



Post-irradiation relaxation in vitreous arsenic/antimony trisulphides

V. Balitska^{a,b}, Ya. Shpotyuk^{a,c,d,*}, J. Filipecki^d, O. Shpotyuk^{a,d}, M. Iovu^e

^a Institute of Materials of SRC "Carat", 202, Stryjska str., Lviv, 79031, Ukraine

^b Lviv State University of Vital Function Safety, 35, Kleparivska str., Lviv, 79023, Ukraine

^c Faculty of Electronics of the Ivan Franko National University of Lviv, 50, Dragomanova str., Lviv, 79005, Ukraine

^d Institute of Physics of Jan Dlugosz University, 13/15, al. Armii Krajowej, Czestochowa, 42200, Poland

^e Center of Optoelectronics, Institute of Applied Physics, 1, Academiei str., Chisinau, Moldova

ARTICLE INFO

Article history:

Received 16 April 2010

Received in revised form 14 June 2010

Available online 20 August 2010

Keywords:

Chalcogenide vitreous semiconductors;

Relaxation;

Topological defects

ABSTRACT

Instability caused by high-energy γ -irradiation was 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 obtained results being treated within a two-state trapping model. The observed decrease in the positron trapping rate of the glasses tested just after irradiation was explained due to renovation of destroyed covalent chemical bonds. This process was governed by monomolecular relaxation kinetics agreed well with corresponding changes in fundamental optical absorption edge.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Chalcogenide vitreous semiconductors (ChVS) have been in a sphere of high interests because of their application in advanced IR optics, information photonics and telecommunication [1, 2].

Post-technological radiation modification route was shown recently to be one of most effective ways to prepare these disordered solids with the best exploitation properties [3]. This unique ability was attributed to specific type of radiation-induced structural defects that appeared in ChVS as pairs of charged over- and under-coordinated atoms [3]. However, these defects introduced additional metastability in radiation-modified properties in view of ChVS tending towards equilibrium after irradiation. Thus, it was observed experimentally that ChVS subjected to high-energy γ -irradiation demonstrated time drift in their physical properties in dependence on glass composition [3, 4]. In part, in Ge-based and mixed As–Ge-based ChVS, this process was governed by stretched-exponential kinetics close to bimolecular one with character durations over a few months [3, 4]. However, in ChVS of arsenic trisulphide As_2S_3 and related compositions such as quasibinary As_2S_3 – Sb_2S_3 , the post-irradiation relaxation attains quicker monomolecular kinetics decaying over a few days [5].

This difference allows principal mismatch in structural interpretation of both instabilities, nevertheless, each of them can originate from the same *in-situ* bond-destructive state caused by high-energy irradiation. To clarify the underlying mechanism of the observed post-irradiation relaxation, we have studied free volume evolution in

vitreous $v-(As_2S_3)_{1-x}(Sb_2S_3)_x$ irradiated by ^{60}Co γ -quanta using positron annihilation lifetime (PAL) spectroscopy.

2. Experimental

ChVS samples of quasibinary $v-(As_2S_3)_{1-x}(Sb_2S_3)_x$ system ($x = 0, 0.1, 0.2, 0.3$) were prepared by melt quenching using high-purity (99.9999%) initial ingredients [5]. The obtained glassy ingots were cut into disks of ~ 1 mm thickness and polished to high optical quality. To remove mechanical strains that appeared after quick cooling, the samples were additionally annealed near their glass transition temperature.

Radiation treatment was performed by ^{60}Co γ -quanta with 1.25 MeV average energy and absorbed dose close to 2 MGy in normal conditions of a stationary radiation field as was described elsewhere [3]. No special measures were taken to prevent uncontrolled thermal annealing of the samples, while maximum temperature during irradiation did not exceed 320–330 K.

