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A. Uedono, Lumei Wei, S. Tanigawa, R. Suzuki, H. Ohgaki, et al.. Characterization of SiO₂ films grown on Si substrates by monoenergetic positron beams. Journal de Physique IV Proceedings, 1993, 03 (C4), pp.C4-177-C4-183. 10.1051/jp4:1993424 . jpa-00251467

HAL Id: jpa-00251467

<https://hal.science/jpa-00251467>

Submitted on 1 Jan 1993

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Characterization of SiO₂ films grown on Si substrates by monoenergetic positron beams

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Abstract

Variable-energy positron beams were utilized to characterize SiO₂ films grown on Si substrates. For a SiO₂ film grown by wet oxidation, a high formation probability of positronium (Ps) was found by measurements of Doppler broadening profiles of the annihilation radiation and those of lifetime spectra. For the SiO₂ films grown by a chemical vapor deposition technique, the formation probability of Ps was found to decrease. This was attributed to interactions between positrons and -OH bonds and to the trapping of positrons by point defects. In order to know annihilation characteristics of Ps in the SiO₂ films in more detail, a lifetime spectrum for a vitreous silica glass was also measured.

1. Introduction

The application of positron annihilation to studies of condensed materials and lattice defects in solids has contributed a substantial amount of valuable information.¹ The development of variable-energy positron beams has demonstrated that monoenergetic positrons can be utilized as a nondestructive surface and subsurface probe.² By measuring Doppler broadening profiles as a function of incident positron energy, one can detect defects under the subsurface region. This technique was also used to study SiO₂ films grown on Si substrates and SiO₂/Si interfaces.³⁻²⁰ However, since information derived from measurements of Doppler broadening profiles is limited, annihilation characteristics of positrons in the SiO₂ film or at the SiO₂/Si interface are not well understood. Since lifetime spectra of positrons can be decomposed into several components corresponding to different annihilation states, measurements of lifetime spectra can provide more information than the analysis of Doppler broadening profiles. In the present paper, therefore, we applied a pulsed monoenergetic positron beam in order to measure lifetime spectra of positrons for the SiO₂ films deposited on the Si substrates by a chemical vapor deposition (CVD) technique and by wet oxidation.

2. Experimental

The specimens used in the present experiment were a high purity vitreous silica glass (v-SiO₂) and SiO₂ films grown on Si substrates by a CVD technique and by wet oxidation. The SiO₂ films were deposited by an atmospheric-pressure chemical vapor deposition (APCVD) using tetraethylorthosilicate (TEOS, Si(OC₂H₅)₄) and O₃. A deposition apparatus of APCVD was described elsewhere.²¹ The SiO₂ film deposited by CVD using SiH₄ and N₂O and that by wet oxidation were also studied. The growth conditions of those films are listed in Table I.

The monoenergetic positron beam line installed at the University of Tsukuba was used for the present experiments.²² In this system, monoenergetic positrons were moderated from high-energy (< 0.5 MeV) positrons emitted from a ²²Na source. Obtained monoenergetic positrons were guided by a magnetic field through multiple discrete acceleration lenses and struck the specimen with an adjusted energy between 0

keV and 30 keV. Doppler broadening profiles of the annihilation radiation with a total count of about 5×10^5 were measured by a Ge detector as a function of incident positron energy. The annihilation spectrum was characterized by the S parameter.

A pulsed monoenergetic positron beam line constructed at the Electrotechnical Laboratory was used in order to measure lifetime spectra for the SiO_2 films. The detail of the system was described elsewhere.²³ An intense monoenergetic positron beam ($10^7 \text{ e}^+/\text{s}$) was produced by an electron beam with an energy of 75-MeV and with a pulse width of $1 \mu\text{s}$ (50 pulse/s). The obtained positrons were stored in a linear-storage section and a stretched positron beam was guided into a pulsing system. The width of bunched positrons was about 150 ps and the counting rate of about 200 counts/s was achieved at the average electron current of 2 mA. The lifetime spectra were obtained by measuring the time interval between the timing signal derived electrically from the pulsing system and the annihilation γ -ray detected by a BaF_2 scintillation detector. About 2×10^5 counts were accumulated for each lifetime spectrum. These spectra were resolved into two components with a time resolution of about 250 ps by using RESOLUTION²⁴.

