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Stimulated relaxational transformations in amorphous chalcogenide films

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Irreversible changes of refractive index of as-deposited As_xS_{1-x} amorphous films in course of physical ageing is studied using a prism-coupling technique. These changes result from an initiating effect of an optical mode in the film waveguide. It is shown that amorphous chalcogenide films can undergo structural and “mechanical“ relaxational transformations triggered by sub-bandgap light irradiation. An approach based on floppy modes is proposed to understand the response and irreversible relaxation changes of structural, mechanical and optical properties of nanoinhomogeneous amorphous chalcogenides.

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1. Introduction

The main properties of amorphous chalcogenide films deposited in vacuum noticeably differ from those of bulk glasses. The basic reason for these differences lies in the methods of obtaining the non-crystalline materials providing different types of phase transitions between states of aggregation of matter. In comparison with glasses, amorphous films possess much higher degree of the state non-equilibrity. Films are characterized by much more intense flow of long-time relaxational changes of structural characteristics and a number of structurally sensitive properties due to their physical ageing and under external factors of low intensity [1-6].

Specific features of the non-equilibrium state of amorphous films can be affected by the presence of effects of surface interphase interaction at the substrate/film and film/environment interfaces. Film media are characterized by sample geometry, close to 2-dimensional, when directions, parallel and orthogonal to the substrate are, in general, non-equivalent. Evidently, these results in an even greater discrepancy in the behaviour of films and glasses since for the former interfacial interactions can enhance probability of appearance of anisotropic and statistically inhomogeneous properties [7-9]. Both substrate attraction and simple size effects substantially influence morphology and location of so-called “weak spots” and “voids” preferentially formed in the film volume which can possess preferential spatial orientation [8,10]. Usually for their consideration a concept of “free volume” is invoked. The above voids are considered as low electron-density configurations [10].

While in out-of-equilibrium state, amorphous chalcogenide As_xS_{1-x} ($0.18\leq x<0.44$) films under consideration in the post-condensational period are characterized by particularly essential changes of their properties [9]. The reason for such behaviour is derived from the consequences of structural transformations of mostly polymerizational type which noticeably modify structural state of a disordered medium at intermediate and mesoscopic order. The most noticeable irreversible changes are supposed to result from multiple acts of cooperative transformations of local structural regions [9]. Durable processes of self-relaxation transformations (i. e. not induced by additional external factors) should not be treated as exclusively thermally activated; they are to an essential degree controlled entropically. As-deposited fresh As-S films under investigation are characterized by complex transformation processes in which a greater part of the amorphous matrix atoms participate. Hence comes the necessity of finding internal driving forces enabling the acts of cooperative atomic rearrangements (local relaxation events).

In our analysis we dwelt upon a clear affinity of relaxation changes of structural, mechanical and optical characteristics for as-deposited amorphous chalcogenide films [9,11,12]. We took into account that due to pronounced spatial and dynamical inhomogeneities, typical for as-deposited amorphous film media, the latter demonstrate a relaxational behaviour typical for so-called weakly-connected networks. Besides covalent non-crystalline materials, this category also includes Alexander’s soft materials [13], models of static forces in granular packs [14], rigidity percolation models [15] etc.

While considering non-ergodic systems in modeling irreversible structural and "mechanical" relaxation transformations, the possibilities of traditional molecular dynamics are essentially limited [16]. Instead, a concept of potential energy landscape appears much more promising and fruitful [17]. For topologically disordered media one can explore only a restricted portion of total phase space. In other words, only a limited ranges of length and time scales can be probed. For weakly connected networks of amorphous chalcogenides intense structural transformations require multiple acts of cooperative atomic rearrangements when the role of so-called floppy modes becomes decisive. The latter are collective modes potentially capable to propagate at the distance between any particles in a nanoinhomogeneous medium. The nonlocality of the floppy modes suggests relaxation via extended events. Such system more efficiently explores inherent structures (local energy minima [17]). For amorphous chalcogenides the possibility of irreversible transformations is provided by cumulative and competing effects at self-consistent interactions for separated conditionally rigid and soft atomic configurations [9].

