

Photo-induced covalent-bond switching in amorphous arsenic selenide

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A microstructural mechanism of photoinduced transformations in amorphous films of arsenic selenide was studied with IR Fourier-spectroscopy technique in 300-100 cm^{-1} region. It was shown that stage of irreversible photostructural changes was connected with cooperative process of coordination defect formation accompanied by homopolar chemical bonds switching in heteropolar ones. On the contrary, reversible photoinduced effects were caused by heteropolar chemical bonds switching in homopolar ones, as well as additional channel of bridge heteropolar bonds switching in short-layer ones. The both processes were associated with formation of anomalously coordinated defect pairs and accompanying atomic displacements at the level of medium-range ordering. The developed mathematical simulation procedure testified that the observed kinetics of reversible photo-induced transformations corresponded to well-known stretched-exponential relaxation function, tending to bimolecular behavior rather than to single-exponential monomolecular one.

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1. Introduction

Amorphous chalcogenide semiconductors (AChS) possess a unique ability to change their physical-chemical properties at the influence of external factors, first of all, the absorbed light photoexposure. These so-called photoinduced effects (PhIE) are put in the basis of AChS-related xerography and lithography, CD-erasable media, memory-switching devices, photosensitive recording elements, etc. [1]. They reveal themselves clearly in the changes of optical properties of vacuum-deposited thin AChS films [1-3], while bulk and powder samples are characterized only by relatively slight PhIE [4].

In the most typical cases, the absorbed light photoexposure leads to long-wave shift of fundamental optical transmission edge (a so-called photoinduced darkening effect) and refractive index increase in strong dependence on thin film composition and light treatment parameters (photon energy or wavelength, ambient temperature, exposure duration, light intensity, etc.). Thermal annealing near glass transition temperature of the corresponding chalcogenide glass restores initial optical properties of the photoexposed thin film so that the observed changes become reversible in the following multiple cycles of photoexposure and thermal annealing. The irreversible component of these changes is important only in the first-cycle photoexposure of as-prepared AChS films [1-4].

Physical features of the above PhIE were well studied more than 3 decades ago [2,3], but a number of controversies concerning our understanding of their microstructural nature are still remained up to now. In spite of the majority of authors stand at the ground of so-called photostructural model for the reversible PhIE,

associated them with short- and intermediate-range ordering changes within glass-forming network [4,5], the adequate schemes of these changes are too speculative. This is obviously caused by difficulties in the direct observation of local atomic structure transformations in disordered solids such as AChS. The reversible PhIE are relatively weak as they embrace no more than 5-7 % of atomic nodes concentration. The sensitivities of conventional amorphographical techniques operating with useful information obtained at the general background of the whole integrated signal are insufficient for this purpose. Only in the case of amorphous a-As₂S₃ films, the reversible photostructural transformations can be relatively simply identified as covalent-bond switching using Raman spectroscopy data [6]. Nevertheless, the main result of this experiment was connected only with quantitative estimation of reversibly transformed bonds (near ~6 %), while initial and finite products of covalent-bond switching (the types of destructed and newly created bonds) were not identified exactly.

Later, we established that necessary information on the microstructure mechanism of PhIE could be accurately obtained with "differential" IR Fourier-spectroscopy technique, dealing with a part of the photoexposure-induced vibrational spectrum, but not the whole integrated spectrum [7]. Multiple accumulation of this deducted signal, when fast Fourier transformation is used, allows us to reach sensitivity at the ~1 % level of switching bonds. Thus, in particular, it was proved that reversible photostructural transformations in a-As₂S₃ films were explained by heteropolar As-S bonds switching in homopolar As-As and S-S ones, accompanied by simultaneous formation of specific coordination topological defects represented themselves as pairs of anomalously coordinated (under- and over-coordinated)

atoms with opposite electrical charges (negative and positive ones, respectively) [7-10]. These changes were not restricted by short-range ordering structural transformations, stretching into intermediate range over 3-5 coordination spheres due to accompanied relaxation processes around re-switched covalent bonds in good correspondence to known EXAFS data [11,12].

