Vol. **107** (2005) *ACTA PHYSICA POLONICA A* No. 5

Proceedings of the 35th Polish Seminar on Positron Annihilation, Turawa, Poland 2004

Variable-Energy Positron Annihilation as Highly Sensitive Nanoporosimetry for Porous Thin Films

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Positron annihilation was applied to measuring critical pore sizes in various materials. In recent years, positron annihilation with a variable-energy positron beam has emerged as a powerful tool for the investigation of porous thin films synthesized as low-k dielectrics, high performance gas sensor materials, and so on. This paper is a brief overview of recent progress in nanopore characterization of thin films by means of positron annihilation with a description of several important issues relevant to positron annihilation.

PACS numbers: 78.70.Bj, 78.55.Mb

1. Introduction

Positron annihilation (PA) has been applied to measuring critical pore sizes in polymers, porous oxides, and other systems [1–3]. There are several advantages of PA over other methods; it is nondestructive, sensitive to holes of 0.3–50 nm in size and can detect buried, isolated pores that are not accessible to conventional probes. In recent years, PA with a variable-energy positron beam has emerged as a powerful tool for the investigation of porous thin films (tens nm up to several μm in thickness) [3–24].

Up to date various classes of porous thin films, synthesized as low-k dielectrics [25], high performance gas sensor materials [5], etc., have been studied by PA with variable-energy positron beams. Majority of target films are of silicate or its related derivatives, such as silicon oxide, hydrogen-silsesquioxane (HSQ), methyl-silsesquioxane (MSQ), hexamethyldisiloxane, and trimethylsilane. The film preparation methods include spin-on-glass fabrication, plasma enhanced chemical vapor deposition (PECVD) and physical vapor deposition (PVD) such as evaporation and sputtering. In the spin-on-glass fabrication, for example, pores are introduced into a film through the thermal decomposition of a sacrificial additive (porogen).

Two techniques in PA are commonly used: positron annihilation lifetime (PAL) and γ-ray measurements. The former measures the lifetime of spin-parallel *ortho*-positronium (*o*-Ps), whereas the latter measures the positron 3γ annihilation probability ($I_{3\gamma}$) and the Doppler broadening of annihilation radiation (DBAR) characterized by line-shape (S) and wing (W) parameters.

In free space, *o*-Ps annihilates into 3γ-rays with an intrinsic lifetime of 142 ns. If *o*-Ps is localized in a closed pore, it annihilates with a lifetime shorter than 142 ns by a 2γ pick-off process. The *o*-Ps lifetime is well correlated with the pore dimension [1–4], and the pore size can be evaluated by the PAL technique. In the presence of open pores, *o*-Ps can escape from the film surface into vacuum. Thus the fraction of *o*-Ps self-annihilation, i.e., $I_{3\gamma}$, determined from the relative fraction of 3γ annihilation with energies lower than 511 keV [5, 19], may provide useful information on film porosity. The S parameter defined as the ratio of the integral counts around a small window centered at 511 keV to the total 511 keV annihilation peak counts reflects the annihilation of low-momentum positron–electron ($e^+ - e^-$) pairs, whereas the W parameter defined as the ratio of the counts of a wing region in the 2γ photo-peak to the total peak counts reflects the annihilation of high-momentum $e^+ - e^-$ pairs.

In this paper, the usefulness of PAL and DBAR techniques for nanopore characterization of thin films is described, briefly summarizing recent progress in this research field with emphasis on several important issues relevant to PA. We then discuss different effects of paramagnetic defects based on our recent experimental results for various nonporous and porous silicate films obtained by DBAR and 3γ annihilation measurements [26].

2. Positronium annihilation lifetime

Current research on porous thin films by PA is mainly motivated by the practical importance of the pore size characterization of porous thin films in semiconductor industry. Nanoscale pores present in porous films have been successfully studied with respect to the conditions of film preparation: deposition time and gas pressure for sputtered silica film [5, 9], deposition bias power for PECVD SiOCH-based film [14], film-forming particle size [11], decomposition of porogen [15], composition of precursor solution [10, 20, 21] and molecular weight of porogen [22] for spin-on-glass MSQ-based films, which illustrates "the great strength" [16] of PAL techniques for evaluating pore dimension.