It should be emphasized that formation of the disordered medium of an as-deposited amorphous film is accompanied by formation of non-uniformly distributed local internal mechanical stresses which may play very different roles in subsequent evolutional changes. As we had noted earlier, in disordered media the stored elastic energy is treated as one of the main driving motives (forces) at dynamic redistributions of energy from microscopic degree of freedom to cooperative ones and vice versa [18]. In the configurational space of the amorphous medium cooperative degrees of freedom will be activated, what results in interactions of a higher (mesoscopic) hierarchical level being involved in the transformation processes.

Understanding of interrelation and interdependence of the relaxational behaviour of structural and mechanical characteristics of As-S amorphous films is even more important because of the real prospects of involvement of chalcogenide materials in nanofabrication applications. On the other hand, conditions of reliable functioning of optoelectronic and integrate-optic devices where applications of amorphous chalcogenide films are desirable, should be specified.

Here we present the studies of post-condensation changes of refractive index of vacuum-deposited As-S films under active stimulating effect of optical waveguide modes (λ=633 nm), capable of triggering the processes of relaxational structural transformation in the amorphous film medium.

2. Experimental

Standard vacuum evaporation techniques, fabrication procedure and construction details of optical waveguides based on fresh amorphous films of As-S have been described in detail elsewhere [5,9].

A prism-coupling technique was used to measure the refractive index of the as-evaporated films. The guided waves (λ=633 nm) were generated with a crystal GaP prism. Refractive index n_f measured with the light for which the electric field vector runs in the film plane. The accuracy of the refractive index measurements is 10^{-4}. All experiments were carried out at room temperature.

Earlier we have shown the existence of two threshold values of intensities for wave-guiding optical modes from the spectral transparency region, capable of initiating irreversible changes in optical properties of as-deposited a-As-S films. Thus, two cases of conditions for the resonance excitation of optical modes depending on the density of light flux (λ=633 nm) directed at the front facet of a prism-coupler can be specified [9,12]:

1) $3 \leq P \leq 15$ W·cm^{-2}, where the action of optical modes can stimulate irreversible "photo-structural" changes in the refractive index;

2) $10^2 \leq P \leq 10^3$ W·cm^{-2}, when the detrimental effects with optical "recording" by the optical mode in the wave-guiding channel are observed.

In the present work we consider the first case for the excitation of wave-guiding modes only (P=5.5 W·cm^{-2}).

While studying the effect of "self-recording" by the wave-guiding light, the mode of automatic continuous tuning of the corresponing angular characteristics by a goniometer was performed in order to provide the resonance conditions of excitation of TE_0 type mode (λ=633 nm). The first measurements of n_f were carried out in about 15 min after the film preparation procedure having been finished. They were periodically reproduced in certain periods of time, each time in new parts of the film waveguide. This has enabled to study the effect of physical ageing on the "photosensitive" properties of the films under their durable storage at conventional laboratory conditions.

For the quantitative evaluation of the effect of "self-recording" by an optical mode we have introduced a parameter of the film "photosensitivity" $N = \Delta n_{\mathrm{f}} \cdot \Delta t_{\mathrm{exp}}^{-1}$ which characterized the "dynamics" of stimulated enhanced increase of the film refractive index within the waveguide channel with continuous propagation of the recording wave-guiding optical mode. The "photosensitivity" parameter *N,* taken as the evaluation parameter, was determined by adjustment of optimal dose of mode radiation (λ=633 nm), continuously interacting with the film material, when we managed to keep within almost linear dependence of n_f on the propagation time of the wave-guiding optical mode. In our experiments it corresponded to the duration of the time interval of resonant propagation of the mode radiation $\Delta t_{\mathrm{exp}} = 10 - 15$ min.

3. Results and discussion

Fig. 1 illustrates the effect of ageing of a-As-S films of various compositions on the parameter of the waveguide layer "photosensitivity" *N* introduced here. The films under investigation have not been exposed to any activating effect of external factors (illumination, thermal treatment).