The lifetime spectrum for the v- SiO_2 specimen was also measured by a conventional system using a $^{22}\text{NaCl}$ positron source with a strength of $7 \times 10^5 \text{ Bq}$ deposited on a kapton foil ($t = 7.5 \mu\text{m}$). This measurement was performed by a fast-fast system with BaF_2 scintillators attached to XP2020Q (Philips) photomultiplier tubes. The time resolution curve was about 200 ps and each lifetime spectrum contained about 5×10^6 counts. The spectrum was resolved into three components by using RESOLUTION. This spectrum was also analyzed by a numerical Laplace inversion technique²⁵.

Table I: The growth condition of the SiO_2 films.

specimen	growth condition	substrate temp. ($^\circ\text{C}$)	atmosphere	film thickness (nm)
TEOS/ O_3 No. 1	APCVD	370	TEOS& O_3 (5.6 %)	312
TEOS/ O_3 No. 2	APCVD	400	TEOS& O_3 (5.6 %)	322
TEOS/ O_3 No. 3	APCVD	430	TEOS& O_3 (5.6 %)	288
TEOS/ O_3 No. 4	APCVD	400	TEOS& O_3 (0.56%)	305
$\text{SiH}_4/\text{N}_2\text{O}$	CVD	800	SiH_4 & N_2O	600
Thermal Oxide	thermal oxidization	1000	H_2O & O_2	506

3. Results and Discussion

Figure 1 shows the lifetime spectrum for the v- SiO_2 specimen. From the figure, it can be seen that Ps formed with very high probability in the v- SiO_2 specimen. This lifetime spectrum was decomposed into three components and the results are summarized in Table II. Figure 2 shows the annihilation rate probability density function²⁵ for the v- SiO_2 specimen. From Fig. 2, it is clearly seen that the obtained lifetime spectrum can be decomposed into three components. In Table II, the long-lived component was attributed to the pick-off annihilation of ortho-Ps.

It is well known that the annihilation of para-Ps in a delocalized state can be detected in a single crystal quartz by measurements of two-dimensional angular correlation radiation (2D-ACAR). Berko *et. al.*²⁶ and Ikari and Fujiwara²⁷ reported a narrow peak located at zero momentum corresponding to the self-annihilation of para-Ps with an energy width near the resolution of the measuring system and peaks located at positions corresponding to a Bloch state of Ps. These peaks suggest the self-annihilation of para-Ps from the delocalized state. For the v- SiO_2 specimen, however, the annihilation of such free para-Ps was not observed.²⁸

From Table II, the intensity corresponding to the pick-off annihilation of ortho-Ps was 52 %. The formation probability of Ps in a crystalline quartz is far less than this value.^{26,27} Because of the high sensitivity of positrons for vacancy-type defects, almost all positrons are considered to be trapped by

Table II. The lifetimes and their intensities for the v- SiO_2 specimen.

τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	I_1 (%)	I_2 (%)	I_3 (%)
0.145(2)	0.82(2)	1.821(7)	27.1 (1)	21.4 (5)	51.5 (6)

Fig. 1. The lifetime spectrum for the v-SiO₂ specimen.

Fig. 2. The annihilation rate probability density function for the v-SiO₂ specimen ($t=1/\lambda$).

Fig. 3. The lifetime spectrum for the SiO₂ film with a thickness of 506 nm grown by wet oxidation.

such defects in amorphous materials. If a specimen contains open-space defects such as microvoids or pores, positrons can form Ps in such regions under some conditions. Thus the formation of Ps in the v-SiO₂ specimen is considered to be enhanced by the trapping of positrons in open-space defects. Since the lifetime of ortho-Ps increases with increasing size of open-space defects in molecular solids,²⁹ one can obtain information about open-space defects in the v-SiO₂ specimen.

In Table II, since the value of τ_1 is close to the lifetime of para-Ps (125 ps), τ_1 is mainly attributed to the self-annihilation of para-Ps. τ_2 can be associated with the annihilation of positrons or that of Ps trapped by open-space defects. From Table II, the value of I_3/I_1 was obtained as 1.9. Since the ratio of the formation probability of ortho-Ps to para-Ps is 3, the short-lived component (I_1) can be attributed to not only the annihilation of para-Ps but also that of positrons.

Figure 3 shows the lifetime spectrum for the SiO₂ film with a thickness of 506 nm grown by wet oxidation measured by the pulsed monoenergetic positron beam. The lifetime spectrum was decomposed into two components and the results are summarized in Table III. From Table II, the weight average of τ_2 and τ_3 , τ_{2+3} , was obtained as 1.5 ns and its intensity (I_2+I_3) was 72.9 %. The value of τ_{2+3} is in good agreement with τ_2 obtained for the SiO₂ film grown by wet oxidation. The value of I_2 for the SiO₂ film is smaller than the value of I_2+I_3 for the v-SiO₂ specimen. Since the formation of Ps needs larger open spaces or a lower electron density than the volume or electron density around point defects, the trapping of positrons by point defects is considered to suppress the formation probability of Ps. Uedono *et al.*³⁰

Table III. The lifetimes and the intensities for the SiO₂ film grown by wet oxidation.

