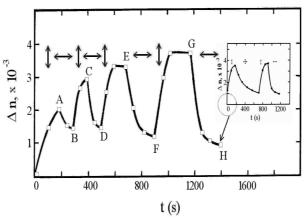

Fig. 3. Inducing and erasing of the photo-induced birefringence $\Delta n = n_z - n_y$ in amorphous $As_{0.4}S_{0.6}$ films by alternating the polarization state of linearly polarized light. Vertical and horizontal arrows denote the polarization state of $\lambda = 514$ nm beam (I = 60 mW·cm^{-2}). The insert shows the inducing of the birefringence with linearly polarized light and its erasing by circularly polarized light.

At it is seen from the compositional dependence of photo-induced reversible birefringence for the as-evaporated and annealed films (Fig. 4), the two curves show nearly the similar character up to 30 at. % As.

One should pay attention to the fact that the compositional dependences of inherent (Fig.1) and photo-induced (Fig.4) optical anisotropies are different. The inherent anisotropy has a maximum in the vicinity of 30 at. % As and correlates with the concentration of "flat" vapour particles. However, the magnitude of photo-induced anisotropy grows monotonically with increasing As part and correlates with the concentration of molecular-like vapour particles.

It was earlier stated by us that for this compositional range the short-range order of the atomic structure of As-Se films may be described by the model, which considers the combination of pyramidal $AsSe_{3/2}$, quasi-tetrahedral $Se=AsSe_{3/2}$ and some other structural units [31,32]. They are defined as basic building blocks of disordered self-organized networks of the films with compositions in the vicinity of 30 at. % As. We believe that the maximum in the concentration dependence Δn (Fig. 1) is due to availability of large layered clusters of $S(Se)=AsS(Se)_{3/2}$ structural units. For analogue glasses presence of such structural units is very important with regard to some peculiar properties of their elastic backbones. Such glasses are defined as those relating to the so-called intermediate phase [8, 33].
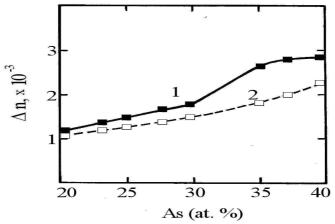
Fig. 4. Compositional dependences of the maximal achieved photo-induced reversible birefringence in "fresh" (1) and annealed (2) As_xS_{1-x} amorphous films.

The manifestation of nanoscale phase separation effects in films masks more subtle elastic ones related to rigidity transitions. The appearance of large layered clusters with well-coordinated $S(Se)=AsS(Se)_{3/2}$ structural units in the amorphous network optimizes self-organized two-dimensional layered structures of the films with compositions in the vicinity of $As_2S(Se)_5$. Taking into consideration the appearance of inherent anisotropy such optimization can be interpreted as follows.

Firstly, the manifestation of anisotropy is due to large layered clusters in the matrix of the film. The optimal chemical composition for such clusters is $As_2S(Se)_3$. At 30 at. % As the film composition is noticeably enriched in sulphur or selenium in comparison with the optimal one. The excess of S(Se) is more pronounced because of a considerable part of As – rich molecular-like clusters. As a result large layered clusters for films in the vicinity of 30 at. % As are noticeably enriched in chalcogen. The $S(Se)=AsS(Se)_{3/2}$ s.u. bind the excess of chalcogen in large layered clusters with optimal pyramidal configurations. Consequently, the formation of some short chains consisting of S(Se) atoms is blocked. As a result the sizes are reduced and large layered clusters fail.

Secondly, molecular-like structural fragments are wedged between large layered clusters, "forcing them out". In such local sites the layers gradually diverge, forming the voids. These voids can be energetically favourable when double S(Se) = As bonds in large layered clusters are formed.

Note that the optimization of the film structure by $S(Se)=AsS(Se)_{3/2}$ structural units does not only set the maximal optical anisotropy but ensures the minimal attenuation of guiding optical modes in thin-film waveguides of the corresponding compositions [22]. On the other side, we incline to consider that an important role in the relaxation reduction of inherent optical anisotropy is also played by processes where molecular fragments and sites of large layered clusters with $S(Se)=AsS(Se)_{3/2}$ s. u. take part. Summarizing the above relationships, we stress the importance of molecular phase separation in the manifestation of optical anisotropy effects in as-evaporated films.

The mechanism of photo-induced anisotropy in chalcogenide materials has been discussed already [2-4,34], but its microscopic nature has been unclear and controversial so far. We prefer those models which are based on mesoscopic structural changes through co-operative fragmentary arrangements for photo-induced anisotropy (linear dichroism and birefringence) [34-36]. A lot of experimental results count in favour of such models: 1. The behaviour of changes in low-frequency Raman spectra with illumination of the polarized light [3,35]. 2. EXAFS analysis data of light polarization-dependent structural changes in As-Se films [37]. 3. Kinetics of photo-induced dichroism [38] and birefringence [34] in amorphous chalcogenides, which are described by stretched exponential functions (the Kohlraush's exponential law). Besides, this kinetics indicates to the existence of some hierarchy in structural organization of the system where corresponding metastable transformations are realized [6].

