Photo-induced cooperative covalent-bond switching in amorphous arsenic selenide

O Shpotyuk¹,²,³, V Balitska¹ and J Filipecki²

¹Lviv Scientific Research Institute of Materials of SRC "Carat", 202, Stryjska str., Lviv, UA-290031, Ukraine
²Institute of Physics of Jan Długosz University, 13/15, Al. Armii Krajowej, Częstochowa, PL-42201, Poland
E-mail: shpotyuk@novas.lviv.ua

Abstract. A microstructural mechanism of photoinduced transformations in amorphous arsenic selenide films 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 in a favour of defect-related origin of the reversible photo-thermally-induced transformations, since their kinetics corresponded to known stretched-exponential dependence, tending to bimolecular behaviour rather then to single-exponential one.

1. Introduction

Amorphous chalcogenide semiconductors 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 xerography and lithography, CD-erasable media, memory-switching devices, photosensitive recorders, etc. [1-3]. Physical features of the above PhIE were well studied more than 3 decades ago, but a number of controversies concerning our understanding of their microstructural nature are still remained up to now.

This situation is obviously caused by difficulties in the direct observation of local atomic structure in disordered solids. The reversible PhIE are relatively weak as they embrace no more than 10 % of atomic nodes concentration. The sensitivities of conventional amorphographical techniques operating with useful information at the general background of the whole integrated signal are insufficient for this. Only in the case of amorphous a-As₂S₃ films, the reversible photostructural transformations can be relatively simply identified as covalent-bond switching processes using Raman spectroscopy [4]. The main result of this experiment was connected only with numerical 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 showed that necessary information on the PhIE mechanism could be accurately obtained with “differential” IR Fourier spectroscopy, dealing with a part of the photoinduced spectrum, but not the whole integrated one [5]. Thus, in part, it was proved that reversible photostructural transformations in a-As₂S₃ 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 [5,6].

³ To whom any correspondence should be addressed.
Because of good distinction of different vibrational bands as well as structural network models well-developed for this specimen [3,6], the a-As$_2$S$_3$ film can be consider as a model object to study photostructural transformations. However, this situation becomes more complicated for a-As$_2$Se$_3$ films, while reversible PhIE are quite sharply expressed in them too [1,2]. The IR vibrational spectrum of this specimen contains a large number of absorption bands overlapping in the narrow range of 275-100 cm$^{-1}$ [7,8]. As a result, the direct observation of photostructural changes in a-As$_2$Se$_3$ is problematic, but IR Fourier-transform spectroscopy is expected to be more informative in this case.

2. Experimental
The investigated a-As$_2$Se$_3$ 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$^{-1}$ region. The powder of bulk a-As$_2$Se$_3$, obtained by direct synthesis from 99.999 % purity constituents was used. The prepared films were exposed by absorbed light of He-Ne laser (633 nm) at 25 mW/cm$^2$ power density during 120 min and then annealed at 430 K during 30 min. These conditions ensure 20-25 nm shift in optical absorption edge with 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 vibrational bands of a-As$_2$Se$_3$. The positive ∆D values were associated with appeared structural complexes, while the negative ones – with destructed complexes.

It is well known that vibrational bands of a-As$_2$Se$_3$ are grouped in the narrow 275-100 cm$^{-1}$ spectral domain [7-10]. Apart from $\nu_3$=217 cm$^{-1}$ mode of symmetric valence vibrations of As-Se bonds in pyramidal AsSe$_3$ units [7,8], the sharply defined vibrations of short-layer As-Se bonds at 243 cm$^{-1}$ [7] and intermolecular modes of deformation As-Se-As vibrations at 172 and 274-269 cm$^{-1}$ [8] are revealed in IR spectra. This is a consequence of partial keeping of main structural features proper to crystalline As$_2$Se$_3$ in amorphous state [3]. If interatomic As-S distances for both bridge and short-layer fragments change slightly in crystalline As$_2$S$_3$, this distance in spiral chains along C axis is 0.011 nm shorter than in bridge complexes in c-As$_2$Se$_3$ [9]. To identify the absorption bands of structural units based on homopolar As-As (230, 140 and 120 cm$^{-1}$) and Se-Se (270, 260, 250-230, 144-136 cm$^{-1}$) bonds, the experimental results on amorphous a-As and a-Se were taken into account [9,10].

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-As$_2$Se$_3$ films.

3.1. Stage of irreversible photostructural transformations
Structural transformations observed at the stage of irreversible photodarkening in as-prepared a-As$_2$Se$_3$ 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 figure 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 As-Se valence vibrations in pyramidal AsSe$_3$ units [7,8], 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) [9,10].

The similar changes have been observed by us previously in photoexposed as-prepared a-As$_2$S$_3$ films [5,6]. Using this analogy between a-As$_2$S$_3$ and a-As$_2$Se$_3$, it is possible to conclude that irreversible photostructural transformations correspond to cooperative switching of homopolar As-As and Se-Se covalent bonds in heteropolar As-Se ones. 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 [3].
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-As$_2$Se$_3$, previously discussed by us elsewhere [6]. Only 4 topological schemes shown in figure 2 correspond to homopolar-heteropolar bond switching (the corresponding bond-switching reaction is given below each scheme), since other ones are associated with bond-conserving switching (without changes in bond type). Consequently, (As$_2^-$, Se$^+_3$) and (As$^{4+}$, Se$_1^-$) defects are main products of the irreversible photostructural transformations in as-prepared a-As$_2$Se$_3$ films, the upper index meaning the electrical charge state and the lower one – the number of covalent bonds. It should be noted that heteropolar As-Se 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 complexes.