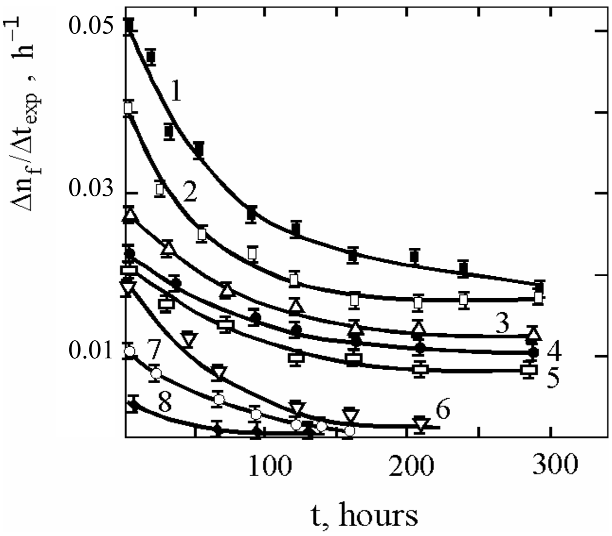

Fig. 1. Changes of the "photosensitivity" parameter $N = \Delta n_f \cdot \Delta t_{exp}^{-1}$ of As_xS_{1-x} films at optical coupling zone versus laboratory storage duration (x=0.44 (1); 0.40 (2); 0.35 (3); 0.30 (4); 0.28 (5); 0.25 (6); 0.20 (7); 0.17 (8)).

In the films with arsenic content below 17 at. % the effect of "self-recording" by an optical mode, as well as ageing-induced changes in n_f, are practically absent. However, with the increase of As content in as-deposited films the investigated "photosensitivity" parameter $N = \Delta n_f \cdot \Delta t_{exp}^{-1}$ noticeably increased. Compositional dependences of the parameter N at different stages of physical ageing are shown in Fig. 2 (curve 1 corresponds to as-deposited films; curve 2 – to the samples having been stored during a month at conventional laboratory conditions). The highest "photosensitivity" to the waveguide mode light was observed for the samples with $x \geq 0.30$.

Note that the "photosensitivity" of films with $0.17 < x < 0.25$ decreased to small values already during a couple of days after their deposition. In our opinion, the most noticeable initial changes result from the fact that at the moment of the film preparation procedure being finished the films are still capable of intense curing of especially gross defects of the structure (nanovoids, pores, fluctuation nanoinhomogeneities, non-equilibrium local atomic configurations etc). At initial predominance of soft atomic configurations in the amorphous film matrix the sensitivity of the film material within the above compositional interval to the wave-guiding mode radiation naturally decreases with physical ageing.

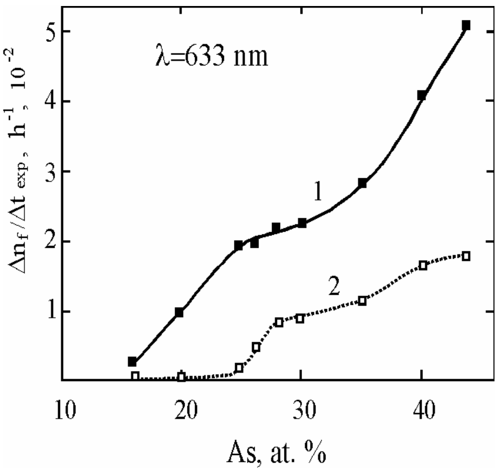

Fig. 2. Compositional dependence of the "photosensitivity" parameter $N = \Delta n_f \cdot \Delta t_{exp}^{-1}$ of As_xS_{1-x} films at the optical coupling zone immediately after deposition (1) and after 1 month of natural ageing (2).