However, as pointed out in previous papers [16, 18], the PAL techniques have some limitations. They require that *o*-Ps must form in the material, and that *o*-Ps formed is able to diffuse into the pores of interest. In addition to this, in the case that a film has a large amount of open, highly interconnected porosity, the lifetime of *o*-Ps is significantly altered from that in the pores because of *o*-Ps escaping from film [5, 18]. For the determination of the pore sizes in such films, they have to be capped so that *o*-Ps is kept from escaping into vacuum.

A more important requisite, but unsolved, is pore size calibration from the *o*-Ps lifetime for mesoporous materials. Several independent models, though not completely validated, have been proposed for describing the correlation between the pore size and *o*-Ps lifetime. Comparison of pore sizes between PAL combined with these models and other methods such as conventional nitrogen adsorption exhibits fair agreement between each other, but with significant scattering in both positive and negative directions. An important role may be played by pore surface chemistry, which influences the behavior of *o*-Ps in the pores but not the pore size determination by other methods. For example, free radicals on the pore walls may partially quench *o*-Ps [27], resulting in a shorter lifetime than those predicted by the above models and a smaller pore size. A better calibration may be obtained using porous materials with the well-defined surface states and pore size.

For the practical use of PA in industry, essential is the standard sample for calibrating the measuring system as well as ensuring the confidence of the obtained positron lifetime data. For more accurate pore size determination, as mentioned above, calibration between *o*-Ps lifetimes and pore sizes for thin films must be accomplished. An international round robin test of various porous low-k films was performed by the groups of University Yamanashi, IMEC (Belgium), NIST (USA) and University Michigan (USA) to compare the results of PAL, small angle neutron scattering, ellipsometric porosimetry, and conventional gas adsorption [17].

3. Positron 3γ annihilation probability

The intensity $I_{3\gamma}$ for porous films may be related to film porosity. A strong correlation between $I_{3\gamma}$ and refractive index, which serves as a measure of film total porosity as long as its optical constants are influenced only by the presence of pores, was reported for sputtered silica films [6]. The open porosity of MSQ-based films prepared with various amounts of porogen was qualitatively discussed using the ratio of fractions of 3γ decay signals due to open and closed pores [19]. Wang et al. asserted that the conclusion is supported by the results of positron lifetime data observed for a similar system [21]. A comparative study with other methods such as X-ray reflectivity, gas adsorption and transmission electron microscopy (TEM) observation is further required for the transformation of positron 3γ data to porosity.

Analysis of the variation of $I_{3\gamma}$ with incident positron energy ($I_{3\gamma}$ depth-profiling) on the basis of a one-dimensional diffusion model provides the *o*-Ps traveling length normal to the film surface [19, 22]. This length has been discussed in relation to the pore interconnectivity [19]. We recently reported that the *o*-Ps traveling lengths for silica sputtered films containing highly interconnected, column-like open pores were well comparable to the corresponding Knudsen diffusion lengths of *o*-Ps [12]. This suggests that for films with highly interconnected nm scale open pores the diffusion of *o*-Ps may be approximated as that of a classical particle inside the pores, and hence comparison between the experimental and Knudsen (theoretical) diffusion lengths may be of help to study the film pore morphology [12].

4. Line-shape S parameter and S–$I_{3\gamma}$ plot

DBAR is useful to characterize porous materials. So far several studies on porous low-k films have been conducted using S and W parameters. The S parameters of MSQ-based porous films have been measured as a function of incident positron energy [22, 23]. Large values of the S parameters observed in most cases for as-deposited films were attributed to the contribution of spin--antiparallel *para*-Ps (*p*-Ps) annihilation in pores and/or with unknown impurity. In a study of the effect of heat treatment on the S parameter for SiOCH-based PECVD film, Brusa et al. [24] reported that the S parameter, relatively high for as-prepared film, decreases with increasing heat treatment temperature above 600°C. These authors related the decrease in the S parameter to the variation of the film stoichiometry.

While film composition significantly influences the S parameter [28], another factor should also be taken into consideration to interpret DBAR data: free radicals that affect Ps formation and annihilation. Nonporous silica sputtered films, containing different types of paramagnetic centers, i.e., P_b and E', have been examined systematically [7]. It was observed that the S parameter increases with increasing P_b concentration. In the presence of E' centers, it decreases with increasing the radical concentration. These variations of S parameters were attributed, respectively, to increased and decreased contributions of low-momentum *p*-Ps self-annihilation to the 2γ photo-peak. P_b centers cause Ps spin conversion (*o*-Ps → *p*-Ps), while E' centers lead to the suppression of *p*-Ps formation (along with *o*-Ps formation).

