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Positron-lifetime study on porous silicon with a monoenergetic pulsed positron beam

Ryoichi Suzuki, Tomohisa Mikado, Hideaki Ohgaki, Mitsukuni Chiwaki, and Tetsuo Yamazaki
Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba, Ibaraki 305, Japan

Yoshinori Kobayashi
National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305, Japan

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Positron-lifetime measurements have been performed on anodized porous silicon as a function of temperature by using a monoenergetic pulsed positron beam. In the lifetime spectra, a long-lived component, which can be attributed to orthopositronium formed at the surface of pores, has been observed. The intensity and the lifetime of the orthopositronium component were found to be strongly influenced by the sample temperature and the annealing temperature. A dramatic increase in the orthopositronium intensity after annealing at 300–400 °C suggests a reduction of positron traps near the surface due to a microstructural change. A temperature-reversible change of the orthopositronium lifetime after annealing at 400 °C suggests that there exist thermally activated dangling bonds at the pore surface at high temperatures. The present study revealed that positron lifetime is highly sensitive to changes in microstructure and pore surface conditions in porous Si.

Porous silicon, obtained by anodization of silicon (Si) single crystals in HF acid solutions, has promoted considerable interest because of its unique properties due to a large surface area[1] and low-dimensional quantum-size crystalline structures.[2] In recent years, porous Si has become a subject of intensive investigation not only in fundamental phsyics but also in electronic technology because of its potential for integrated circuits[3] and light-emitting devices.[4] The structure and properties of porous Si have been found to be strongly influenced by Si crystal characteristics, anodization conditions, and thermal treatments.[5–7] However, there are still unanswered questions regarding the microstructure and pore surface properties which affect the characteristics of porous Si.

Positron-annihilation experiments have been successfully used to study electronic structure, microstructural defects, surface properties, chemical reactions, etc.[8–10] While there are various positron-annihilation techniques, each of which possesses unique features, positron-lifetime spectroscopy is the most widely used technique to study microstructual defects, free volumes, and chemical reactions in various materials.[10] Positron lifetimes depend on electron density at the site of the positron and can be used to characterize the nature of the positron trapping site. Furthermore, if positronium (Ps), the bound state of the positron-electron pair, forms in the sample, the lifetime and intensity of the orthopositronium (*o*-Ps) component gives us valuable information on free volume sizes, chemical properties, etc.[10]

To date, only a few positron-annihilation studies have been performed on the porous silicon system. Cruz and Pareja[11,12] applied the conventional positron-lifetime technique to porous silicon samples, and they found that the intermediate lifetime τ_2 strongly depends on the anodization conditions, annealing temperatures, and silicon crystal properties. More recently, Itoh, Murakami and Kinoshita[13] found a long-lived ($\sim$ 25 ns) component and they reported that the component depends on the sample conditions. However, a high intensity of substrate component included in those spectra makes it difficult to perform detailed analyses, because the conventional lifetime technique uses high-energy positrons (β^+ rays of radio isotope sources) which have a large penetration depth of several hundred micrometers for porous Si.

In recent years, a monoenergetic pulsed positron beam generated from slow positrons enables us to perform positron lifetime spectroscopy on thin films, near surface regions, and surfaces.[14–18] Furthermore, it has been possible to measure a long-lived *o*-Ps component using an intense positron beam.[19] The present authors have successfully investigated large vacancy-type defects in thin films of hydrogenated amorphous Si, diamond, and SiO_2, all of which have long-lived *o*-Ps components, by the use of an intense pulsed positron beam at the Electrotechnical Laboratory (ETL).[16–18]

In this paper, we report a positron-lifetime study of the *o*-Ps component in porous Si as a function of sample temperature and annealing temperature by using the intense pulsed positron beam.

The porous Si sample was made from a polished *n*-type Si (001) wafer (Sb doped, $3 \times 10^{15}/cm^3$, $15 \times 20 \times 0.5$ mm^3 in size). The wafer was mounted at the bottom of an electrolysis cell which contains an electrolyte of $HF:H_2O:C_2H_5OH$ 1:1:2. The wafer was anodized for 10 min at room temperature at a current density of 60 mA/cm^2 with a platinum cathode. The thickness of the porous Si layers can be estimated as an order of 10 μm.[1,2,6] The sample was exposed in air for two days.