PAL measurements were performed at room temperature in different moments after irradiation using conventional fast-fast coincidence system with ORTEC spectrometer [6]. The radioactive ^{22}Na isotope placed between two sandwiched ChVS samples was used as a positron source. The PAL spectra were recorded in normal-measurement statistics that evolved near 10^6 elementary annihilation events. This allows to determine PAL parameters (positron lifetimes τ_1, τ_2 and their intensities $I_1, I_2 = 1 - I_1$, as well as bulk τ_B and average positron lifetimes τ_{av} and positron trapping rate κ_d) within a two-state positron trapping model [6, 7] using LT program [8].

By taking into account that within a conventional accuracy in both positron lifetimes τ_1 and τ_2 (± 0.005 ns) and their intensities I_1 and I_2

* Corresponding author. Institute of Materials of SRC "Carat", 202, Stryjska str., Lviv, 79031, Ukraine.

E-mail address: shpotyuk@novas.lviv.ua (Y. Shpotyuk).

(± 0.010) limited by the effect of source correction, spectrometer calibration and possible uncertainties because of non-identical sample installation in the measuring chamber [7] the adequate description of fine-changing positron trapping processes is difficult, the following algorithm for PAL data treatment was applied. The first short lifetime τ_1 was assumed to be equal exactly to 0.200 ns in all studied samples whichever their chemical composition. This assumption was grounded on our previous PAL measurements for $v\text{-As}_2\text{S}_3$ as the model sample with a character layer-like structural motive formed by corner-shared $\text{AsS}_{3/2}$ pyramids [9]. The same structural motive is proper for $v\text{-(As}_2\text{S}_3)_{1-x}(\text{Sb}_2\text{S}_3)_x$ composed by mixture of identical $\text{AsS}_{3/2}$ and $\text{SbS}_{3/2}$ pyramids [10]. Under this assumption, the constant value of first positron lifetime $\tau_1 = 0.200$ ns reflects the similarity in basic positron trapping event in defect-free network of $v\text{-(As}_2\text{S}_3)_{1-x}(\text{Sb}_2\text{S}_3)_x$, which is accepted to be identically arranged for all studied compositions ($x = 0, 0.1, 0.2$ and 0.3). Within this approach, the fine changes in defect-related positron trapping modes caused by irradiation are gathered in positron trapping rate κ_d . The similar procedure of positron lifetime fixing was successfully applied previously to describe defect-related positron trapping modes in dielectric oxyaluminate ceramics [11].

3. Results

Positron trapping modes of non-irradiated $v\text{-(As}_2\text{S}_3)_{1-x}(\text{Sb}_2\text{S}_3)_x$ measured just after irradiation and 1 month later are presented in Table 1.

It should be noted that under the condition on fixed short positron lifetime $\tau_1 = 0.200$ ns, the second or defect-related lifetime τ_2 is also constant (close to 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), reflecting in such a way the same nature of positron trapping centre in all tested samples.

The decaying kinetics of positron trapping rate κ_d for γ -irradiated $v\text{-As}_2\text{S}_3$ and $v\text{-(As}_2\text{S}_3)_{0.8}(\text{Sb}_2\text{S}_3)_{0.2}$ samples are shown in Fig. 1 (the similar dependencies for ChVS samples with $x = 0.9$ and 0.7 are not reproduced in Fig. 1). The normalization procedure was carried out for κ_d values (shown as full circuits) taken just after irradiation and 1-month later in a stationary regime. For comparison, we also introduced 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 circuits) and fitted with single-exponential relaxation function (red line) [5]. It is obvious that both normalized kinetics (for optical transmission and positron trapping rate) coincide well in its main features. Therefore, the same structurally-sensitive process is responsible for these changes in each ChVS sample. 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 [3].

Table 1

Dynamic post-irradiation PAL parameters of $v\text{-(As}_2\text{S}_3)_{1-x}(\text{Sb}_2\text{S}_3)_x$, in normal-measurement PAL statistics treated within a two-state positron trapping model at fixed $\tau_1 = 0.200$ ns.