In the case of porous materials, the situation becomes more complicated, because of an important role played by *o*-Ps self-annihilation emitting 3γ-rays with lower energies outside the 511 keV 2γ peak [6]. At a constant Ps formation probability an increase in $I_{3\gamma}$ reduces the contribution of the high-momentum *o*-Ps pick-off component to DBAR, resulting in an increase in the S parameter [6, 7]. This effect can be expressed as

$$(1-I_{3\gamma})S=\left(\frac{3}{4}f-I_{3\gamma}\right)S_{o-\mathrm{Ps}}+\frac{1}{4}fS_{p-\mathrm{Ps}}+(1-f)S_{\mathrm{e}^+}$$

$$\text{with}\qquad S_{\mathrm{e}^+}\sim S_{o-\mathrm{Ps}}\ll S_{p-\mathrm{Ps}}, \tag{1}$$

where f is the Ps formation probability, and $S_{o-\mathrm{Ps}}$, $S_{p-\mathrm{Ps}}$, S_{e^+} represent S values due to *o*-Ps, *p*-Ps and positron 2γ annihilation, respectively* [6, 7].

Figure 1 shows a plot of the S parameter versus $I_{3\gamma}$ for various nonporous and porous silicate films, some of which have paramagnetic centers P_{b} or E' (see the caption of the figure). The solid line is a fit of the data for annealed radical-free films indicated by the closed symbols to Eq. (1). As one can see, the data for radical-free films are well reproduced by Eq. (1). The data for films with P_{b} are shifted to higher S values from the line for radical-free films, while those with E' deviate to smaller S values, clearly demonstrating that the S parameter and DBAR depend both on radicals and $I_{3\gamma}$.

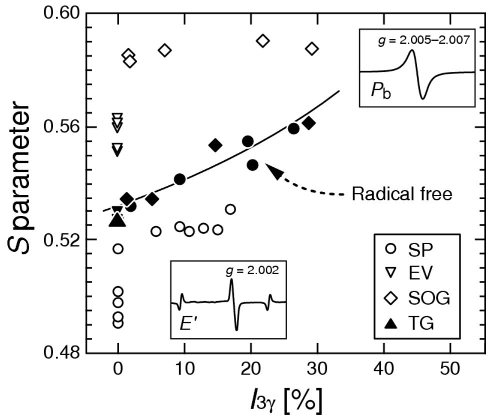

Fig. 1. Plot of S parameter versus positron 3γ annihilation probability ($I_{3\gamma}$) for various nonporous and porous silicate thin films. Open and closed symbols represent data obtained for as-deposited and annealed (600°C) films, respectively. The data for thermally-grown (TG) silica film is also included. The presence of paramagnetic P_{b} centers in spin-on-glass HSQ-based (SOG) and evaporated silica (EV) films and E' centers in sputtered silica (SP) films was confirmed by electron spin resonance spectroscopy, as shown in the insets. Radical-free samples were prepared by elimination of radicals in as-deposited films by annealing. The solid line is a fit of the data for radical-free films to Eq. (1).

W parameter is sensitive to relatively high-momentum electrons, and is very useful to identify positron annihilation sites in nonporous materials. Plot of this parameter versus S gives a straight line for a change of a nonporous sample from one state to another, which is caused by the variation of a single factor such as defect concentration. However, as is evident from the above discussion the W parameter for porous materials is influenced by 3γ annihilation (conversely to the S parameter it decreases with increasing $I_{3\gamma}$). We believe that the anomalous

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[*] This equation does not take account of Ps spin conversion, which alters the *ortho-para* ratio of Ps from 3:1.

nonlinear variation of W versus S for porous low-k films [23, 24] is due to the effect of 3γ annihilation. Thus, in addition to the factors which influence DBAR for nonporous materials, the effect of 3γ annihilation has to be taken into consideration for the correct interpretation of the $S-W$ plots for porous materials.

5. Summary

We have presented a brief review which highlights recent progress in thin film nanopore characterization by the PAL and DBAR techniques. New PA techniques such as positronium time-of-flight (Ps TOF) [29], age-momentum correlation (AMOC) [13], and angular correlation of annihilation radiation (ACAR) [30, 31] have emerged, which are complementary to those mentioned above. Further cross-correlating investigations using these independent techniques will promisingly contribute to more sophisticated, comprehensive pore characterization by PA.

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