

## IRREVERSIBLE RELAXATION TRANSFORMATIONS IN AMORPHOUS CHALCOGENIDES

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In this paper we report the results of the study of changes in optical properties of as-deposited  $As_xS_{1-x}$  ( $0.15 \leq x \leq 0.43$ ) amorphous films depending on the composition and physical aging processes under ambient laboratory conditions. The possible nature of the obtained experimental facts is discussed in terms of the local relaxation events in the potential energy landscape approach for amorphous heterogeneous material at the nanoscale level. The post-condensation irreversible transformations in amorphous chalcogenide films as a result of competing effects of interactions for mutually separated local rigid and soft atomic configurations have been considered.

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### 1. Introduction

Nowadays the two kinds of the amorphous state for chalcogenides, namely bulk glasses and amorphous films are largely studied. One should remember that the amorphous films possess a considerably higher non-equilibrium state comparing to bulk glasses [1-4]. This is due to the peculiarities of the organization of their local structure, in which the incomplete chemical ordering is related to incommensurably greater molecular phase separation (the heterogeneity at the nanoscale level). Such a non-crystalline medium can be considered as a non-ergodic system with the excess entropy. As-deposited amorphous films are characterized especially by high non-equilibrium. In the post-condensation period they suffer durable relaxation characterized by structural changes. The most intensive changes are due to polymerization. Such processes are very often considered as physical ageing under ambient external conditions. Non-equilibrium relaxation changes are effected in the form of cooperative transformations of local structural regions and allow to reach the total free energy minimum for the system. Meanwhile, passing through intermediate metastable states the system diminishes the initial inherent mechanical stresses [5,6]. In As-S amorphous films studied by us such irreversible transformations of local structure condition the changes in the parameters of photosensitivity, microhardness, Newtonian viscosity, dissolution in chemical solvents, deformation rate under load. Such changes take place most dramatically in the presence of initiating electromagnetic irradiations [1,2-4].

Thus, the study of spontaneous changes in structurally sensitive properties of as-deposited film structures based on  $As_xS_{1-x}$  ( $0.15 \leq x \leq 0.43$ ) is undoubtedly important for future developments

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of optoelectronics, integrated optics and nanotechnology in which amorphous structures are successfully used as the information media with potentially overhigh recording resolution [7,8].

Besides, in technological procedures of recording one should take into account that amorphous chalcogenides “remember” the previous structural state depending on their properties from own thermal (technological) prehistory. The “instantaneous” structural state will define sensitivity, recording contrast, etching selectivity of an inorganic resist for the film medium. This fact should also be borne in mind to keep stable characteristics of waveguiding film components in the elements of integrated-optical and optoelectronic devices to be developed.

On the other side, a thorough study of the irreversible relaxation changes in structurally sensitive parameters, i.e. such as dielectric constants and the refractive index gives the ponderable information which can elucidate the mechanisms of structural transformations of the amorphous chalcogenide films and influence of vacuum deposition conditions on them.

Earlier by using high-sensitive waveguiding technique we studied a dark relaxation behaviour of the refractive index  $n_f$  in as-deposited As-S amorphous films with relatively high As content [9,10]. The revealed peculiarities in the kinetics of changes in  $n_f$  allowed us to conventionally distinguish three typical time intervals of its post-condensation growth:

a) initial (some first days of dark storage) with sufficiently intensive changes in the refractive index which we estimate as those connected to a great extent with the presence of technologically imported “gross” defects of the structure (microvoids, pores, “fluctuation” microinhomogeneities, greatly non-equilibrium local atomic configurations, etc) that reveal themselves most at the mesoscopic level;

b) noticeably more durable (some months of dark storage) “basic” transformation changes conditioned by different type – irreversible structural transformations of local regions of the structure. Under steady storage of the film the refractive index achieves the level of conditionally proper “saturation” for the given film, when the indicated time interval is finished.

c) the largest long-term (some years of periodic observations) “fluctuation” stage of transformations with much weaker, entirely insufficient relaxation changes in the refractive index.

