Positron trapping by defects in vitreous silica at low temperature

1995 J. Phys.: Condens. Matter 7 5139

(http://iopscience.iop.org/0953-8984/7/26/019)

J. Phys.: Condens. Matter 7 (1995) 5139–5149. Printed in the UK

Positron trapping by defects in vitreous silica at low temperature

Akira Uedono†, Takao Kawano‡, Shoichiro Tanigawa†, Akira Urano§, Michihisa Kyoto§ and Hisayoshi Itoh‖

† Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305, Japan
‡ Radioisotope Centre, University of Tsukuba, Tsukuba, Ibaraki 305, Japan
§ Analytical Characterization Centre, R & D Group, Sumitomo Electric Industries Ltd, 1 Taya-cho, Sakae-ku, Yokohama 244, Japan
‖ Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute, Watanuki, Takasaki, Gunma 370-12, Japan

Received 17 October 1994, in final form 27 March 1995

Abstract. Annihilation characteristics of positrons in vitreous silica (v-SiO_2) were studied in the temperature range between 20 K and room temperature (RT). In the measured temperature range, almost all positrons are trapped by open spaces and annihilate mainly from positronium (Ps) states. Lifetimes of ortho-Ps increase with increasing temperature, where the distribution of the lifetimes at 20 K is shallower than that at RT. This fact was attributed to the thermal expansion of the open spaces and the broadening of their size distribution. In the temperature range between 170 K and 200 K, a certain structural transition of the open spaces was found. The transition temperature is decreased by electron irradiation or by the presence of hydroxyl groups. These results were attributed to the fact that an activation energy of the transition was lowered by the introduction of defects.

1. Introduction

Vitreous silica (v-SiO_2) is well recognized as the most promising fibre material for optical communication systems. v-SiO_2 is also used as an optical lens in excimer laser systems for the lithography of large-scale integrated devices. For v-SiO_2, a high resistance against ionizing, particle radiation and high-energy lasers is required because such irradiation induces optical absorptions [1]. The positron annihilation technique has become an established tool in the study of defects in materials [2]. With this technique, the concentration of point defects for a detectable response is about 0.1 ppm, and there are no restrictions regarding specimen conductivity or specimen temperature. Dannefaer *et al* [3] demonstrated that positrons can be used as a nondestructive and sensitive probe for defects in crystalline quartz and v-SiO_2. They also reported that positrons implanted in v-SiO_2 annihilate from positronium (Ps) states, that is, a hydrogen-like bound state between a positron and an electron. By using this technique, Uedono *et al* [4] studied point defects introduced by electron irradiation in v-SiO_2. It was found that the formation probability of Ps was decreased by the irradiation. The observed inhibition of the Ps formation was attributed to the trapping of positrons by point defects introduced and/or activated by the irradiation. Since positrons annihilate from Ps states with high probability [3, 4], studies of behaviours of Ps in v-SiO_2 are important. Recently, Watauchi *et al* [5] reported the

0953-8984/95/265139+11$19.50

detailed annihilation characteristics of Ps in v-SiO_2 by using age–momentum correlation measurements. In the present paper, we report the study of annihilation characteristics of positrons in v-SiO_2 by measurements of lifetime spectra of positrons in the temperature range between ~20 K and room temperature.

2. Experiment

Synthesized v-SiO_2 specimens used in the present experiment were supplied from Sumikin Quartz Products, Inc. These specimens were grown by the vapour phase axial deposition technique. The specimens with different OH concentrations (<5 ppm and <200 ppm) were prepared. Major impurities in these specimens were Al (<0.04 ppm) and Ca (<0.04 ppm). The concentration of Na was under the detection limit. In order to introduce defects, the specimens were irradiated with 3 MeV electrons up to a dose of 1×10^{18} e cm^{-2}. The temperature of the specimens was kept at ~70 °C during the irradiation.

Positron lifetime spectra were measured by a conventional fast–fast system at 21 K and room temperature (RT). The full width at half maximum (FWHM) of the time resolution of the system was ~200 ps. Each lifetime spectrum contains 8×10^6 counts. By using the same set-up, lifetime spectra were measured as a function of temperature. At each temperature, the observed lifetime spectrum contained about 1×10^6 counts. The lifetime spectrum of positrons, $I(t)$, is represented by

$$I(t) = \sum_{i=1}^{n} \alpha_i \lambda_i \exp(-\lambda_i t) \tag{1}$$

where α_i is the fraction of positrons annihilating with the ith lifetime, τ_i ($= 1/\lambda_i$) and n is the number of annihilation modes. In the present experiment, $I(t)$ was analysed by using computer codes developed by Kirkegaard *et al* [6]. Equation (1) can be expressed in a continuous decay form:

$$I(t) = \int_0^\infty \alpha(\lambda)\lambda \exp(-\lambda t)\, d\lambda. \tag{2}$$

