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Coordination defects in chalcogenide amorphous semiconductors studied by positron annihilation lifetime

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Abstract

Defect formation processes in chalcogenide vitreous semiconductors of the ternary As–Ge–S system, induced by the ^{60}Co γ-irradiation with 2.82 MGy absorbed dose, are studied using positron lifetime measurements. The obtained results are explained at the level of both short- and medium-range ordering in the framework of coordination topological defects model modified with free-volume microvoids formation.

Keywords: Positrons; Semiconductors; Chalcogenides; Glasses

1. Introduction

Positron annihilation method is a powerful instrument for the experimental study of solids at different levels of their structural hierarchy [1]. It is characterized by a high sensitivity to local changes associated with point and linear defects, impurities and inhomogeneities, crystallites and phase incorporates, microvoids and atomic clusters.

The application of this method for disordered solids, such as chalcogenide vitreous semiconductors (ChVS), gives very important and sometimes exclusive information on their structural features as well as on microstructural transformations, induced by different kinds of high-energetic ionizing irradiation. The coordination topological defects (CTD) model for these radiation-induced effects in the binary ChVS was created [2,3] in the framework of well-known D^+–D^- point charged defects concept developed by Mott et al. [4]. As a rule, only data of vibrational spectroscopy methods (such as the Raman, IR Fourier spectroscopy) were obtained on the basis of the above model.

The aim of the present investigations is to obtain additional data on the CTD in the ternary As–Ge–S ChVS of stoichiometric As_2S_3–GeS_2 and non-stoichiometric As_2S_3–Ge_2S_3 cross-sections using positron annihilation lifetime technique.

2. Experimental

The investigated bulk samples of ternary 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 a well-known melt quenching method described previously elsewhere [5].

The prepared ChVS samples were irradiated by γ-quanta with an accumulated dose of 2.82 MGy and a dose power of 20 Gy/s in the normal conditions of stationary radiation field, created in the closed cylindrical cavity owing to concentrically established ^{60}Co (E = 1.25 MeV) sources.

The measurements of positron annihilation lifetimes were carried out using an ORTEC spectrometer with the FWHM (full-width at half-maximum) resolution of

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0.270 ns. The ^{22}Na isotope with 0.74 MBq activity was used as a positron source placed between two identical samples, forming a "sandwich" system. The positron lifetimes were calculated from the LT computer program [6] using a single exponential function as well as a sum of two weighted exponential functions fittings.

3. Results and discussion

The positron lifetime characteristics of the investigated ChVS samples before and after γ-irradiation are presented in Table 1. Let us try to explain these results taking into account the previously obtained experimental data of other authors [7–10].

There are two principally different approaches to the interpretation of the positron lifetime measurements in the ChVS.

The first one, developed by Kobrin and Shantarovich with co-workers in the 1980s [7–9] on the basis of the CTD concept, prefers the positron annihilation processes in the ChVS at the negatively charged "dangling" bonds. It was assumed on the basis of numerous experimental data for the various ChVS systems (however, without strong theoretical calculations) that the main types of these CTD were characterized by the following lifetimes—0.32 ns (S_1^-), 0.37 ns (As_2^-) and 0.42 ns (Ge_3^-). The upper index in the CTD signature indicates the charged electrical state, and the lower one, the number of neighbouring atoms. The experimentally observed positron annihilation lifetime components were treated as a superposition of various combinations of these lifetimes with each other, as well as lifetimes of positron annihilation on non-localized free electrons (0.2 ns) or microcrystalline inclusions (0.5 ns). Thus, only topological changes at the short-range ordering level were taken into account in this consideration. However, in this way it is difficult to explain the positron annihilation lifetimes less than 0.32 ns, because the free-electron concentration is typically too low in the ChVS [11].

