OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 7, No. 11-12, November - December 2013, p. 1029-1031

Positron life time spectroscopy as a method to study of the defect degree materials with disordered structure

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The paper presents the use of positron lifetime spectroscopy PALS to study the defect degree of structures of disordered materials, research materials were used as samples: the metallic glass, oxide glass, chalcogenide glass and polymer. As a result of the measurements obtained curves describing the dependence of the number of counts of acts of annihilation as a function of time. The distribution of positron lifetime spectra was carried out on three components. The calculated parameters uptake of positron and positronium in structurally disordered materials studied allow to draw conclusions about the degree and nature of defects of studied materials.

(Received December 3, 2012; accepted November 7, 2013)

Keywords: Positron annihilations, Disordered materials, Free volumes

1. Introduction

With the progressive development of the science of modern disordered materials, the interest of how they are structured keeps growing. The purpose of this work is to demonstrate that positron lifetime spectroscopy (PALS) can be successfully used for studying defect of disordered structures.

Positron annihilation is the process of changing the whole mass of both, particles and their kinetic energy into energy of photons of electromagnetic radiation.

$$2m_e c^2 + E_+ + E_- = \sum_i h\nu_i \quad (1)$$

where:
$\sum h\nu$ – emerging energy photons
m_e – rest mass of the electron and positron
c – speed of light
$E_+ E_-$ – corresponding kinetic energy of the positron and electron.

Therefore, the study of photons generated in the process of annihilation, provides information about the electron positron pair annihilation. The annihilation process follows certain general laws of conservation, such as the conservation of total energy, total angular momentum, total linear momentum, and parity.

During the annihilation of the antiparticles and particles the emission of quanta gamma takes place and it equals (2 γ) or (3 γ). Annihilation may occur between free positrons and electrons or between particles in a bound state positronium (Ps). Ps is generally not found in metals, but is found in molecular materials, metals oxides, molecular liquids and gasses and its annihilation parameters reflects the properties of containing host medium.

The energy of annihilating posistronium undergoes the termalization phenomenon. This results in a rapid decrease of energy associated with scattering of positrons and excitation center, as well. The positron last value of its energy (10 – 50 eV) loses for interaction with matter and at the same time can create positronium with one of the surrounding electron [1,2].

Positronium exists in two spin states. One is called para-positronium (p-Ps) in which the positron and electron spins are anti-parallel. The other state, ortho-positronium (o-Ps), corresponds to parallel particle spins. In the condensed matter the positron creates mainly o-Ps state.

The lifetime of o-Ps is reduced due to interaction of o-Ps with electrons from surrounding matter (pick-off annihilation) and decay into two gamma rays. Thus, three positron lifetimes (τ_1, τ_2, τ_3) are often found in polymers. These lifetimes, from shortest to longest, are believed to be due to the self-annihilation of p-Ps, the annihilation of free positrons, and the pick-off annihilation of o-Ps, respectively The o-Ps is formed in the free volume holes of size two times bigger than the diameter of a hydrogen atom. Its lifetime determines the size of holes [3-5].

Local free volume occur due to irregular molecular packing in the materials. Structural changes are combined with changes in free volume [6,7]. In this paper the relationship between the lifetime of ortho-positronium o-Ps, and the size of free volume were describe by Tao – Eldrupa model. It assumes that o-Ps trapped inside the spherical free volume may decay spontaneously by three quantum annihilation or by "pick-off" process.

The Tao-Eldrup model was elaborated for small free volumes, like vacancies in solids, voids in polymers, bubbles forced by Ps in liquids. In order to simplify the

calculations, the well of finite depth is substituted by infinitely deep one but broadened by, which is needed to reproduce the value of in finite well radius R. Furthermore, a very successful semi-empirical relationship between the o-Ps lifetime (τ_3) and the average radius R (nm) of free volume holes in the spherical approximation is given by the following equation [5-7]:

$$\tau_3(ns) = 0.5\left[1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R+\Delta R}\right)\right]^{-1} \qquad (2)$$

where ΔR = 0.166 nm is fitted empirical electron layer thickness. By fitting equation 2 with measured τ_3 values, R and free volume size V_f can be evaluated:

$$V_f = \frac{4}{3}\pi R^3 \qquad (3)$$

The relative intensity of the longest component, I_3, is generally correlated to the density of holes, which can be considered as a kind of trapping centres for Ps. A semi-empirical relation may be used to determine the fraction of free volume (f_v) in polymers as:

$$f_v = CV_f I_3 \qquad (4)$$

where:
V_f – is the free volume calculated from τ_3, using Eq. (2) with a spherical approximation,
I_3 – (in %) is the intensity of long-lived component,
C – is an empirical parameter, which can be determined by calibrating with other physical parameters.

2. Experimental

The PALS measurements were done using a fast-fast coincidence system ORTEC operating at room temperature (for experimental construction see Fig. 1) with a time resolution of 0.270 ns (FWHM).

System of circle layers, of 10mm diameter and 1.2 mm thickness formed each tested sample. A Na^{22} isotope positron source of 4×10^5 Bq activity was situated between two identical samples, forming a "sandwich" system.

