On the atomistic origin of radiation-structural relaxation in chalcogenide glasses: the results of positron annihilation study

Ya. Shpotyuk[*,1,2,4], **A. Ingram**[3], **J. Filipecki**[4], **and M. Hyla**[4]

[1] Ivan Franko National University of Lviv, Faculty of Electronics, 50, Dragomanova str., Lviv 79005, Ukraine
[2] Institute of Materials of Scientific Research Company "Carat", 202 Stryjska str., Lviv 79031, Ukraine
[3] Institute of Physics, Mathematics and Chemistry of Opole Technical University, 75 Ozimska str., Opole, Poland
[4] Institute of Physics of Jan Dlugosz University, 13/15 al. Armii Krajowej, Czestochowa, Poland

* Corresponding author: e-mail y_shpotyuk@mail.ru, Phone: +38 032 2638303

Instability effects caused by high-energy γ-irradiation are studied in $(As_2S_3)_{1-x}(Sb_2S_3)_x$ glasses (x=0, 0.1, 0.2 and 0.3) using positron annihilation lifetime spectroscopy, the results being treated within two-state trapping model in both normal and high-measurement statistics. The observed decrease in positron trapping rate of the glasses tested just after γ-irradiation was explained due to renovation of destroyed covalent chemical bonds. This process was governed by monomolecular single-exponential relaxation kinetics agreed well with corresponding changes in the fundamental optical absorption edge.

1 Introduction High-energetic irradiation is known to be one of most effective factors modifying different types of disordered solids in many purposeful device applications [1]. This statement is quite meaningful in application to chalcogenide vitreous semiconductors (ChVS) – the glassy alloys of chalcogen atoms (S, Se or Te) with elements from IV-V groups of the Periodic Table obtained by melt quenching [2, 3].

Recently, at the example of quasibinary As_2S_3-Sb_2S_3 ChVS, it was shown that radiation-induced functionality is unstable, revealing a monotonic decay in the value of low-energetic shift of fundamental optical absorption edge (the effect known as radiation-induced darkening) [2, 4]. This post-irradiation relaxation is supposed to be connected with specific types of structural defects changing local electric charge and coordination of constituting atoms [4]. The whole process of radiation-induced defect creation attains destruction-polymerization character, e.g. one covalent bond is destroyed under irradiation, but another one is formed instead of this [2, 3]. So these coordination-topological defects appear by pairs involved over-coordinated atoms with excess of positive electric charge and under-coordinated atoms with excess of negative electric charge, which keep an overall electroneutrality of irradiated ChVS.

An alternative possibility exists for direct destruction of covalent chemical bonds just under high-energy irradiation. The weakened covalent bonding cannot be renewed in covalent networks, possessing a sufficient amount of free volume in the vicinity of destroyed covalent bond [5]. Nevertheless, because of homolytical nature of bond breaking [3], the created structural instability forms also a pair of diamagnetic under-coordinated atoms, one of them being negatively-charged and other being positively-charged. Just this type of coordination-topological defects was shown to be responsible for electron-induced dichroism in glassy As_2S_3-Sb_2S_3 [6].

Whichever the case, one of the created defects is under-coordinated with character excess of negative electric charge and accompanied free volume due to lack of destroyed covalent bond. Within bond-free solid angle concept of Kastner [7], it can be easily estimated that maximal value of additional free volume as high as 43 Å^3 in stoichimetric glassy As_2S_3 is proper to under-coordinated

sulphur atoms forming S_1^- defects (the upper index denotes electrical charge and lower denotes local atomic coordination) [8, 9]. For comparison, the corresponding value of free volume attached to under-coordinated arsenic atom in glassy As_2S_3 (As_2^- defect) is only 33 $Å^3$ [8, 9]. In just post-irradiation state, the content of such defects can rise to a few percents in respect to the overall concentration of atoms, giving a measurable shift in fundamental optical absorption edge of ChVS [2, 4].

The created coordination-topological defects cause time instability in the irradiated ChVS samples, since they spontaneously annihilate after irradiation (under storage in normal temperature conditions), renewing the destroyed covalent chemical bonds. This work is aimed to identify the atomistic nature of the above radiation-induced defects in As_2S_3-Sb_2S_3 ChVS, associated them with excess of additional free volume, using positron annihilation lifetime (PAL) measurements. The PAL method was chosen by us as one of the most sensitive experimental tool to study free-volume associations in solids despite their structural-chemical nature [5, 8].