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

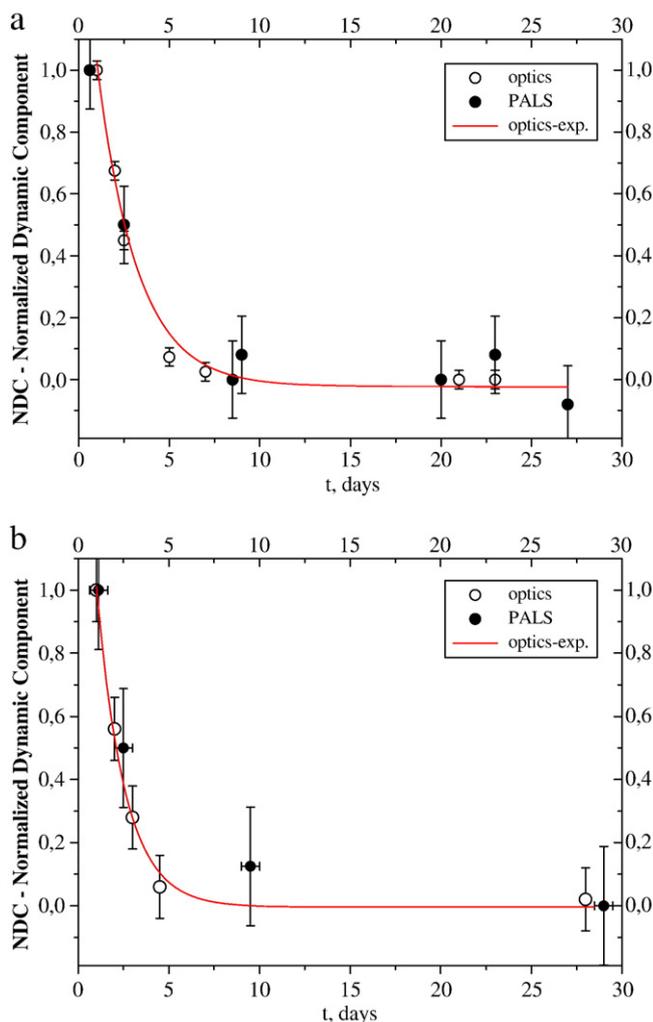


Fig. 1. Normalized kinetics of post-irradiation decrease in positron trapping rate κ_d (full circuits) for $v\text{-As}_2\text{S}_3$ (a) and $v\text{-(As}_2\text{S}_3)_{0.8}(\text{Sb}_2\text{S}_3)_{0.2}$ (b) compared with corresponding optical transmission changes (open circuits) fitted by single-exponential function (red line) [6].

4. Discussion

Thus, the above results for $v\text{-(As}_2\text{S}_3)_{1-x}(\text{Sb}_2\text{S}_3)_x$ are in strong contrast to previous study on As-Ge-based ChVS [3, 4], where bimolecular post-irradiation relaxation kinetics with character time constants near a few months was dominant. The measured extra-short values of post-irradiation relaxation times along with single-exponential post-irradiation kinetics testify in favor of underplaying processes associated with under-coordinated atoms arising from direct bond destruction, as in the case of electron irradiation [12]. It is obvious that such processes are quicker in time giving small values of character time constants.

In the case of studied ChVS, the process of post-irradiation relaxation attains an activation-like single-exponential character owing to spontaneous renovation of destroyed chemical bonds. Since corresponding relaxation times are only slightly modified with glass composition (all being close to 2 days [5]), these changed are supposed to be associated with coordination topological defects only in As-based sub-matrix. Within analogy on electron-induced metastability [12], the defects responsible for monomolecular relaxation in $v\text{-(As}_2\text{S}_3)_{1-x}(\text{Sb}_2\text{S}_3)_x$ can be identified as under-coordinated atoms in the form of As_2^+ and S_1^- (the super- and subscript in defect signature mean charge state and local covalent-bonded coordination, respectively) with character intrinsic

free volumes owing to destroyed As–S covalent bonds. The similar defects are impossible in Sb-based sub-matrix because of lower dissociation barrier for Sb–S covalent bonds [1]. This feature explains well the observed compositional tendency in positron trapping rate κ_d for γ -irradiated $v\text{-(As}_2\text{S}_3)_{1-x}(\text{Sb}_2\text{S}_3)_x$ shown in Table 1 and Fig. 1.