In (2), $I(t)$ is a Laplace transform of the decay probability density function, $\alpha(\lambda)\lambda$. A numerical Laplace inversion technique for the deconvolution of lifetime spectra was developed by Gregory [7]. This method used to analyse the lifetime spectra contains high total counts (8×10^6), where the lifetime spectrum of a well annealed Ni specimen was used for the reference spectrum.

3. Results and discussion

3.1. Annihilation characteristics of positrons in v-SiO_2 at room temperature

In this section, annihilation characteristics of positrons in the unirradiated specimen with OH concentration of <5 ppm are mainly discussed. The observed lifetime spectra of 8×10^6 counts can be decomposed into three components. In this analysis, the values of τ_1 were obtained as 0.13–0.14 ns for the unirradiated and the irradiated specimens. These first lifetimes were longer than the intrinsic lifetime of para-Ps (p-Ps, $\tau = 0.125$ ns) [2]. This means that the first component derived by the three-component analysis was a superposition of the annihilation of p-Ps and the annihilation of positrons with a short lifetime. Thus, the lifetime spectra containing 8×10^6 counts were decomposed into four components, where the value of τ_1 was fixed at 0.125 ns. The same analysis was performed in the previous

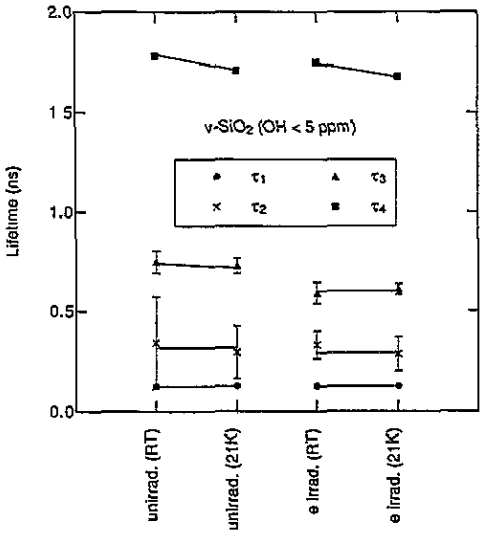

Figure 1. The lifetimes for the v-SiO_2 specimens with OH concentration of <5 ppm before and after the irradiation. The measurement was performed at room temperature and 21 K. The lifetime spectra were decomposed into four components, where the first lifetime was fixed as the lifetime of p-Ps (0.125 ns).

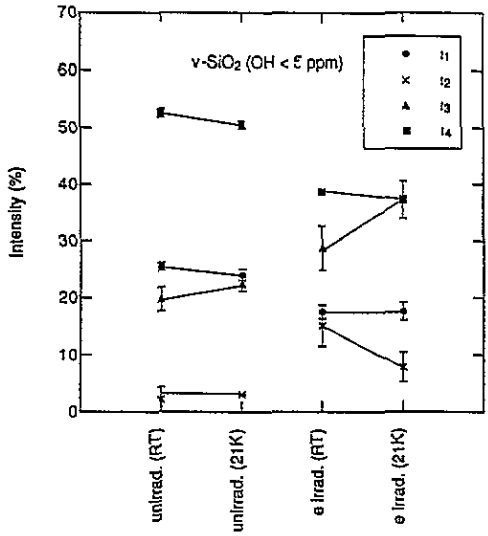

Figure 2. The intensities for the v-SiO_2 specimens with OH concentration of <5 ppm before and after the irradiation.

experiments [4, 9]. Figures 1 and 2 show the lifetimes and the corresponding intensities respectively, for the v-SiO_2 specimens with OH concentration of <5 ppm at 21 K and RT. In these figures, the first component can be attributed to the annihilation of p-Ps. For the unirradiated specimen, a ratio of $I_3 + I_4$ to I_1 was calculated as 3.0 at 21 K and 2.8 at RT. Since these values are close to the ratio of the formation probability of ortho-Ps (o-Ps) to that of p-Ps (3) [2], both the third and the forth components can be attributed to the annihilation of o-Ps. Uedono *et al* [4, 10] reported that almost all Ps is trapped by open spaces in v-SiO_2. Since the lifetime of o-Ps decreases with decreasing the size of the open spaces [11], the difference between the value of τ_3 and that of τ_4 is considered to be due to a difference in the size of such spaces. The second component might be attributed to the annihilation of positrons trapped by point defects. Since the statistical error of the second lifetime was large, a detail of this annihilation mode is not discussed. As shown in figure 2, the intensity of this component was increased by the irradiation. The species of defects detected by the second component is discussed in section 3.3.

