Application Of Positron Beams For The Characterization Of Nano-scale Pores In Thin Films

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Abstract. We applied three positron annihilation techniques, positron 3γ-annihilation spectroscopy, positron annihilation lifetime spectroscopy, and angular correlation of annihilation radiation, to the characterization of nano-scale pores in thin films by combining them with variable-energy positron beams. Characterization of pores in thin films is an important part of the research on various thin films of industrial importance. The results of our recent studies on pore characterization of thin films by positron beams will be reported here.

INTRODUCTION

The control of nano-scale pores is important in various applications of thin films, examples of which are high-performance coatings, sensors, separation membranes, and low-dielectric constant (low-k) insulators for the next generation of ultralarge-scale integrated circuits (ULSI). Positronium (Ps), which is the hydrogen-like bound state between a positron and an electron, is a powerful probe that can be used in the characterization of pores in various materials.¹ There are several advantages of positronium porosimetry over other techniques for pore characterization: it is nondistractive; it is sensitive to holes of 0.3-50 nm in size; and it can detect buried, isolated pores that are undetectable by such conventional techniques as nitrogen adsorption. In this paper, we explain the principle and experimental techniques of high-sensitivity positronium porosimetry for thin films and describe several applications to silicon oxide based thin films.

PRINCIPLE AND EXPERIMENTAL TECHNIQUE

In many insulating materials, a fraction of positrons can combine with an electron to form Ps, which is either spin anti-parallel para-positronium (p-Ps) or spin parallel ortho-positronium (o-Ps). Both p-Ps and o-Ps can be used for pore characterization.

Para-Ps has an intrinsic self-annihilation lifetime of 125 ps, and it decays into two 511 keV γ-rays. When p-Ps is at rest, the two γ-rays are emitted in exactly opposite directions. If p-Ps has a momentum, the angle between the two γ-rays is deviated, by an amount proportional to the magnitude of the momentum, from 180 degree. The angular correlation of annihilation radiation determines the distribution of the deviations from 180 degree (Fig. 1a).

In a vacuum, o-Ps annihilates into 3 γ-rays (<511 keV) with an intrinsic lifetime of 142 ns. If trapped in a pore, o-Ps primarily decays into 2 γ-rays with a lifetime shorter than 142 ns upon collision with the pore wall, where the positron in o-Ps annihilates with one of the bound electrons having opposite spin. This 2γ decay process of o-Ps is called ‘pick-off’
annihilation. Since the probability of finding o-Ps on the pore surface is higher for smaller pores, o-Ps lifetime is shortened with decreasing pore size. Therefore, in the case of a trapped o-Ps, the o-Ps lifetime provides information on the size of the pore (Fig. 1b). In the presence of open pores, o-Ps trapped in a pore may escape from the film and undergo the intrinsic 3γ-decay in free space. Hence, the probability of 3γ decay serves as a measure of open porosity (Fig. 1c).

There are three experimental techniques in positronium porosimetry. They are angular correlation of annihilation radiation (ACAR), positron annihilation lifetime spectroscopy (PALS), and positron 3γ-annihilation spectroscopy. As mentioned above, ACAR gives information on the momentum distribution of p-Ps, which is sometimes related to pore connectivity. PALS measures o-Ps lifetime, which is correlated with the size of a closed or capped pore. The fraction of 3γ-annihilation is obtained from energy distribution of annihilation radiation, and it provides information on the open porosity. Combining of the techniques with variable-energy positron beams makes it possible to characterize thin films. Variable-energy positron beams suitable for positron 3γ-annihilation spectroscopy can be obtained with high-energy positrons from a radioactive source. More intense beams for ACAR and PALS can be produced with a linear accelerator and with a nuclear reactor.

### APPLICATIONS

Here, we present some applications of positronium porosimetry to silicon oxide based thin films. The data were obtained with an isotope-based positron beam at the Delft University of Technology. Sputter-deposited silicon oxide films have been applied as sensors and high-performance coatings. The former requires open pores to provide paths of gas molecules, whereas low open porosity is required for the latter to prevent gas molecules from moving into materials through open pores. In this study, we investigated the effect of film deposition condition on the pore size and structure using positronium porosimetry.