In the same as-deposited amorphous films we have revealed a metastable natural optical anisotropy (birefringence  $\Delta n \sim 10^{-2}$ ), whose optical axis is directed perpendicularly to the film surface [9-11]. We have observed the irreversible decrease in birefringence almost “synchronously” with dark relaxation transformations up to the rise of the refractive index  $n_f$  (the polarization direction belongs to the film surface). The inherent potential of irreversible relaxation transformations of the local structure at physical aging of the film has not been realized completely at the moment of conditional saturation of respective optical parameters, the second region of their “basic” time changes being finished. Besides, the amplitudes of respective irreversible changes in  $n_f$  and  $\Delta n$  at the thermal annealing or band-gap light irradiation ( $\Delta n \rightarrow 0$ ) appeared to be three-four times larger.

Earlier in electron-microscopic studies of before-crystallization transformations of the local structure close to the origin of as-deposited As-S(Se) films it was uniquely stated that irreversible structural transformations do not relate to the short-range order but mainly include the intermediate and mesoscopic orders [12]. It is considered that the most intensive structural transformations in such objects are connected with irreversible redistributions of intermolecular (interatomic) bonds in the vicinity of “free” internal surfaces of mesoscopic structural fragments which are mutually separated [13]. As a result, the optically anisotropic as-deposited amorphous films which possess the features of the chemical ordering during relaxation transformations (including cross-polymerization connectivity of the structural fragments) become more disordered with a loss of the medium-range structure. Such topological and structural changes require the motion of atoms and the bonding rearrangements [1,2]. A great role in transformations of the local structure of as-deposited films is assigned to “isolated” molecular  $As_4S_4$  and  $S_n$  fragments and some other configurations [3,14-16]. The substantial part of the “wrong” homopolar bonds is eliminated during their post-condensation storage and under the initial acts of thermal annealing or light illumination.

The peculiarities of spontaneous and stimulated relaxation changes in as-deposited a-As-S films allowed us to estimate their behaviour as typical characteristic for dissipative fluctuational structures [17]. The specificity of the organization of the film structure (incomplete chemical ordering in connection with the nanoscale phase separation) is the relevant basis of non-ergodic character of irreversible relaxation transformations. When analyzing the non-equilibrium dynamics

of such relaxation transformations the complex multi-particle problem should be solved [17,18]. This requires to consider multiply changes in the microscopic structure (local relaxation events). A great role is paid by cooperative interactions that include collective spatial atomic displacements when self-consistent “intensification” of fluctuation local structural transformations becomes possible. The direction and intensity of all these processes are defined by contradirectivity (competitions) of contributions which are defined through configurational and collective entropies in “homogenization” transformations for initially demixed amorphous medium at the nanoscale level [17,18].

In the present work the changes connected with irreversible transformations defined in optical characteristics of a-As-S films during their physical ageing under ambient laboratory conditions have been studied.

## 2. Experimental

Experimental measurements were conducted using the as-evaporated a-As<sub>x</sub>S<sub>1-x</sub> (0.15 ≤ x < 0.44) films. The deposition was carried out by making use of the standard vacuum evaporation technique at a pressure of 5 × 10<sup>-5</sup> Torr. As<sub>x</sub>S<sub>1-x</sub> glasses were used as the initial material for evaporation. These samples were prepared by means of the conventional melt quenching procedure.

The alloys were then vacuum-deposited onto a pre-cleaned silica glass substrate at the substrate temperature of 300 K. A typical evaporation rate was 3-4 nm·s<sup>-1</sup>. To check the chemical composition of films the electron probe microanalysis method was realized. The film thickness ranged from 0.9 to 1.2 μm.

A prism-coupling technique was used to measure the refractive index and thickness of the films. The guided waves (λ=633 nm) were generated with a crystal GaP prism. The experimental procedure has been described in detail elsewhere [19].

The accuracy of the refractive index measurements is 10<sup>-4</sup>. All experiments were carried out at room temperature.

