

PACS 61.43.Fs, 61.80.Ed, 78.20.-e

On the origin of radiation-induced metastability in vitreous chalcogenide semiconductors: The role of intrinsic and impurity-related destruction-polymerization transformations

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Abstract. Radiation-optical effects in vitreous chalcogenide semiconductors are comprehensively analyzed as resulting from both *intrinsic* and *impurity-related* redistribution of covalent chemical bonds known also together as *destruction-polymerization transformations*. Two types of experimental measuring protocols can be used to study radiation-induced effects within *ex-situ direct* or *in-situ backward* measuring chronology, the latter being more adequate for correct separated testing of competitive inputs from both channels of destruction-polymerization transformations. Critical assessment is given on speculations trying to ignore intrinsic radiation-structural transformations in As₂S₃ glass in view of accompanying oxidation processes. In final, this glass is nominated as the best model object among wide group of vitreous chalcogenide semiconductors revealing the highest sensitivity to radiation-induced metastability.

Keywords: vitreous chalcogenide semiconductors, glasses, optical spectroscopy, X-ray diffraction, γ -irradiation, oxidation.

Manuscript received 15.09.14; revised version received 26.11.14; accepted for publication 19.02.15; published online 26.02.15.

1. Introduction

The problem of induced metastability has still been actual since the time of the first experiments on photostructural transformations in vitreous chalcogenide semiconductors (VChS) in the earliest 1970-s [1-3]. In fact, this problem deals with nature of defective states in VChS caused by destruction of existing bond arrangement following structural relaxation towards metastable state with new distribution of covalent chemical bonds. This process was consequently defined as *destruction-polymerization transformation* (DPT)

[2, 3], meaning that photoinduced metastability is directly related to modified bond distribution in a glassy matrix obeying the known (8-N) rule [4].

Under these circumstances, it is quite understandable, that covalent chemical bonds being destructed by absorbed light or other acting external factors (such as high-energy γ -irradiation [5, 6], for instance), can be renewed *intrinsically* via direct interaction of bond-constituting atoms with the nearest neighbors forming a channel for *own (intrinsic) bond switching*, or *extrinsically* due to interaction with impurity chemical environment. In the first case,

diamagnetic pairs of over- and under-coordinated atoms possessing an excess of positive and negative electric charges (*charged defects*), respectively, appear in a glassy backbone [4-6]. Alternatively, this process can proceed as non-defect structural transformation, provided two covalent bonds are simultaneously switched [7]. In the latter case, some kinds of impurity products can be formed preferentially at the VChS surface [5, 8], the most essential being induced by interaction with absorbed oxygen, which replace chalcogen in its bonding states within glassy network. For As-based VChS, formation of arsenic oxide is favorable from the thermodynamic viewpoint for both S- and Se-type environment [4, 9]. Therefore, *intrinsic (own) DPTs* occur to be permanently admixed to *extrinsic (impurity)* ones, forming a complicated picture of competitive input in the overall balance of induced effects. So, methodological route allowing unbiased observation of these channels has attained a vital importance, especially in respect to implementation of externally-induced functionality in a variety of VChS systems [5].

Incorrect presentation of interrelation between own and impurity-type induced processes, such as radiation-structural effects in vitreous $v\text{-As}_2\text{S}_3$ considered in ref. [10], appears as an artifact of many inconclusive findings on their eventual nature. Thus, for example, the broadening of the first sharp diffraction peak (FSDP) in $v\text{-As}_2\text{S}_3$ (which, by overall opinion, is a manifestation of medium-range ordering at the atomistic length scales ranging from a few to $\sim 10 \text{ \AA}$ [11-13]) due to radiation-induced oxidation [14] was mistakenly ascribed to own structural changes [15], they being imagined as fully identical to reversible photoexpansion [16, 17]. An obvious difference in the origin of photo- and radiation-induced metastability was thus ignored at all. It is well known, in case of photoexposure, this metastability is triggered by excitation of lone-pair p -electrons [18], while over-barrier atomic displacements become important under high-energy irradiation [6, 19]. It means that some excitation processes causing essential optical changes, which are principally impossible under photoexposure, can be indeed activated under radiation influence [6]. In a naive sense, the author [10] tries to exclude parasitic impact of oxidation in the overall radiation-induced effect due to experiments arranged within *in-situ* measuring protocol, which in fact has no any relation to the observed misbalance between *intrinsic* and *extrinsic* radiation-induced effects.