One should note explicit affinity of the compositional dependences characterizing the kinetics of relaxational increment of the refractive index n_f at physical ageing of the films [9] and variation of the "photosensitivity" parameter N under study. The variation of the latter is related to the initiating of irreversible changes in the waveguide channel due to the excitation of optical mode of moderate intensity (exceeding the first intensity threshold limit).

We are inclined to treat the effect of "self-recording" by an optical mode in fresh films of a-As-S system as triggering of "relaxational" changes, initiated by light waves at the zone of their waveguide propagation. The obtained dependences contain important information to elucidate the possible nature of the irreversible relaxational transformations in the film material under physical ageing.

Fig. 3 shows the compositional dependences of coefficients A_{sw} and k_{sw} of an approximating function $N = A_{sw} \cdot \exp(-k_{sw} \cdot t)$ where t is the postcondensational film storage time. This is an interpolating function describing relaxational changes of the "photosensitivity" parameter N in course of the film physical ageing.

One should distinguish between separate components of the irreversible changes of refractive index determined by physical ageing ("self-relaxation" process), and by complementary stimulation of changes by weakly absorbed light waves. The intensity of both components is given by characteristic "instantaneous" (waiting) relaxation times, i. e. the "background" level of relaxational transformations having been achieved by the instant of measurement. We take into account the fact that in our case the range of distribution of relaxation times is rather wide. The kinetics of the irreversible changes of n_f (separately those determined by the physical ageing and those due to the effect of "self-recording" by the waveguide mode) more or less adequately reflects the specific features of the structurally non-equilibrium state of the amorphous films. These specific features are determined by the character of topological and chemical disorder and correspond to the incomplete chemical ordering and molecular phase separation inherent to the medium.

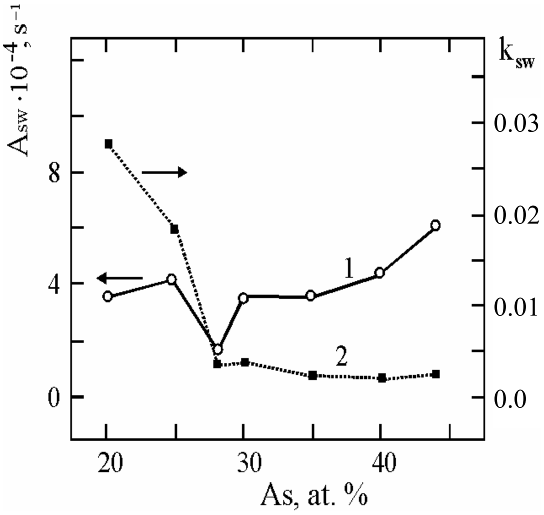

Fig. 3. Compositional dependences of the calculated coefficients A_{sw} (1) and k_{sw} (2) for the interpolating functions of temporal variation of the "photosensitivity" parameter $N = \Delta n_f \Delta t_{exp}^{-1}$ for As_xS_{1-x} films at optical coupling zone.

The features being revealed in the dependences under analysis can be conveniently treated in the framework of potential energy landscape formalism [17]. We treat separately the contributions to the transformation processes of configurational (topological) entropy and flexibility (communal) entropy. In dynamic transformations of the latter both harmonic and anharmonic contributions are involved, meanwhile its value directly depends on the number of floppy modes [15].

In view of this seems quite understandable that the films with $x<0.17$ lack of "photosensitivity", since the disordered micristructure of such films is treated as stochastically organized. Since the amorphous network practically does not contain specific fragmentary formations related to the existence of so-called conditionally "rigid" atomic configurations, no fixation of statistically random structural transformations in the film optical characteristics is achieved.

When conditionally "rigid" cluster formations are incorporated in the amorphous film local structure, or, in other words, when elements of chemical ordering are introduced into an amorphous matrix, one should take into account competing effects of the configurational and flexibility entropies on the processes under investigation. At the increase of arsenic concentration the achieved dynamic balance of the entropy component variation dictates the film relaxational behaviour, drastically different from the statistically random network. We assume that for the films with $0.17<x<0.25$ a considerable part of the residual entropy is released during relaxational transformations in the first few days after preparation. Therefore, with their further ageing, photorelaxation processes, initiated by excitation of an optical mode of moderate intensity in the waveguide channel, are almost unnoticeable. For the samples under study it can be explained by postulating that irradiation by the optical mode can access mostly short-time elements of the relaxation spectrum.