Experiments were performed under high-vacuum ($\sim 10^{-8}$ Torr) conditions. A variable-energy pulsed positron beam generated from an intense positron beam at the ETL was used for the positron-lifetime measurement. The positron-lifetime spectra were measured with an apparatus similar to that of Ref. 19, modified for sample heating. The operating frequency of the pulsing system was 4.1 MHz and each lifetime spectrum was

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measured within a time range of ~ 120 ns with a channel width of 119.8 ps. The positron-lifetime spectra were measured at an implantation energy of 2 keV to minimize the effect of backscattered positrons to the analysis of the spectra. The implantation profile of the 2-keV positrons can be approximated by the derivative of a Gaussian[9] with a mean depth of 12 μg/cm^2. Since the positron diffusion length of porous Si is considerably shorter than that of crystalline Si, most of the implanted positrons would annihilate in the porous Si layer.

At the first step of the experiment, a lifetime spectrum was measured at 25 °C. Then, the sample temperature was elevated to 200 °C. In order to study both thermal behavior and annealing behavior, four heating cycles were carried out by changing the peak temperature from 300 °C to 600 °C with an interval of 100 °C. Since the vacuum pressure of the present experiment was insufficient for surface studies at room temperature, we chose 200 °C as the minimum temperature of the heating cycles to prevent the adsorption of residual gases, such as H_2O.

In each heating cycle, the sample temperature was elevated stepwise with an interval of 50 °C from 200 °C to the peak temperature, then lowered stepwise with an interval of 100 °C. In each step, the temperature was kept for approximately 3000 s, and a positron-lifetime spectrum was taken. For each spectrum, 1×10^5–3×10^5 counts were accumulated. Data taking of several steps failed due to the instablility of the positron beam.

Figure 1 shows the positron-lifetime spectra at the sample temperatures of 25 °C, 300 °C, and 500 °C. The spectra of 300 °C and 500 °C were measured at the peak of the heating cycles. As shown in Fig. 1, a well-separated long-lived component, which actually is a mixture of two or more lifetime components, was observed in the spectra and both the intensity and lifetime of this component are dramatically changed as a function of the temperature. The long-lived component can be attributed to the o-Ps formed at the surface of the pores because of following reasons: A short-lved component which can be attributed to parapositronium was found and the intensity increases as that of the long-lived component increases. It is well known that the positrons implanted in the near-surface region diffuse back to the surface and then form Ps at the surface of crystalline Si; furthermore, Ps formation at void surface has been found in hydrogenated amorphous Si.[16,20]

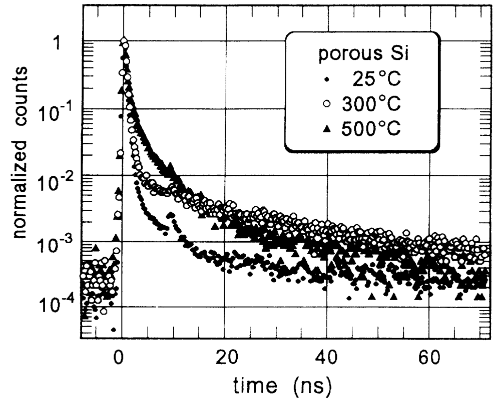

FIG. 1. Positron-lifetime spectra of the anodized porous Si film at the sample temperatures of 25 °C, 300 °C, and 500 °C. The spectrum of 25 °C was measured before the heating cycles, and the spectra of 300 °C and 500 °C were measured at the peak of the heating cycles. A satellite peak at around 10 ns is due to backscattered positrons.

The lifetime spectra were resolved into three or four exponentially decaying components by a nonlinear least-square-fitting program,[21] and the o-Ps component was resolved as the third component and the fourth component. The second component which has 350–550-ps lifetime can be attributed to positrons trapped at vacancy-type defects. Unfortunately, it is difficult to discuss temperature dependence of the second component because relatively large fluctuation resulted from the wide channel width and low statistics.

Figure 2 shows the temperature dependences of (a) the intensity and (b) the lifetime of the long-lived o-Ps component. Solid circles in Fig. 2 indicate the sample temperature dependence measured at virgin temperature of the heating cycles, and open circles indicate the temperature dependence measured at lowered temperature of 200 °C from the peak temperature (i.e., annealing temperature) of the heating cycles. The lifetime (τ_L) and intensity (I_L) in Fig. 2 were obtained from the fitting parameters τ_3, τ_4, I_3, and I_4, as $\tau_L = (\tau_3 I_3 + \tau_4 I_4)/(I_3 + I_4)$ and $I_L = I_3 + I_4$, respectively.