Recently, some of the present authors showed that simple elimination of oxidized surface layer from irradiated VChS allowed restoration all the FSDP parameters, keeping essential radiation-induced darkening in optical absorption of $v\text{-As}_2\text{S}_3$ [20, 21]. So, these effects can be attributed to preferential changes in local atomic configurations at the level of short-range structural ordering. Such transformations are known to evolve a few percent of atoms ($\sim 10^{20} \dots 10^{21} \text{ cm}^{-3}$) [5-7,

18, 19], being most pronounced in loosely-packed atomic matrices, which are insensitive to medium-range structural correlations responsible for the FSDP [22, 23].

So, an actual question appears in respect to this critical assesment: *What is a way to study intrinsic radiation-induced DPT in VChS, since their occurrence is so hidden by competitive oxidation input?* In this work, we shall present an adequate methodological solution of this problem exemplified by high-dose radiation-induced optical changes observed in $v\text{-As}_2\text{S}_3$.

2. Experimental

The samples of $v\text{-As}_2\text{S}_3$ were prepared by conventional rocking-melting-quenching technique using respective quantities of high-purity (not less than 99.999%) As and S in evacuated and sealed fused silica ampoules. The mixture of precursors was melted in a rocking furnace with further air-quenching to a glassy state, which was controlled visually by a characteristic conchoidal fracture and confirmed by XRD analysis. Then, the glass samples were annealed at $140 \text{ }^\circ\text{C}$ to eliminate residual mechanical stress frozen during the melt-quenching procedure. All prepared specimens were cut as plane-parallel plates of 1.5 mm in a thickness and carefully polished to high optical quality.

The γ -irradiation treatment was carried out at the ambient conditions in a closed cylindrical cavity of concentrically located ^{60}Co sources (the mean energy of γ -quanta 1.25 MeV) with 0.7 kGy/h dose rate at temperature not exceeding $30 \text{ }^\circ\text{C}$. The overall duration of γ -irradiation treatment was 6 months and total accumulated dose during this period was $\sim 3 \text{ MGy}$. It is well known that under such conditions, both intrinsic (own) and extrinsic (impurity-related) structural transformations (first of all, the radiation-induced oxidation) are well activated [5, 20, 21].

Optical transmission spectra of the samples were recorded in the fundamental absorption edge region using AvaSpec-2048 spectrometer (*Avantes*, Netherlands) with a maximum associated error of $\pm 1 \%$. These measurements were performed one month after γ -irradiation. In such a way, the dynamic (transient) quick-decaying changes [5, 6, 24] were exhausted, and only the static (just residual) optical effect left in the γ -irradiated glasses.

Two types of experimental measuring protocols were applied to study γ -induced effects in $v\text{-As}_2\text{S}_3$, these being realized in *direct* and *backward* measuring chronology.

In the former, the optical transmission spectra were recorded *ex-situ* for the same glass sample taken in non-irradiated (just before irradiation) and γ -irradiated states (one month after irradiation). To minimize errors due to inadequate repetition of measuring cycles separated over period more than 6 months, the tested sample was positioned in a measuring chamber in respect to probe light beam using special marks drawn on its surface.

The second type of optical measurements was performed *in-situ* in *backward measuring chronology*, since only the same γ -irradiated sample was used to reproduce just irradiated and further annealed states. The investigated γ -irradiated sample was kept in the same position in respect to the probe light beam during all stages of thermal treatment, the air-flow heating and cooling being provided in a specially adjusted temperature chamber with the constant rate (5 K/min) and uncertainty in the temperature control at the level of ± 0.5 K.

3. Results and discussion

Transmission spectra in the region of fundamental optical absorption edge of the same $v\text{-As}_2\text{S}_3$ sample measured in *direct chronology*, so just before (initial unirradiated state) and after γ -irradiation, are shown in Fig. 1.

The saturation level of optical transmittance of initial $v\text{-As}_2\text{S}_3$ (Fig. 1, curve 1) was close to about 69...70%, so corresponding in respect to the Fresnel formula $T = 2n/(n^2+1)$ to the refractive index n reaching ~ 2.5 , which is well agreed with the known literature data [25, 26]. Since the white arsenolite As_4O_6 layer appeared due to decomposition-oxidation reaction activated by high-energy ionizing radiation can be easily removed from surface by wet polishing [20, 21, 27, 28], we presented the resulting spectra for both cleaned and uncleaned samples (Fig. 1, curves 3 and 2, respectively). Some of these rhombohedral arsenolite crystallites attain a few μm , while majority of them has smaller sub-micrometer sizes [20, 21]. So, these inclusions act as effective scattering centers depressing optical transmission in near-band-gap region (due to Rayleigh scattering), as well as in mid-IR optical transmission region (preferentially due to Mie scattering losses) [29, 30]. Thus, not only saturation level, but also the slope of optical transmission spectrum are essentially changed in γ -irradiated VChS sample (Fig. 1, curve 2).