Therefore, we can consider a-As₂S₃ film as a model object to study photostructural transformations in AChS. It is explained, in part, by a good distinction of different vibrational bands corresponding to main structural fragments of a-As₂S₃ with homo- and heteropolar covalent bonds [13,14], as well as by structural network models well-developed for this specimen [15].

However, this situation becomes more complicated for a-As₂Se₃ films, while reversible PhIE are quite sharply expressed in them too (but with less amplitude) [1,4]. The IR vibrational spectrum of this AChS specimen contains a large number of absorption bands overlapping in the narrow range of 275-100 cm⁻¹ [16,17]. As a result, the direct observation of photostructural changes in a-As₂Se₃ is too problematic, but IR Fourier-transform spectroscopy is expected to be more informative in this case.

2. Experimental

As to the preparation of the investigated a-As₂Se₃ thin films and other experimental details, it should be noted that correct study of PhIE mechanism at the both irreversible and reversible stages needs:

1) using of especially prepared specimens, determined by technological parameters of deposition, thickness, molecular and atomic chemical composition, etc., which possess sharply defined PhIE;

2) correct formation of the reversible channel of PhIE owing to subsequent cycles of absorbed light photoexposure and thermal annealing at the temperatures of 20-30 K less than glass transition point;

3) experimental proving of the PhIE reversibility, i.e. observation of mutually opposite changes of relatively equal amplitudes in multiple cycles of photoexposure and thermal annealing.

Unfortunately, in some cases these requirements have not been kept leading finally to sufficient divergences in the developed interpretations.

The investigated a-As₂Se₃ films of 2 μm thickness were vacuum-deposited at 10-15 nm/s rate on substrates made of especially prepared radiation-modified polyethylene, having a softening temperature over 430 K and high transparency in 300-100 cm⁻¹ spectral region. The powder of bulk a-As₂Se₃ glass obtained by direct synthesis from 99,999 % purity constituents was used as raw materials. The correspondence between compositions of bulk glass, thin films and stoichiometric As₂Se₃ compound was confirmed by electron probe microanalysis ("Camebax", France).

The prepared films were exposed by absorbed light of He-Ne laser (633 nm) at power density of 25 mW/cm² during 120 min and then thermally annealed at 430 K during 30 min. These conditions ensure a 20-25 nm reversible shifts in optical absorption edge with a full absence of non-linear effects proper to extra-high or low light intensities.

The IR Fourier-transform measurements were performed in 300-100 cm⁻¹ region using IFS-113V "Bruker" spectrometer. The occurring structural transformations were determined by corresponding optical density D changes in the main own vibrational bands of a-As₂Se₃. The positive ΔD values were associated with appeared complexes, while the negative ones – with destructed complexes.

It is well known that vibrational bands of a-As₂Se₃ are grouped in the narrow 275-100 cm⁻¹ spectral domain [16-19]. Apart from ν₃=217 cm⁻¹ mode of symmetric valence vibrations of As-Se bonds in pyramidal AsSe₃ units [16,17], the sharply defined vibrations of short-layer As-Se bonds at 243 cm⁻¹ [16] and intermolecular modes of deformation As-Se-As vibrations at 172 and 274-269 cm⁻¹ [17] are revealed in IR spectra. This is a consequence of partial keeping of main structural features proper to crystalline As₂Se₃ in amorphous state [20]. If interatomic As-S distances for all structural units (bridge and short-layer ones) slightly change in crystalline As₂S₃, this distance in spiral chains along C axis is 0.011 nm shorter than in bridge complexes in c-As₂Se₃ [20]. In order to identify the absorption bands of structural fragments based on homopolar As-As (230, 140 and 120 cm⁻¹) and Se-Se (270, 260, 250-230, 144-136 cm⁻¹) chemical bonds, the experimental results on amorphous a-As and a-Se were taken into account [18,19].

3. Results and discussion

The methodology of our experimental research is grounded on a sequence of individual stages caused by photoexposure or thermal annealing of the prepared a-As₂Se₃ films.