Sputter-deposited silicon oxide films were deposited on Si substrates at different argon pressures ranging from 0.25 to 2.0 Pa using a magnetron sputtering system (ANELVA). Not only the as-deposited (uncapped) samples but also the samples with capping layer were prepared. A 100 nm thick silicon oxide capping layer without open porosity was deposited on top of the films. Figure 2 shows the argon pressure dependence of the 3γ o-Ps decay fraction (I3γ) as a function of incident positron energy E (I3γ-E plot) for the uncapped and capped samples. We can see in Fig. 2a...
that $I_{3\gamma}$ is very small at $E>20$ keV. This is because most of the positrons are injected in the Si substrate and annihilate there without Ps formation.

With decreasing $E$ from 20 keV, more positrons are implanted into the silicon oxide film. We note that $I_{3\gamma}$ values at 2-7 keV are different for films prepared at different argon pressures; $I_{3\gamma}$ significantly increases with increasing argon pressure from 0.25 to 1.5 Pa. The enhancement of $I_{3\gamma}$ with argon pressure indicates that film porosity increases with argon pressure. Fig. 2b clearly shows that the $I_{3\gamma}$ values at 2-7 keV are reduced by the capping. From this result, we can conclude that the films have open pores; the $o$-Ps atoms that would otherwise escape into the vacuum through open pores are confined in the pores by the capping and decay into $2\gamma$ rays by the pick-off annihilation process, which reduces $I_{3\gamma}$.

To investigate the effect of argon pressure on pore size, we conducted PALS of the capped samples at $E=5.5$keV (Fig. 3). The $o$-Ps lifetime obtained by three-component analysis is summarized in Table 1, along with refractive index of uncapped films. The lower refractive index for the films deposited at higher argon pressure is consistent with higher porosity mentioned above. Also included in Table 1 are the characteristic pore sizes estimated from the $o$-Ps lifetime using a simple empirical equation between the pore size and $o$-Ps lifetime. The pore size increases with increasing argon pressure from 0.25 to 1.5 Pa, and the characteristic pore size shows a maximum radius of 2.6 nm at 1.5 Pa. The variation of the pore size as a function of argon pressure is correlated with the decrease of the refractive index, which indicates that film open porosity increases with total porosity.

<table>
<thead>
<tr>
<th>Ar pressure (Pa)</th>
<th>$o$-Ps lifetime (ns)</th>
<th>R (nm)</th>
<th>Refractive index</th>
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<tbody>
<tr>
<td>0.25</td>
<td>13.7 ±0.2</td>
<td>0.8</td>
<td>1.457</td>
</tr>
<tr>
<td>0.5</td>
<td>28.9 ±0.2</td>
<td>1.3</td>
<td>1.430</td>
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<td>1.0</td>
<td>46.1 ±0.2</td>
<td>2.3</td>
<td>1.390</td>
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<tr>
<td>1.5</td>
<td>49.5 ±0.3</td>
<td>2.6</td>
<td>1.376</td>
</tr>
<tr>
<td>2.0</td>
<td>42.7 ±0.2</td>
<td>2.1</td>
<td>1.401</td>
</tr>
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</table>

Pore-introduced Hydrogen-silsesquioxane (HSQ) Spin-on-glass Films

In order to develop next-generation ULSI devices, researchers are trying to produce low dielectric constant (low-$k$) materials, which reduce the interconnect RC (resistance $R$ and capacitance $C$) delay. Pore-introduction to material reduces its dielectric constant, and pore-introduced hydrogen-silsesquioxane (HSQ) spin-on-glass film is one of the candidates for the low-$k$ material. As pore structures strongly affect film properties including mechanical strength and moisture uptake, characterization of the pore structure is important in the development of new low-$k$ materials.

