Available online at www.sciencedirect.com
SCIENCE DIRECT®
Physica B 340–342 (2003) 960–964
PHYSICA B
www.elsevier.com/locate/physb

A nanoscale characterisation of extended defects in glassy-like As_2Se_3 semiconductors with PAL technique

O. Shpotyuk[a,b,*], A. Kovalskiy[a], J. Filipecki[b], M. Hyla[b], A. Kozdras[c]

[a] *Lviv Scientific Research institute of Materials of SRC, Scientific Research Company "Carat", 202, Stryjska str., Lviv 79031, Ukraine*
[b] *Pedagogical University, 13/15, al. Armii Krajowej, Czestochowa 42201, Poland*
[c] *Opole Technical University, 75, ul. Ozimska, Opole 45370, Poland*

Abstract

A meaningful interpretation of positron lifetime characteristics for glassy-like g-As_2Se_3 is developed taking into account calculations of Jensen et al. (J. Non-Cryst. Solids 170 (1994) 57) for positrons trapped by free-volume extended defects in orthorhombic As_2Se_3 and void volume distribution for 146-atoms layer-biased model of amorphous As_2Se_3 presented by Popescu (J. Non-Cryst. Solids 35–36 (1980) 549). The obtained results are compared for samples having different thermal pre-history. Two groups of experimental results with close lifetime characteristics are distinguished for each of the investigated samples. This feature is explained in terms of average positron lifetime by applying two-state positron trapping model for mathematical treatment of the obtained spectra.

Keywords: Extended defects; Glass; Positron annihilation

1. Introduction

A great number of experimental results on positron annihilation lifetime (PAL) characteristics of chalcogenide vitreous semiconductors (ChVS) [1] was accumulated during last three decades [2–5]. Systemising this data, one can observe an essential discrepancy for ChVS obtained in different research laboratories, sometimes considerably exceeding the experimental error-bar acceptable for this method. The glassy-like g-As_2Se_3 serves as a typical example for this situation.

Firstly, this ChVS was studied by Alekseeva et al. at the end of the 1970s [2,3], the investigated samples were prepared in two modifications quenched from 750°C and 600°C. Despite close positron lifetimes for both modifications ($\tau_1 \approx 0.20-0.22$ ns and $\tau_2 \approx 0.36-0.37$ ns), the g-As_2Se_3 samples prepared in more non-equilibrium conditions of water-ice quenching from 600°C demonstrated larger I_2 intensity for long PAL component. This result was explained in terms of specific point-type charged defects proper to ChVS [1].

In 1994, Jensen et al. [4] obtained PAL characteristics for g-As_2Se_3 water-ice-quenched from 650°C, which were in obvious contradiction to the data of Alekseeva et al. [2,3]. The short positron lifetime τ_1 was as high as 0.29 ns, while the second component intensity I_2 jumped up to

*Corresponding author. Tel.: +380-322-631065; fax: +380-322-63-22-28.
E-mail address: shpotyuk@novas.lviv.ua (O. Shpotyuk).

0921-4526/$ - see front matter
doi:10.1016/j.physb.2003.09.173

0.75. To explain these results, the theoretical calculations of positron lifetimes for vacancy-type defects in crystalline c-As_2Se_3 were performed on the basis of Puska's model [6,7]. It was assumed that not point-type charged defects but only extended vacancy-type voids were responsible for positron trapping in both c-As_2Se_3 and g-As_2Se_3. However, it was adopted a fully identical origin for these positron traps in chalcogenide crystals and glasses, despite significant differences between them [1].

Recently, our PAL experiments with g-As_2Se_3 water-quenched from 850°C [5] testified rather in a favour of Alekseeva's data for water-ice-quenched from 600°C modification of this specimen [3]. However, it has remained unclear whether this contradiction caused by pre-history of the samples or more deep reasons lying in their structural specificity.

This controversy can be resolved, provided not only calculations for positron lifetimes in vacancy-type traps of c-As_2Se_3 [4], but also void volume distribution for possible structural model of g-As_2Se_3 presented by Popescu yet in 1980 [8] will be taken into account.

2. Experimental

Two identical g-As_2Se_3 samples were prepared from high-purity elemental constituents, and the standard rocking furnace technique followed by water quenching from 850°C was applied [1]. After synthesis, all ingots were cut into plates ($\sim$1.5 mm in thickness) and polished to optical quality. Hereafter, these kinds of samples will be referred as "as-prepared".