3. 1. Stage of irreversible photostructural transformations.

Structural transformations observed at the stage of irreversible photodarkening due to absorbed light photoexposure of as-prepared a-As₂Se₃ films correspond to homopolar As-As and Se-Se covalent bonds switching in heteropolar As-Se ones. This result is obvious from IR Fourier-transform spectrum shown in Fig.1 as an increase in the intensities of vibrational bands associated with As-Se bonds (217, 243, 172, 274-269 cm⁻¹), especially in the region of 217 cm⁻¹ band proper to symmetric valence As-Se vibrations in pyramidal AsSe₃ units [16,17], as well as a decrease in the intensities of homopolar-bond vibrations at 230, 140, 120 cm⁻¹ (As-As bonds) and 270, 260, 250-230, 144-136 cm⁻¹ (Se-Se bonds) [18,19].

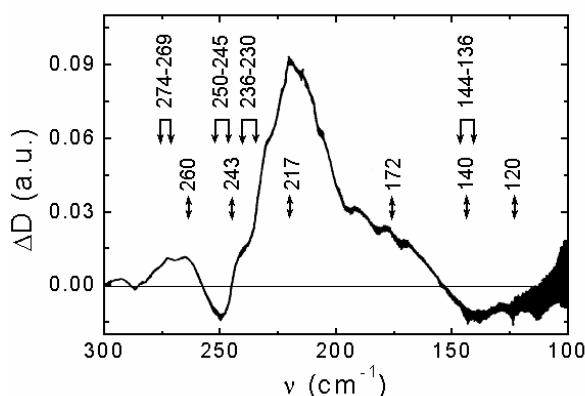


Fig.1. IR Fourier-transform spectrum of additional optical density in as-prepared a-As₂Se₃ films induced by first-cycle photoexposure (the irreversible photodarkening stage).

The similar changes have been observed by us previously in photoexposed as-prepared a-As₂S₃ films [7,8]. Using this analogy between a-As₂S₃ and a-As₂Se₃, it is possible to conclude that irreversible photostructural transformations correspond to cooperative switching of homopolar As-As and S-S covalent bonds in heteropolar As-S ones (the homopolar-heteropolar covalent-bond switching). This process is accompanied by formation of coordination topological defects, which appear in a glassy-like network by pairs (negative and positive, under- and overcoordinated ones), keeping its electrical neutrality and average covalent-bonded connectivity. Electrical states and structural configurations of these defects were described previously in terms of D-centres or unsaturated dangling bonds [21], valence alternation pairs [22], intimate valence alternation pairs [23] or self-trapped excitons [24].

Taking into account that final defect-enriched structural state depends not only on destroyed bond, but also on its nearest atomic arrangement, we can introduce 16 topological schemes of the corresponding structural transformations for a-As₂Se₃, previously discussed by us elsewhere [8-10]. Only four topological schemes shown in Fig.2 correspond to homopolar-heteropolar bond switching, since another ones are associated with bond-conserving switching (without changes in bond type). Consequently, (As₂⁻, Se₃⁺) and (As₄⁺, Se₁⁻) defects are main products of the irreversible photostructural transformations in as-prepared a-As₂Se₃ films, the upper index in the defects signature meaning the electrical charge state and the lower one – the number of covalent bonds. It should be noted that heteropolar As-Se covalent bonds appeared at the irreversible stage of PhIE instead of destructed homopolar As-As and Se-Se ones exist within both short-layer heteropolar As-Se and long-bridge heteropolar As-Se-As covalent bonds.

The only possible alternative way to explain these results is structural polymerization process including transformation of As₄Se₄ and Se₂ molecular fragments in heteropolar-bond-based homogeneous AsSe_{3/2} network

without any changes in atomic coordination [6]. This process is possible only at high concentration of initial molecular fragments with homopolar covalent bonds. Simultaneously two different homopolar bonds (As-As and Se-Se) are destroyed and two heteropolar ones (As-Se) appear instead of them. All four atoms forming initial homopolar bonds should occupy such sites in a glassy network, which can be well transformed in new configuration containing two heteropolar bonds without strong atomic rearrangement. This requirement must be satisfied only for two atoms, provided coordination topological defects appear. Hence the probability of photoinduced coordination defect formation in a-As₂Se₃ is higher in comparison with photoinduced defect-free polymerization. The latter is probably dominant in as-prepared AChS films during their thermal annealing near glass transition temperature, when atomic migrations can be essentially activated [13,14].

