Positron annihilation characteristics in multi-wall carbon nanotubes with different average diameters

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Abtract. Positron lifetime spectroscopy was used to study multi-wall carbon nanotubes. The measurements were performed in vacuum on the samples having different average diameters. The positron lifetime values depend on the nanotube diameter. The results also show an influence of the nanotube diameter on the positron annihilation intensity on the nanotube surface. The change in the annihilation probability is described and interpreted by the modified diffusion model introducing the positron escape rate from the nanotubes to their external surface.

1. Introduction

Soon after their discovery, multi-wall carbon nanotubes (MWNTs) became promising high technology materials with a wide variety of possible applications. The influence of synthesis conditions on the quality and physical properties of MWNTs was studied by various methods [1, 2, 3, 4, 5]. Recently, positron techniques have been considered to be useful methods for studying nanomaterials [4, 6, 7, 8, 9, 10, 11, 12, 13, 14]. The unique sensitivity of the positron techniques for probing properties and special imperfection structures of material is due to positron trapping in the low-electron density regions (such as surfaces, interstitial sites, free volumes, and voids) of real solids [15]. Early studies reported on different values of positron lifetime and annihilation probability on the surface of the nanotubes [4, 5, 7, 8, 9, 10]. Our previous study also showed that the presence of amorphous structure, the kind and concentration of defects as well as the presence of possible catalytic agents can affect the positron annihilation data. It was also indicated that the positron lifetime on the external surface of the nanotubes could be related to the external surface area of the nanotube, which depends on the average nanotube diameter [6].

In the present work lifetime spectroscopy (LT) is used to study positron annihilation characteristics of high quality MWNT samples produced by Thermal Chemical Vapor Deposition (CVD) technique with different average diameters [2, 11]. The samples were carefully selected to avoid the influence of the amorphous fraction, of the defects as well as of the catalytic agents in the experimental data. Besides, a modified positron diffusion model for the nanomaterial was used to include the positron escape rate from the nanotubes in the positron annihilation probabilities.

2. Experimental

Samples of multiwall carbon nanotubes with average diameters (*d*) in the range of 50-100 nm were investigated by transmission electron and atomic force microscopy [2, 6, 11]. The high quality samples were selected for LT measurements which will be referred to as M1 (d≈50 nm), M2 (d≈60 nm), M3 (d≈75 nm), M4 (d≈80 nm), M5 (d≈90 nm) and M6 (d≈100 nm). The powder samples were densely packed and pressed by c. 5 MPa into pellets. The ^{22}Na source (of c. 20 MBq activity kept between thin Al foils) was inserted between two identical pellets and this sandwich was then covered with a thin Al foil. LT measurements were carried out with the sample in vacuum using a conventional fast-fast spectroscopy with a time resolution of 210 ps. The spectra were recorded in a Microfast 16k PC MCA with integral counts of $2\text{x}10^6$. Data evaluation was carried out using the LT v. 9 program applying a source correction of 10% and accounting for annihilation in the various aluminium foils.

3. Results and discussion

In our previous studies [6, 11], the LT spectra of MWNTs samples were decomposed into three lifetime components. The short lifetime component τ_1 (≈215 ps as case of positron annihilation in graphite [9, 14]) was assigned to originate from positron annihilation in the nanotubes, the characteristic lifetime τ_2 to the annihilation on the external surface of the nanotubes, and the longer lifetime component τ_3 (≈1 ns) was related to the formation of positronium in defects and/or free volumes [6, 11]. A similar result was also indicated by Kun et al [9]. However, for the high quality samples of this study, the long lifetime component τ_3 was not observed in any of the LT spectra. It seems that positronium formation is negligible in the high quality samples. The positron lifetime spectra are shown in figure 1.