One should pay attention to a plateau in the analyzed compositional dependences observed for the amorphous films in the range $0.23 \leq x \leq 0.28$ (corresponding to a "dip" of the A_{sw} parameter and a decrease of the k_{sw} parameter in curves 1 and 2, Fig. 3). These features show a good correlation with the approximating dependencies of self-relaxation changes in the refractive index [9] obtained for samples of a nearly similar origin.

Bulk glasses of similar composition also possess corresponding structurally determined threshold features in certain physical properties [19]. This fact was related to the divergence from "stochastically agglomerational" (disordered) forms of glass structure organization and treated as a consequence of self-organizing processes at the amorphous network formation due to quasitetrahedral $S{=}AsS_{3/2}$ and pyramidal $AsS_{3/2}$ structural units being introduced into the glass matrix. Fresh films typically are in out-of-equilibrium state and are characterized by a considerably higher residual entropy; therefore, any unambiguous comparative analogies with bulk glasses for percolational (threshold) features in compositional dependences of optical characteristics require a particularly reserved approach.

The films of the vicinity of $As_2S(Se)_5$ composition are distinguished by a number of characteristic features: maximal natural optical anisotropy [5,18], combined with minimal values of a reversible component of scalar photodarkening effect [20], low attenuation of optical modes in film optical waveguides [21], non-trivial elasto-plastic behaviour of the amorphous medium in the presence of band-gap light illumination [4,22]. The latter feature was revealed at the background of a pronounced photosoftening effect. We consider these features of the films with the above threshold content of As to be determined by a relatively compact self-organized amorphous network (a disposition to minimize the internal molar volume). Their topology is determined by a combination of optimally coordinated structural units in conditionally "rigid" cluster formations, joined by "soft" bridge S_n chains.

The chain formations serve the main elements of the structural softness of the chalcogen-enriched film medium. It is natural that with approaching As_2S_5 composition when the concentration and length of the intermediate chalcogen-based chain elements are expectedly reduced ($n=2 \div 3$) [9], distinct thresholds in structure-sensitive characteristics are observed. We considered the experimentally observed features as consequences of the self-organization phenomenon [18] and treated them in the framework of a known "chains-crossing model" [23]. This also means that for the films of the vicinity of the As_2S_5 composition the decisive role of the flexibility entropy in the processes of relaxational transformations should become noticeably restricted. These films, if having undergone considerable sponateneous and stimulated irreversible transformations (resulting in a noticeable reduction of the residual entropy [24]), are close to the equilibrium state of configurational entropy.

On the other hand, fresh films of the above "threshold" composition, and, to a smaller extent, As-enriched samples are characterized by a distinct anisotropy of topologically deficient microstructure. This favours their noticeable optical anisotropy [5,18]. Besides, the nanoinhomogeneous medium of vacuum-deposited a-As_xS_{1-x} samples with $x>0.30$ is initially characterized by anisotropic distribution of local mechanical stresses. The inherent "mechanical" anisotropy can in different way result in the character of both spontaneous (at physical ageing at normal laboratory conditions) and stimulated (e.g. triggered by a weakly absorbed optical mode) transformations. In general, anisotropic stress contributes to the free energy of the disordered system, the changes in the anisotropy drive the system from one free energy minimum to the other. Locally anisotropic mechanical strain is, at least in a number of cases, even capable of slowing down relaxational transformations. The relaxational behaviour of an amorphous chalcogenide film on a substrate essentially differs from that of a film, separated from the substrate. Undoubtedly, for an amorphous medium with a distinct anisotropy of the topologically deficient microstructure at the evaluation of the role of the mechanical component of relaxational transformations one should take into account the orientational degree of freedom. An essential role belongs to anisotropic interactions determined by the substrate surface.