The results obtained earlier while studying the resonance excitation of optical modes in film waveguides based on as-deposited a-As-S films allowed us to distinguish three typical conditions for them depending on the density of light flux directed at the front facet of a prism-coupler (λ=633 nm) [9,10]:

- a) P < 0.25 W·cm<sup>-2</sup>, when the light action of optical modes on optical characteristics of the film in the waveguiding channel is certainly absent;
- b) P = 3÷15 W·cm<sup>-2</sup>, when the light action of optical modes from the spectral transparency region of the amorphous film material can stimulate small irreversible “photostructural” changes in the refractive index;
- c) P = 10<sup>2</sup>÷10<sup>3</sup> W·cm<sup>-2</sup>, when the detrimental effects with optical “recording” by the optical mode in the film waveguiding channel are observed, and as a result the intermode conversion of light energy and a strong growth in attenuation of optical waves occurred.

In the present work among possible conditions for the excitation of guiding optical modes we have made use of the first one only. It is absolutely correct in respect to the definition of film parameters.

## 3. Results and discussion

Fig. 1 shows the post-condensation changes in n<sub>f</sub> for a-As<sub>x</sub>S<sub>1-x</sub> films of different compositions deposited onto cold substrates. The films were kept under ambient laboratory conditions all the time.

If one compares them with similar dependences of dark irreversible relaxation changes in n<sub>f</sub> which were earlier studied for As-enriched a-As-S films [9,10], it is possible to conclude that the main peculiarities of the parameter behaviour are similar, too. In both cases three preset stages of transformations mentioned above are present (the latter, of small intensity but especially long-term

stage is not depicted in Fig. 1). In the presence of scattered (indirect) laboratory illumination the respective processes of changes of optical parameters are “accelerated” at each stage of transformations (for first two time intervals – approximately twice or three-times). The respective amplitudes of the relative increment in  $n_f$  before the moment of conditional “saturation” of the refractive index are noticeably larger. This undoubtedly testifies to the fact that the weak (scattered) natural illumination creates a stimulating (accelerating) effect on irreversible transformations of the local nanoinhomogeneous structure (especially for As-rich films).

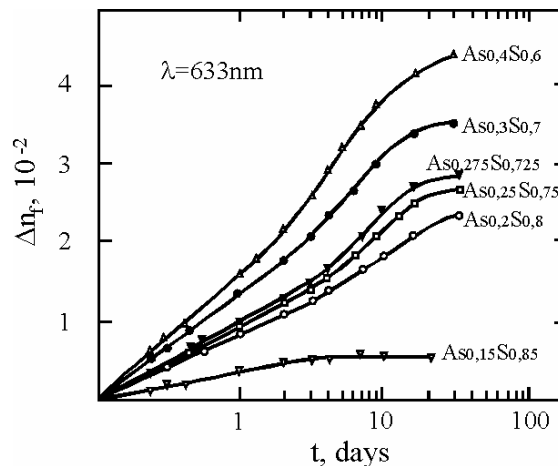


Fig. 1. The relaxation of the refractive index for a- $\text{As}_x\text{S}_{1-x}$  films during their post-condensation storage.

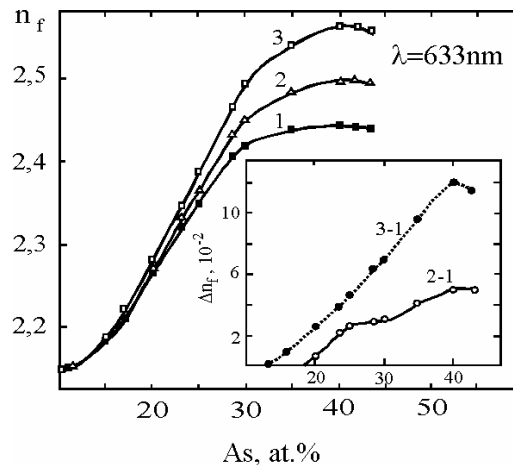


Fig. 2. The concentration dependencies of the refractive index  $n_f$  for a- $\text{As}_x\text{S}_{1-x}$  films taken just after deposition (1), after one-month laboratory storage (2) and next one-and-half hour thermal annealing (3). The insert shows the respective increments of the refractive index of the films: after their natural ageing (2-1) and after thermal annealing (3-1).