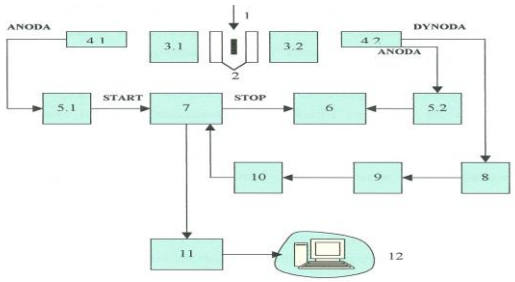

Fig. 1. Block scheme of the spectrometer. 1 – positron source (^{22}Na); 2 – two identical parallel flat sample; 3.1,3.2 – scintillators (KL 236); 4.1,4.2 – photomultiplier (RCA8575); 5.1,5.2 – constant fraction discriminator (ORTEC473A); 6 – converter time to amplitude (ORTEC 467); 7 – delay line (ORTEC 425A); 8 – preamplifier (ORTEC 113); 9 – amplifier (ORTEC 471); 10 – single channel analyzer amplitude (ORTEC 455); 11 – multichannel analyzer (TUKAN 8K); 12 – PC computer.

Positron lifetime investigations were carried out for four different amorphous materials:
S1 – metallic glass $Ni_{78}Si_9B_{13}$
S2 – chalcogenide glass As_2S_3;
S2 – oxide glass $PbO\text{-}Bi_2O_3\text{-}Ga_2O_3$;
S3 – contact lens - polymer Comfilcon A.

3. Results

The analyses of the positron annihilation were performed using the LT program [8]. The study provide qualitative information about the changes of concentration, size and type of defects in the structure of the investigated materials. Fig. 2 shows an example of an experimental spectrum of positron lifetime curve.

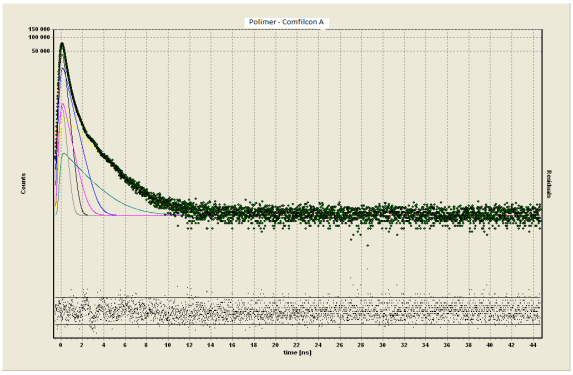

Fig. 2. An example of the positron lifetime spectrum.

Table 1 contains the values of, life times τ and their intensities I. In Table 2 the calculated values of radius R, and the size of free volume V_f and the fraction of free volume f_v are derived from equations (2), (3) and (4) and summarized.

Table 1. Lifetime values τ and their intensities I.

Sample	τ_1 [ns]	I_1 [%]	τ_2 [ns]	I_2 [%]	τ_3 [ns]	I_3 [%]
S1	0.191 ± 0.004	100	-	-	-	-
S2	0.226 ± 0.008	72.62 ± 0.63	0.383 ± 0.043	27.21 ± 0.48	-	-
S3	0.247 ± 0.008	96.13 ± 0.76	0.671 ± 0.073	3.24 ± 0.36	3.69 ± 0.26	0.617 ± 0.061
S4	0.193 ± 0.005	64.18 ± 0.52	0.495 ± 0.055	28.86 ± 0.84	3.210 ± 0.28	8.65 ± 0.15

Table 2. Calculated values of radius R, the size of free volume V_f and the fraction of free volume f_v.

Sample	R [nm]	V_f [10^{-30} m^3]	f_v [a.u.]
S1	-	-	-
S2	-	-	-
S3	0.394	256.07	171.82
S4	0.377	224.35	1933.90

Positron lifetime spectra of all tested samples were calculated for three components τ_1, τ_2 and τ_3. For the metallic glass sample only one component τ_1 was obtained. While for the chalcogenide glass two components τ_1 and τ_2 occurred. In the case of oxide glass sample and polymer three components τ_1, τ_2 and τ_3 were achieved. The component τ_1 is related to the free annihilation of positrons in the amorphous state. It is a result of the positron location in the vacancy-sized free volumes and in the lattice defects, as well. The second component τ_2 is related with the occurrence of volume defects which appear on the grain boundaries of point monovacancy defects. The appearance of the component τ_3 is related to the annihilation of ortopositronium (process "pick-off") [1,2]. This component is associated with the presence of free volume in the sample within the size twice time bigger then the size of a hydrogen atom. The component τ_3 appeared only in two samples such as oxide glass and the contact lens (polymer Comfilcon A). The τ_3 component of sample S4 is related to the existence of free volumes (voids) of nano-sizes in the polymer structure of the contact lens – polymer Comfilcon A [10]. On the other hand the same parameter τ_3 in case of oxide glass sample can be attributed to imperfections in the packing order of molecules as a vibration degrees of freedom and some rotational motions. Moreover the appearance and the value of parameter τ_3 in case of glass strongly depend on their composition. This parameter is sensitive for short range order formed by a bridging oxygen (BO) bond. The more components of glass as a modifiers which addition leads to break-up of the bridging bonds, the vibration degree of freedom in the structure is smaller [11]. The correlation of τ_3 with chemical composition of glass should be further investigated. To explain this phenomena the authors carrying out studies with use of simple oxide glass composition [12]. The aim of this work was not to analyze the exact defects in the samples, but only to demonstrate that the method of positron lifetime spectroscopy PALS shows the difference degree of defects for different materials with disordered structure. The trapping of the positron in the open-volume defects sites with sizes in the sub-nanometer range defects is based on the formation of an attractive potential at these sites, such as an imperfections in the packing order of molecules-vibration degrees of freedom vacancies, vacancy agglomerates, and dislocations.

Acknowledgments

The authors would like to thank for the tested samples: contact lenses (Comfilcon A) from Cooper Vision Company and chalcogenide glass As_2S_3 from the Science Company "Carat" in Lviv (Ukraine).

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