3.2. Annihilation characteristics of positrons in v-SiO_2 at low temperature

Figure 3 shows the positron lifetime distribution function for the unirradiated v-SiO_2 specimen with OH concentration of <5 ppm obtained by the Laplace transform technique. The mean lifetimes of the components at 0.5 ns $< t <$ 1 ns and 1 ns $< t <$ 2.5 agreed with the value of τ_3 and that of τ_4 derived by the four-component analysis. In figure 3, therefore, the component at 0.2 ns $< t <$ 0.3 ns can be attributed to the superposition of the first and the second component obtained in the four-component analysis. At 21 K, the mean lifetime of o-Ps at 1 ns $< t <$ 3 was shorter and the lifetime distributions were narrower than those

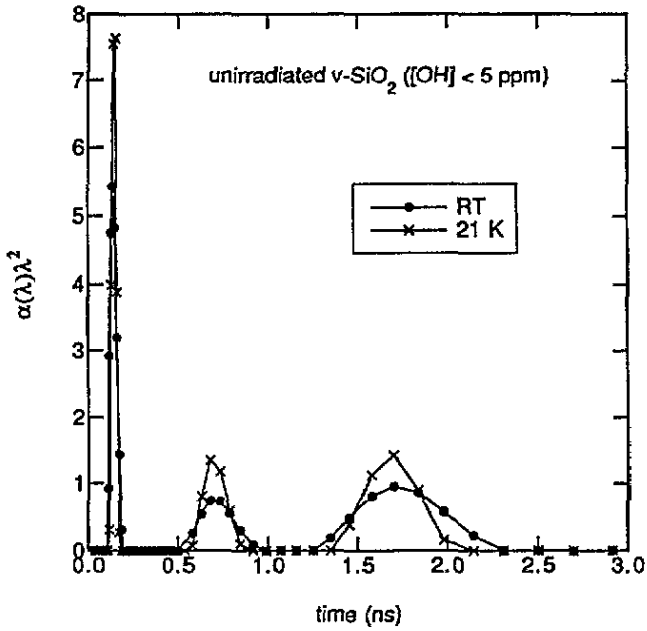

Figure 3. The positron lifetime distribution function for the unirradiated v-SiO_2 specimen with OH concentration of <5 ppm.

at RT. The decrease in the value of τ_4 was also observed in the four-component analysis (figure 1). The observed decrease of the lifetime and the narrow lifetime distribution can be attributed to the decrease in the size of the open spaces and the narrowing in the size distribution of such spaces at low temperature.

In order to know the temperature dependence of the lifetimes and the intensities, lifetime spectra were measured in the temperature range between 21 K and RT. Figures 4 and 5 show the lifetimes and the intensities for the unirradiated v-SiO_2 specimen with OH concentration of <5 ppm. In this experiment, since the total counts of each spectrum were not high enough for the four-component analysis, the spectra were decomposed into three components. In figure 4, the temperature dependence of τ_2 and that of τ_3 were found to be linear and τ_1 was almost constant in measured temperature range. The temperature dependences of τ_2 and τ_3 can be attributed to the thermal expansion of the open spaces. The temperature dependences of the lifetimes were fitted by assuming a linear relationship. The results are shown in figure 4. For the unirradiated specimen, the obtained temperature coefficient for the second lifetime was $1.8(5) \times 10^{-4}$ ns K^{-1} and that for the third lifetime was $2.7(2) \times 10^{-4}$ ns K^{-1}. This result means that the thermal expansion rate of the larger open spaces was larger than that for the smaller open spaces.

