RADIATION-INDUCED OPTICAL EFFECTS IN CHALCOGENIDE SEMICONDUCTOR GLASSES

Article · January 2017
DOI: 10.21175/RadJ.2017.02.021

CITATIONS
0

READS
14

3 authors, including:

M. Shpotyuk
Lviv Polytechnic
30 PUBLICATIONS 114 CITATIONS
SEE PROFILE

Sergii Ubizskii
Lviv Polytechnic
102 PUBLICATIONS 536 CITATIONS
SEE PROFILE

All content following this page was uploaded by M. Shpotyuk on 02 November 2017.
The user has requested enhancement of the downloaded file.
RADIATION-INDUCED OPTICAL EFFECTS IN CHALCOGENIDE SEMICONDUCTOR GLASSES

O. Shpotyuk1-3*, M. Shpotyuk4, S. Ubizskii*1

1Institute of Materials of SRC “Carat”, Lviv, Ukraine
2Vlokh Institute of Physical Optics, Lviv, Ukraine
3Jan Dlugosz University of Czestochowa, Czestochowa, Poland
4Lviv Polytechnic National University, Lviv, Ukraine

Abstract. A variety of methodological resolutions suitable to identify unambiguously radiation-induced effects in chalcogenide glassy semiconductors is analyzed in details. The radiation-optical effects in chalcogenide glasses are comprehensively considered as resulting from both intrinsic and impurity-related redistribution of covalent chemical bonds known as destruction-polymerization transformations. Two types of experimental measuring protocols are utilized to study the radiation-induced effects within ex-situ direct or in-situ backward chronology, the latter being more adequate for correct testing of competitive inputs from both channels of destruction-polymerization transformations. A critical assessment is given on misleading speculations of some authors ignoring intrinsic radiation-structural transformations in glassy As2S3 in view of accompanying oxidation and thermally-induced physical-ageing processes. In final, the As2S3 glass is nominated to be the best model object among a wide group of chalcogenide glassy semiconductors revealing the highest sensitivity to radiation-induced metastability.

Key words: Chalcogenide glassy semiconductors, optical spectroscopy, γ-irradiation, metastability, oxidation

1. INTRODUCTION

Radiation-induced effects (RIEs) were perfectly justified in chalcogenide glassy semiconductors (ChGSs) since the earliest 1960s, the time of extensive research followed after a pioneer invention of N.A. Goryunova and B.T. Kolomiets on semiconductor properties of these glasses. Afterwards, in the 1970s and 1980s, the microstructure mechanism of the radiation-induced metastability in different ChGSs became a subject of a scrupulous study in view of many promising applications in radiation dosimetry and radiation-guided modification technologies (see, e.g. ref. [1] and literature therein).

Now, it is commonly accepted that destruction-polymerization transformations (DPTs), i.e. destruction of some covalent chemical bonds in a favor of other ones, followed by structural relaxation towards thermodynamic equilibrium (the phenomenon known as radiation-assisted physical ageing [2]), are principal determinant of RIEs [3-7]. From a purely methodological viewpoint, the RIEs study assumes the development of unprecedented experimental probes to separate contributions arising entirely from radiation-induced DPTs and those caused by the accompanied structural relaxation. The destructed covalent bonds can be renewed in ChGSs intrinsically due to direct interaction of bond-constituting atoms with their neighbors forming a channel for intrinsic bond-switching, or extrinsically due to the interaction with some impurities, thus forming a channel for extrinsic bond-switching. In the former, the pairs of over- and under-coordinated atoms that possess an excess of the positive and negative electrical charge appear [1,8,9]. The latter is ascribed to some kinds of impurities formed at the surface of the irradiated ChGSs, the most essential being induced by interaction with oxygen, replacing chalcogen in its bonding configurations within the glass network [1].

Thereby, the intrinsic RIEs in ChGSs are permanently admixed to impurity-related extrinsic ones, forming a complicated scenario of their competitive contribution in an overall balance of detected RIEs. Many of these RIEs are accompanied by relaxation phenomena, such as those typical for multinary bulk ChGSs [10-16] and thin chalcogenide films [17-23].