In Fig. 2 the concentration dependencies of  $n_f$  in a-As-S films taken in three states just after deposition (1), at the moment of reaching the state of the conditional saturation of parameter  $n_f$  (2) and with one-and-half hour thermal annealing at softening temperature  $T_g$  (3) are given. As a consequence of detailed analysis of  $n_f$  behaviour on the second “basic” region of relaxation transformations it appeared to be possible to interpolate time dependences of the given parameter increment by the functional dependence  $Y(t) = (\Delta n_f)_{\max} - (\Delta n_f) = A \cdot \exp(-kt)$ , where  $A$  and  $k$  are some parameters. Here we confined the time stage of changes under consideration by the initial countdown of days ( $t_0=3$ ) after preparing the film and final moment of reaching 90% by the

refractive index  $n_f$  from its maximal increment value  $(\Delta n_f)_{\max}$  on the “basic” stage of transformations. In Fig. 3 are given the concentration dependencies of calculated coefficients  $A$  and  $k$  with respect to the obtained approximating dependences of relaxation changes in the refractive index.

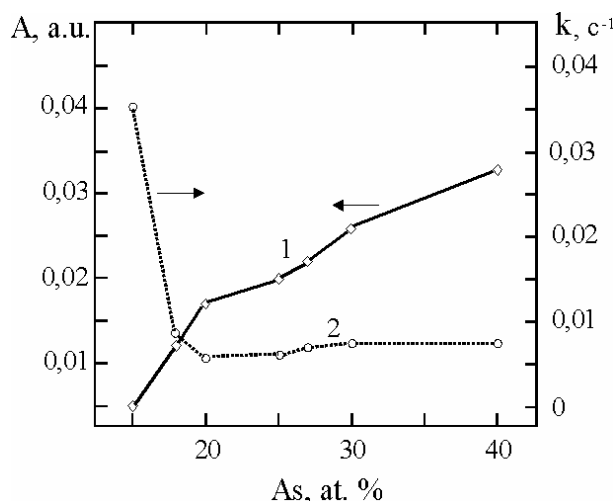


Fig. 3. The concentration dependencies of  $A$  (1) and  $k$  (2) parameters for interpolating functions of relaxation changes of  $Y(t) = (\Delta n_f)_{\max} - \Delta n_f(t)$  parameter in  $\text{As}_x\text{S}_{1-x}$  films.

While interpreting the results we proceed from the unified general scheme of the estimate of both spontaneous (at the physical ageing) and stimulated by external factors structural transformations of nanoinhomogeneous structure of as-deposited films. Within it is possible to depict the revealed peculiarities of the behaviour of structurally sensitive optical parameters under study.

In physical dynamic processes the exponential character of the increment of some parameter  $\Delta x = A \exp(-kt)$  mainly corresponds to such magnitudes whose change is due to the transitions between two (or several) states of local regions of the system under study. The parameter presets total concentration of those local regions (configurations) which are included into these transitions. However, the parameter  $k$  is defined by a specific mechanism of the transitions themselves, i.e. by the probability of their behaviour under existing conditions, in particular.

In similar dependences which represent various processes of the relaxation changes, the ability to show indirectly the presence of some hierarchy of spatial and spatial-temporal inhomogeneities of the disordered medium and correlation degree of atomic rearrangements. As a result, the “non-ergodicity” degree of relaxation transformations is assigned to the parameters of such kind (first of all to parameter  $k$ ) [20,21].