The experimental PAL measurements were performed with ORTEC spectrometer using ^{22}Na source placed between two sandwiched g-As_2Se_3 samples [7].

The obtained spectra were decomposed by LT computer program [9], the best results corresponding to two-component fitting procedure. We used five measured PAL spectra for the investigated pair of g-As_2Se_3 samples; they differed by a total number of counts in the range of 800,000–1200,000. Each of these spectra was multiply treated owing to slight changes in the number of channels, annihilation background and time shift of the spectrum. Firstly, the parameters of PAL spectrum with the long-lived part were calculated and, then, the number of channels was reduced in such a way to cut off the long-lived annihilation background. This procedure was quite a reasonable one, since there were no long-lived components ($\tau > 1$ ns) in the measured spectra. Only results with FIT parameter determined owing to statistically weighted least-squares routine, which were quite close to 1.0 (the optimal FIT range—from 0.95 to $\sim$1.1), were left for the further treatment. At the next stage, this FIT value and the determined PAL characteristics were controlled in dependence on annihilation background and spectrum time shift, the results showing slight changes being selected by us. It must be noted that source correction and spectrometer resolution function were kept constant for all spectra.

By accepting that two-state positron trapping model [7,8] is valid for g-As_2Se_3, the numerical parameters of this model (bulk lifetime τ_B, average lifetime $\bar{\tau}$ and positron trapping rate κ_d) were calculated using τ_1, τ_2, I_1 and I_2 values obtained with applied fitting procedure [7].

Taking into account that PAL characteristics of ChVS are sufficiently dependent on their thermal pre-history [2–5], additional measurements were performed with g-As_2Se_3 samples aged during 3 years at the normal conditions and annealed during 12 h near T_g ($\sim$150°C). This thermal route permits one to avoid structural strains and inhomogeneities appeared because of too sharp cooling [1]. These kinds of samples will be denoted henceforth as "thermally aged".

3. Results

Two-component fitting parameters of LT computer program, describing positron annihilation in as-prepared and thermally aged g-As_2Se_3 samples within two-state positron trapping model, are gathered in Tables 1 and 2, respectively. We used two different procedures to select the optimal sets of PAL results.

Table 1
PAL characteristics of as-prepared g-As_2Se_3

Result	Fit	τ_1 (ns)	τ_2 (ns)	I_2 (a.u.)	τ_B (ns)	$\bar{\tau}$ (ns)	κ_d (ns^{-1})
No. 1	1.002	0.19	0.37	0.62	0.27	0.30	1.6
No. 2	**1.003**	**0.20**	**0.37**	**0.60**	**0.28**	**0.30**	**1.4**
No. 3	**1.004**	**0.20**	**0.37**	**0.60**	**0.28**	**0.30**	**1.4**
No. 4	**1.037**	**0.20**	**0.37**	**0.60**	**0.28**	**0.30**	**1.4**
No. 5	0.933	0.21	0.37	0.59	0.28	0.30	1.3
No. 6	1.006	0.21	0.37	0.58	0.28	0.30	1.3
No. 7	1.112	0.22	0.35	0.12	0.23	0.24	0.2
No. 8	**0.980**	**0.22**	**0.37**	**0.54**	**0.28**	**0.30**	**1.0**
No. 9	**0.984**	**0.22**	**0.37**	**0.54**	**0.28**	**0.30**	**1.0**
No. 10	**0.986**	**0.22**	**0.37**	**0.54**	**0.28**	**0.30**	**1.0**
No. 11	**0.988**	**0.22**	**0.37**	**0.54**	**0.28**	**0.30**	**1.0**
No. 12	**0.990**	**0.22**	**0.37**	**0.54**	**0.28**	**0.30**	**1.0**
No. 13	**1.023**	**0.22**	**0.37**	**0.54**	**0.28**	**0.30**	**1.0**
No. 14	1.227	0.24	0.34	0.55	0.29	0.30	0.7

