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Journal of Non-Crystalline Solids 326&327 (2003) 268–272
JOURNAL OF NON-CRYSTALLINE SOLIDS
www.elsevier.com/locate/jnoncrysol

Radiation-induced defect formation in chalcogenide glasses

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Abstract

The modified model of native and radiation-induced microvoid-type positron traps in vitreous chalcogenide semiconductors is developed to explain compositional features of positron annihilation lifetime measurements in stoichiometric As_2S_3–GeS_2 and non-stoichiometric As_2S_3–Ge_2S_3 chalcogenide glasses before and after γ-irradiation.

PACS: 61.43.Fs; 61.82.Fk; 78.70.Bj

1. Introduction

The positron annihilation lifetime (PAL) technique is known to be especially effective in studying irradiation damage in different kinds of crystalline materials [1]. However, the analogous investigations for topologically disordered solids are less successful because of their specific nature.

The essence of the present investigation is to develop the modified model of native and induced microvoid-type positron traps in vitreous chalcogenide semiconductors (VChSs) and to check this model for the ternary As–Ge–S VChSs.

2. Experimental

The investigated bulk VChSs of stoichiometric $(As_2S_3)_y(GeS_2)_{1-y}$ ($y = 0.1$–0.6) and non-stoichiometric $(As_2S_3)_x(Ge_2S_3)_{1-x}$ ($x = 0.2$–0.4) systems were prepared by the known melt-quenching method [2]. All ingots were sliced into 1 mm thick disks with 10–12 mm diameter and polished to a high optical quality. The prepared samples were irradiated by γ-quanta with an accumulated dose of 2.82 MGy and dose power of a few Gy/s in the conditions of stationary radiation field of ^{60}Co ($E = 1.25$ MeV) source.

The PAL measurements were carried out with Ortec spectrometer (0.270 ns resolution) [3]. The ^{22}Na isotope (0.74 MBq activity) was used as positron source placed between two identical samples, forming a 'sandwich' system [1]. The one component fit with positron lifetime τ_1, or the two-component fit with positron short τ_1 and long τ_2

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0022-3093/$ - see front matter
doi:10.1016/S0022-3093(03)00406-X

lifetimes, revealed themselves with I_1 and I_2 relative intensities ($I_1 + I_2 = 1$), were chosen using the LT computer program [4]. The average positron lifetime $\bar{\tau}$ was calculated as $I_1 \cdot \tau_1 + I_2 \cdot \tau_2$.

3. Results

The obtained PAL data for the investigated As–Ge–S VChSs before and after γ-irradiation are accumulated in Table 1.

It is obvious that before γ-irradiation all VChS samples of stoichiometric cut-section are characterized by one PAL component of $\tau_1 \approx 0.36$ ns. In the case of non-stoichiometric As_2S_3–Ge_2S_3 ChVSs, the As-enriched non-irradiated glasses are characterized by one lifetime for positrons ($\tau_1 \approx 0.34$ ns), but two lifetimes ($\bar{\tau} = 0.322$ ns) appear in the $(As_2S_3)_{0.2}(Ge_2S_3)_{0.8}$ sample.

The fulfilled mathematical treatment shows the appearance of two PAL components in both stoichiometric and non-stoichiometric glasses after γ-irradiation (Table 1), the calculated τ_B values remaining at the same high level as in the previous case of $(As_2S_3)_{0.2}(Ge_2S_3)_{0.8}$.

4. Discussion

It should be noted that two principally different approaches to interpretation of PAL data in VChSs have been proposed up to now. The first one [5] prefers the positron annihilation on point-like coordination topological defects (CTDs), while the second one is based on theoretical calculations for vacancies in crystalline As_2Se_3 [6]. However, none of these approaches can be accepted entirely to explain experimental features of positron annihilation in VChSs [3].

We assert that positron trapping in VChSs occurs rather on native open-volume microvoids, but their origin is principally different in comparison with crystalline counterparts of these compounds. The main statements of the native open-volume microvoids concept can be summarized as follows:

(1) the native microvoids of atomic sizes appear in VChSs in result of local bond-charge density distribution (bond-free solid angle microvoids [7]), technologically frozen atomic fluctuations and topological inconsistencies between different glass-forming units (geometrical microvoids);

Table 1
PAL characteristics for boundary compositions of the investigated stoichiometric $(As_2S_3)_y(GeS_2)_{1-y}$ and non-stoichiometric $(As_2S_3)_x(Ge_2S_3)_{1-x}$ VChSs