τ_1 (ns)	τ_2 (ns)	I_1 (%)	I_2 (%)
0.25 (2)	1.543(7)	35.5 (3)	64.5 (3)

Fig. 4. The lifetime as a function of incident positron energy for the SiO_2 films grown by wet oxidation with different substrate temperatures.

Fig. 5. The intensity as a function of incident positron energy for the SiO_2 films grown by wet oxidation with different substrate temperatures.

found that the formation probability of Ps in the $\nu\text{-SiO}_2$ specimen was drastically decreased by the trapping of positrons into point defects introduced by electron irradiation. Thus, the low formation probability of Ps in the SiO_2 film can be attributed to the trapping of positrons by point defects. The inhibition of the Ps formation will be discussed in a latter section.

Figures 4 and 5 show the lifetime and the intensity as a function of incident positron energy for the SiO_2 films grown by wet oxidation, where the substrate temperature was 650 °C and 1000 °C, respectively. From Fig. 4, it was found that the lifetime corresponding to the pick-off annihilation of ortho-Ps, τ_2 , decreased with decreasing the substrate temperature. This result suggests that the size of voids or pores in the SiO_2 film grown with the low substrate temperature is smaller than that in the SiO_2 film grown with the high substrate temperature.

Fig. 6. The lineshape parameter S as a function of the incident positron energy for the SiO_2 films fabricated by the CVD technique and by wet oxidation.

Figure 6 shows the S parameter as a function of incident positron energy for the SiO_2/Si specimens fabricated by the CVD technique and by wet oxidation. The mean implantation depth of positrons² is shown below the horizontal axis in the figure together with the incident positron energy E . At high E (25~30 keV), the values of the S parameter were found to approach the constant value. This indicates that almost all positrons are implanted into a bulk Si at this energy range. Thus, this saturated value is the characteristic value of the S parameter for the positron annihilation in the bulk Si. In regions of E between 2 keV and 4 keV, the S - E relations were found to be nearly flat for all specimens. This means that these values correspond to the annihilation of positrons in the SiO_2 films.

For the thermal oxide film, a dip in the S - E plot was observed at $E=7\sim 8$ keV. The decrease of the S parameter at the SiO_2/Si interface was reported by Nielsen *et al.*⁷, Lynn *et al.*⁸ and Rubloff *et al.*¹¹. They found that the annihilation characteristics of positrons trapped by the SiO_2/Si interface were very sensitive to hydrogen exposure. The decrease of S at the SiO_2/Si interface can be attributed to the strong interaction between positrons and the

Fig. 7. The lifetimes of positrons and Ps for the SiO₂ films fabricated by CVD and by wet oxidation.

Fig. 8. The intensities for the SiO₂ films fabricated by CVD and by wet oxidation.

hydrogen modified interface.⁸ For the CVD-SiO₂ films, the characteristic values of S for the SiO₂ film, S_{SiO_2} , were lower than S_{SiO_2} for the thermal oxide film. For the APCVD-SiO₂ films grown by using TEOS/O₃, it was found that S_{SiO_2} increased with increasing substrate temperature (samples No. 1~3) and it decreased with decreasing the concentration of O₃ (sample No. 4).

The lifetime spectra of positrons for the SiO₂ films grown by the CVD technique were measured at $E=2$ keV. From Fig. 6, almost all positrons are considered to annihilate in the SiO₂ film at this energy. The observed spectra were decomposed into two components and results are shown in Figs. 7 and 8. From Fig. 7, the value of τ_2 for the thermal oxide film is found to be smaller than that for the CVD-SiO₂ films. This means that the size of voids in the thermal oxide film is smaller than that for the CVD-SiO₂ films. From Fig. 8, it can be seen that the values of I_2 for the APCVD-SiO₂ films grown by using TEOS/O₃ were smaller than I_2 for the SiO₂ film grown by wet oxidation. This shows that the formation of Ps is inhibited in these specimens. The value of I_2 increased with increasing substrate temperature and it decreased with decreasing the concentration of O₃. The behavior of S for the SiO₂ films is good agreement with that of I_2 . Since the annihilation from the para-Ps state produces γ rays with very sharp energy width, the annihilation of para-Ps increases the value of the S parameter. Thus the S parameter is sensitive for the annihilation of para-Ps. These results suggest that the annihilation characteristics of positrons in the SiO₂ films are mainly dominated by the formation probability of Ps.