3.2. Stage of thermal bleaching of irreversible PhIE
The following thermal annealing of photoexposed as-prepared a-As$_2$Se$_3$ films causes the similar changes in IR spectrum, but with more than twice smaller intensities of the main vibrational bands (see figure 1). This feature was observed previously in a-As$_2$S$_3$ films too [6].

We can explain this result by thermally-induced annihilation not all, but only a half part of coordination defects appeared at the previous stage of photoexposure. As it testified from figure 2, in the nearest neighbourhood of (As$_2^-$, S$^+_3$) and (As$^{4+}$, S$_1^-$) defect pairs, formed via 1 and 3 schemes, only high-energetic heteropolar As-Se bonds exist (their dissociation energy is 2.26 eV, while dissociation energies of homopolar As-As and Se-Se bonds are 2.07 eV and 2.14 eV, respectively [3,11]). These defect pairs are thermally stable, but two other ones with homopolar As-As and Se-Se bonds (schemes 2 and 4 in figure 2) annihilate by switching in heteropolar As-Se bonds in full agreement with our results shown in figure 3. In such a way, the glass network relaxes towards more thermodynamically equilibrium state with lower concentration of coordination defects. 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-As$_2$Se$_3$ films treated by absorbed light and thermally annealed are ready to demonstrate the reversible PhIE in the following cycles of treatment.

3.3. Stages of reversible photo- and thermally-induced structural transformations
As it follows from figure 4a, the third-cycle photoexposure of a-As$_2$Se$_3$ 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 AsSe$_3$ (217 cm$^{-1}$) and bridge As-Se-As (274-269, 172 cm$^{-1}$) units.
The next annealing is fully reversible (figure 4b). In multiple photoexposure thermoannealing cycles these changes of optical density $\Delta D$ can be repeated with a very small irreversible component.

It is estimated that no more than 3% of atoms are involved in the observed PhIE. In contrast to a-As$_2$S$_3$, showing the reversible photostructural transformations due to heteropolar-homopolar bond switching, the a-As$_2$Se$_3$ films contain an additional channel connected with 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 (As$_2^+$, Se$_3^-$) and (As$_4^+$, Se$_1^-$) defect formation. Taking into account topological schemes of irreversible PhIE discussed in 3.1 and 3.2, the complete topological scheme of reversible photo-thermally-induced bond switching with heteropolar-bond-based pyramidal AsSe$_3$ units as initial structural fragments can be presented (see figure 5). The heteropolar-heteropolar bond switching (see figure 6) corresponds to (As$_2^+$, As$_4^+$) defect formation.

Instead of destructed bridge As-Se-As unit, the short-layer heteropolar As-Se bond appears forming As$_4^+$-Se$_2^0$-As$_3^0$ structural chain.

It should be emphasized that bent vibrations ($\nu<170$ cm$^{-1}$) are dominant in the additional optical density spectrum of the reversibly treated a-As$_2$Se$_3$ films (figure 4) as they are more sensitive to intermolecular medium-range structural changes [2]. 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-As$_2$Se$_3$ films in good accordance to the preference of irreversible short-range structural transformations [2].
As to intermediate “light-in” processes between initial and final states in figures 5 and 6, we believe, at the basis of “in-situ” EXAFS data for a-Se [12], they include photoexcitation of lp-electrons localized on Se atoms, formation of new dynamic bond and, finally, relaxation of the created disturbance through destruction of another bond accompanied by medium-range atomic displacement.

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

**Figure 5.** Reversible photo-thermally-induced structural transformations in a-As$_2$Se$_3$ connected with heteropolar-homopolar bond switching.

**Figure 6.** Reversible photo-thermally-induced structural transformations in a-As$_2$Se$_3$ connected with heteropolar-heteropolar bond switching.
3.4. On the kinetics of the observed photostructural transformations

The kinetics of the reversible photodarkening was studied to obtain the complementary confirmation on the defect-related origin of the corresponding structural changes in a-As$_2$Se$_3$ films. This kinetic dependence was typical one, showing a character sharp increase in optical transmittance with time followed a more extended saturation [1-3]. Using mathematical fitting procedure developed at the basis of general differential equation of photoinduced degradation [13], it was established that stretched-exponential relaxation function [14] was the absolutely best to adequately describe this behaviour. By comparing mono- and bimolecular functions, the strong preference of the former was proved. Since this kind of relaxation kinetics corresponds to interaction of specific defect pairs of opposite nature (such as electrons and holes, vacancies and interstitials) [15], we accept this fact as an additional confirmation for defect-related origin of the studied photostructural effects in a-As$_2$Se$_3$.

4. Conclusions

The PhIE mechanism of in a-As$_2$Se$_3$ films was studied by IR Fourier-transform spectroscopy in 300-100 cm$^{-1}$ range. It is shown that irreversible photostructural transformations in as-prepared films are connected with coordination defect formation accompanied by homopolar As-As and Se-Se covalent-bond switching in heteropolar As-Se ones. The subsequent thermal annealing of these films causes the same changes in IR spectra as in the case of their photoexposure, but corresponding intensities of 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.

The reversible photostructural transformations are caused by two different types of bonds switching. The first type is heteropolar-homopolar bond switching, while the second one is switching of heteropolar bridge bonds in heteropolar short-layer ones. The both processes are connected with coordination defects and atomic displacement at more extended medium-range ordering level.

The developed mathematical simulation procedure testifies in a favour of defect-related origin of the investigated photo-thermally-induced structural transformations, since their kinetics corresponds to stretched-exponential low, tending to bimolecular behaviour rather then to single-exponential one.

5. References

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