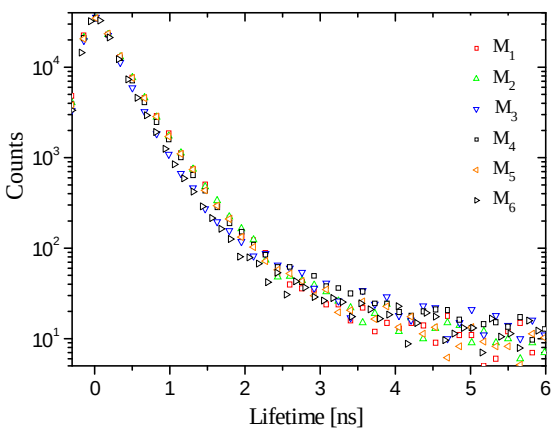

Figure 1. Positron lifetime spectra of the samples of various diameters

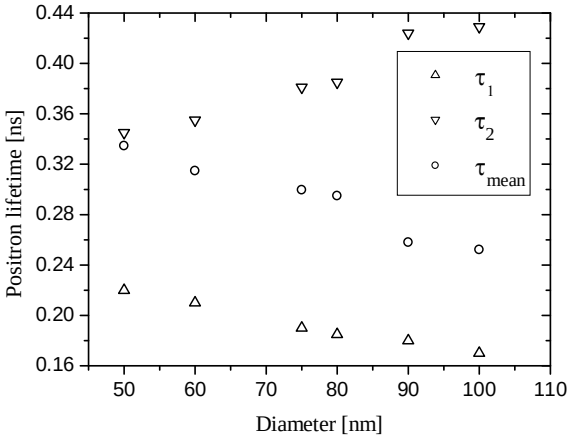

Figure 2. Positron lifetimes versus the average diameter of the samples

Figure 2 shows the correlation between the positron lifetimes and the average nanotube diameter. The short lifetime and the mean lifetime component (τ_1 and $\tau_{mean}= (I_1.\tau_1+I_2.\tau_2)/(I_1+I_2)$, respectively,) of the positrons are decreasing upon increasing average nanotube diameter. Similarly, the mean positron lifetime was found to decrease with increasing particle size in ZnO [16] and silver [17] nanoparticles. Conversely, the characteristic lifetime (τ_2) assigned to positron annihilation on the external surface of the nanotubes increases with increasing average nanotube diameter. The increase of the diameter of the nanotubes leads to an increase of the external surface area as well as the interstitial region volume among the nanotubes. Hence, the increase of τ_2 can be interpreted by assuming that the larger the diameter of the nanotube, the larger the chance for the positron to get attached to the external surface so the longer the resulting lifetime will become [6, 11]. This result may also explain many different values of the characteristic positron lifetime in the early experiments performed by different authors [4, 5, 7, 8, 9, 10] and also reflects some conditions for MWNT synthesis with different average diameters (not shown here).

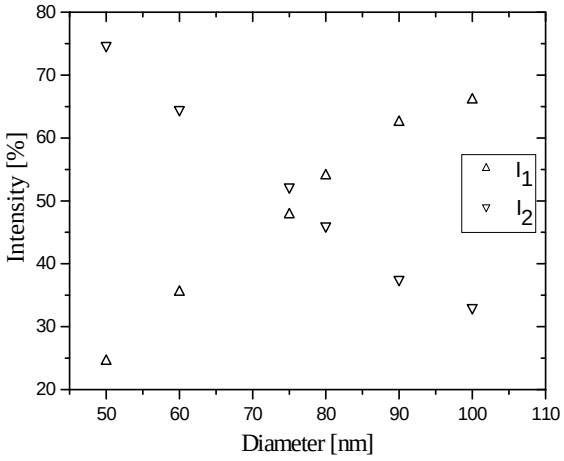

Figure 3. Positron annihilation intensities of samples with different average diameters.