While analyzing the irreversible transformations we take into account the unstable (dynamic) character of anisotropic local stress redistribution. The latter can favour cooperative and spatially correlated motions, meaning that the dynamics of transformations is heterogeneous. We distinguish between the above spatially localized anisotropic stresses and so-called atomistic-level stresses being ascribed to the redundant strains experienced by individual atoms [13].

Transitions between various energy minima with resulting minimization of total free energy occur most effectively in mutual consistence of processes of relaxational transformations. Involvement of mechanical component to the analysis of the relaxational behaviour of the nanoinhomogeneous medium of amorphous films enables quite natural and correct modeling of collective processes of irreversible structural transformations which require multiple acts of atomic rearrangements and displacements. For the objects under investigation an important element providing spontaneous ("self-relaxation") structural modifications is derived from the possibility of consecutive plastic events, localized within so-called shear transformation zones (STZ) [25]. A separate STZ-like event generates spatially much more dispersed elastic non-affine atomic displacements [26,27]. In potential energy landscape concept the consequences of corresponding interactions dictating the irreversibility of "self-relaxation" transformations, are fixed in configurational space topology as annihilations and creations of inherent structures [26]. The stored elastic energy is dissipated each act of a plastic shear induced annihilation what can stimulate further consecutive transformations. Directions of low curvature on the potential energy surface are responsible for nucleating the cascade of local transformations. Floppy modes, actively participating in irreversible transformation processes, acquire a "shear-transformational-like" quadrupolar character [27]. Floppy modes play a predominant role in the retention of non-affine elastic displacement fields via which energy is dynamically redistributed in the vicinity of the reorganized STZ [27]. Note that As-enriched fresh a-As-S films possess 2-D layered "geometrical network" (with preferential orientation and no periodicity). These cumulative atomic displacements and stress fields result in changes which are reminiscent of narrow lines of sliding. The latter should affect the character and intensity of irreversible changes in a number of structure-sensitive properties. A greater part of integrated changes is deried from the consequences of accumulation of local atomic rearrangements in the film due to consecutive series of avalanche-like elementary shear-transformation sub-events [27].

In the course of a-As-S and a-As-Se film vacuum deposition and in the initial post-condensation period, opposite in sign and, as can be supposed, spatially anisotropic mechanical strain at the substrate/film interface are known to be detected [4,11]. Their generation is derived from intense relaxational transformations, accompanied for arsenic sulphide and selenide films by the processes of dilatation and contraction in the film plane, respectively. The reason for the observed difference in the a-As-S and a-As-Se film behaviour can be found in a considerably higher intensity of the relaxational changes demonstrated by As-Se in the initial post-condensation period.

Amorphous As-Se films are characterized by more pronounced "smooth" morphology of the amorphous network. In the course of deposition or immediately after the preparation procedure having been finished, spontaneous transformations are directed to the removal of gross structural defects, characterized by a preferential spatial orientation. The corresponding changes within the "weak spots" and planar "voids" are accompanied by thickness decrease and constricting stresses arising at the film/substrate interface [4,6]. Meanwhile, at the condensation of a-As-S, characterized by locally much more inhomogeneous microstructure, a trend to irreversible transformations within distinguished "microvolumes" predominates, the nature of local interactions in this case being rather of cohesive than adhesive type. Experimentally it was revealed as appearance of stretching mechanical stresses at the film/substrate interface.

Hence, in the post-condensation period a-As-S(Se) films undergo intense "self-relaxation" transformations when local mechanical stresses are effectively minimized and, accordingly, total free energy is reduced. The "smooth" morphology of highly inhomogeneous films, at the initially present anisotropy of local stress distribution is especially favourable for activation of the shear-like transformations. The topologically layered microstructure of the amorphous network gives high probability of collective rearrangements of atoms in the vicinity of the "free surface" of the molecular layers to affect essentially the mechanical and optical properties. In the photodarkening effect the corresponding changes are derived from general lone pair – lone pair interactions yielding a widening of valence band and band gap narrowing [28]. The film refractive index is extremely sensitive to local structural transformations.