In figure 5, the third intensity was almost constant in the temperature range between 21 K and 170 K. At 170–200 K, it increased and kept a constant value above 200 K. The temperature dependence of the second intensity corresponded to that of the third intensity, where the first intensity was almost constant in the measured temperature range. Thus, the observed changes in the value of I_2 and I_3 can be attributed to the change in the trapping rate of positrons or Ps into two different open spaces. The trapping rate of positrons into defects, κ, can be expressed by [8]

$$\kappa = v_+ \sigma_+ C \tag{3}$$

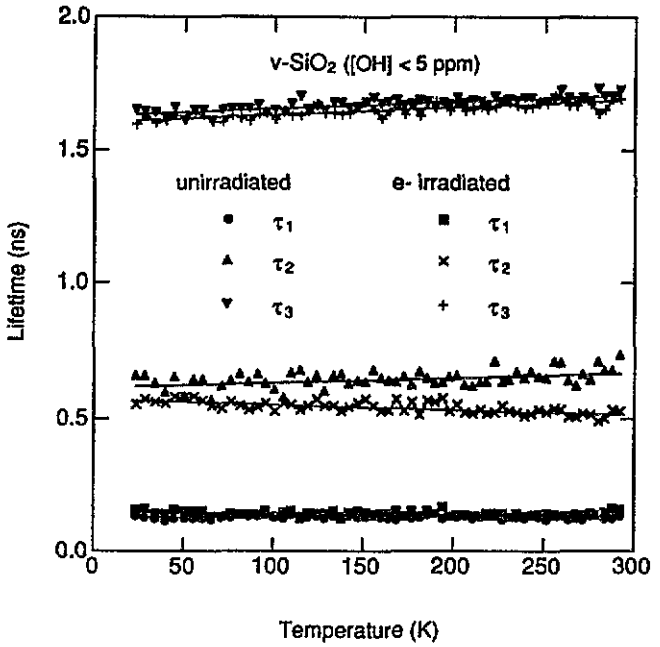

Figure 4. The lifetimes for the v-SiO_2 specimen with OH concentration of <5 ppm before and after the irradiation as a function of temperature. In this measurement, the lifetime spectra were decomposed into three components.

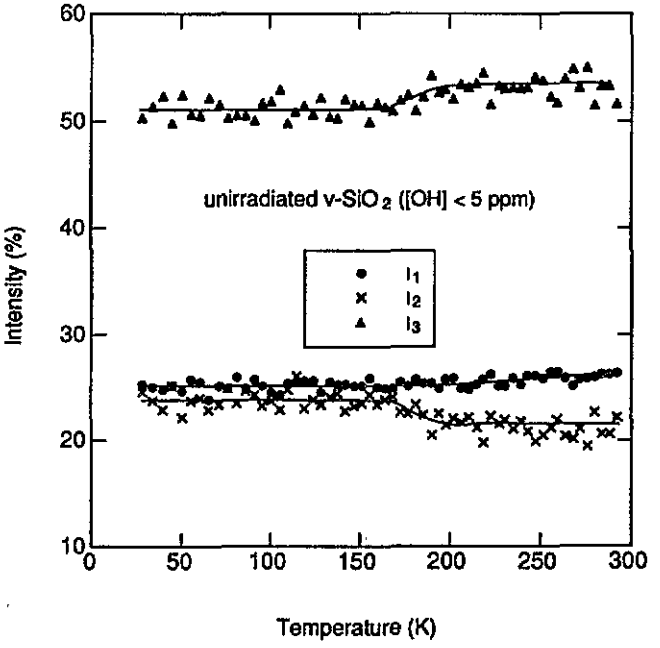

Figure 5. The intensities for the unirradiated v-SiO_2 specimen with OH concentration of <5 ppm as a function of temperature.

where v_+ ($= \sqrt{2kT/m_+}$) is the thermal velocity of positrons, σ_+ is the trapping cross-section of the defects and C is the concentration of the defects. v_+ is unlikely to cause the stepwise changes observed in the I_3–T relationship. In v-SiO_2, it is expected that σ_+ for neutral defects does not depend on temperature [3]. σ_+ for negative charge defects might be explained by a capture process involving an emission of a phonon cascade [12]. Within a semiclassical approach to the cascade process, the capture cross-section varies with temperature as T^{-n}. Thus, it can be concluded that the temperature dependences of v_+ and σ_+ are unlikely to represent the stepwise changes observed at 170–200 K.