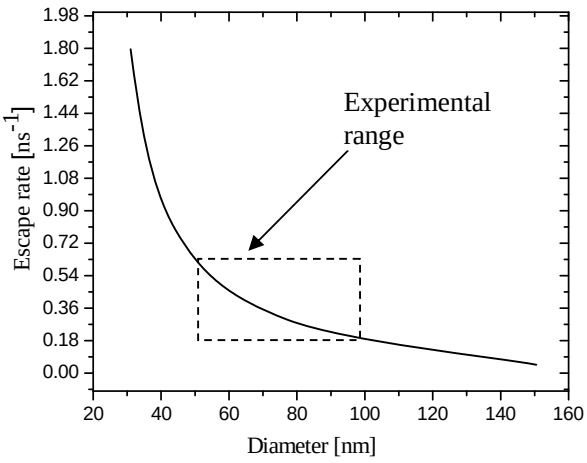

Figure 4. The escape rate versus the nanotube average diameter

The result of the LT measurements indicate that the intensity of the positron lifetime component associated with the external surfaces is decreasing as a function of average nanotube diameter (figure 3). Actually, for the nanomaterial or the fine-grain powder, the surface to volume ratio is inversely proportional to the diameter but proportional to the escape probability of positron to the surface [15, 18]. This suggests that the escape probability of the positrons decreases with increasing nanoparticle diameter. To account for the latter, positron diffusion theory developed for nanomaterials was considered [13, 15]. We suppose that the diffusion length of the thermalized positrons in the MWNTs is approximately equal to that in the graphite material. Indeed, in MWNTs the distance between the coaxially rolled graphene sheets is approximately equal the distance between the graphene sheets in graphite (≈ 0.34 nm) [1, 5]. As a result, the thermalized positron diffusion length in MWNTs can be calculated by $L \approx \sqrt{\tau_f . D} = 102$ nm, where, τ_f = 215 ps and $D = 0.49 \text{x} 10^{-4} m^2 s^{-1}$ are the bulk positron lifetime and the positron diffusion coefficient in the graphite material, respectively [9, 14]. Therefore, if the radius (half of the diameter) of the nanotube is below 100 nm, the thermalized positrons diffusing in the nanotube can escape to the external surface before annihilation [12]. The positron annihilation intensity on the external surface of the nanotube can be approximated as

$$I_2 \approx \frac{\alpha D}{\alpha D + d^2(\lambda_1 - \lambda_2)} \quad (1)$$

and the positron escape rate *k* from the nanotube can be calculated using

$$k \approx \alpha D / d^2 \quad (2)$$

where α, *d*, I_2 are the shape and construction parameter of the nanotube, the average nanotube diameter and the annihilation intensity on the external surface of the nanotube, respectively. Additionally, λ_1 and λ_2 are the positron annihilation rates in and on the external surface of the nanotube. The value of α ≈ 0.034 determined by experimental data fitting of equation (1) was used for calculating the escape rate *k* versus the average nanotube diameter in equation (2). The results show the influence of the the average nanotube diameter on the positron escape rate to the external surface of the nanotubes (figure 4). In the average nanotube diameter range below 30 nm (the small diameter range), the positron escape rate is very large, consequently the positron annihilation mainly occurs on the external surface of nanotubes. This is confirmed by the single lifetime component found in the small diameter MWNTs samples by the early studies [4, 5, 7]. Conversely, in the nanotube diameter range above 100 nm the escape rate is about one order of magnitude smaller than for the small diameter range, and the positrons predominantly annihilate

in the nanotubes. The MWNT diameters in this study cover the range of 50-100 nm, therefore, the positrons annihilate both in and on the external surface of the nanotubes.

4. Conclusions

In this study, the correlation between the positron lifetimes with the average nanotube diameter was established for high quality multi-wall carbon nanotube samples produced by the Thermal CVD technique. The short and mean lifetime components decrease as the average nanotube diameter increases. The results also indicate the dependence on nanotube diameter of the probability of positron annihilation on the external surfaces of the nanotubes. A modified diffusion model was applied to the multi-wall nanotubes and an escape rate k was introduced for the positrons from the nanotubes to the surface to properly account for the positron annihilation probability in and on the external surface of the nanotubes. The present study may contribute to a better understanding of positron annihilation in MWNTs and the obtained results will be applied to better control the synthesis process of nanotubes.

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