Mills[22] reported that the Ps formation at Si surface is a thermally activated phenomenon; the activation energies for Si(100) and Si(111) surfaces are 0.17 and 0.49 eV, respectively. In the present case, however, no significant difference in the o-Ps intensity was found in Fig. 2(a) up to 400 °C. This might be the result of the lowered activation energy of Ps formation due to hydrogen atoms.[20]

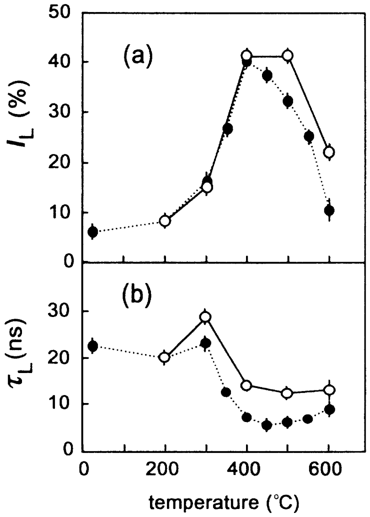

FIG. 2. The temperature dependence of the long-lived component for the anodized porous Si. (a) I_L vs temperature and (b) τ_L vs temperature. The solid circles show the sample temperature dependence measured at the virgin temperatures and the open circles show the annealing temperature dependence measured at lowered temperature of 200 °C.

A dramatic increase in I_L was found from 300 °C to 400 °C. Two factors should be considered for the intensity increase: one is change of surface conditions, which causes an increase of Ps formation probability, and the other is a reduction of positron traps near the surface of the pores, which increases the effective positron diffusion length and the number of positrons that diffuse to the pore surface. It is known that desorption of hydrogen from dihydride species of the pore surface occurs in the range between 200 °C and 400 °C.[5,23–25] However, hydrogen is considered to be an impurity which decreases the activation energy of Ps formation as discussed before. Meanwhile, microstructual change in porous Si was observed in the range between ~ 300 °C and 400 °C by x-ray multiple-crystal diffractometry.[6] This agrees well with the sharp increase in I_L from 300 °C to 400 °C. Thus, the reduction of positron traps due to the microstructural change, such as structural relaxation, reduction of microcrystalline boundaries, etc., would mainly contribute to the I_L increase from 300 °C to 400 °C.

A sharp decrease in I_L was found between 500 °C and 600 °C. A similar phenomenon was observed on a hydrogenated amorpohus Si film which has a high concentration of voids.[18] Two factors should be considered about this phenomenon: one is a change of pore surface conditions, and the other is the reduction of pore surface area due to large structural change. It is known that the hydrogen effuses from monohydride species in the range of 500 °C–600 °C.[24,25] Furthermore, a significant reduction of the pore surface area was observed at 500 °C by a gas desorption technique.[25] Both of them are well correlated to the I_L decrease in Fig. 2(a) and we cannot conclude from the present data whether the hydrogen effusion or the large structual change is dominant for the I_L decrease. Clarification of the phenomenon is presently under study.

As shown in Fig. 2(a), I_L measured at 200 °C after annealing at 500 °C and 600 °C is significantly higher than that measured at the virgin temperatures of 500 °C–600 °C. This is not consistent with the temperature dependence of Ps formation at Si surfaces proposed by Mills.[22] A rapid quenching of Ps atoms due to high dangling-bond density at the surface might reduce the *o*-Ps intensity at high temperatures.[20]

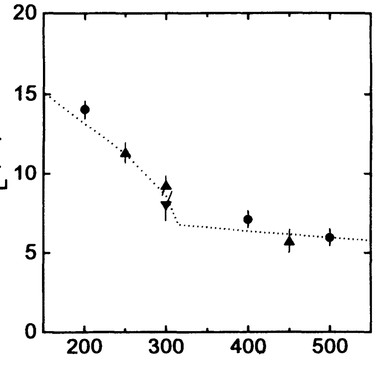

FIG. 3. The lifetime of the long-lived component vs the sample temperature in the latter half of the second heating cycle and the former half of the third heating cycle. The solid circles show the peak or bottom of the heating cycles, the down triangle shows the temperature lowering step of the second heating cycle, and the up triangles show the temperature elevating steps of the third heating cycle. The dotted curve is fit by Eq. (1).