In the present experiment, the diffusion length of positrons, L_d, was measured by using a monoenergetic positron beam. L_d is given by $L_d = \sqrt{D_+/\kappa_{eff}}$, where D_+ is the diffusion coefficient of positrons and κ_{eff} is the effective escape rate of positrons from the diffusion process. The details of this technique were described elsewhere [13]. The Doppler broadening profiles were measured as a function of incident positron energy for the unirradiated v-SiO_2 specimen with OH concentration of <5 ppm at 21 K and RT. By using the one-dimensional diffusion model of positrons, the value of L_d was derived from the observed relationship between the S parameter and the incident positron energy [9]. The obtained values of L_d at 21 K and RT were 20.9 ± 0.4 nm and 19.7 ± 0.5 nm, respectively. This means that the trapping process of positrons did not change significantly in this temperature range. At low temperature, positrons might be trapped by defects with shallow trapping potential. Since the size of the open spaces detected by the second component is large enough to form Ps, these defects are not shallow traps. Thus, the observed temperature dependences of I_2 and I_3 can be attributed to the change in the value of C for two different open spaces. For v-SiO_2, since open spaces are considered not to be isolated from nearby open spaces, a change in the structure of open spaces might affect that of nearby open spaces. The thermal expansion of the open spaces detected by the third component was larger than that detected by the second component. With increasing temperature, the expansion of the open spaces detected by the third component is considered to decrease with the value of C for the open spaces detected by the second component. The different temperature coefficient may cause the structural transition of the open spaces. The transition temperature was found to be affected by the introduction of point defects or by the presence of hydroxyl groups. These phenomena are discussed in sections 3.4 and 3.5, respectively.

3.3. Inhibition of the Ps formation by electron irradiation

Uedono *et al* [4, 14] and Watauchi *et al* [5] reported effects of the electron irradiation on annihilation characteristics of positrons. According to their results, positrons were trapped by point defects introduced by the irradiation. Since the formation of Ps needs larger open spaces or a lower electron density than the volume of or electron density around point defects, the trapping of positrons by such defects suppresses the formation of Ps. As shown in figure 2, the value of I_2 was increased by the irradiation; in turn, the values of I_1 and I_4 were decreased. These facts mean that the inhibition of the Ps formation due to the trapping of positrons by point defects introduced by the irradiation. The species of the point defects is not clear at this stage. It was suggested that Si vacancies, oxygen divacancies and relaxed oxygen vacancies are candidates for the point defects introduced and/or activated by the irradiation [4].

For the irradiated specimens, the values of $(I_3 + I_4)/I_1$ were calculated as 3.7. Since the value of I_3 was increased by the electron irradiation, the third component for the irradiated specimen can be attributed to the superposition of the annihilation of o-Ps and that of positrons. The lifetime of such positrons is considered to be close to the value of τ_3. Thus,

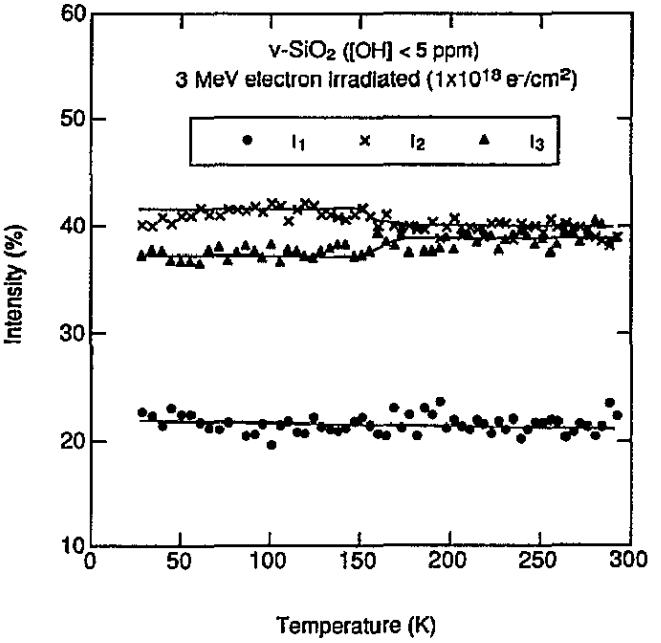

Figure 6. The intensities for the irradiated v-SiO_2 specimen with OH concentration of <5 ppm as a function of temperature.

the inhibition of the Ps formation is attributed not only to the trapping of positrons by point defects but also to that by vacancy clusters.

3.4. Positron annihilation in irradiated v-SiO_2 at low temperature

Figures 4 and 6 show the lifetimes and the intensities for the irradiated v-SiO_2 specimen with OH concentration of <5 ppm. In figure 4, the temperature dependences of τ_1 and τ_3 agreed with those for the unirradiated specimen; however, the temperature coefficient of τ_2 was found to be negative. As shown in figure 2, for the irradiated specimen, the value of I_2 decreased and that of I_3 increased at low temperature. Figure 7 shows the value of $(I_2 + I_3)/I_1$ as a function of temperature for the unirradiated and the irradiated v-SiO_2 with OH concentration of <5 ppm. For the irradiated specimen, the value of $(I_2 + I_3)/I_1$ was almost constant in the measured temperature range. These facts mean that the positrons detrapped from the point defects do not form Ps. Such positrons are considered to be trapped by the vacancy clusters and annihilate without forming Ps. Therefore, the negative temperature dependence of τ_2 can be attributed to the detrapping of positrons from the point defects and the increased annihilation probability of positrons in vacancy clusters at low temperature.