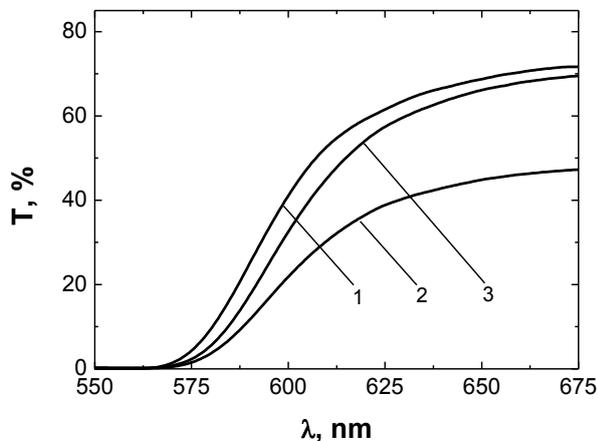


Fig. 1. Optical transmission spectra of $v\text{-As}_2\text{S}_3$ measured in *direct chronology* for initial unirradiated (1), uncleaned γ -irradiated (2) and cleaned γ -irradiated (3) states.

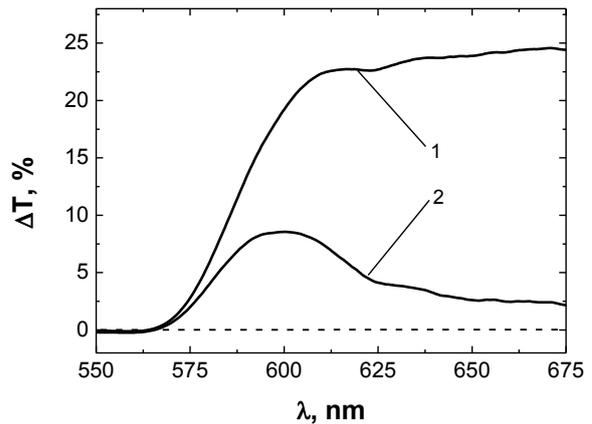


Fig. 2. Optical transmission difference for unirradiated and γ -irradiated $v\text{-As}_2\text{S}_3$ samples measured in *direct chronology* for uncleaned (1) and cleaned (2) surface.

Under such drastic changes in optical transparency, it is difficult to make unambiguous conclusions on intrinsic long- or short-wave shift in the fundamental optical absorption edge (respectively called darkening or bleaching). If only intrinsic changes occur, the close-to-parallel shift of optical transmission edge leads to bell-shaped difference curve with well-defined maximum, sharp high-energetic edge and more extended low-energetic “tail” for compared unirradiated and γ -irradiated samples [5]. Instead of this, the optical transmission difference for these samples with uncleaned surfaces demonstrates a characteristic step-like behavior ending by obvious close-to-saturation trend (see Fig. 2, curve 1), which is also similar to that for $v\text{-As}_2\text{S}_3$ irradiated by 2.41 MGy dose shown in [10]. So, under these circumstances, it is impossible to estimate (even roughly) an input from pure intrinsic changes in the overall balance of radiation-induced DPT.

The simplest way to avoid this problem within measuring procedure arranged in *direct chronology* is to remove the appeared arsenolite layer by delicate hand polishing with a moistened cotton swab [20, 27, 28]. As a result, we can record the optical transmission spectrum of cleaned γ -irradiated $v\text{-As}_2\text{S}_3$ sample (Fig. 1, curve 3) with saturation level tending towards one of the initial sample (Fig. 1, curve 1), the obtained optical transmission difference being shown by curve 2 in Fig. 2 (which is evidently like to one character for γ -induced darkening [5]).