Glass composition (x, y; Z)	Before γ-irradiation	After γ-irradiation	
		Experimental values	Average lifetime
$As_{28.6}Ge_{9.5}S_{61.9}$ ($y = 0.6$; $Z = 2.48$)	$\tau_1 = 0.364 \pm 0.002$ ns	$\tau_1 = 0.277 \pm 0.002$ ns; $I_1 = 67 \pm 1\%$ $\tau_2 = 0.386 \pm 0.003$ ns; $I_2 = 33 \pm 1\%$	$\bar{\tau} = 0.313 \pm 0.003$ ns
$As_{6.25}Ge_{28.125}S_{65.625}$ ($y = 0.1$; $Z = 2.63$)	$\tau_1 = 0.364 \pm 0.004$ ns	$\tau_1 = 0.282 \pm 0.009$ ns; $I_1 = 53 \pm 1\%$ $\tau_2 = 0.397 \pm 0.010$ ns; $I_2 = 47 \pm 1\%$	$\bar{\tau} = 0.336 \pm 0.010$ ns
$As_{16}Ge_{24}S_{60}$ ($x = 0.4$; $Z = 2.64$)	$\tau_1 = 0.340 \pm 0.003$ ns	$\tau_1 = 0.275 \pm 0.010$ ns; $I_1 = 55 \pm 1\%$ $\tau_2 = 0.392 \pm 0.013$ ns; $I_2 = 45 \pm 1\%$	$\bar{\tau} = 0.328 \pm 0.013$ ns
$As_8Ge_{32}S_{60}$ ($x = 0.2$; $Z = 2.72$)	$\tau_1 = 0.239 \pm 0.006$ ns; $I_1 = 43 \pm 1\%$ $\tau_2 = 0.385 \pm 0.005$ ns; $I_2 = 57 \pm 1\%$	$\tau_1 = 0.243 \pm 0.017$ ns; $I_1 = 33 \pm 1\%$ $\tau_2 = 0.387 \pm 0.009$ ns; $I_2 = 67 \pm 1\%$	$\bar{\tau} = 0.339 \pm 0.017$ ns

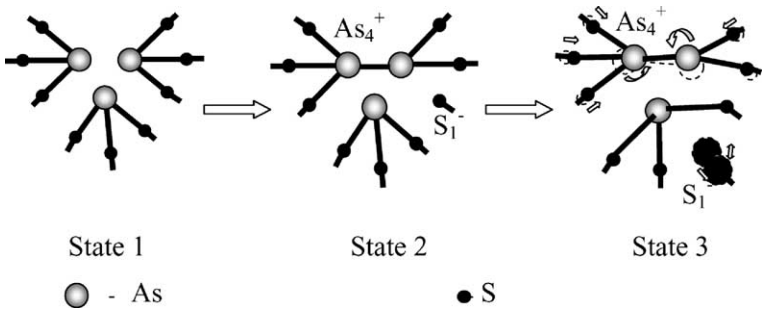

Fig. 1. Bond switching in vitreous As_2S_3 with a simultaneous separation of the created CTDs.

(2) all types of the above microvoids are stabilized during melt quenching;
(3) the volume distribution of the above microvoids is determined by glass composition;
(4) these microvoids are counterparts of neutral vacancy-type defects in crystals, they being effective traps for positrons with character lifetimes ranging from 0.20 to 0.25 ns up to 0.5 ns.

A principally another part of microvoids can be created in a glassy-like network by a number of external influences (high-energetic irradiation) at $T \ll T_g$. These induced microvoids are associated mainly with intrinsic open spaces, appeared owing to structural transformations (bonds switching, atomic displacements) in the nearest vicinity of some atomic configurations, especially those containing CTDs [2]. This process is shown in Fig. 1 at the example of (S_1^-, As_4^+) defect formation (superscript – electrical charge, subscript – atomic coordination) in amorphous As_2S_3, caused by photoexposure [8]. It is clear that appearance of As–As covalent bond instead of destructed As–S one at the positively charged As_4^+ CTD leads to the local densification of the nearest atomic package, while in the vicinity of the negatively charged S_1^- CTD the atomic network is distorted with open volume formation (is cross-hatched in Fig. 1). This conclusion is in a good agreement with experimental results obtained using EXAFS [9] and DAXS [10] techniques.

The CTD-based microvoids can be effective traps for positrons with 0.3–0.5 ns individual lifetimes (due to dependence presented in [5]), they being very strong trapping sites because of Coulomb attraction of positrons with negative charge. The medium-range ordering transformations associated with open-volume microvoids offer the necessary conditions for CTD stabilization, preventing their self-disappearing (CTDs are separated at the final state 3 of bond-switching scheme shown in Fig. 1). Taking into account an electrical charge of under-coordinated atom, where induced microvoid is mainly spaced, we can identify this kind of extended defects in VChSs as the counterpart of negatively charged vacancy-type defects in crystals [1].

