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Positron lifetime study of native vacancy-like defects in chalcogenide glasses

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Abstract

Modified model for positron annihilation in vitreous chalcogenide semiconductors is developed to explain a number of previously obtained results on positron lifetime measurements in glassy As–Ge–S of stoichiometric As_2S_3–GeS_2 and non-stoichiometric As_2S_3–Ge_2S_3 cut-sections.

Keywords: Positron annihilation; Chalcogenide glasses; Open-volume void

1. Introduction

Recent progress in semiconductor science is known to be determined, to a great extent, by measuring possibilities of different experimental techniques giving vital information on their atomic and electron-defect sub-systems. Positron annihilation lifetime spectroscopy belongs to methods equally suitable for different solid-state substances despite their structural hierarchy.

The essence of the present investigation is to develop the modified native open-volume void (NOVV) model for positron trapping in vitreous chalcogenide semiconductors (VChS) taking into account a microstructural nature of their glass-forming network and to check this model at the example of previously investigated As–Ge–S glass system (Shpotyuk et al., 2001).

2. Experimental

The investigated bulk VChS of stoichiometric As_2S_3–GeS_2 (6 compositions) and non-stoichiometric As_2S_3–Ge_2S_3 (5 compositions) cut-sections were prepared by well-known melt quenching method (Feltz, 1986). Positron lifetime measurements were carried out using ORTEC spectrometer with 0.270 ns resolution. The ^{22}Na isotope (0.74 MBq activity) was used as positron source placed between two identical samples, forming a "sandwich" system. The measured lifetime spectra were fitted by LT computer program (Kansy, 1996), using either single exponential function or sum of two weighted exponential functions convoluted with measured resolution function of the spectrometer.

3. Results and discussion

It should be noted that two principally different approaches to the interpretation of positron lifetime measurements in VChS have been proposed until now. The first one, developed in the 70-s (Alekseeva et al., 1978), prefers the positron annihilation in VChS on native negatively charged "dangling" bonds or the so-called point coordination defects (Feltz, 1986). The second approach, presented by Jensen et al. (1994), is based on theoretical calculations for positrons trapped by open-volume vacancy-type defects (vacancies and their clusters) in crystalline As_2Se_3. However, none of these approaches can be accepted entirely to explain

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the experimental features of positron annihilation in VChS.

The main declaration of the proposed alternative model is that the NOVV could be effective trapping sites for positrons in VChS, but their origin principally differs from one proper to crystalline counterparts of these compounds. The proposed NOVV model could be summarized in the form of the following statements:

(1) the NOVV of atomic sizes appear in a fully saturated covalent-linked VChS network in the result of stereometric specifics in local bond-charge density distribution around chalcogen and pnictogen atoms (Kastner, 1973), atomic fluctuations frozen technologically at melt quenching (Sanditov and Bartenev, 1982) and topological inconsistencies between different glass-forming units (Feltz, 1982);
(2) all types of the above NOVV are stabilized technologically in VChS structure during melt quenching;
(3) distribution of the above NOVV is determined mainly by glass composition;
(4) these NOVV are the effective traps for positrons with character lifetimes ranging from 0.20–0.25 up to 0.5 ns.

Taking into account that there are no significant electron-density flashes within full-saturated VChS network (Feltz, 1986), we can identify the above NOVV as the counterparts of neutral vacancy-type defects in crystals (Krause-Rehberg and Leipner, 1999).

If the effective positron lifetime correspondent to the statistical maximum in open-volumes distribution of the above NOVV is quite close to non-trapped positron lifetime τ_B, or if positron annihilation with free electrons is of low intensity, the observed positron annihilation spectra will not be decomposed by the chosen computer program giving only one lifetime component. Otherwise, two lifetimes, sufficiently remote from τ_B value, will appear in VChS having wider open-volume distribution of the NOVV.

The obtained experimental results on positron lifetime measurements in As–Ge–S VChS (Table 1) can be correctly considered within above model. The positron lifetime measurements show that all VChS samples of stoichiometric As_2S_3–GeS_2 cut-section are characterized by one average positron lifetime $\tau_1 \approx 0.36$ ns. We connect this component with positron trapping on the continuous row of NOVV proper to these VChS with the mean positron lifetime quite closed to the bulk one (τ_B). Under these conditions, only one lifetime component can be revealed in the measured spectra. The similar situation was observed previously in some ternary VChS, such as AsGeS, $AsGe_{0.2}Te$, AsGeSe, $AsGe_{0.2}Se$ (Singh et al., 1987).

Table 1
Positron lifetime characteristics for boundary compositions of As–Ge–S VChS

VChS		Positron lifetime characteristics
Cut-section	Chemical formula	
As_2S_3–GeS_2	$As_{28.6}Ge_{9.5}S_{61.9}$	$\tau_1 = 0.364 \pm 0.002$ ns
As_2S_3–GeS_2	$As_{6.25}Ge_{28.125}S_{65.625}$	$\tau_1 = 0.364 \pm 0.004$ ns
As_2S_3–Ge_2S_3	$As_{16}Ge_{24}S_{60}$	$\tau_1 = 0.340 \pm 0.003$ ns
As_2S_3–Ge_2S_3	$As_8Ge_{32}S_{60}$	$\tau_1 = 0.239 \pm 0.006$ ns, $I_1 = 0.43 \pm 0.01$; $\tau_2 = 0.385 \pm 0.005$ ns, $I_2 = 0.57 \pm 0.01$

The results of positron annihilation measurements for two boundary non-stoichiometric As_2S_3–Ge_2S_3 VChS compositions are presented in Table 1 too. It is obvious that the As-enriched glass is characterized by the sole lifetime for positrons ($\tau_1 \approx 0.34$ ns), but two lifetime components appear in $As_8Ge_{32}S_{60}$ sample. Such separation of short and long lifetime components is observed only in the Ge-enriched non-stoichiometric VChS of this system. So the effective lifetime correspondent to the maximum in statistical distribution of the NOVV in these glasses is distant far from the defect-free bulk lifetime τ_B, leading finally to the two-component decomposition of the measured positron lifetime spectra. It could be supposed that this effect is caused by principally different structural motives in the investigated VChS-two-dimensional layer-like one, based mainly on $AsS_{3/2}$-pyramids, and three-dimensional cross-linked one, based mainly on $GeS_{4/2}$-tetrahedra (Feltz, 1986). The same conclusion is valid for some mono-, binary and a large number of metal-doped ternary VChS (Alekseeva et al., 1978; Jensen et al., 1994; Singh et al., 1987).

Thereby, the developed NOVV model is quite meaningful one for quantitative and qualitative interpretation of the results on positron lifetime measurements in the investigated As–Ge–S VChS.

4. Conclusions

The results of positron lifetime measurements in vitreous As–Ge–S samples of both stoichiometric As_2S_3–GeS_2 and non-stoichiometric As_2S_3–Ge_2S_3 cut-sections are well explained within the modified model considering different types of native open-volume trapping sites in VChS.

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