The second approach is based on the theoretical lifetime calculations for the positrons trapped by the so-called open volume defects (vacancies and vacancy clusters) in crystalline As_2Se_3. It was carried out by Jensen et al. at the beginning of the 1990 in order to explain the experimentally observed results on positron lifetime measurements in glassy As_2Se_3 [10]. It was stated that not intrinsic negatively charged CTD, but only microvoids of 25–100 Å^3 volume in the form of As- (0.262 ns) and Se-monovacancies (0.274 ns), As—Se divacancy (0.316 ns) and As—Se_3 quadruple vacancy (0.368 ns) were responsible for the positron trapping. The lowest value of the positron lifetime (0.240 ns) was attributed to non-trapped positron annihilation in defect-free bulk crystalline As_2Se_3. Apart from this, the experimental evidences for the CTD formation processes in the ChVS

Table 1
Positron lifetime characteristics for boundary compositions of the investigated stoichiometric $(As_2S_3)_y(GeS_2)_{1-y}$ and non-stoichiometric $(As_2S_3)_x(Ge_2S_3)_{1-x}$ ChVS systems before and after γ-irradiation with 2.82 MGy dose

Glass composition	Before γ-irradiation (ns)	After γ-irradiation with 2.82 MGy dose	
		Experimental values (ns)	Mean lifetime (ns)
$y = 0.6$	$\tau_1 = 0.3638 \pm 0.0002$	$\tau_1 = 0.277 \pm 0.002$; $I_1 = 0.67 \pm 0.01$ $\tau_2 = 0.386 \pm 0.003$; $I_2 = 0.33 \pm 0.01$	$\tau = 0.313 \pm 0.003$
$y = 0.1$	$\tau_1 = 0.3644 \pm 0.0004$	$\tau_1 = 0.282 \pm 0.009$; $I_1 = 0.53 \pm 0.05$ $\tau_2 = 0.397 \pm 0.010$; $I_2 = 0.47 \pm 0.05$	$\tau = 0.336 \pm 0.010$
$x = 0.4$	$\tau_1 = 0.3396 \pm 0.0003$	$\tau_1 = 0.275 \pm 0.010$; $I_1 = 0.55 \pm 0.06$ $\tau_2 = 0.392 \pm 0.013$; $I_2 = 0.45 \pm 0.06$	$\tau = 0.328 \pm 0.013$
$x = 0.2$	$\tau_1 = 0.239 \pm 0.006$ $I_1 = 0.43 \pm 0.02$ $\tau_2 = 0.385 \pm 0.005$ $I_2 = 0.57 \pm 0.02$	$\tau_1 = 0.243 \pm 0.017$; $I_1 = 0.33 \pm 0.05$ $\tau_2 = 0.387 \pm 0.009$; $I_2 = 0.67 \pm 0.05$	$\tau = 0.339 \pm 0.017$

are quite convincing [2,3,15] and, consequently, they cannot be rejected fully without any serious arguments.

So none of these approaches can be accepted entirely to explain the experimental results of the positron annihilation measurements in the ChVS.

We believe that positron trapping in the ChVS occurs on microvoids, but their association with the CTD must be taken into account too.

A part of the microvoids have a fluctuating nature and can be frozen technologically at melt quenching [12–15]. Their volumes in the ChVS are typically as high as 15–30 $Å^3$, which is less than the volumes of discrete atomic vacancies introduced in Ref. [10]. This value of 15–30 $Å^3$ can be reduced even to 5–10 $Å^3$ by accepting that fluctuation microvoids are probably connected with boundary shifts of bridge chalcogen atoms [15]. These native microvoids of atomic and sub-atomic sizes lead to a lower compactness of glassy-type atomic network in comparison with the crystalline structures. It means that these native free-volume microvoids can be the traps for positrons with characteristic lifetimes less than 0.25–0.30 ns (due to the dependence of the positron lifetimes on open volumes presented in Ref. [10]).

But the other part of the microvoids can be created in the ChVS structure by external influences as a result of atomic transformations at the medium-range ordering level in the nearest vicinity of the negatively charged CTD (CTD-based microvoids). This process is shown schematically in Fig. 1 in the example of (S_1^-, As_4^+) CTD formation in amorphous As_2S_3, caused by photoexposure [16]. It is clear that the appearance of an additional As—As covalent chemical bond instead of the destructed As—S one at the positively charged As_4^+ defect leads to the local densification of the atomic package, while near the negatively charged S_1^- CTD the atomic network is distorted with free-volume microvoid formation (which is crosshatched in Fig. 1).