The basis for our interpretation is the nanostructural inhomogeneity of a-As-S films [3,4,17]. The peculiarities of the organization of such structure are the inclusion of at least two types of local atomic relaxation subsystems into the processes. The first of them relates to conditionally “rigid” atomic states (configurations), mainly spatially “concentrated” within layered and molecular cluster formations. The second subsystem relates to “soft” local atomic configurations, having additional degrees of freedom in the configurational space. The presence of the given interacting subsystems, to our mind, is defined by a high level of the molecular phase separation in as-deposited films of amorphous chalcogenides. The similar specificity of local structure conditions the behaviour of long-term relaxation transformations with multiply acts in the form of cooperative rearrangements of separate atomic groups (acting relaxing units) through the breaking and switching of inter-atomic bonds [22].

As a result of metastability of amorphous films such cooperative relaxation transformations have a well-defined activation character. Thus, in the process of relaxation the transition of a

separate local atomic configuration from one structural state to the other requires crossing over the energy barrier.

So, long relaxation changes under ambient laboratory conditions are defined by structural transformations of local configuration of the amorphous network, each of the configuration passes gradually via intermediate labile states overcoming energy barriers which separate them. In such cooperative character of stretched relaxation transformations the structure of local atomic configurations is revealed as constantly changing, dynamic, non-stationary. Due to changes in a separate relaxing unit the corresponding change (local relaxation event) creates favorable conditions for further structural transformations with corresponding displacements of atomic configurations in the nearest vicinity. For the latter it may be considered as the formation of the evolution potential for the elements of the rearranged local subsystem. So, the set of spatial-temporal atomic configurations obtained for each moment of structural transformation defines the further trajectory of possible structural changes resulting in the decrease of total free energy [17,18].

The similar behaviour of the relaxing system in its thermodynamical environment can be adequately depicted within the configurational space energy landscape approach [21]. The potential energy landscape formalism clearly separates the vibrational and configurational contributions in thermodynamical quantities. The heterogenous potential energy landscape dynamics is defined through the sum of the vibration-like motions within minimal energy valleys (usually called inherent structures) and transitions between energy minima (basins). An active role is assigned to entropy components which reflect existing various configurations and the curvature of the potential energy function at its minima. The potential energy barriers prevent from the relaxation in the system. The largest drastic relaxation transformations are accompanied by multiply two-stage acts of overcoming the saddle-point energy barriers (by a descent path in the energy surface) with corresponding collective microstructural rearrangements resulting in the transition of some structural fragments (atomic groups) to new topology and energy states. The irreversible local relaxation events occur when the inherent structures annihilate during a collision with saddle-points. During ageing the system gradually explores the basins associated with equilibrium configurations. The system has been brought to a more stable configuration with higher potential energy barriers when the local curvature of energy minima changes measurably. The important point of our approach in this work is the fact that we stress the necessity of taking into account the contribution of soft atomic configurations in dynamic structural transformations. This contribution is defined by including the so-called floppy modes into the process as collective motions that provide the pathways across the phase space [23].

We also suppose that in the complex character of the processes and competitions (energy contradirectivity) of contributions defined by configurational and communal entropies, the amorphous film becomes able to relax with smaller losses of energy in various irreversible transformations. In this aspect it means that for our objects these transformations are realized by reaching the energy dissipation minimum [17,18]. A special condition of such behaviour is the balance of contributions of elements reflecting both structural "rigidity" and soft atomic configurations. The former are localized in the form of atomic configurations with the definite set of inherent structures, "concentrated" in relatively stable cluster formations within strong covalent bonds. The "channels" for the transformation of stored or exported from the outside energy for providing non-equilibrium structural transformations are formed in correlational interactions for such configurations through other atomic groups [24,25]. Separated molecular fragments and inter-cluster regions of the amorphous matrix are the structural centre-point of soft atomic configurations. The ability of S(Se) atoms to vary easily their own coordination number is an important factor in relaxation transitions for structurally flexible chalcogene-containing compounds.

We stress one more important peculiarity: the presence of self-organization motive in spontaneous and stimulated relaxation structural transformations in amorphous chalcogenides. This feature makes their behaviour quite different from other amorphous films. In particular, from oxides, for which the dominant is the structure rigidity as well as the weakness of residual van-der-Waals forces and enhanced ionicity of interatomic bonds. However, the polymeric materials have, mainly, an excessively soft structure that conditions a different specificity of kinetics of relaxation transformations.