In realistic conditions, the hierarchical complexity in RIEs reveals at both time-probing and space-holding levels. The former are defined by metastable structural changes detected just after irradiation, which are composed of static (i.e. time-independent or residual) and dynamic (i.e. spontaneously decaying or instable) components, while the second are affected by the locality of the DPTs occurring in sample’s bulk [1].
2. MATERIALS AND METHODS

2.1. Samples preparation, radiation treatment and optical measurements

The As-S glasses were prepared by conventional melt-quenching route using the respective quantities of high-purity elemental ingredients, as was described in more details elsewhere [7, 24, 25]. The glasses cut as plane-parallel 1.5 mm thick plates and carefully polished to high optical quality were annealed before irradiation at temperature 20 K below the glass transition temperature $T_g$ to eliminate mechanical stresses frozen within quick cooling.

The $\gamma$-irradiation was carried out at the ambient conditions of a stationary $^{60}$Co radiation field (an average energy of $E=1.25$ MeV). The duration of $\gamma$-treatment (up to 6 months) allows the accumulation of the total dose of $\Phi=2-10$ MGy. Under such conditions, both intrinsic and impurity-related DPTs are known to be activated [24-27].

Optical transmission spectra of the studied ChGSs were recorded in the region of a fundamental absorption edge using AvaSpec-2048 spectrometer (Avantes, Netherlands) with a maximum error-bar of ± 1 %. Measurements were performed one month after finishing $\gamma$-irradiation. In such a way, the majority of dynamic decaying changes [1, 28] were exhausted, and only static RIEs were detected.

2.2. Methodology of RIE detection

Two principally different experimental measuring protocols can be utilized to unambiguously identify the RIEs in ChGSs; these being realized within the continuous (in-situ measurements in direct and/or backward measuring chronology for the same control sample affected by irradiation) or discontinuous (ex-situ measurements for control-irradiated sample before and after irradiation, or two samples, one being kept in control-irradiated and other being in reference-unirradiated) cycles (see Fig. 1).

In direct measurements chronology (see Fig. 1a), the optical transmission spectra are recorded ex-situ for the same glass sample taken necessarily in a sequence of the following states:

(1) non-irradiated initial state (i.e. sample taken just before irradiation);
(2) $\gamma$-irradiated state (i.e. sample taken one month after irradiation);
(3) near-$T_g$ thermally-annealed state (i.e. deeply aged sample);
(4) rejuvenated state (i.e. sample affected to over-$T_g$ heating-cooling cycle).

Each of the stages is needed for the chosen ChGS to completely represent the optical signature of the RIEs. To minimize the errors owing to inadequate repetition of too prolonged experimental optical measurements (non-reproducibility of multiple measuring cycles), the glass is positioned in a spectrometer chamber in respect to the probe-light beam, using special marking on its surface. However, the effects of physical ageing in the irradiated ChGS (if any) cannot be resolved adequately within this method.

Therefore, the experimentally measured numerical parameters concerns, in fact, a cumulative input from RIEs and physical ageing.

In principal, the ex-situ measurements in a direct chronology can be realized for two identical ChGS samples taken as the control (i.e. irradiated) and reference (i.e. unirradiated). However, in this case, the samples' identity should be precisely controlled on each stage, as it becomes the main source of false in addition to non-reproducibility of multiple measuring cycles and unresolved radiation-assisted physical ageing (see Fig. 1a).

Within in-situ measurements (see Fig. 1b) in a backward chronology, the optical transmission spectra...
are recorded for the same γ-irradiated ChGS sample used to reproduce a sequence of the following states:

(1) just irradiated state (i.e. the ChGS sample measured after γ-irradiation);
(2) annealed state (i.e. the γ-irradiated sample affected to thermal annealing in a spectrometer chamber);
(3) rejuvenated state (i.e. the thermally-aged γ-irradiated sample affected to rejuvenation heating-cooling route [2] in spectrometer chamber).

