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Coordination positron-trapping centers in vitreous chalcogenide semiconductors

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A model of radiation-induced coordination topological defects with an associate open volume is developed in order to explain the experimental results on positron annihilation lifetime measurements in γ-irradiated vitreous chalcogenide semiconductors of the ternary As–Ge–S system. It is shown that, contrary to the native open-volume microvoids frozen technologically at thermodynamic equilibrium near a glass transition, the principally different part of void-type defects can be created as a result of ^{60}Co γ-irradiation. They are associated mainly with structural transformations (atomic displacements) at the medium-range ordering level in the nearest vicinity of some metastable atomic configurations, especially those containing the negatively charged coordination topological defects.

1. Introduction Vitreous chalcogenide semiconductors (VChSs) or, in other words, wide-gap semiconducting compounds of chalcogen atoms (S, Se or Te, but not O) with some elements from the IV-th and V-th groups of the Periodic Table (typically As, Ge, Sb, Bi, etc.) [1], are unique solid state materials, showing the effect of changes in their physical properties under the influence of high-energetic ionizing radiation, such as ^{60}Co γ-quanta with an average energy of more than 1 MeV [2, 3]. These changes are caused by specific radiation-induced structural transformations, connected with so-called coordination topological defects (CTDs) [4, 5]. These defects are created in the form of diamagnetic pairs of over- and under-coordinated atoms in a glassy-like network with positive and negative electrical charge, respectively [1, 4, 5].

The microstructural mechanism of this process is well studied in vitreous v–As_2S_3 [2, 3]. However, the similar transformations were not considered previously neither for v–GeS_2, nor for more complicated cross-linked VChSs with two-, three- and four-fold coordinated atoms.

2. Experimental details The investigated bulk v–$(As_2S_3)_y(GeS_2)_{1-y}$ (y = 0.1 – 0.6) glasses were prepared by a well-known melt-quenching method [1]. Finally, 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 close to 3 MGy and a dose power of a few Gy/s in the normal conditions of a stationary radiation field of a ^{60}Co (E = 1.25 MeV) source.

Positron lifetime measurements (^{22}Na isotope with 0.74 MBq activity) were carried out using an ORTEC spectrometer with 0.270 ns resolution [6]. The measured lifetime spectra were fitted by the LT

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computer program [7], using either a single exponential function or a sum of two weighted exponential functions convoluted with the measured resolution function of the spectrometer. The one-component fit with a positron lifetime τ_1, or the two-component fit with positron short τ_1 and long τ_2 lifetimes, revealed themselves with I_1 and I_2 relative intensities, were chosen in dependence on the reduced chi-squared values. The average positron lifetime $\bar{\tau}$ was calculated as $I_1 \cdot \tau_1 + I_2 \cdot \tau_2$. The overall accuracy of the positron lifetime determination is at the level of ~0.01 ns, while the I_1 and I_2 intensities are typically measured with ~1 – 2% deviation.

3. Results and discussion Using the method of topological-mathematical simulation of CTD formation, previously well developed for vitreous As_2S_3 [4, 5], and taking into account a number of experimental results of IR Fourier spectroscopy of additional γ-induced reflectivity [8], it can be concluded that the observed radiation-induced changes in the investigated VChSs are explained by increase in the content of one chemical bonds (mainly As–S) and decrease in the content of other (mainly Ge–S).

The topological scheme of this bond-switching reaction is shown in Fig. 1. Two atoms with "wrong" coordination appear in the result of this process – As_4^+ and Ge_3^- (the upper index in the defect signature means the electrical charge of the atom, and the lower one the number of nearest covalent-linked atoms). It is clear that the appearance of the As–S covalent chemical bond instead of the destructed Ge–S one at the positively charged As_4^+ defect leads to the local densification of the nearest atomic package, while in the vicinity of the negatively charged Ge_3^- defect the electron charge-density is lowered because of the lack of one covalent bond (Ge–S). So the atomic network is distorted near negatively charged under-coordinated Ge-atom with open volume formation (crosshatched in Fig. 1, state 3). It means, in other words, that structurally intrinsic open-volume space (microvoid) appears near the above Ge_3^- defect. Its volume is estimated to be at the level of atomic and super-atomic sizes, taking into account numerical parameters of v–As–Ge–S network [1]. This microvoid is supposed to be an effective trap for positrons with individual lifetimes close to 0.3–0.5 ns (due to the dependence of positron lifetimes on open volumes presented in [9]), it being a very strong trapping site due to the Coulomb attraction of positrons.