The above–mentioned correlation in compositional (concentration) dependences of the amplitude of photo-induced anisotropy and the concentration of $As_4S(Se)_4$ molecules justifies an important role of these clusters embedded in the glassy matrix in the process of this anisotropy being

induced. The authors of articles [37,39] are of the same opinion. To our mind, the phenomenological microscopic mechanism of optical anisotropy may be described by polymerization-depolymerization processes [40]. The main role in such processes is given to dynamic spatial rearrangement of atomic bonds in the sites of "contacting" of large layered and "closed" isolated $As_4S(Se)_4$ molecules between themselves. At illumination of samples by the linear polarized light some As-As bonds of such little clusters preferentially "break" which were approximately parallel to the electric field vector of the light. At the same time some homopolar As-As bonds perpendicular to the electric field vector are restored with the participation of $As_4S(Se)_4$ molecules [39]. Such corporative dynamic microscopic reconstructions result in photo-induced optical anisotropy. Note that with illumination the redistribution of local mechanical stresses has to occur in the nanostructured film matrix. These local stresses are anisotropic by themselves. We emphasize that the elastic energy is one of main driving motives at dynamic energy redistributions from microscopic degrees of freedom to co-operative ones, and vice versa. Similar conceptions agree well with that of the film medium of amorphous chalcogenides as dissipative fluctuational structures. The characteristic (with distinct maxima) temperature and spectral variations of photo-induced birefringence in As_2S_3 films may be an indirect support of this statement [34].

Fig.5 illustrates the microscopic model of photo-induced anisotropy proposed by us which shows the refractive index value and the orientation of separated "optical-active" structural clusters forming the layers respective to the orientation of the electric field vector of linearly polarized light. These layers are seen to be oriented perpendicularly to the electric field vector. The refractive index values in Fig.5 correspond to $As_{0.4}S_{0.6}$ film.
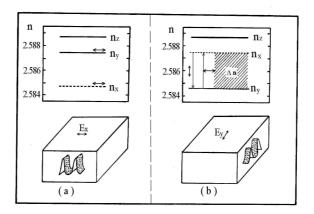

Fig. 5. Schematic illustration of oriented layer clusters which can be produced by linearly polarized light with horizontal (a) and vertical (b) directions of electric vector orientation. For the sake of simplicity, only parts of "oriented" clusters are illustrated. The upper part shows the refractive indices and the transitions between the mutually orthogonal states (shadowed area).

Summarizing the analysis conducted we state the following.

1. Self-organization phenomena are of great importance while forming the films of As-S(Se) systems. They lead to the realization of nanostructural clustering and nanoscale molecular phase separation in the structural network of these films.

2. The anisotropy of the inherent structure for a considerable part of vapour phase particles and that of their condensation conditions parallel and perpendicular to the film plane favour the formation of specific structural anisotropy of the amorphous network of As-S(Se) films.

3. The structural anisotropy of as-deposited As-S(Se) films creates their inherent optical anisotropy. The structural relaxation of films in post-condensation period causes the decrease in the inherent optical anisotropy.

4. Under certain conditions at illumination of As-S(Se) films the structural changes with 'memorization" of new structural states of its previous topological structure take place in the

amorphous matrix of films. Structural transitions between these metastable states condition on reversible photo-induced anisotropy.

5. Separated molecular $As_4S(Se)_4$ structural units are of great importance for both reversible and irreversible optical anisotropies.

6. Structural mechanisms which condition on the effects of stimulated optical anisotropy include complex dynamic corporative reconstructions of chemical bonds and changes with redistributions of local mechanical stresses in the amorphous matrix of films.

4. Conclusions

The inherent optical anisotropy in as-evaporated As-S(Se) films has been observed, its axis being normal to the film plane. It has been shown to be unstable, diminishing during the sample storage in the dark, disappearing under annealing and illumination by the unpolarized light. The appearance of the anisotropy results from the self-organization phenomena (nanostructural clustering and nanoscale phase separation) in virgin samples.

$AsS(Se)_{3/2}$, $S(Se)=AsS(Se)_{3/2}$ and especially $As_4S(Se)_4$ and $S(Se)_n$ ones are considered to be basic molecular units initiating the formation of the anisotropic structure.

The photo-induced birefringence has also been considered. The model based on anisotropic deformation of the distorted layer clusters has been proposed to explain photo-induced anisotropy.

The synergetic approach to the formation of amorphous thin films and post-condensed behavior of the amorphous chalcogenide films has been discussed.

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