Let us try to explain the obtained PAL data in vitreous As–Ge–S before and after γ-irradiation (Table 1) at the basis of this modified model for positron trapping in VChSs.

The one PAL component ($\tau_1 \approx 0.36$ ns) in non-irradiated VChSs of stoichiometric cut-section corresponds to alone microvoid-related annihilation channel (or several channels with close lifetimes), unresolved by the used computer program. In other words, we connect this result with positron trapping on a relatively broaden row of the native open-volume microvoids proper to As_2S_3–GeS_2 VChSs.

By applying the two-state positron trapping model [1] to vitreous $(As_2S_3)_{0.2}(Ge_2S_3)_{0.8}$, which is characterized by two lifetimes with $\bar{\tau} = 0.322$ ns, the effective bulk non-trapped positron lifetime $\tau_B = 0.305$ ns can be obtained. However, this τ_B value is too large to be accepted as the actual bulk positron lifetime. So we assert that positron annihilation from defect-free bulk state has a very small probability in comparison with defect-related annihilation processes [1]. This result can be

more reasonably treated in terms of saturation trapping of positrons in several types of intrinsic open-volume defects created technologically. Such approach explains in a good manner the high τ_B value and observed decomposition in the PAL spectra owing to some distinguished maxima in statistical void volume distribution of these positron traps.

The calculated τ_B values for γ-irradiated VChSs of both systems remain at the same high level, as in the previous case. So the above version on saturation of positron trapping in open-volume defects can be used further to explain PAL data, at least two different types of CTD-based open-volume microvoids being created in γ-irradiated samples.

In stoichiometric VChSs, the first lifetime ($\tau_1 \approx 0.28$ ns) seems to be responsible for positron annihilation on CTDs with the shortest lifetime and, presumably (but with a very negligible probability), on free electrons. The former is probably connected with S_1^--based positron traps. The second lifetime ($\tau_2 \approx 0.39$ ns) can be attributed to the superposition of the biggest lifetimes, which are character for positrons trapped on As_2^+- and (or) Ge_3^--based microvoids. According to the relative intensities for these PAL components, it can be concluded that S_1^- defects are dominant in As-enriched VChSs, while the role of Ge_3^- defects rise with Ge content. Consequently, these conclusions are in a full agreement with main compositional features in the investigated VChSs.

Another important conclusion is obvious from average lifetime interpretation of the obtained PAL data. It was found that $\bar{\tau}$ value decreases after γ-irradiation in stoichiometric glasses, showing a release in their total open volume. Hence, the CTDs appear mainly in such spatially extended regions of a glassy-like network, which have the lowest atomic compactness. These regions involve the native microvoids with largest open volumes, characterized by the longest positron lifetimes. They disappear under γ-radiation, giving a rise for CTD-based microvoids with the above lifetimes.

The structure of non-stoichiometric ChVSs becomes more defective after γ-irradiation too. It is clear that role of long PAL component enhances with Ge content in these glasses owing to Ge_3^--based microvoids, giving a good explanation for the previously studied concentration dependence of radiation-induced optical effects in this system [11].

The observed increase in $\bar{\tau}$ for γ-irradiated $(As_2S_3)_{0.2}(Ge_2S_3)_{0.8}$ sample (0.322 and 0.339 ns before and after irradiation, respectively) says in a favour of uniqueness of the observed radiation-structural transformations. The total open volume in this sample enlarges after irradiation owing to $\bar{\tau}$ increase. It indicates that the CTD-formation processes take place more or less uniformly throughout a whole glassy-like network, but not only in the vicinity of the largest native microvoids, as in the previous case of stoichiometric glasses. We suppose this is possible owing to a high content of homopolar covalent bonds in Ge-enriched non-stoichiometric VChSs [2], resulting in principally another type of radiation-induced effects [11].

Thus, in the framework of the developed approach, we can well explain all compositional features of PAL data in the ternary As–Ge–S VChSs of both stoichiometric As_2S_3–GeS_2 and non-stoichiometric As_2S_3–Ge_2S_3 cut-sections before and after γ-irradiation.

5. Conclusions

The experimental PAL data prove the essential role of CTD-based open-volume microvoids in radiation-induced effects in the ternary As–Ge–S VChSs of stoichiometric As_2S_3–GeS_2 and non-stoichiometric As_2S_3–Ge_2S_3 cross-sections. The developed modified model of native and induced open-volume microvoids describes well the compositional features of these changes.

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