![FIGURE 3. Positron lifetime spectra at $E=3$keV of capped samples.](image)

![FIGURE 4. $I_{3\gamma}$ as a function of incident positron energy for (a) uncapped and (b) capped samples.](image)
HSQ films with a thickness of ca. 500 nm were fabricated by spin-coating of precursor solutions of triethoxysilane and porogen with an acidic catalyst on Si substrates followed by subsequent curing. By varying the porogen concentration, the samples with different porosities (KN50, YU65, YK48, and KI31 in the order of increasing additive concentration) were prepared. Porogen was not added to the precursor solution for KN50. The atomic density of the films was determined by Rutherford backscattering spectrometry (RBS) using a software on the assumption that the composition of the film was Si$_2$O$_3$H$_3$, and the film thickness was measured by spectroscopic ellipsometry. The atomic density decreases with increasing porogen concentration, so the total porosity increases in the order of KN50, YU65, YK48, and KI31. Capped samples were prepared by sputter-deposition of a silicon oxide layer with a thickness of 60 nm on top of each sample.

![FIGURE 5. $L_{\omega-P}$ as a function of film atomic density.](image)

![FIGURE 6. 2D-ACAR spectra for (a) KI31 and (b) KN50 at a positron energy of 3keV. The indications $p_x$ and $p_y$ represent momentum parallel and perpendicular to the sample surface, respectively.](image)
Fig. 4a and 4b show the $I_{3\gamma}E$ plots for the uncapped and capped samples, respectively. Capping considerably reduces $I_{3\gamma}$ for the films, except KN50, and we conclude that these films have open porosity. As the $o$-Ps atoms escape through the open pore to a vacuum, the escaping ability of $o$-Ps characterized by the $o$-Ps escaping length $L_{o Ps}$ gives information about open pore connectivity. $L_{o Ps}$ can be obtained by data analysis program for variable-energy positron beam experiment. Figure 5 shows $L_{o Ps}$ as a function of the atomic density of the film. The $L_{o Ps}$ value for the sample with the highest atomic density (KN50) is ca. 2 nm, which is close to the $o$-Ps diffusion length in SiO$_2$ obtained from $\nabla D\tau$, where $D$ is the Ps diffusion coefficient in bulk SiO$_2$ ($1.45\times10^{-5}$ cm$^2$/s)$^{15}$ and $\tau$ is the $o$-Ps lifetime in the HSQ film of the sample (4.0 ns at $E=3$ keV). Therefore, the $o$-Ps atoms do not escape through interconnected open pores for KN50. The $L_{o Ps}$ value increases as the film atomic density decreases. The pronounced enhancement in $L_{o Ps}$ around 1.1 g/cm$^3$ suggests that the open pore interconnectivity rises rapidly when the density becomes lower than this value.

Information on the connectivity of open pores in the films is also provided by two-dimensional distribution of $p$-Ps momentum, which is obtained by the combined use of a variable-energy positron beam with a two-dimensional ACAR (2D-ACAR) system. Figure 6 shows 2D-ACAR spectra for KI31 and KN50 samples at $E=3$ keV. In the figure, $p_x$ and $p_y$ represent momentum parallel and perpendicular to the sample surface, respectively. A narrow peak in the central position for each spectrum is due to $p$-Ps annihilation. An asymmetric broadening is observed for KI31; the cross-sectional momentum distribution for $p_y$ is broader than that for $p_x$. Furthermore, for KI31, the two-dimensional momentum distribution is off-centered toward the positive $p_x$ (film surface) direction. On the assumption that the spectrum is superimposed by Gaussian components, a centered component due to $p$-Ps annihilation in closed pores and an off-centered component with a momentum of ca. $1.5\times10^{-3}$ m$_0$c in the direction toward the surface due to $p$-Ps flying were obtained. Thus, some of the $p$-Ps atoms formed in the HSQ film of KI31 fly toward the film surface direction through interconnected pores. The asymmetry of 2D-ACAR spectrum is not observed for KN50, indicating that the sample has no open pore. The results obtained by 2D-ACAR are consistent with those by positron $3\gamma$-annihilation measurement.

**REFERENCES**

1. For example, Abstract in 7$^{th}$ International Workshop on Positron and Positronium Chemistry (PPC7), 2002, Knoxville Tennessee, USA.

12. RBS measurements were conducted with a 935keV He⁺ beam from a 990keV single-ended accelerator (Kobe Steel LTD. MBX1010-HX). The beam was perpendicularly incident to the sample surface with a spot size of 1mm in diameter. The backscattered particles were detected at an angle near 180° using an annular surface barrier detector with a resolution of 17keV. The spectra were analyzed using a software, Micro I ANA (Kobe Steel LTD).