For the unirradiated specimen, the value of $(I_2 + I_3)/I_1$ increased with decreasing temperature, and it just coincided with the ratio of the formation probability of *o*-Ps to that of *p*-Ps below ~50 K. This fact is also attributed to the detrapping of positrons from native point defects at low temperature. In this case, the positrons detrapped from the native point defects annihilate from Ps states. In figure 6, the values of I_3 were smaller than that those for the unirradiated specimen (figure 5). This is due to the inhibition of the Ps formation by the irradiation. The temperature dependences of the intensities for the

irradiated specimen were found to be similar to those for the unirradiated one. In figure 6, the value of I_3 was almost constant in the temperature range between 21 K and 150 K. At 150–160 K, it increased and kept a constant value above 160 K. The corresponding decrease in the value of I_2 was also observed. As discussed in section 3.2, the observed steps in the I_2–T and the I_3–T relationships were attributed to the structural transition of the open spaces. For the irradiated specimen, the transition temperature (~150 K) was lower than that for the unirradiated specimen (~180 K). It is well established that electron irradiation introduces broken bonds such as E' centres [15]. The E' centre is point defects observed by measurements of electron spin resonance (ESR), and it was assigned to an electron trapped by a tribonding Si atom which is similar to the structure of an asymmetrically relaxed oxygen vacancy. From the observed decrease of the transition temperature, an activation energy required for the transition is considered to be lowered by the introduction of such broken bonds.

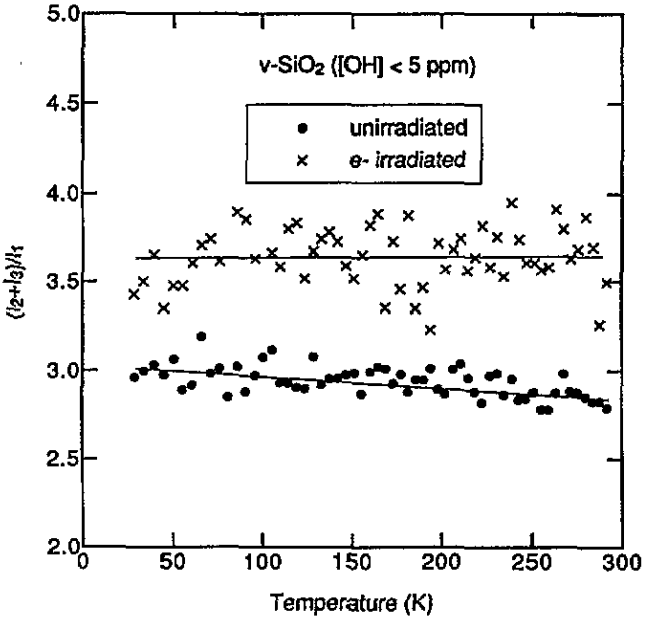

Figure 7. The value of $(I_2 + I_3)/I_1$ as a function of temperature for the v-SiO_2 specimen with OH concentration of <5 ppm before and after the electron irradiation.

3.5. Annihilation characteristics of positrons in v-SiO_2 with high OH concentration at low temperature

Figures 8–10 show the lifetimes and the intensities for the v-SiO_2 specimen with OH concentration of <200 ppm before and after the irradiation as a function of measuring temperature. As shown in figures 9 and 10, the effect of the electron irradiation on the value of I_3 was smaller than that for the specimen with low OH concentration (figures 5 and 6). A similar suppression of the inhibition of the Ps formation in the specimen with high OH concentration was reported by Uedono *et al* [4]. Galeener and co-workers [16, 17] reported the suppression effect of hydroxyl groups on the introduction of E' centres by x-ray irradiation. They suggested that the introduction of E' centres can be attributed to an

activation of pre-existing defects by the irradiation, where the activation involves the transfer of electrons or holes to or from previously existing broken bonds. These pre-existing broken bonds are considered to be suppressed by hydroxyl groups. In the present experiment, E' centres were probed by measurements of ESR. ESR spectra were measured at ~9.43 GHz and 0.04 mW microwave power. The resonance of E' centres with $g = 2.001$ was observed, where the g value was determined using the known number of Mn^{2+} spins in MgO. The integrated intensity of a signal corresponding to E' centres for the specimen with high OH concentration was 25% lower than that for the specimen with low OH concentration. Therefore, for the specimen with high OH concentration, the observed small difference between the value of I_3 for the unirradiated specimen and that for the irradiated one can be attributed to the suppression effect of hydroxyl groups on the introduction of point defects.