3. 2. Stage of thermal bleaching of irreversible PhIE

The following thermal annealing of as-prepared a-As₂Se₃ films photoexposed by absorbed light to saturation of long-wave shift of optical transmittance edge causes the same changes in IR vibrational spectrum. However, the intensities of the main vibrational bands associated with structural fragments based on homo- and heteropolar covalent bonds (see Fig.1) are more than twice smaller. This feature was observed previously in a-As₂S₃ films too [8].

We can explain this result by thermal recombination not all, but only a half part of coordination defects appeared at the previous stage of photoexposure. As it testified from Fig.2, in the nearest neighbourhood of (As₂⁻, S₃⁺) and (As₄⁺, S₁⁻) coordination defects, formed via 1 and 3 schemes, only high-energetic heteropolar As-Se bonds exist (their dissociation energy is equal to 2.26 eV, while dissociation energies of homopolar As-As and Se-Se chemical bonds are 2.07 eV and 2.14 eV, respectively [20,25]). These defects are thermally stable, but two other defect pairs (schemes 2 and 4 in Fig.2), having homopolar As-As and Se-Se bonds, annihilate by switching in heteropolar As-Se ones in full agreement with the obtained result (Fig. 3). In such a way, the glass network relaxes in a more stable structural state with lower concentration of coordination defects.

It is significant that, in the case of irreversible PhIE and their thermal bleaching, the greatest changes occur in 240-190 cm⁻¹ spectral domain, which corresponds to stretch-type vibrations.

The as-prepared a-As₂Se₃ films treated by absorbed light and thermally annealed are ready for reversible PhIE observation in the next cycles of treatment.

3. 3. Stages of reversible photo- and thermally-induced structural transformations.

As it follows from Fig.4a, the third-cycle photoexposure of a-As₂Se₃ film increases the content of structural complexes based on heteropolar short-layer As-Se bonds (243 cm⁻¹), as well as homopolar Se-Se (260, 250-245, 236-230, 144-136 cm⁻¹) and As-As (230, 140, 120 cm⁻¹) ones, formed instead of pyramidal AsSe₃ (217 cm⁻¹) and bridge As-Se-As (274-269, 172 cm⁻¹) units. The next annealing is fully reversible (see Fig.4b). In multiple photoexposure-thermoannealing cycles these changes of optical density ΔD can be repeated with a very small irreversible component.

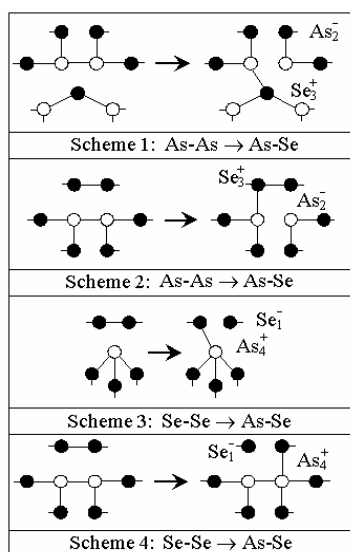


Fig. 2. Topological schemes of covalent-bond switching explained irreversible photostructural transformations in as-prepared a-As₂Se₃ films.