2 Experimental The studied ChVS samples of $(As_2S_3)_{1-x}(Sb_2S_3)_x$ system (x=0, 0.1, 0.2, 0.3) were prepared by conventional melt quenching route using high-purity initial ingredients as it was described in details elsewhere [4]. The samples were irradiated with ^{60}Co γ-quanta source (mean energy of 1.25 MeV), the absorbed dose being close to 2 MGy. No special measures were taken to prevent uncontrolled thermal annealing of the samples, while maximum temperature during irradiation did not exceed 320 K.

The PAL measurements were performed at room temperature using conventional fast-fast coincidence system with an ORTEC spectrometer and radioactive ^{22}Na isotope placed between two sandwiched ChVS samples, the PAL spectrum being recorded in normal- and high-measurement statistics evolving near 1 and 5 millions of elementary positron annihilation events, respectively [10, 11]. This allows definition of PAL parameters (both positron lifetimes τ_1, τ_2 and their intensities I_1, $I_2=1-I_1$, bulk τ_B and average τ_{av} positron lifetimes and positron trapping rate κ_d) within two-state positron trapping model [10] using LT computer program [12]:

$$\tau_{av} = \frac{\tau_1 I_1 + \tau_2 I_2}{I_1 + I_2}, \tag{1}$$

$$\tau_b = \frac{I_1 + I_2}{\dfrac{I_1}{\tau_1} + \dfrac{I_2}{\tau_2}}, \tag{2}$$

$$k_d = \frac{I_2}{I_1}\left(\frac{1}{\tau_b} - \frac{1}{\tau_2}\right). \tag{3}$$

To control the radiation-induced darkening effect, the spectral dependences of optical transmission τ of the studied ChVS samples were measured in 200-900 nm range in different time periods after irradiation (from 1 to 40 days) using "Specord M-40" device, the maximal error of measurements being no more 0.5%. Further, we calculate the normalized dynamic component in the optical transmission of the irradiated samples in the range of fundamental optical absorption edge, all quantifications being made on the wavelength of maximum effect.

3 Results and discussion Positron trapping modes of $(As_2S_3)_{1-x}(Sb_2S_3)_x$ ChVS measured in normal statistics just after irradiation and one month later are presented in Table 1. In our calculations we accept that the first short lifetime τ_1 is equal exactly to 0.200 ns in all samples whichever their composition. This assumption is grounded on previous PAL measurements for glassy As_2S_3 as model object characterized by layer-like structural motive built of corner-shared $AsS_{3/2}$ pyramids [13]. The same structural organization is proper to $(As_2S_3)_{1-x}(Sb_2S_3)_x$ ChVS composed by mixture of identical $AsS_{3/2}$ and $SbS_{3/2}$ pyramids [14]. Under this approach, the fine changes in defect-related positron trapping modes caused by high-energy irradiation are reflected in positron trapping rate κ_d.

Table 1 Positron trapping modes of $(As_2S_3)_{1-x}(Sb_2S_3)_x$ ChVS measured in normal statistics (τ_1=0.200 ns)

x	Treatment stage	τ_2, ns	I_2, a.u.	κ_d, ns^{-1}
	Before γ-irradiation	0.360	0.86	1.91
0.0	Just after γ-irradiation	0.355	0.84	1.83
	One month after γ-irradiation	0.359	0.77	1.71
	Before γ-irradiation	0.362	0.82	1.83
0.1	Just after γ-irradiation	0.361	0.80	1.78
	One month after γ-irradiation	0.359	0.76	1.68
	Before γ-irradiation	0.366	0.78	1.77
0.2	Just after γ-irradiation	0.362	0.77	1.72
	One month after γ-irradiation	0.358	0.75	1.65
	Before γ-irradiation	0.364	0.76	1.71
0.3	Just after γ-irradiation	0.359	0.75	1.66
	One month after γ-irradiation	0.359	0.73	1.62

It should be noted that under condition on fixed τ_1=0.200 ns, the defect-related lifetime τ_2 is also constant (0.36 ns), along with other positron trapping modes such as bulk and average positron lifetimes ($\tau_B \approx$ 0.31 ns and $\tau_{av}\approx$0.33 ns, respectively), testifying in a favor of the same nature of positron trapping centres in all tested samples.