The highest functional reliability can only be provided within this measuring protocol, owing to the complete elimination of the errors associated with (i) the sample reinstallation in a spectrometer chamber and (ii) time separation between subsequent cycles of optical transmission spectra recording for ChGS samples in different states. The contribution of the impurity-related and intrinsic DPTs can be efficiently separated also only within this measuring protocol. Realistically, the in-situ measurements cannot be simply realized in a direct measuring chronology because of difficulties in reliable and highly-reproducible conditions for the unified radiation- and thermally-induced treatment.

3. Results and discussion

3.1. RIES in a direct measuring chronology

The transmission spectra in the fundamental optical absorption edge of the same stoichiometric As₂S₃ glassy sample measured in a direct chronology, so before (initial thermally-annealed or aged state) and after γ-irradiation with Φ=10.0 MGy dose and subsequent cycles of thermal annealing at different temperatures are shown in Fig. 2.

![Figure 2. Optical transmission of As₂S₃ glass (d=1 mm) measured in direct chronology for initial thermally-annealed (aged) state (1), γ-irradiated (Φ=10.0 MGy) state (2) and further thermally aged states due to annealing at 330 (3), 370 (4), 380 (5), 395 (6), 420 (7) and 440 K (8)](image)

The long-wave shift in the optical transmission of the γ-irradiated ChGS corresponds to the radiation darkening effect [1], which cannot be resolved unambiguously under such ex-situ measuring conditions, as originated from both intrinsic and impurity-related DPTs. Further thermal annealing at growing temperatures, which are close to glass transition temperature Tg, tends optical transmission towards the initial state (with character threshold-like behavior [1]), but this renovation is only partial, because of the competitive contribution from the radiation-induced surface oxidation.

Thus, the initial thermally-aged (curve 1, Fig. 2) and final after-irradiation thermally-aged (curve 8, Fig. 2) states essentially differ in As₂S₃ glass before and after γ-irradiation, so it is impossible to distinguish between them, unless complete cycle of measurements (curve 1 – curve 2 – curves 3:4:5:6:7:8, Fig. 2) is performed. The intrinsic and impurity-related DPTs (preferentially due to oxidation) cannot be separated at all in these experiments arranged in a direct measuring chronology. The only resolution is to fully eliminate the oxidized layer from the surface of γ-irradiated ChGSs and renew the optical measurements for this cleaned sample within the same thermal-treatment cycles.

Fortunately, this resolution is fully applicable for the group of glassy binary arsenic sulfides As-S (incl. stoichiometric As₅S₃), since the layer of rhombohedral arsenuite AsₓOₙ₋₃ₓ, appeared due to the decomposition-oxidation reaction activated under normal conditions by high-energy irradiation, can be easily removed from the sample’s surface by simple wet cleaning [29-31]. Such arsenuite crystallites act as effective scattering centers, depressing the optical transmission in the near-band-gap region (due to Rayleigh scattering), as well as in the mid-IR optical transmission region (preferentially due to Mie scattering losses) [32]. This specificity is well-illustrated by Fig. 3 showing two principally different positions of the optical transmission edge for uncleaned and cleaned γ-irradiated As₂S₃ glass. It is seen that, not only the saturation level, but also the slope of the optical transmission curve are essentially modified in the uncleaned γ-irradiated stoichiometric As₂S₃ glassy sample affected to surface oxidation.

Noteworthy, this methodological resolution is principally unacceptable for Ge-based ChGSs like glasses of ternary As-Ge-S system [1,3], where the residual effect caused by germanium oxide cannot be simply eliminated due to water insolubility of GeO₂ species [33]. In other words, in RIES in Ge-based ChGSs studied in direct measuring chronology, we can never distinguish (even roughly) the intrinsic “pure” radiation-induced changes like in binary As-S glasses. So the attempts of some authors [34,35] claiming the Ge-based ChGSs (like glasses of stoichiometric GeS₂-As₂S₃ cut-section) as the ideal model object for RIES are simply wrong and entirely misleading.