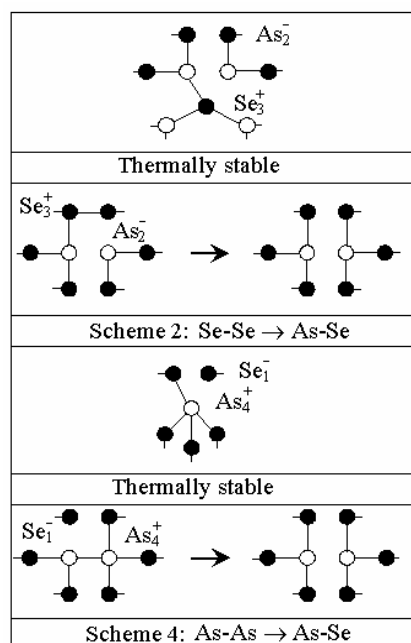


Fig. 3. Topological schemes of covalent-bond switching explained first-cycle thermal annealing of

photoexposed as-prepared a-As₂Se₃ films.

It is estimated that no more than 3 % of atoms are involved in the observed PhIE. In contrast to a-As₂Se₃, showing the reversible photostructural transformations due to heteropolar-homopolar bond switching, the investigated a-As₂Se₃ films contain an additional channel connected with long-bridge heteropolar As-Se-As bonds switching in short-layer ones of the same type (the heteropolar-heteropolar bond switching). The heteropolar-homopolar bond switching can be attributed to (As₂⁻, Se₃⁺) and (As₄⁺, Se₁⁻) defect formation. Taking into account topological schemes of irreversible PhIE discussed in 1 and 2, the complete topological scheme of reversible photo-thermally-induced bond switching with heteropolar-bond-based pyramidal AsSe₃ units as initial structural fragments can be presented (see Fig. 5). The heteropolar-heteropolar bond switching (see Fig. 6) corresponds to (As₂⁻, As₄⁺) defect formation. Instead of destructed bridge As-Se-As unit, the short-layer heteropolar As-Se bond appears forming As₄⁺-Se₂⁰-As₃⁰ structural chain.

The observed small shift in the spectral position for some IR absorption bands (no more than 10 cm⁻¹), in particular, the long-wave shift of bent modes at 172 and 274-269 cm⁻¹ (see Fig. 4), are produced by strong relaxation processes at the reversible stage because of increased intermolecular interaction between defect-based structural groups. At the stage of irreversible PhIE, these features were relatively negligible (Fig. 1).

It should be emphasized that bent vibrational modes ($\nu < 170$ cm⁻¹) are dominant in the additional optical density spectrum of the reversibly treated a-As₂Se₃ films (Fig.4) as they are more sensitive to intermolecular (interlayer) interactions [4]. It testifies that medium-range ordering structural changes (rotations and displacements of atomic blocks) are very important in the observed effects. Simultaneously, the intensities of stretch-type vibrational modes in 300-200 cm⁻¹ spectral region are stronger than ones of bent-type vibrational modes at the stage of first-cycle photoexposure of as-prepared a-As₂Se₃ films in good accordance to the preference of irreversible short-range structural transformations [4].

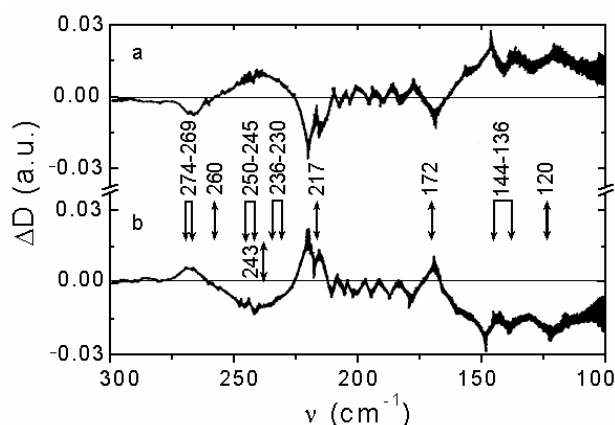


Fig. 4. IR Fourier-transform spectrum of additional optical density in $a\text{-As}_2\text{Se}_3$ films induced by third-cycle photoexposure (a) and subsequent thermal annealing (b).