Note once again that in As_xS_{1-x} amorphous films for which the threshold of 30 at. % As has been overcome, the mode self-recording effect is especially strong. The revealed features are in agreement with our vision in according to which intense post-condensation irreversible transformations in amorphous media should be derived from competing effects of interactions for mutually separated local rigid and soft atomic configuration sites [9]. For the objects under investigation an essential role is given to involvement of partly fragmented molecular formations of As_4S_4- and As_4S_3-type into the transformation processes. The observed trend to transformations is related particularly with the excessive As-As homopolar bonds arising from the non-stoichiometry of amorphous network. In the fresh films the concentration of "wrong" bonds is especially high, and the corresponding sites of their localization are considered as softer ones. Introduction of the above partially separated molecular fragments dictates the behaviour of the amorphous network, whose backbone is formed by conditionally "rigid" cluster formations. The areas of the "soft" sites can, in our opinion, be related to so-called regions of negative shear modulus [29]. The presence of areas with negative shear modulus leads to relaxational unstability of the amorphous network; however, the domains of negative modulus are partially stabilized by surrounding regions of positive modulus over longer length scales.

With such approach to the elucidation of possible microscopic mechanism of cooperative relaxation processes for arsenic-enriched As-S(Se) films one could expect to observe the maximal values of amplitude components of irreversible (fresh samples) and reversible (thermally annealed films) scalar changes in the effects of photodarkening and photostimulated increase of refractive index. On the other hand, the observed behaviour of objects under investigation from the vicinity of As_2S_5 composition (to the most extent this concerns the reversible changes of optical parameters) show that dynamical equilibrium states for these irradiated and thermal annealed films appear to be close what could be expected. It should be emphasized that while considering photostimulated transformations a proper attention should be paid to a drastic modification of rheological properties of amorphous films under light illumination. Our understanding of the nature of the photorelaxation changes, for which photosoftening effect is of special importance, correlates with the model of slip motion of layered clusters proposed by Shimakawa et al. [30], first of all with the consideration of scalar photodarkening effect in a-$As_2S(Se)_3$. Note that among the two popular terms *photosoftening* and *photofluidity* the latter is less adequate for photoinduced local transformations. In our opinion, the term *fluidity* can be involved into the analysis of postcondensational non-equilibrium behaviour of amorphous chalcogenides to the same extent, as it can be applied to the phenomena for which collective displacements and rearrangements of particles are naturally introduced in the framework of granular packing and sandpile models [14]. For these models the term yielding is more appropriate.

On the other hand, in a-As-S related to the above trends are traced in compositional dependences of amplitudes of reversible component of birefringence, being induced during photoexcitation by polarized band-gap light [18]. Our logic agrees with the mechanism of arising of photostimulated anisotropy in amorphous chalcogenides proposed by Tanaka [31] which predicts segmental alignments in atomic (molecular) scales. Moreover, Tanaka assumed lightwave-initiated anisotropic alignment of segmental layers under illumination with light having altering polarization. We are convinced that the array of experimental data from the studies of newly discovered vector effects exhibiting dependence on the polarization of the incident laser beam – anisotropic mass transport [32], anisotropic photoinduced deformations or optomechanic effect [33], confirms the mechanism proposed by Tanaka. Under illumination of As-enriched films by linearly polarized light when a distinct anisotropy in the photosoftening effect is observed [34], non-affine "internal" motions of atomic groups should be revealed in the anisotropic response of an amorphous medium. The existence of quadrupolar fluctuations in elastic fields and consequent long-range interactions between STZs is considered as an organizing dominant factor of anisitropic complex transformations which determine the mechanism of photostimulated birefringence formation. This phenomenon is also favoured by the fact that at the local level amorphous chalcogenides are characterized by chirality [35]. Thus, in order to understand the nature of the most noticeable vector optical effects, first of all those related to the anisotropic photodiffusion [31-34], one should take into account the posiibilities of localization and dynamical redistributions of the anisotropic stresses. A topical issue is elucidation of behaviour of the "mechanical" subsystem in the anisotropic response of an inhomogeneous amorphous medium to the external initiating factors. It becomes clear that one should not discard the possibility of irreversible transformations where the structure nodification will be determined by mesoscopic order as well. Hence, anisotropic alignment of segmental conditionally "rigid" molecular fragments (clusters) becomes possible. It is also clear that indirect reaction of a nanoinhomogeneous amorphous medium to the change of polarization of the initiating light waves is complex. In particular, this is confirmed by the specific features of vector effects in short-time (several minutes of action) and long-time (several hours) intervals during photoexcitation under polarized band-gap illumination [32]. One can expect that, contrary to photostimulated anisotropic phenomena where spatial reorientation of "rigid" molecular fragments is important (birefringence, photodichroism or optomechanical effect), more durable processes of anisotropic photodiffusion will be best revealed in the films with high photosoftening.