On the other side, we note that the structural inhomogeneity of as-deposited amorphous chalcogenide films requires to take into account an inhomogeneity of phononic subsystems – inharmonic atomic vibrations of inter-cluster bonds (residual van-der-Waals interactions due to dihedral angle forces and lone pair electron interactions). This can result in a shear non-stability and the possibility of regrouping separate atomic groups in the intercluster space. The latter is initially stored as an elastic deformation energy, accumulated in the nanoinhomogeneous network of as-deposited film. Separated local regions define the redistribution of local strains and support a finite stress in the post-condensation period. The key basis for non-trivial structurally-conditioned mechanical properties for the amorphous medium under analysis is the diverging length scale at the level of intermediate and mesoscopic orders [26]. The latter is also associated with a loss of rigidity, particularly, in comparison with bulk glasses.

It is reasonable to admit that occurring repulsive interactions for local structural fragments in the inter-cluster space are able to be revealed in photo-expansion effects, best defined for as-deposited a-As-S(Se) films. Probably, it would be worth taking into account as a separate aspect the consideration of the processes of photostimulated changes within Shimakawa and co-authors' original model [27]. We especially stress that the most intensive dynamic manifestations of the photo-expansion in such objects coincide with the temporary intervals of such changes: a maximal decrease in the internal mechanical stresses and the most intensive effect of photo-softening, the most “destructive” dynamics in the medium-range order transformations of the local structure [28-30]. This also relates to the stimulated irreversible annihilation of non-stable natural optical anisotropy in the films of similar origin [9-11].

The relevant basis for the estimate of elasto-plastic behaviour of the amorphous chalcogenides in irreversible relaxation transformations, as we have already mentioned, is taking the heterogeneous geometrical structure into account. This is properly achieved within the conception of the potential energy landscape. The elementary plastic and shear events are localized in space and completely separated. The revealed clear features of spatial-temporal organization in relaxation changes of the mechanical properties can be associated with the fact that in the disordered media highly heterogeneous plastic and strong non-affine elastic displacements show the distinct hierarchy at the length scale [26]. Speaking about co-existence of relaxation subsystems in the form of rigid and soft local atomic configurations in the structure of the amorphous film we consider it possible to correlate them with “shear transformation zones”, viz. the so-called regions of positive shear modulus and regions of negative shear modulus [31]. The latter are characterized by a typical size of some interatomic distances which is much less than the ones for elastic inhomogeneities [26]. In terms of the idea about the affinity with relaxation changes of structural and mechanical parameters the analysis of evolution of the plastic properties for amorphous chalcogenides under band-gap light irradiation by using micro- and nanoindentation methods could be the most effective [32]. Such specific behaviour could be reasonably associated with the dynamic divergence of the elastic constants at the nanoscale level.

Taking into consideration the above mentioned idea, we will try to find the explanation of the revealed threshold peculiarities in the concentrational dependences shown in Figs. 2 and 3. The  $\text{As}_x\text{S}_{1-x}$  films with small As content ( $x < 0.15$ ) do not really demonstrate post-condensation relaxation changes in  $n_f$  that is conditioned both by the existence of mainly soft atomic configurations in them and “stochastic” character of the structural connectivity of the amorphous film network. Though they possess distinct features of the molecular phase separation in the form of chains and rings of chalcogens, their structure is almost free from elements of chemical ordering. Such peculiarities of the amorphous network give it the possibility to relax to a more stable state due to easily carried out collective displacements of local atomic configurations. However, the general statistically averaged structural motive of the given films almost does not change. As just the statistically averaged structural state of amorphous materials defines the majority of their physical properties, such relaxation processes are not revealed for  $n_f$  values. It is interesting that these objects (as-deposited As-S films with high chalcogen content) demonstrated the non-monotonous changes in the refractive index under band-gap illumination [33]. The nature of the revealed non-monotonous behaviour is associated with the so-called interatomic dynamical bonds, included into weak processes of irreversible photostructural transformations. Such a peculiarity is typical for the relaxation

transformations and photo-responses in the amorphous medium which are related to the topological floppy phase within the framework of a well-known Phillips-Thorpe model [34].