By analogy with [5], the possible explanation for this phenomenon can be given in terms of intrinsic DPT [1-3] via atomistic structural rearrangement accompanied by switching of heteropolar As-S bonds into homopolar As-As ones. Such transformations lead to anomalously-coordinated charge-uncompensated atoms, which appear in VChS by pairs in respect to reaction



In this scheme proposed by L. Tichy [31], the indexes without parentheses stand for the number of atoms, while the indexes in parentheses stand for local atomic coordination. So, the fraction of heteropolar As-S bonds decreases due to irradiation and, simultaneously, the fraction of homopolar As-As bonds increases in excellent agreement with known experimental evidences [7, 31-34]. Noteworthy that non-zero long-wave remainder in optical transmission difference ΔT for unirradiated and γ -irradiated v -As₂S₃ samples tested in *direct chronology* (Fig. 2) is evidently produced by time retardation in subsequent measuring cycles.

Therefore, the above *direct-chronology* measuring has a lot of disadvantages, most of them being related with significant separation between subsequent cycles of optical spectra recording for initial (before irradiation) and final (after γ -irradiation) VChS samples (this period has lasted even few months). The impossibility to reproduce reliably exploitation characteristics of measuring equipment and ambient environmental conditions is principal obstacle restricting this procedure. Simultaneous measuring for different VChS samples, one of them being unirradiated and other one being γ -irradiated, allows only partial solution, since eventual diversity between such samples. The optimal testing methodology for intrinsic radiation-optical changes is to arrange the measuring cycles for the same sample ensuring as small as possible time separation between its states.

This breakthrough idea can be well provided by *backward-chronology* measurements arranged for the same γ -irradiated VChS sample. In this case, the γ -induced effect is considered as consisting of difference in optical transmission between γ -irradiated and subsequently thermally annealed states. This investigation is grounded on the prerequisite that below- T_g thermal annealing γ -induced change arises in VChS restoring the initial glass structure [1, 5, 25, 31]. In our research, we made one more step to enrich the highest accuracy, performing all post-irradiation measurements within *in-situ* regime, so the investigated γ -irradiated sample was kept in the same position in respect to the probe light beam during all subsequent cycles of thermal annealing. Thereby, this *in-situ* measuring protocol allows full exclusion of inaccuracies associated with sample placing in a spectrometer. To distinguish intrinsic and impurity-related radiation-induced effects, we also start our experiments with carefully cleaned VChS sample free of products of radiation-induced oxidation on the surfaces.

The experimental optical transmission spectra of γ -irradiated and further annealed v -As₂S₃ sample (being recorded at the same 25 °C temperature in according to the above described *backward-chronology* protocol) are shown in Fig. 3. It can be easily seen that saturation levels of optical transparencies for both spectra coincide, indicating high precision of this investigation. At the same time, the optical bleaching effect is evident as a result of thermal annealing of γ -irradiated v -As₂S₃ or,

alternatively, the γ -induced darkening observed in respect to annealed sample. The curve of corresponding optical transmission difference ΔT for γ -irradiated and further annealed sample in Fig. 4 has a predicted asymmetric bell-like shape with all necessary constituents (well-defined maximum, sharp high-energetic edge and extended low-energetic “tail”). Remarkably, both high- and low-energetic $\Delta T(\lambda)$ edges decrease with a reasonable accuracy of optical measurements to zero level, the maximal value of γ -induced changes exceeding 10% for $\lambda \sim 600$ nm.

Of course, the above methodological procedure can be successfully applied for each VChS system to study its realistic intrinsic response on radiation influence. In this view, the reference on Ge-As-S system as free of products of radiation-induced oxidation and, consequently, more suitable to study own structural changes, which was declared in [10], is a simple misunderstanding. The VChS of this Ge-As-S system also demonstrate a pronounced response on prolonged γ -irradiation with various doses (0.1...10.0 MGy) dependent, in main, on As₂S₃ content, especially within GeS₂-As₂S₃ cut-section [35-39] (if slighter topological variations near average coordination 2.67 within Ge₂S₃-As₂S₃ cut-section are neglected). White arsenolite layer on the surface of just γ -irradiated Ge-As-S glasses was always detected in our experiments [35-39], it was always carefully eliminated before further optical measurements. It seems also important to note that oxidation is not related alone to the absorbed dose of irradiation, since environmental conditions, especially water moisture, act as catalyst in this process [27]. So, under over-barrier conditions of high-energy γ -irradiation, the process of arsenic oxidation (appearance of As₄O₆ crystallites) can proceed towards formation of volatile H₂S [40], which can significantly reduce residue of S in a glassy matrix.