The average positron lifetimes τ_{av} of these samples determined in high-measurement statistics are presented in Table 2. The decrease in τ_{av} value was observed in all samples tested 1 day after γ-irradiation, this effect being inhibited with Sb_2S_3 content. The same ChVS samples studied 1 month after irradiation show additional decrease in τ_{av} with analogous compositional trend. So the most essential

Phys. Status Solidi C **8**, No. 11–12 (2011)

3165

changes occur in pure As_2S_3 (the initial τ_{av}=0.339 ns drops down to 0.331 ns in just after-irradiation state with further tending towards 0.322 ns during 1-month natural storage).

Table 2 Average positron lifetimes τ_{av} for $(As_2S_3)_{1-x}(Sb_2S_3)_x$ ChVS determined in high-measurement statistics (τ_1=0.200 ns)

| ChG composition, x	Average positron lifetime τ_{av}, ns		
	before γ-irradiation	1 day after γ-irradiation	1 month after γ-irradiation
0.0	0.339	0.331	0.322
0.1	0.333	0.327	0.320
0.2	0.328	0.323	0.318
0.3	0.324	0.319	0.316

These changes (see Tables 1 and 2) testify that structural shrinkage followed by further enhancement during post-irradiation storage dominates in the γ-irradiated ChVS samples of $(As_2S_3)_{1-x}(Sb_2S_3)_x$ system. The observed radiation-induced densification (decrease in molar volume) is complex, being composed of two parts. The first part is connected with weakening of covalent bonding owing to *in-situ* under-irradiation electronic excitations. Because of decrease in overall number of Lagrangian constraints per atom during prolonged high-energy irradiation (near two months), this process is followed by significant atomic shrinkage. In addition, coordination topological defects accompanied by additional free volume owing to lack of one covalent chemical bond on under-coordinated atom appear [2]. The former process dominates causing overall decrease in τ_{av} in just-γ-irradiated ChVS. The further after-irradiation renovation in covalent bonding leads to annihilation of these under-coordinated defects in respect to τ_{av} decrease in 1-month stored samples (Table 2).

The kinetic dependence of positron trapping rate κ_d for γ-irradiated $(As_2S_3)_{0.9}(Sb_2S_3)_{0.1}$ glass is shown in Fig. 1 (the similar dependencies for other ChVS samples are not reproduced in this Fig. 1). The normalization procedure was carried out for κ_d values (shown as full circles) taken just after irradiation and one-month later in a stationary regime. For comparison, we also introduce the analogous dependencies for normalized optical transmission changes measured for each ChVS sample in the range of fundamental optical absorption edge at the wavelength of maximum effect (open circles) and fitted with single exponential relaxation function (red line). It is obvious that both control parameters (optical transmission and positron trapping rate) coincide well in its main features for each sample. So the same underlying structurally-sensitive process can be supposed to be responsible for these changes. By accepting that only dropping tendency is clearly observed in positron trapping rate κ_d after γ-irradiation, it can be assumed that this process is associated with decrease in structurally-intrinsic free volume in ChVS [5].

These results contradict obviously to previous study on As-Ge-based ChVS [2, 15], where bimolecular post-irradiation relaxation kinetics with character times near a few months dominates. The measured extra-short values of post-irradiation relaxation times as high as 2 days along with single-exponential post-irradiation kinetics [4] testify in a favor of underplaying processes associated with under-coordinated atoms arising from direct bond destruction.