Slight decrease in positron trapping rate κ_d (Table 1) in $v\text{-(As}_2\text{S}_3)_{1-x}(\text{Sb}_2\text{S}_3)_x$ observed just after γ -irradiation can be attributed to overall shrinkage of glassy-like matrix caused by Coulomb attraction between network fragments involving opposite-charged coordination defects. This process is assumed to be responsible for γ -induced increase in microhardness and other mechanical properties of ChVS too [3].

5. Conclusions

The relaxation kinetics observed in a two-state positron trapping rate is shown to correlate well with corresponding changes in the optical properties of γ -irradiated $v\text{-(As}_2\text{S}_3)_{1-x}(\text{Sb}_2\text{S}_3)_x$. These results are explained in terms of under-coordinated topological defects originated from radiation-destroyed covalent chemical bonds.

Acknowledgement

The authors acknowledge support from the Science and Technology Center in Ukraine (Project No. 3745). YaSh is kindly grateful to the assistance offered by the International Visegrad Fund.

References

- [1] A. Feltz, A. Feltz, *Amorphous and Vitreous Inorganic Solids*, Mir, Moscow, 1986.
- [2] X. Zhang, H. Ma, J. Lucas, J. Optoelectron. Adv. Mater. 5 (2003) 1327–1333.
- [3] O.I. Shpotyuk, in: R. Fairman, B. Ushkov (Eds.), *Semiconducting Chalcogenide Glass 1: Glass Formation, Structure, and Simulated Transformations in Chalcogenide Glasses. Semiconductors and Semimetals*, vol. 78, Elsevier Academic Press, Amsterdam-Boston-London-New York-Oxford-Paris-San Diego-San Francisco-Singapore-Sydney-Tokyo, 2004, pp. 215–216.
- [4] O.I. Shpotyuk, A.P. Kovalskiy, E. Skordeva, E. Vateva, D. Arsova, R.Ya. Golovchak, M.M. Vakiv, Phys. B. Cond. Matt. 271 (1999) 242–247.
- [5] Ya.O. Shpotyuk, V.O. Balitska, O.I. Shpotyuk, M. Iovu, J. Optoelectron. Adv. Mat. 11 (2009) 2079–2082.
- [6] O. Shpotyuk, J. Filipecki, Free Volume in Vitreous Chalcogenide Semiconductors: Possibilities of Positron Annihilation Lifetime Study, WSP Ed, Czestochowa, 2003.
- [7] R. Krause-Rehberg, H.S. Leipner, *Positron Annihilation in Semiconductors, Defect studies*, Springer-Verlag, Berlin-Heidelberg-New York, 1999.
- [8] J. Kansy, Instr. Meth. Phys. Res. A374 (1996) 235–244.
- [9] M. Hyla, J. Filipecki, O. Shpotyuk, M. Popescu, V. Balitska, J. Optoelectron. Adv. Mat. 9 (2007) 3177–3181.
- [10] E.I. Kamitsos, J.A. Kapoutsis, I.P. Culeac, M.S. Iovu, J. Phys. Chem. B 101 (1997) 11061–11067.
- [11] O. Shpotyuk, J. Filipecki, H. Klym, A. Ingram, Bull. Lviv Univ. Ser. Phys. 43 (2009) 199–208.
- [12] V.O. Balitska, O.I. Shpotyuk, Nucl. Instr. Meth. Phys. Res. B 166–167 (2000) 521–524.