It is well known that the high concentrations of H₂O and -OH bonds can be observed in APCVD-SiO₂ films grown by using TEOS/O₃.³¹ A reaction between TEOS and O₃ is described as

H₂O created during the formation of the SiO₂ film could be trapped by open-space defects or it terminates Si dangling bonds. The contents of H₂O and bonding structures in the APCVD-SiO₂ films were analyzed by a moisture evolution analyzer and Fourier transform infrared spectroscopy (FTIR). From the measurements, it was found that the concentration of -OH bonds in the APCVD-SiO₂ films decreased with increasing substrate temperature and it increases with increasing the concentration of O₃. Thus, the inhibition of the Ps formation is considered to relate with the concentration of -OH bonds.

In solid materials, the formation of Ps is expressed by "super model".³² Therefore, the formation of Ps is affected by a number of available electrons or positrons. Since an oxygen-vacancy (E' center) is known to be a hole trap in SiO₂,^{33,34} such defects also can trap positrons. However, for the APCVD-SiO₂ films grown by using TEOS/O₃, these defects are considered to be terminated, because of the high concentration

of -OH bonds. Thus, the concentration of the E' center in the thermal oxide film is considered to be higher than that for the APCVD-SiO₂ films grown by using TEOS/O₃. Therefore, it can be concluded that the inhibition of the Ps formation is attributed to a strong interaction between positrons and -OH bonds in SiO₂ films. For the SiO₂ films with the high concentration of -OH bonds, positrons are considered to be trapped by -OH bonds and annihilate before the formation of Ps. The decrease of S at the SiO₂/Si interface was attributed to the strong interaction between positrons and the hydrogen modified SiO₂/Si interface. The reaction between positrons and -OH bonds is considered to be similar to that between positron and hydrogen at the SiO₂/Si interface.

From Figs. 6 and 8, the value of S_{SiO_2} and the intensity of the second component for the CVD-SiO₂ film grown by using SiH₄/N₂O were lower than those for the thermal oxide film. This means the inhibition of Ps formation in this specimen. A reaction between SiH₄ and N₂O is described as

where H₂O is not included during the formation of the SiO₂ film. From the measurement of FTIR, no peak corresponding to -OH bonds was observed for this specimen. Thus, the inhibition of the Ps formation can not be attributed to -OH bonds for the CVD-SiO₂ film grown by using SiH₄/N₂O. A composition of SiO₂ films grown by using SiH₄/N₂O is known to be SiO_x ($x < 2$).³⁵ Because of the lack of -OH bonds, the concentration of E' center is considered to be high in this specimen. Thus, the first candidate for the inhibition of the Ps formation for the CVD-SiO₂ film using SiH₄/N₂O is the trapping of positrons by point defects such as the E' center.

4. Conclusion

We have presented the characterization of SiO₂ films by using monoenergetic positron beams. In order to know the annihilation characteristics of positrons in the SiO₂ films in more detail, the lifetime spectrum for the v-SiO₂ specimen was also measured by the conventional fast-fast system. From a comparison between the results for the v-SiO₂ specimen and those for the SiO₂ film grown by wet oxidation, it was found that the lifetime corresponding to the pick-off annihilation of ortho-Ps for the v-SiO₂ specimen were close to those in the SiO₂ film. However, the intensity associated with the annihilation of ortho-Ps for the SiO₂ film is lower than that in the v-SiO₂ specimen. This can be attributed to the trapping of positrons by point defects and the resultant inhibition of the Ps formation. For the SiO₂ film grown by wet oxidation, the lifetime of ortho-Ps is found to increase with increasing substrate temperature. This suggests that the size of voids increases with increasing the substrate temperature. For the CVD-SiO₂ films, the formation probability of Ps was found to be very sensitive to the growth condition of the SiO₂ films. In the CVD-SiO₂ films, the formation probability of Ps was found to be lower than that in the SiO₂ film grown by wet oxidation. The formation probability of Ps increased with increasing the substrate temperature and it decreased with decreasing the concentration of O₃. The inhibition of Ps formation in the APCVD-SiO₂ film was attributed to the trapping of positrons by -OH bonds. The present investigation showed the possibilities for the study of pores on the nanometer scale in the SiO₂ films grown on Si substrates.

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