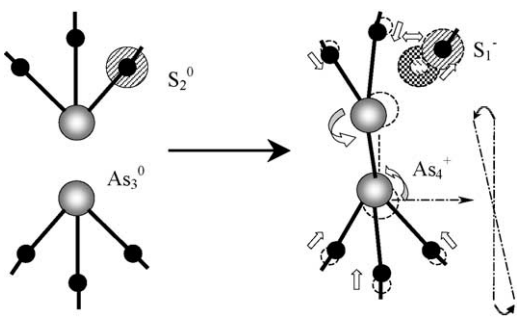

Fig. 1. A topological scheme illustrating the process of additional free-volume formation in the vicinity of the negatively charged S_1^- coordination defect.

It is difficult to quantitatively estimate the real volume of the created CTD-based microvoids for different kinds of the negatively charged CTD, but their appearance in the vicinity of the negatively charged CTD provides the effective positron trapping with characteristic lifetimes given by Kobrin and Shantarovich with co-workers [7–9].

The positron annihilation lifetime measurements show that before the γ-irradiation, all the ChVS samples of the stoichiometric system (the experimental data for two of them with maximal content of As_2S_3 and GeS_2 are presented in Table 1) are characterized by one mean positron lifetime of ~0.36 ns.

The fulfilled computer treatment of the obtained results shows the existence of two lifetime components after γ-irradiation: short- and long-lived ones. The first one ($\tau_1 \sim 0.28$ ns) seems to be responsible for positron annihilation on the native free-volume microvoids and S_1^- CTD with an associated free volume. The second lifetime ($\tau_2 \sim 0.39$ ns) is attributed to the superposition of lifetimes for positrons trapped on Ge_3^- and As_2^- CTD (with associated microvoids). According to the ratio of these short- and long-lived components (see Table 1), it can be concluded that the S_1^- CTD are dominant in the As_2S_3-enriched ChVS compositions. On the contrary, the role of the Ge_3^- CTD becomes more essential with GeS_2 content in the investigated stoichiometric ChVS.

The results of the positron annihilation measurements for two-boundary non-stoichiometric ChVS compositions are also presented in Table 1. It is established that the As-enriched non-irradiated glasses are characterized by a lone mean lifetime of positrons (~0.34 ns), while two lifetime components (with average lifetime $\tau = 0.322$ ns) appear with high Ge content in the $(As_2S_3)_{0.2}(Ge_2S_3)_{0.8}$ sample. The short-lived component ($\tau_1 \sim 0.24$ ns) can be explained similarly as in the case of the irradiated stoichiometric ChVS. The same interpretation is proper for a long-lived component of $\tau_2 \sim 0.39$ ns. We treat the latter by positron annihilation on the trapping sites of the Ge_3^- and As_2^- CTD. Such a separation of short- and long-lived components is observed only in the Ge-enriched non-stoichiometric ChVS. It is well known that these samples have a very small atomic compactness [11] and, finally, a high level of structural defectiveness. So, we conclude that a large concentration of the electrically charged CTD with extremely great amount of associated CTD-based microvoids initially exist as positron traps in these glasses.

The structure of the non-stoichiometric ChVS (similar to stoichiometric ones) becomes more defective after the γ-irradiation. As a result, two positron lifetime components with the above attributions to traps on the negatively charged CTD (with associated microvoids) and native free-volume microvoids appear. It is clear that the role of long-lived positron trapping is enhanced

with Ge content in the investigated ChVS owing to the Ge_3^- CTD ($\tau \sim 0.42$ ns) in good accordance with the previously studied concentration dependence of radiation-induced optical effects in this system [5].

4. Conclusions

The obtained results on the positron annihilation lifetime measurements in the ternary As–Ge–S ChVS of stoichiometric $As_2S_3-GeS_2$ and non-stoichiometric $As_2S_3-Ge_2S_3$ cross-sections prove the essential role of the CTD formation processes in the observed radiation-induced effects. The developed modified model of the CTD formation associated with free-volume microvoids at the levels of both short- and medium-range ordering describes well the compositional features of these effects.

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