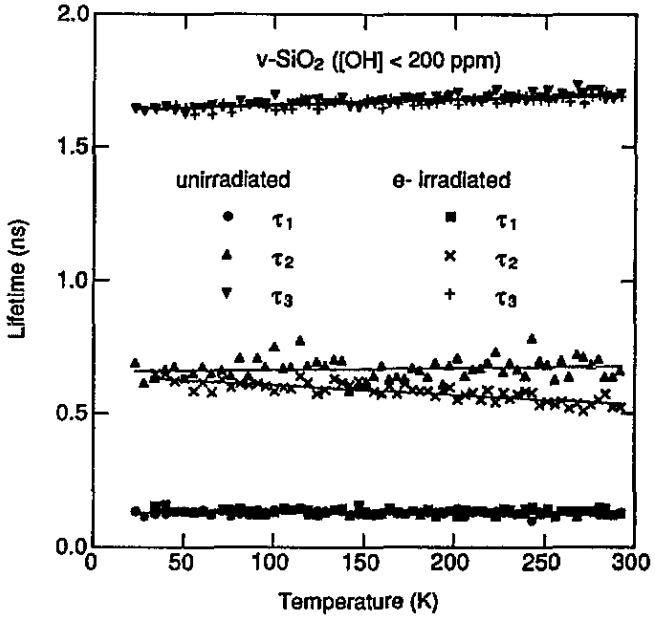

Figure 8. The lifetimes for the v-SiO_2 specimens with OH concentration of <200 ppm before and after the irradiation as a function of temperature.

In figure 8, the temperature dependence of the lifetimes was found to be close to that for the specimen with low OH concentration. In figure 9, the increase in the value of I_3 was observed at 130–150 K. This transition temperature was lower than that for the unirradiated specimen with low OH concentration. In the v-SiO_2 specimen with high OH concentration, hydroxyl groups terminate Si–O bonds as a formation of Si–OH. Thus, an activation energy of the transition is considered to be lowered by the termination of Si–O bonds. For the irradiated specimen (figure 10), the transition was observed in the temperature range between 130 K and 200 K. The lower transition temperature was close to that for the unirradiated specimen with high OH concentration and the upper transition temperature was close to that for the unirradiated specimen with low OH concentration. A recoil of hydrogen atoms or hydroxyl groups by the irradiation could generate Si–O bonds. Thus, the broadening of the transition temperature is considered to be attributed to the broadened species of the open spaces under circumstances such as the termination of Si–O bonds and the regeneration of such bonds.

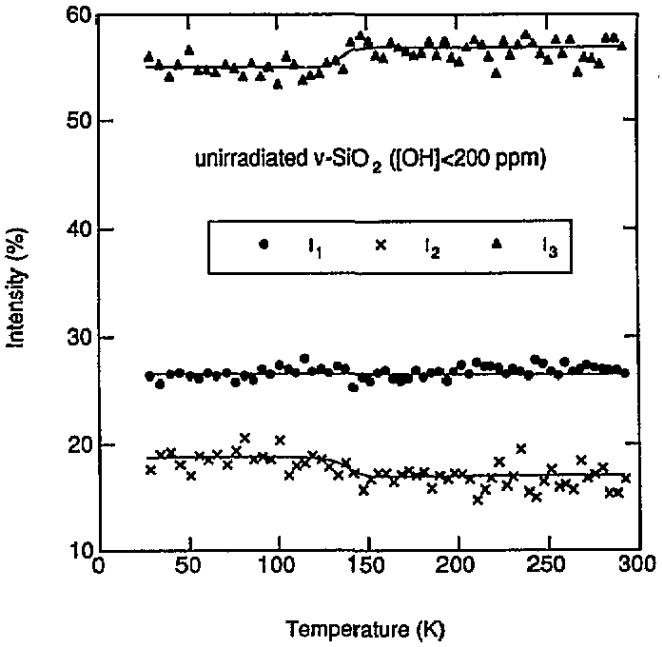

Figure 9. The intensities for the unirradiated v-SiO_2 specimen with OH concentration of <200 ppm as a function of temperature.