Table 2
PAL characteristics of thermally aged g-As_2Se_3

Group	Number of results	FIT	τ_1 (ns)	τ_2 (ns)	I_2 (a.u.)	τ_B (ns)	$\bar{\tau}$ (ns)	κ_d (ns^{-1})
No. 1	4	1.133	0.145	0.34	0.75	0.25	0.29	3.1
No. 2	4	1.092	0.18	0.36	0.67	0.27	0.30	1.85
No. 3	5	1.019	0.20	0.37	0.60	0.28	0.30	1.4
No. 4	3	1.087	0.21	0.37	0.58	0.28	0.30	1.2
No. 5	9	1.031	0.225	0.385	0.50	0.285	0.30	0.9

As to as-prepared g-As_2Se_3 samples, we left only 14 sets of experimental results with the smallest FIT values, having rounded off each of them (to a reasonable fitting and systematic error of ± 0.01 ns in positron lifetime and ± 0.01 in component intensity), and eliminated ones with the same PAL parameters. They are presented in Table 1 in the sequence of τ_1 increase, and the absolutely best data being additionally distinguished by bold characters. Thanks to such an arrangement, one may observe a number of certain regularities.

The results Nos. 7 and 14 should be ignored because of too high FIT values. In addition, the former seems to be physically unreal due to extremely low bulk positron lifetime τ_B (0.23 ns). The remaining 12 results can be divided into two large groups with the smallest FITs: the first one (results Nos. 2, 3 and 4) with $\tau_1 \approx 0.20$ ns, $\tau_2 \approx 0.37$ ns, $I_2 \approx 0.60$ and $\kappa_d = 1.4\,ns^{-1}$ and the second one (results from Nos. 8–13) with $\tau_1 \approx 0.22$ ns, $\tau_2 \approx 0.37$ ns, $I_2 \approx 0.54$ and $\kappa_d = 1.0\,ns^{-1}$, both groups having the same bulk τ_B (0.28 ns) and average $\bar{\tau}$ (0.30 ns) lifetimes. The results Nos. 5 and 6 we accept rather as intermediate cases between these groups.

As to thermally aged g-As_2Se_3, the above selection procedure was repeated, but we left a more wide range of 25 experimental results with smallest FITs. Then we distinguish a few groups within this row of results, each of them differing sufficiently from neighbouring one by FIT value. In such a way, five different groups of results were formed (see Table 2).

The first and second groups can be ignored because of too high FITs. The third group is formed by five results with τ_1 values of 0.19 (one result) and 0.20 ns (four results), the smallest average FIT = 1.019 being character for them.

The average FIT value jumps to 1.087 in the fourth group completed with three results having $\tau_1 = 0.21$ ns. It means that the third group is well distinguished at the general background of the selected results. The rest nine results are impossible to divide on separate groups with different FITs. They form the last fifth group of results with sufficiently low average FIT = 1.031.

Therefore, we can conclude that the optimal (the absolutely best) set of PAL parameters is the same in both as-prepared (the first bold-distinguished group in Table 1) and thermally aged (group No. 3 in Table 2) g-As_2Se_3 samples. However, each kind of these ChVS can be simultaneously characterised by another set of PAL parameters with higher lifetime, thermally aged samples having the larger τ_2 and lower I_2 values (group No. 5 in Table 2) in comparison with as-prepared g-As_2Se_3 samples (the second bold-distinguished group in Table 1).

4. Discussion

In accordance to Jensen's calculations [4], the defect-free orthorhombic c-As_2Se_3 is characterised by bulk positron lifetime of $\tau_B = 0.240$ ns. The higher fraction of structurally intrinsic-free volume leads to higher τ_B values in a glassy-like state. That is why the results with $\tau_B \leqslant 0.24$ ns marked as No. 7 in Table 1 and that obtained by Alekseeva et al. in 1977 [2] should be eliminated as physically unreal ones.

Further, the extremely high value of $\tau_B = 0.35$ ns obtained in Ref. [4] seems too doubtful to be accepted as actual bulk positron lifetime for g-As_2Se_3 prepared with conventional melt–quenching route. It may be assumed that these samples water-ice-quenched from 650°C contained a great content of additional structural imperfections, strained knags and bubbles, disappearing in more-equilibrium conditions. As a result, the two-state model does not well describe the real positron trapping processes in these samples. The conventionally prepared g-As_2Se_3 is expected to characterise by smaller τ_B value.