Distinct relaxation processes with the residual fixed change in  $n_f$  are observed in the films with somewhat larger sulphur content, i.e. at  $x \geq 0.15$  (Figs. 1,2,3). We consider that just in the vicinity of composition with  $x \approx 0.15$  in the amorphous film matrix among "soft" atomic configurations the separate "rigid" local atomic configurations are able to reveal themselves. It is reasonable to admit that the appearance of such configurations is conditioned by the growth in the content of arsenic atoms. In the vicinity of the composition with  $x = 0.15$  approximately 5-6 chalcogen atoms, on average, corresponds to each As atom. For such compositions two neighbouring As atoms are covalently bonded between themselves across 3-4 intermediate chalcogen atoms at statistically equal distribution of atoms in the amorphous matrix. We consider that "rigid" atomic configurations are localized in the vicinity of those arsenic atoms between which not more than 3 intermediate chalcogen atoms are located. Relaxation structural transformations with decreasing of the internal free energy of films are conditioned by the rearrangement of the whole amorphous matrix. But only when structural changes in "rigid" local atomic configurations reach a sufficient level, this has to be revealed experimentally as the change in  $n_f$ , particularly due to the statistical averaging of structural parameters throughout such configurations. The "rigidity" peculiar to them allows to "fix" such changes that are described as the exploration of acting minima of the potential energy landscape by the system and as a result the local energy barriers will grow.

As to the values of parameters  $A$  and  $k$  (Fig. 3) the concentration of relaxation "rigid" local atomic configurations is very small ( $A \approx 0.015$  arbitrary units) and the probability of relaxation transitions is very large ( $k \approx 0.035$ ) in the films with  $x \approx 0.15$ . These conditions assure a rapid completion of relaxation processes (large  $k$ ), however, totally weak relaxation changes in the structure and  $n_f$  parameter (small  $A$ ) are reached.

With increasing the As concentration from  $x = 0.15$  to  $x = 0.20$  a sharp decrease in the parameter  $k$  and strong monotonous rise in parameter  $A$  are observed. This will have a great influence upon the passing of relaxation processes reflected in the changes of the optical parameters. We associate such changes with considerable increase in the concentration of "rigid" local atomic configurations. We draw a special attention to the fact that the change in relative concentration of arsenic atoms only by a factor of 1.3 causes the rise in the concentration of potential relaxation units (according to parameter  $A$ ) by a factor of more than 3.5. To our mind, due to such behaviour in the given concentrational region introducing each new As atom into the film network causes the creation of additional "rigid" atomic configuration on the local area where this atom is situated. Besides, local atomic configurations connected with one or two nearest neighbours to accepted As atoms are transformed into "rigid" ones. That is, introducing each new As atom causes the formation of approximately  $3.6/1.3 \approx 2.9$  of additional "rigid" local atomic configurations in its vicinity for the amorphous matrix. Because such "approaching" rigid configurations begin to "overlap" between themselves, their relaxation rearrangement is confined by the "rigidity" of the structure of neighbouring local atomic configurations. As a consequence, the probability of the relaxation structural transformations decreases sharply (according to parameter  $k$  by a factor of 7). Within the framework of the potential energy landscape model it will mean the increase in the height of local energy barriers.

For compositions of films with  $x > 0.20$  parameter  $k$  remains constant. Therefore we consider that in the vicinity of compositions of films with  $x \approx 0.20$  the majority of "rigid" local atomic configurations "interact" directly in relaxation processes with the nearest neighbouring "rigid" atomic configurations. Such a situation becomes typical for the amorphous matrix in which about 4 chalcogen atoms correspond to one As atom. The latter responds to the structure in which neighbouring As atoms are, on average, connected with two intermediate chalcogen atoms.