Hence, the above direct-chronology measurements have a lot of disadvantages, most of them being connected with time separation and uncertainties between the subsequent cycles of optical transmission spectra recording for initial (thermally-aged rejuvenated) and final ChGSs (i.e. cleaned or uncleaned after γ-irradiation). The impossibility to reproduce reliably the exploitation characteristics of the measuring equipment in different conditions is the main obstacle restricting this approach. Simultaneous measurements for different ChGSs samples (one being
unirradiated and other being γ-irradiated) allows only partial solution, because of the eventual uncontrolled diversity between samples. Therefore, the optimal testing methodology for intrinsic RIEs is to arrange the measuring cycles for the same ChGS sample, ensuring as small as possible time separation between its different states.

With respect to the optical transmission spectra of stoichiometric As$_2$S$_3$ glass measured in a direct chronology for different final states (compare optical transmission spectra shown on Fig. 2 and 3), it is worth to underline that incomplete elimination of the surface oxide layer results only in the partial restoration of initial optical transmission curve. In other words, it means that the γ-irradiated ChGS sample with some remainders of the oxidation products is always in a more darkened final state as compared with different initial ChGS samples, both thermally-annealed or rejuvenated ones.

This finding is of archetypal importance for the repeatable use of these ChGSs in multiple irradiation-annealing measuring cycles (such as those employed in industrial dosimetric systems). Indeed, in this case, the previously γ-irradiated ChGS samples affected by either thermal annealing or rejuvenation heating-cooling treatment essentially differ from the initial samples not affected by such γ-irradiation at all (compare optical transmission spectra for initial glassy As$_2$S$_3$ on Fig. 2 and two samples shown on Fig. 3).

This approach convincingly discredit some recent speculations [35] which try to ascribe the difference in the optical transmission spectra of two ChGS samples (As$_2$S$_3$ and Ge$_{0.5}$As$_{2}$S$_{3.5}$), measured a decade after γ-irradiation (Φ=2.41 MGy), to intrinsic RIEs. Without comparison for these glasses before irradiation, these data cannot be accepted as a real signature of RIEs. Indeed, in [35], it is ignored that difference in optical transmission spectra could be in these ChGSs just before irradiation, especially if it is accepted that these ChGSs have been affected before to a few subsequent irradiation-annealing cycles (see, for example, the results on γ-irradiation with doses Φ=2.2 MGy [3,36,37] and Φ=1.0 MGy [38,39]).

Most importantly, the shift of optical absorption edge of ChGSs measured in a static position some time after irradiation is a signature of intrinsic RIEs in this glass only in respect to the position of this absorption edge before irradiation.

### 3.2. RIEs in a backward measuring chronology

The breakthrough resolution in RIEs identification is provided by the optical measurements arranged in backward chronology for the same γ-irradiated ChGS sample. The principal γ-induced optical effect is considered as consisting of the difference in optical transmission spectra for ChGS sample in γ-irradiated and subsequently thermally annealed states.

The corresponding measuring protocol is based on the prerequisite that arises intrinsic γ-induced effect below-$T_g$ thermal annealing, restoring the initial glass structure [1-3]. In our research, we made one more step to achieve the highest accuracy, performing post-irradiation measurements in-situ, i.e. the tested γ-irradiated ChGS sample was always kept in the same position in respect to the probe-light beam during all cycles of thermal treatments (thermal annealing near $T_g$ or rejuvenation heating-cooling route).

Thus, this in-situ measuring protocol allows full exclusion of inaccuracies associated with sample’s holding in a spectrometer chamber. To distinguish intrinsic and impurity-related RIEs, we also perform our experiments with carefully cleaned ChGS samples free of any products of radiation-induced oxidation (however, in this case, the impurity-related RIEs can be simply decompose from intrinsic RIEs even for uncleared γ-irradiated ChGSs).

The optical transmission spectra of the γ-irradiated (with Φ=3 MGy dose), thermally aged (20 K below $T_g$) and further rejuvenated glassy samples of As$_2$S$_3$ and AsS$_2$ compositions recorded in a backward chronology are shown in Fig. 4.