In similar ways, other types of CTDs (S_1^- and As_2^-) with associated open-volumes are formed in v–As_2S_3–GeS_2. The quantitative values of these open-volumes, we believe, comparing the native (initial) volumes per one atom of main VChS-forming units, as well as the estimated volumes of destroyed covalent chemical bonds [1], increase in a sequence of $S_1^- \rightarrow As_2^- \rightarrow Ge_3^-$. This conclusion was postu-

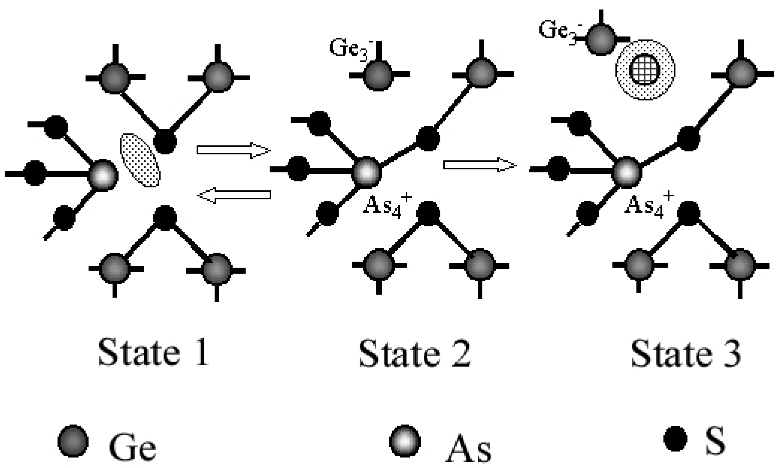

Fig. 1 Topological scheme of the main bond-switching reaction in v–As_2S_3–GeS_2, accompanied by the separation of CTDs with an additional open-volume microvoid.

lated previously in [10] in order to explain the results on positron lifetime measurements in different VChS-systems.

The medium-range ordering transformations associated with open-volume microvoids offer the necessary conditions for CTD-stabilisation in a glass-structure, preventing their self-disappearing (CTDs are separated at the final stage 3 of bond-switching scheme in Fig. 1). It is estimated that this condition is well satisfied, provided that no less than 5 Å distance separates the appeared defects of the created CTD-pair [11]. Taking into account an electrical charge of an under-coordinated atom, where a γ-induced microvoid is mainly spaced, we can identify this kind of extended defects as the counterparts of negatively charged vacancy-type defects in crystals [12].

Let us try to explain the above conclusions at the basis of the experimental results on positron lifetime measurements in this system before and after γ-irradiation (see Table 1).

Positron lifetime measurements show that before γ-irradiation all VChS-samples are characterized by one positron lifetime of $\tau_1 \approx 0.36$ ns. We supposed that the initial concentration of the native CTD-based traps in these glasses is too small for a strong lifetime decomposition. We connect this lifetime component with positron trapping on the continuous row of the native open-volume microvoids proper to VChSs.

The analysis of the spectra with the LT computer program shows the existence of two lifetime components in the investigated As_2S_3–GeS_2 glasses after γ-irradiation: short (τ_1) and long (τ_2) ones. The first one ($\tau_1 \approx 0.28$ ns) seems to be responsible for positron annihilation on free electrons (non-trapped positron annihilation) and, presumably, one of CTD-based open-volume microvoids with the shortest lifetime. The latter is probably connected with S_1^--based positron trapping sites. The second lifetime ($\tau_2 \approx 0.39$ ns) can be attributed to the superposition of the longest lifetimes, which are characteristic for positrons trapped on As_2^-- and Ge_3^--based microvoids. According to the relative intensities for these short ($\tau_1 \approx 0.28$ ns) and long ($\tau_2 \approx 0.39$ ns) components (see Table 1), it can be concluded that S_1^- defects are dominant in As_2S_3-enriched VChSs. Otherwise the role of Ge_3^- defects becomes more essential with the GeS_2 content. These conclusions are in an excellent agreement with the main compositional trends in these VChSs.

Another important conclusion on the nature of radiation-structural transformations is obvious from the average-lifetime interpretation of the obtained results. It was found that the average lifetime for positrons $\bar{\tau}$ decreases after γ-irradiation in the investigated VChSs, showing a release in their total open volume. Hence CTDs appear mainly in such places of a glassy-like network, which have the lowest local atomic compactness. These places involve the native open-volume microvoids with the largest volumes, characterised by the longest positron lifetimes. They disappear under γ-radiation, giving a rise for defect-based microvoids with the above lifetimes.

Table 1 Positron lifetime characteristics of $(As_2S_3)_y(GeS_2)_{1-y}$ VChSs before and after γ-irradiation.

glass composition		positron lifetime characteristics	
chemical formula	y	before γ-irradiation	after γ-irradiation
$As_{28.6}Ge_{9.5}S_{61.9}$	0.6	$\tau_1 = 0.36$ ns	$\tau_1 = 0.28$ ns, $I_1 = 0.67$; $\tau_2 = 0.39$ ns, $I_2 = 0.33$; $\bar{\tau} = 0.31$ ns
$As_{21}Ge_{15.8}S_{63.29}$	0.4	$\tau_1 = 0.35$ ns	$\tau_1 = 0.29$ ns, $I_1 = 0.62$; $\tau_2 = 0.39$ ns, $I_2 = 0.38$; $\bar{\tau} = 0.33$ ns
$As_{11.8}Ge_{23.5}S_{64.7}$	0.2	$\tau_1 = 0.36$ ns	$\tau_1 = 0.28$ ns, $I_1 = 0.53$; $\tau_2 = 0.40$ ns, $I_2 = 0.47$; $\bar{\tau} = 0.34$ ns

4. Conclusion The obtained results on positron annihilation lifetime measurements in the ternary As–Ge–S VChSs of stoichiometric As_2S_3–GeS_2 cross-section prove the essential role of CTD-formation processes on the observed radiation-induced changes. The developed modified model of induced open-volume microvoids describes well the compositional features of these effects.

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