With increasing  $x > 0.20$  parameter  $A$  increases monotonously, too. This increase is considerably slower than in the range of  $0.15 \leq x \leq 0.20$ . The increase in the concentration of arsenic atoms by a factor of two conditions the increase of parameter  $A$  by approximately 1.6 times. Such behaviour of parameter  $A$  testifies to the fact that new "rigid" spatially expanded local configurations are formed in this range of compositions when introducing additional arsenic atoms, i.e.  $\sim 75\%$ . The other fraction of  $\sim 25\%$  of As atoms enters already in existing similar configurations.



Let us also mention the plateau revealed in the vicinity of  $0.25 < x < 0.30$  (insert to Fig. 2) in the obtained concentrational dependences that reflects thresholds in the increment kinetics of  $n_f$  during physical ageing of  $\text{As}_x\text{S}_{1-x}$  films. Earlier while studying the properties of optical waveguides based on the films of the same compositional range we revealed the maximal effect of natural optical anisotropy and minimal values of the attenuation parameter for optical waveguiding modes ( $\lambda=633$  nm) [12,17,30]. We consider that the amorphous matrix of such films is initially better “built” and has a minimal internal molar volume. Such behaviour to a greater extent may be conditioned by the presence of optimally coordinated structural units  $\text{S}=\text{AsS}_{3/2}$  in “rigid” cluster formations. In such a way the organized film structure possesses reduced values of the configurational entropy that is surely reflected in the character of the relaxation changes in  $n_f$ .

Some remarks regarding the appearance of the conditionally saturation state of changes in  $n_f$  in films at storage under ambient laboratory conditions at the moment of the completion of its “basic” relaxation transformations are as follows. The height of local energy barriers with respect to an initially “soft” and further on more and more “rigid” structure of the amorphous network will grow in the process of ageing with a cross-polymerization connectivity. Local relaxation events result in the changes of local coordination numbers. Occasionally, the changes in the concentration of inherent structures (relevant block configurations) and (or) local curvature of energy minima are possible. Such transformations may be considered as gradual self-consistent changes in configurational and commun entropies that result in the minimization of the system free energy. However, with polymerization-structural transformations for inherent structures, probable channels-to-visit defined by the active inclusion into the processes of soft atomic configurations are more and more closed. Due to this fact, the system will not be able to sample these parts of the phase space [23]. With the same ambient laboratory conditions it will mean the removal of prerequisites for “self-organizing” mechanisms of transformations. Thus, the system goes out to a long-term and low-intensity final stage of “fluctuation” changes in  $n_f$  during further physical ageing of the films.

We have also studied the post-condensation changes in optical properties of  $\text{a-As}_x\text{S}_{1-x}$  films under the active stimulating action of the waveguiding mode. The results obtained gave additional arguments in support of the approach proposed while studying the irreversible relaxation transformations in such objects. The revealed peculiarities will be published elsewhere.

#### 4. Conclusions

In this article the post-condensation changes of the refractive index in  $\text{a-As}_x\text{S}_{1-x}$  films during their long-term physical ageing have been studied by the high-sensitive waveguiding technique. The revealed relationships of the parameter behaviour on “basic” regions of long relaxation changes in  $n_f$  in the objects under study are interpreted within a simple model which postulates the existence of specific local relaxing units in their amorphous matrix. Their step by step “actuators” (local relaxation events) are treated as competing effects of interactions for mutually separated conditionally rigid and soft atomic configurations. Each of the local relaxing units relates to a separate conditionally rigid local atomic configuration, marked out in the nanoinhomogeneous film structure. Such configurations to a greater extent define the topography of the potential energy landscape and correspond to those explored local energy minima which are separated by not too high energy barriers. The considerable structural transformations with the integrated changes in optical macro-parameters become possible when the channels-to-visit are formed between separate energy minima (valleys) in the energy landscape. At the trace-level activation under laboratory storage conditions the spontaneous transitions of relaxing local atomic configurations into new structural states with new minima of the energy potential take place, respectively. We especially stress the fact that for significant changes of the local structure the role of floppy modes is active because the crossing of the energy barriers that impair relaxation is provided by them.

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