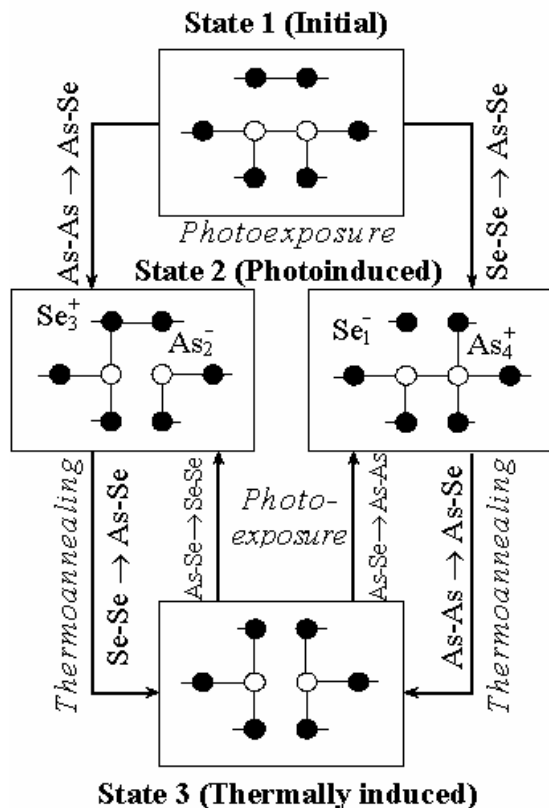


Fig. 5. Reversible photo-thermally-induced structural transformations in $a\text{-As}_2\text{Se}_3$ connected with heteropolar-homopolar bond switching.

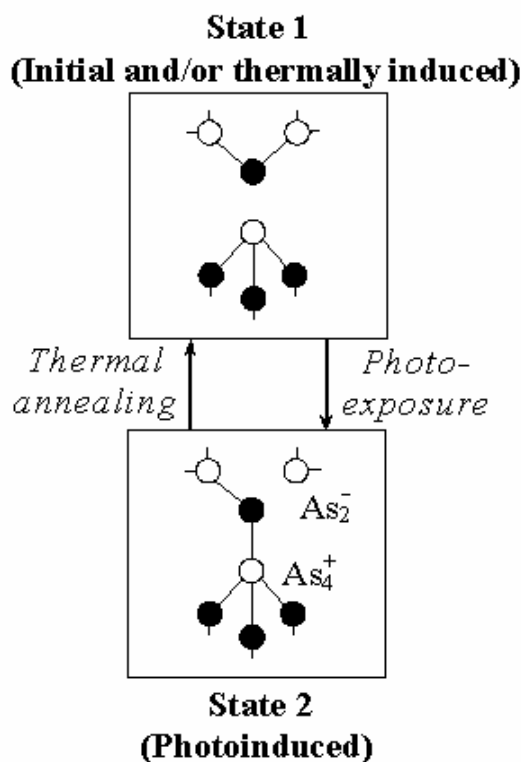


Fig. 6. Reversible photo-thermally-induced structural transformations in $a\text{-As}_2\text{Se}_3$ connected with heteropolar-heteropolar bond switching.

As to intermediate “light-in” processes between initial and final states within described reversible photostructural transformations, we believe, at the basis of experimental results obtained for $a\text{-Se}$ using “in-situ” EXAFS [12], they include the photoexcitation of lp-electrons localized on Se atoms, formation of new dynamic covalent bond with these excited lp-electrons and, finally, relaxation of the created configurational disturbance through destruction of another nearest bond accompanied by medium-range atomic displacement.

3. 4. On the kinetics of the observed photostructural transformations

The mathematical simulation of kinetics of photo-induced structural transformations in the investigated thin films were considered at the basis of general differential equation in power-like form proper to relaxation phenomena in topologically-disordered solids (Table 1, 2) [26]. It was established that well-known stretched-exponential relaxation function [27] was the absolutely best one to adequately describe this behavior. This result is in good agreement with general concept of relaxation phenomena in topologically-disordered substances [26-28] as the investigated thin films are their typical representatives.