The lifetime of the long-lived component measured at 200 °C after annealing at 400 °C and 500 °C is significantly longer than that measured at the virgin temperatures of 400 °C and 500 °C [Fig. 2(b)]. Figure 3 shows sample temperature dependence of τ_L measured in the latter half of the second heating cycle and the former half of the third cycle (i.e., after annealing at 400 °C). The temperature dependence was found to be reversible. This suggests a thermally activated process which affects the lifetime shortening of the *o*-Ps component. There are two factors that shorten the *o*-Ps lifetime at high temperatures: one is an increase of collision rate to the pore surface due to the increase of Ps velocity and/or reduction of pore volume; the other is the change of interaction between the Ps atom and pore surface electrons resulted from the change of pore surface conditions. The pore volume reduction due to thermal expansion of Si ($\sim 8 \times 10^{-6}$/°C) would be negligible in this case. Since the mean pore size of ~ 20 Å estimated from the known relation[26] between *o*-Ps lifetime and radius of free volumes is much larger than the Bohr radius of a Ps atom (1.06 Å), the increase of the collision rate due to the increase of thermal velocity from 200 °C to 400 °C can be estimated from classical thermodynamic theory as 16%. This value is much lower than the decrease ratio of the *o*-Ps lifetime from 200 °C to 400 °C. Therefore, the latter factor would mainly contribute to the lifetime shortening.

He *et al.*[20] reported a similar phenomenon in the experiment on hydrogenated amorphous Si and they speculated that it is due to temperature-reversible hydrogen desorption-adsorption at the inner wall of voids. In the present case, however, this model cannot be adopted, because pores of porous Si are not closed and inside of the pores is vacuum. Thus, we present another model here. That is, dangling bonds are created after hydrogen desorption form dihydride species in the sample annealed at 400 °C. The surface would then reconstruct to lower the dangling-bond density at low temperature so that the surface energy is low. At high temperatures, dangling bonds would be recreated by a thermally activated process, such as temperature reversible surface reconstruction. Those thermally activated dangling bonds can increase probability of *o*-Ps spin conversion and/or chemical reaction of Ps.[10] If the thermally activated process follows continuous phase transition,[27] the critical temperature (T_c) and the critical exponent (β) can be calculated by following way: The *o*-Ps lifetime ($\tau_{o\text{-Ps}}$) is represented by

$$1/\tau_{o\text{-Ps}} = [\lambda_v + (P_p + P_i)A(T)], \qquad (1)$$

where λ_v is the annihilation rate in vacuum; P_p and P_i are the probability of pick-off annihilation and the probability of non-pick-off interaction (spin conversion or chemical reaction), respectively; $A(T)$ is the collision rate to the pore surface wall. Near the critical temperature T_c, we obtain $A(T) = aT^{1/2}$, $P_i = bC_{\rm db}(T) = c - dF(T)$

where a, b, c, and d are constants, $C_{\mathrm{db}}(T)$ is the dangling-bond density, and $F(T)$ is the order parameter of the phase transition. In the continuous phase transition, $F(T)$ is given by

$$F(T) = \begin{cases} [(T_c - T)/T_c]^{\beta} & (T < T_c) \\ 0 & (T \geq T_c). \end{cases} \quad (2)$$

By using a least-squares-fitting program,[28] the critical temperature and the critical exponent were calculated as $T_c = (307 \pm 20)\,^{\circ}\mathrm{C}$ and $\beta = 0.26 \pm 0.07$, respectively.

We cannot discuss from the present results whether the spin conversion or chemical reaction is the dominant interaction between Ps and dangling-bond electron at high temperatures. The measurement techniques, which measure the electron momentum density, e.g., angular correlation of annihilation radiation and Doppler broadening spectroscopy,[8,10] will give us more conclusive information on the annihilation process of Ps atoms.

In conclusion, we have studied the temperature dependence of the long-lived *o*-Ps component in lifetime spectra of porous Si using a monoenergetic pulsed positron beam. The intensity and the lifetime of the *o*-Ps component are strongly influenced by both the sample temperature and annealing temperature. The temperature dependence of the *o*-Ps intensity suggests that a microstructual change, which reduces positron traps near the pore surface, occurred at the temperature range of 200 °C–400 °C. The temperature reversible change of τ_L for the sample annealed at 400 °C suggests that there exists thermally activated dangling bonds at high temperatures. Measurements of the dangling-bond density using the electron spin resonance method, for example, would be an interesting confirming experiment of the above model.

The presented work represents an initial step in the utilization of a monoenergetic pulsed positron beam to study porous Si. Further study, such as depth dependence (positron energy dependence), temperature dependence of τ_2, comparison among different sample growth conditions, should be performed and will lead to better understanding of porous Si.

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