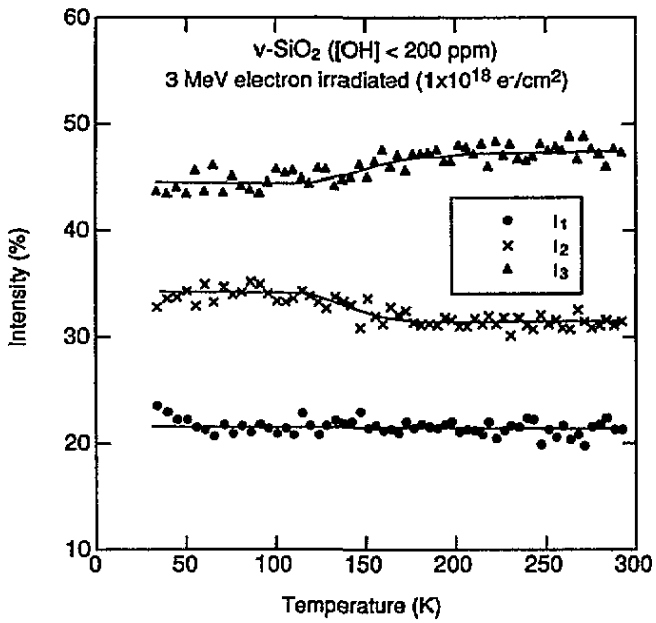

Figure 10. The intensities for the irradiated v-SiO_2 specimen with OH concentration of <200 ppm as a function of temperature.

4. Conclusions

We have investigated annihilation characteristics of positrons in v-SiO_2 at low temperature. Almost all positrons annihilate from Ps states in the temperature range between 21 K and

RT. Two different annihilation modes of *o*-Ps were observed. These were attributed to the pick-off annihilation of *o*-Ps trapped by the open spaces. For the 3 MeV electron irradiated specimens, the inhibition of the Ps formation due to the trapping of positrons by the defects was observed. The lifetimes of *o*-Ps increased with increasing temperature, where the distribution of the lifetimes at RT was broader than that at 21 K. These facts correspond to the thermal expansion of the open spaces and the increase in size distribution of such spaces. The coefficient of the thermal expansion of the larger open spaces was larger than that for the smaller ones. In the temperature range between 170 K and 200 K, the structural transition of the open spaces was observed. The transition temperature was found to be decreased by the irradiation or by the presence of hydroxyl groups. This was attributed to the fact that the activation energy for the structural transition was lowered by the introduction of broken bonds. The present investigation shows that positrons provide a nondestructive probe for the microscopic structure of amorphous SiO_2.

References

[1] Friebele E J 1979 *Opt. Eng.* **18** 552
[2] Hautojärvi P and Vehanen A 1979 *Positrons in Solids* ed P Hautojärvi (Berlin: Springer) p 1
[3] Dannefaer S, Bretagnon T and Kerr D 1993 *J. Appl. Phys.* **74** 884
[4] Uedono A, Kawano T, Tanigawa S and Itoh H 1994 *J. Phys.: Condens. Matter* **6** 8669
[5] Watauchi S, Uedono A, Ujihira Y and Yoda O 1995 *J. Appl. Phys.* **76** 4553
[6] Kirkegaard P, Eldrup M, Mogensen O E and Pedersen N J 1981 *Comput. Phys. Commun.* **23** 307
[7] Gregory R B 1991 *Nucl. Instrum. Methods* A **302** 496
[8] West R N 1979 *Positrons in Solids* ed P Hautojärvi (Berlin: Springer) p 89
[9] Uedono A, Wei L, Tanigawa S, Suzuki R, Ohgaki H, Mikado T, Kawano T and Ohji Y 1994 *J. Appl. Phys.* **75** 3822
[10] Uedono A and Tanigawa S 1993 *Japan. J. Appl. Phys.* **32** 2687
[11] Tao S J 1972 *J. Chem. Phys.* **56** 5499
[12] Lax M 1960 *Phys. Rev.* **119** 1502
[13] Schultz P J and Lynn K G 1988 *Rev. Mod. Phys.* **60** 701
[14] Uedono A, Watauchi S, Ujihira Y and Yoda O 1994 *Hyperfine Interact.* **84** 225
[15] Griscom D L 1988 *The Physics and Technology of Amorphous SiO_2* ed R A B Devine (New York: Plenum) p 125
[16] Galeener F L, Kerwin D B, Miller A J and Mikkelsen J C Jr 1992 *Solid State Commun.* **82** 271
[17] Kerwin D B and Galeenar F L 1992 *Phys. Rev. Lett.* **68** 3208