The optical bleaching effect is evident as a result of thermal ageing in both γ-irradiated samples in full accordance with [2], while rejuvenation occurs an opposite effect. As a result, the optical transmission curves of rejuvenated and γ-irradiated As$_2$S$_3$ glass coincide, giving an evidence on absence of any intrinsic RIEs in this ChGS. In contrast, the fundamental optical absorption edges in stoichiometric As$_2$S$_3$ glass differ essentially in all three states, giving an evidence on comparable intrinsic RIEs and accompanied thermally-assisted physical ageing.

Thus, the high value of RIEs confirms efficiency for both intrinsic and impurity-related DPTs just occurring in stoichiometric As$_2$S$_3$ glass under γ-irradiation. The competitive γ-induced optical darkening resulting from essential oxidation can be excluded from further consideration by the means of wet surface cleaning, allowing “pure” DPTs caused only by the intrinsic bond redistribution. It means that, in real, the stoichiometric As$_2$S$_3$ glass can indeed serve as a model object to study radiation-induced metastability in ChGS systems using different multiexperimantal structural probes.
By finishing, we would like to refer the reader once more to experimentally detected compositional behavior of RIEs in As-S ChGSs measured in-situ in a backward chronology. These samples were irradiated with 0.7 kGy/h dose rate at near-room temperature (300 K) and total accumulated dose $\Phi = 3$ MGy, as was described in more details elsewhere [24]. After irradiation, these ChGSs were additionally affected to annealing near glass transition temperature $T_g$. The resulting curve showing difference in optical transmission $\Delta T_{\text{max}}$ measured in-situ between annealed and $\gamma$-irradiated samples (i.e. detected in a backward measuring chronology) is shown in Fig. 5.

The positive $\Delta T_{\text{max}}$ value (reaching $\sim 10\%$ as seen in Fig. 5) corresponds to long-wave shift of fundamental optical absorption edge caused by $\gamma$-irradiation (or, alternatively, to the darkening effect), while the negative $\Delta T_{\text{max}}$ value (reaching a few % for S-rich ChGSs) is attributed to opposite short-wave shift (alternatively, to the bleaching effect) caused by post-irradiation thermally-assisted physical ageing. Such separation of these contributions (originated from different effects (intrinsic radiation transformations, radiation-induced oxidation, ageing and thermally-assisted ageing) is possible only for measurements arranged in-situ in a backward chronology.

The methodological resolutions suitable to identify unambiguously radiation-induced optical effects in chalcogenide glasses are systematically analyzed and critically compared with alternative approaches. The studied radiation-optical effects are comprehensively considered as resulting from both intrinsic and impurity-related redistribution of covalent chemical bonds in chalcogenide glasses known as destruction-polymerization transformations.

Two types of experimental measuring protocols can be utilized to study the radiation-induced effects within ex-situ direct or in-situ backward chronology, the latter being more adequate for correct testing of competitive inputs arising from the intrinsic and impurity-related transformations, as well as accompanied physical ageing effects. A critical assessment is given on the misleading speculations of some authors ignoring intrinsic radiation-induced structural transformations in glassy As$_2$S$_3$ in view of accompanying processes of radiation-induced oxidation and thermally-induced physical ageing. In final, the stoichiometric As$_2$S$_3$ glass is nominated to be the best model object among a wide group of chalcogenide glasses revealing the highest sensitivity to radiation-induced metastability.

**Acknowledgement**: The paper is a part of research done within the projects No 0116U002578 (subject of Scientific Program funded by Ministry of Education and Science of Ukraine for years 2016-2018). MSh acknowledges financial support from Ministry of Education and Science of Ukraine within the funding program DB/Nanosensor (No 0116U004411).

**REFERENCES**

1. O. I. Shpotyuk, “Radiation-induced effects in chalcogenide vitreous semiconductors,” in *Semiconducting Chalcogenide Glass 1. Glass*
O. Shpotyuk et al., Radiation-induced optical effects..., Rad. Appl., 2017, 2, 94–100


Retrieved on: Jan. 10, 2017


G-Induced_Changes_in_Ge-As-S_Glasses
Retrieved on: Jan. 10, 2017