Therefore, the process of post-irradiation relaxation in the studied $(As_2S_3)_{1-x}(Sb_2S_3)_x$ ChVS has an activation-like monomolecular character owing to spontaneous renovation of destroyed covalent bonds. Since the corresponding relaxation times are only slightly modified with ChVS composition [4], these changed are supposed to be associated with defects only in As-based sub-matrix. Within analogy on electron-induced metastability [6], the coordination defects responsible for monomolecular relaxation in glassy $(As_2S_3)_{1-x}(Sb_2S_3)_x$ can be identified as under-coordinated As_2^+ and S_1^- atoms with character intrinsic free volumes owing to destroyed As-S bonds. This feature explains well the observed compositional tendency in positron trapping rate κ_d shown in Table 1.
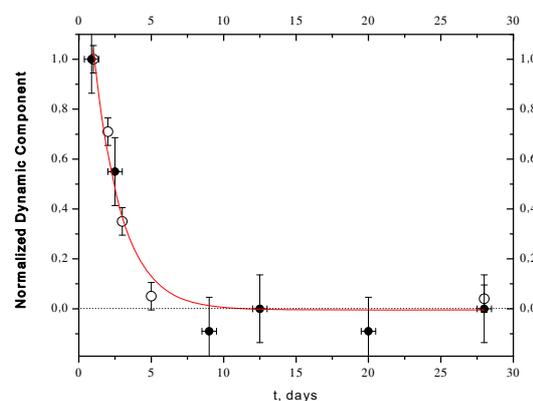
Figure 1 Kinetics behavior of normalized dynamic component in radiation-modified $(As_2S_3)_{0.9}(Sb_2S_3)_{0.1}$ ChVS, determined in optical transmission in the range of fundamental optical absorption edge at the wavelength of maximum effect (open circles) and positron trapping coefficient for two-state positron trapping model with fixed τ_1=0.200 ns (full circles).

4 Conclusions The relaxation kinetics observed in two-state positron trapping rate and average positron lifetime is shown correlate well with corresponding changes in the optical properties of γ-irradiated $(As_2S_3)_{1-x}(Sb_2S_3)_x$ glasses. These results are explained well in terms of under-coordinated topological defects originated from radiation-destroyed covalent chemical bonds.

References

[1] A. K. Pikaev, Modern Radiation Chemistry - Main Principles, Experimental Technique and Methods (Nauka, Moscow, 1985), p. 375.

[2] O. I. Shpotyuk, in: Semiconducting Chalcogenide Glass 1: Glass Formation, Structure, and Simulated Transformations in Chalcogenide Glassess – Semiconductors and Semimetals, edited by R. Fairman and B. Ushkov (Elsevier Academic Press, Amsterdam-Boston-London-New York-Oxford-Paris-San Diego-San Francisco-Singapore-Sydney-Tokyo, 2004), pp. 215-216.

[3] A. Feltz, Amorphous and Vitreous Inorganic Solids (Mir, Moscow, 1986).

[4] Ya. O. Shpotyuk, V. O. Balitska, O. I. Shpotyuk, and M. S. Iovu, J. Optoelectron. Adv. Mater. **11**, 2069 (2009).

[5] O. Shpotyuk and J. Filipecki, Free Volume in Vitreous Chalcogenide Semiconductors: Possibilities of Positron Annihilation Lifetime Study (WSP Ed., Czestochowa, 2003).

[6] V. O. Balitska and O. I. Shpotyuk, Nucl. Instrum. Methods Phys. Res. B **166/167**, 521 (2000).

[7] M. Kastner, Phys. Rev. B **7**, 5237 (1973).

[8] V. Balitska, J. Filipecki, and O. Shpotyuk, Phys. Status Solidi C **6**, 1892 (2009).

[9] O. I. Shpotyuk, J. Filipecki, and V. O. Balitska, J. Optoelectron. Adv. Mater. **10**, 3193 (2008).

[10] R. Krause-Rehberg and H. S. Leipner, Positron Annihilation in Semiconductors: Defect Studies (Springer-Verlag, Berlin-Heidelberg-New York, 1999).

[11] J. Gebauer, F. Rudolf, A. Polity, R. Krause-Rehberg, J. Martin, and P. Becker, Appl. Phys. A **68**, 411 (1999).

[12] J. Kansy, Nucl. Instrum. Methods Phys. Res. A **374**, 235 (1996).

[13] M. Hyla, J. Filipecki, O. Shpotyuk, M. Popescu, and V. Balitska, J. Optoelectron. Adv. Mater. **9**, 3177 (2007).

[14] E. I. Kamitsos, J. A. Kapoutsis, I. P. Culeac, and M. S. Iovu, J. Phys. Chem. B **101**, 11061 (1997).

[15] O. I. Shpotyuk, A. P. Kovalskiy, E. Skordeva, E. Vateva, D. Arsova, R. Ya. Golovchak, and M. M. Vakiv, Phys. B, Condens. Matter **271**, 242 (1999).