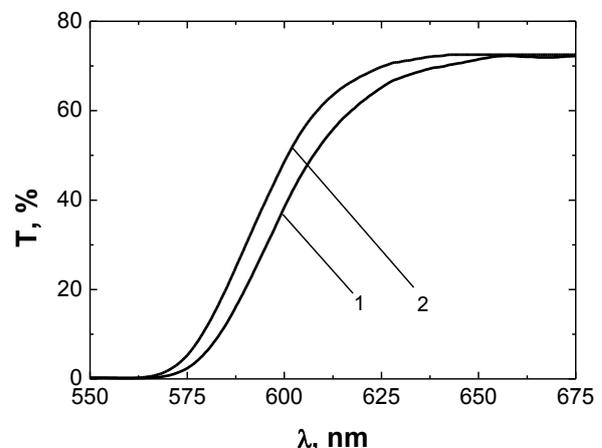


Fig. 3. Optical transmission spectra of v -As₂S₃ measured in *backward chronology* for γ -irradiated (1) and further annealed (2) states (the sample surface was preliminary cleaned from products of radiation-induced oxidation).

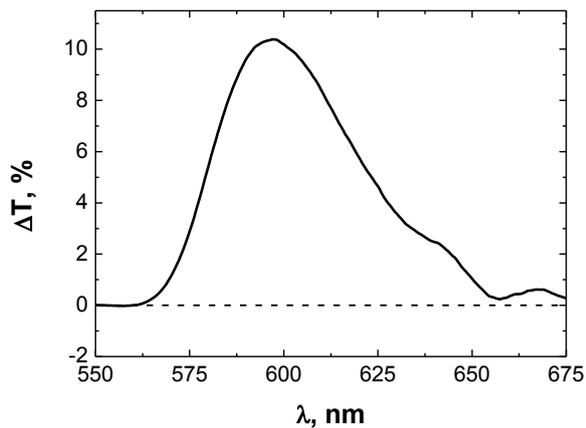


Fig. 4. Optical transmission difference for γ -irradiated and further annealed $v\text{-As}_2\text{S}_3$ measured in *backward chronology* (the sample surface was preliminary cleaned from products of radiation-in

Thus, the high value of γ -induced DPT confirms a thesis on efficient both intrinsic and impurity radiation-structural transformations just occurring in $v\text{-As}_2\text{S}_3$. The competitive γ -induced effects of darkening resulting from essential oxidation can be excluded from consideration by means of wet surface polishing, allowing “pure” DPT caused by intrinsic covalent bond redistribution. It means that, in real, the stoichiometric $v\text{-As}_2\text{S}_3$ can serve as one of the best model objects to study radiation-induced metastability using different experimental structural probes (including such methods as the FSDP-related XRD or positron-electron annihilation spectroscopy [5]) as was reasonably stated more than two decades ago [41–43].

Finally, in respect to this methodological analysis, it seems as simple confuse allegation the conclusion stated in [10] regarding radiation-induced oxidation “...as protective procedure to be used in practice ... for advanced chalcogenide photonics”. Since these water-soluble arsenolite As_4O_6 crystallites (which are ones of the most aggressive poisons and angiogenesis inhibitors [44,45]) can be easily removed from VChS surface by quick wet polishing, it does not worth to be used as protective layer in practical device applications, especially for advanced photonics.

4. Conclusions

Two types of experimental measuring protocols can be applied for correct study of γ -induced optical effects in $v\text{-As}_2\text{S}_3$, these being realized in *direct* and *backward* measuring chronology. In the former, the optical transmission spectra are recorded *ex-situ* for the same glass sample taken in non-irradiated (just before irradiation) and γ -irradiated (one month after irradiation) states. The second type of optical measurements is performed *in-situ*, recording optical transmission spectra

for the same γ -irradiated and further annealed sample. The smallest inaccuracies are shown to be provided within the latter measuring protocol owing to elimination of errors associated with (1) sample reinstallation in a spectrometer and (2) time separation between subsequent cycles of optical spectra recording for initial unirradiated and γ -irradiated samples. As a result, the impacts of impurity-related and intrinsic γ -induced effects on optical transmission spectra can be reasonably separated. It is shown that impurity-related radiation processes (connected mainly with surface oxidation) depresses optical transmission in near-band-gap region, while intrinsic ones (realized as defect formation) shifts optical absorption edge towards larger wavelengths.

Acknowledgement

The authors appreciate acknowledgement for As_2S_3 samples described by T. Kavetsky in [10], while are forced to declare that such samples were never provided to him within joint projects.

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