By comparing mono- (single-exponential) and bimolecular relaxation functions, the strong preference of the former was obtained in all cases under consideration. Since this kind of relaxation kinetics corresponds to interaction of specific defect pairs such as electrons and holes, vacancies and interstitials, etc. [28], we can accepted this fact as an additional confirmation for defect-related nature of photostructural transformations in $a\text{-As}_2\text{Se}_3$ films, these defects being pairs of oppositely charged under- and over-coordinated atoms.

Recently, the similar experimental [29] and theoretical [30] works were devoted to study the mechanism of photoinduced effects in $a\text{-As}_2\text{Se}_3$. In spite of some differences, the both investigations are relevant to covalent-bond switching with an associated coordination defects.

4. Conclusions

The microstructural origin of PhIE in $a\text{-As}_2\text{Se}_3$ films was studied by IR Fourier-transform spectroscopy in the range of $300\text{-}100\text{ cm}^{-1}$. It is shown that irreversible photostructural transformations in as-prepared $a\text{-As}_2\text{Se}_3$ films are connected with coordination topological defect formation accompanied by homopolar As-As and Se-Se covalent-bond switching in heteropolar As-Se ones. These defects can be identified as atomic pairs with uncompensated opposite electrical charges and anomalous

coordination. In the case under consideration, $(\text{As}_2^-; \text{Se}_3^+)$ and $(\text{As}_4^+; \text{Se}_1^-)$ defect pairs are formed.

The subsequent thermal annealing of the photoexposed as-prepared a- As_2Se_3 thin films causes the same changes in IR absorption spectrum as in the case of their photoexposure, but corresponding intensities of the main vibrational bands are more than twice smaller. This result is explained in terms of thermal annihilation of a half part of coordination defects created at the previous stage.

Table 1. Fitting parameters of the relaxation functions describing photoinduced degradation kinetics in as-deposited As_2Se_3 films.

Relaxation function	Fitting parameters				MSD $\times 10^4$
	a	τ	λ	r	
$M_\eta(t) = e^{-\frac{t}{\tau}}$	0.65	4416.1	—	—	129.7
$M_\eta(t) = \left(1 + \frac{t}{\tau}\right)^{-1}$	0.75	2083.7	—	—	99.1
$M_\eta(t) = \left(1 + \frac{t}{\tau}\right)^{-\kappa}$	1.00	6.5	0.17	—	0.9
$M_\eta(t) = \exp\left[-\left(\frac{t}{\tau}\right)^\kappa\right]$	1.37	358.3	0.14	—	1.5
$M_\eta(t) = \left(1 + \left(\frac{t}{\tau}\right)^\kappa\right)^{-r}$	1.11	3.4	1.48	0.13	1.0

Table 2. Fitting parameters of the relaxation functions describing photoinduced degradation kinetics in annealed As_2Se_3 films.

Relaxation function	Fitting parameters				MSD $\times 10^4$
	a	τ	λ	r	
$M_\eta(t) = e^{-\frac{t}{\tau}}$	0.72	5248.5	—	—	82.0
$M_\eta(t) = \left(1 + \frac{t}{\tau}\right)^{-1}$	0.89	2328.5	—	—	76.1
$M_\eta(t) = \left(1 + \frac{t}{\tau}\right)^{-\kappa}$	1.00	28.82	0.18	—	0.5
$M_\eta(t) = \exp\left[-\left(\frac{t}{\tau}\right)^\kappa\right]$	2.46	21.1	0.11	—	0.9
$M_\eta(t) = \left(1 + \left(\frac{t}{\tau}\right)^\kappa\right)^{-r}$	1.11	3.4	1.28	0.13	1.0

The reversible stage of photostructural transformations is caused by two different types of bonds switching. The first type can be presented as heteropolar-homopolar bond switching, while the second one is connected with heteropolar bridge bonds switching in heteropolar short-layer ones. The both processes are accompanied with coordination defect formation and

atomic displacement at more extended medium-range level.

The developed mathematical simulation procedure testified that the observed kinetics of reversible photo-induced transformations corresponded to well-known stretched-exponential relaxation function, tending to bimolecular behavior rather than to single-exponential monomolecular one.

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