Some experimental artefacts, detected at the investigation of a-As-S films, are worth noticing. For example, even a slight amount of oxygen added into the initial compositions resulted in a noticeable increase of relaxational stability of the optical parameters of fresh a-As_2S_3 film [21]. Its optical properties appeared close to those of "undoped" samples after a durable physical ageing or an external effect having initiated the changes. An artificial state of the amorphous medium "oxidization" can be treated as the one for which the role of negative STZs in the irreversible relaxational transformations is essentially restricted. A similar argument should be used at the consideration of the nature of the anomalous behaviour of doped samples of amorphous chalcogenides with small amounts of metals (Sn, Mn, rare-earth ions) [36].

In particular, in [37] a quite reasonable statement was made that for amorphous chalcogenide films a significant role of the mechanical subsystem in the relaxational transformations is revealed in a known phenomenon called dark self-enhancement of holograms (an increase of diffraction efficiency over time without any special treatments). Illumination-induced formation of inhomogeneous, periodically distributed internal mechanical stresses was considered by the researchers of this effect as a decisive factor.

There are reasons to consider that "technological" formation of variable composition gradient, i. e. the procedure of preparation of amorphous chalcogenide nanomultilayers is a precondition for inhomogeneous distribution of local mechanical strains over the gradient structure thickness. This, consequently, can be considered a precondition for a giant photoexpansion effect [38]. The corresponding state is characterized by an increased shear nonstability when the possibility of effective rearrangment of separate atomic groups in the intercluster space increases. The inhomogeneities can be revealed in giant photoexpansion effects.

4. Conclusions

While considering stimulated transformations in amorphous chalcogenide films resulting in irreversible changes of structural, mechanical (elasto-plastic) and optical properties, one should take into account the specific features of spatial and temporal organization of strongly correlated relaxation events. Dynamical heterogeneity is considered as a feature of the slow relaxation dynamics of amorphous media. Existence of the some spatial and dynamical correlations, associated with the soft modes, dictates the correlated behaviour of structural and mechanical subsystems, participating in relaxational transformations. We used the floppy modes to show that not only "self-relaxation" transformations, but also photostimulated changes considered here can be treated as collective phenomena. The corresponding modes with vanishing frequency and restoring forces are required to provide the most intense transformations.

One should emphasize that the microscopic degree of freedom describing disordered structure of amorphous chalcogenides determines the specific features of divergence of the non-affine elastic correlations. Moreover, there are reasons to claim that the rigidity for nanoinhomogeneous media of as-deposited films to a certain extent can be considered as a non-local microscopic property. The correlation length associated with the floppy modes extends over large distances. The floppy modes are related to long-range elastic interactions which are decisive in the final stage of each of the extended relaxation events. An essentail feature of properly organized non-affine elastic contributions can be the fact that in case they being taken into account both linear atomic rearrangements and rotation motion of molecular fragments can be achieved.

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