Since the number of components cannot be determined unambiguously provided actual positron trapping model is unknown, the quite correct interpretation of PAL data should be presented at the basis of average positron lifetime $\bar{\tau}$, which is relatively insensitive to the chosen fitting procedure [7]. The slightly deviated value of $\bar{\tau} \approx 0.30$ ns appears not only in the presented results but also in the experimental data of Alekseeva et al. [3] and Filipecki et al. [5]. So we accepted just these PAL data as the most appropriate ones for g-As_2Se_3.

The observed difference between two groups of experimental PAL results character for each kind of the investigated samples can be explained using a so-called void topology of 146-atoms layer-biased structural model of a-As_2Se_3 [8]. This model (see Fig. 1) contains at least three types of free-volume voids of nanoscale sizes (nanovoids) centred near $\bar{r}_1 \approx 1.5$ Å, $\bar{r}_2 \approx 2.3$ Å, and $\bar{r}_3 \approx 2.9$ Å. They can be effective traps for positrons with character lifetimes in dependence on their trapping rates. Consequently, two separate components in the experimentally measured PAL spectra may differ sufficiently, resulting from different combinations of nanovoids. Presumably, just this feature leads to the above discrepancies in the measured PAL spectra for g-As_2Se_3 prepared in different technological regimes. In accordance to Jensen's calculations [6], the numerical value of long lifetime associated with greatest nanovoids centred near $\bar{r}_3 \approx 2.9$ Å corresponds exactly to $\tau_2 = 0.37$ ns. So just this kind of nanovoids has the highest κ_d, tending the overall process of positron trapping to saturation with constant τ_2 (close to 0.37–0.38 ns) and slightly changed τ_1 lifetimes.

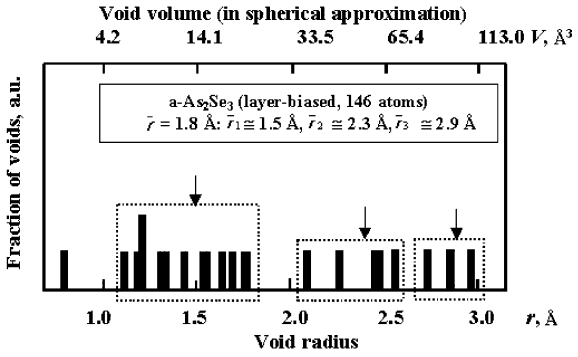

Fig. 1. Void radius (volume) distribution for layer-biased structural model of a-As_2Se_3 [8].

By comparing the optimal sets of PAL data for as-prepared and thermally aged g-As_2Se_3, it should be noted that additional thermal annealing near T_g leads to nanovoid growing. This effect reveals itself on the second set of fitting results as slight increase in τ_1 and more essential increase in τ_2 lifetimes. Since the larger nanovoids are formed by gathering the smallest ones, their relative fraction falls down, leading to the observed decrease in I_2 intensity.

5. Conclusions

The existing contradictions in experimental results of PAL measurements for g-As_2Se_3 can be reasonably resolved within the previous theoretical concepts for positron trapping in free-volume vacancy-type centres of orthorhombic c-As_2Se_3 [4] and void topology for 146-atoms layer-biased computer model of amorphous As_2Se_3 [8]. The observed difference in PAL parameters for as-prepared and thermally aged samples is explained in terms of nanovoid growing.

References

[1] A. Feltz, Amorphe und Glasartige Anorganische Festkörper, Akademie-Verlag, Berlin, 1983.
[2] O.K. Alekseeva, et al., Sov. Fiz. Tverd. Tela 19 (1977) 3452.
[3] O.K. Alekseeva, et al., Phys. Stat. Sol. A 60 (1980) K185.
[4] K.O. Jensen, et al., J. Non-Cryst. Solids 170 (1994) 57.
[5] J. Filipecki, et al., Visnyk Lviv. Univer. Ser. Phys. 33 (2000) 204.
[6] M.J. Puska, et al., Phys. Rev. B 41 (1990) 9980.
[7] R. Krause-Rehberg, H.S. Leipner, Positron Annihilation in Semiconductors. Defect Studies, Springer, Berlin, Heidelberg, New York, 1999.
[8] M.A. Popescu, J. Non-Cryst. Solids 35–36 (1980) 549.
[9] J. Kansy, Nucl. Instrum Methods A 374 (1996) 235.