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Detection of paramagnetic centers on amorphous-SiO_2 grain surfaces using positronium

Haruo Saito, Yasuyuki Nagashima, and Toshio Hyodo
Institute of Physics, College of Arts and Sciences, University of Tokyo, 3-8-1 Komaba, Meguro-ku, Tokyo 153, Japan

Tianbao Chang
Institute of High Energy Physics, Academia Sinica, P.O. Box 2732, Beijing, China

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Angular correlation of positron-annihilation radiation, positron-lifetime spectra, and Doppler-broadening spectra of the annihilation radiation from silica aerogel have been measured in the temperature range between 13 and 295 K. Spin conversion of positronium at the surfaces of the amorphous-SiO_2 grains is observed when the aerogel is irradiated sufficiently by the positrons at low temperatures. This shows that paramagnetic centers are induced on the first layer of the surface of the amorphous-SiO_2 grains by the irradiation. The surface paramagnetic centers are unstable above 150 K and are attributed to a nonbridging oxygen hole center (Si-O $^\cdot$).

It is well known that when amorphous SiO_2 (a-SiO_2) is exposed to ionizing radiation, a variety of paramagnetic defect centers result.[1] These centers have attracted wide attention because of their scientific and technological importance. They are usually studied with ESR or optical spectroscopies. The ESR technique, in particular, has made a great contribution to the detection and definitive identification of many of these centers. The intrinsic paramagnetic centers identified so far include the E' center (an unpaired electron in a Si dangling bond),[2] the nonbridging oxygen hole center,[3] and the peroxy radical.[4] Other intrinsic and extrinsic centers, atomic hydrogen, O_2, Cl_2, etc. are also found.

There have been several studies of paramagnetic centers in a-SiO_2 in connection with surfaces using silica gel[5–14] and crushed silica.[15] The ESR method is mainly used in these studies; the existence of paramagnetic centers on surfaces is demonstrated by observing changes in ESR spectra on introducing gases. This method is effective when the number of the paramagnetic centers in the bulk is negligible,[5,6,15] but ambiguousness about the location of paramagnetic centers sometimes remains because of the large contribution of the bulk centers or complexity of the reaction process between the gases and the centers.

Positrinium (Ps),[16] used in the present work, is the bound state of an electron and a positron. Ps exists in triplet state ($S=1$) or in singlet state ($S=0$). The former is called orthopositronium (o-Ps) and the latter is called parapositronium (p-Ps). In vacuum, o-Ps annihilates into three γ rays, while p-Ps annihilates into two γ rays. The mean lifetimes of the o-Ps and p-Ps in vacuum are 142 ns and 125 ps, respectively; o-Ps thus lives more than 1000 times longer than p-Ps. When positrons are implanted into aggregates of oxide fine grains, Ps atoms are formed in many cases and emitted into the vacant space between the grains.[17] They repeat collisions against the grains till they annihilate into γ rays. They cannot penetrate back into a grain because of the negative Ps work function, and thus interact with the surfaces only. Another property of the Ps atoms is that they undergo spin conversion by interacting with unpaired electrons.[18,19] Hence they can be used as a probe for the paramagnetic centers on the surfaces.

Recently interactions between Ps atoms and irradiation-induced paramagnetic centers on the surfaces of powdered Al_2O_3 (Ref. 20) and MgO (Ref. 21) were reported by Dauwe and co-workers. They investigated behavior of Ps atoms with the positron-lifetime and 3γ coincidence method at low temperatures. They found that the long lifetime of Ps atoms and its intensity decrease with time, and that the decrease rate depends on the activity of the positron source. They attributed this to ortho-para conversion of Ps atoms due to spin-exchange collision with surface paramagnetic centers induced by the irradiation of the energetic positrons. The intensity of the ^{22}Na positron source was 10 μCi when this irradiation effect was observed.

For a-SiO_2 fine powder, lifetime measurement at low temperatures was reported by Kiefl and Harshman.[22] The intensity of the ^{22}Na positron source was 2.5 μCi. The result was different from that for Al_2O_3; the effect of irradiation was not observed.

In this work we performed positron-annihilation measurements in silica aerogel, at various temperatures below 295 K, in order to study whether irradiation effect on Ps atoms, such as in Al_2O_3, is observed in a-SiO_2 or not. Silica aerogel is aggregate of a-SiO_2 ultrafine grains, having a three-dimensional network structure. We measured, with angular correlation of annihilation radiation (ACAR) and Doppler-broadening methods,[23] momentum distribution of Ps atoms in silica aerogel. In the ACAR method the total momentum distribution of the annihilating electron-positron pairs is obtained by measuring the angular distribution of the γ rays from the 2γ annihilation. This method selectively analyzes the γ rays from the 2γ annihilation. In the Doppler-broadening method the momentum distribution is obtained by measuring the energy spectrum of the annihilation γ rays. Since a strong ^{22}Na positron source (25 mCi) was used in the ACAR measurement, the irradiation effect is larger than that of the previous works with the lifetime method. We also measured positron-lifetime spectra. The positron-lifetime and Doppler-broadening spectra were measured changing the irradiation condition. We observed through Ps spin conversion that paramagnetic centers are induced on the surfaces by

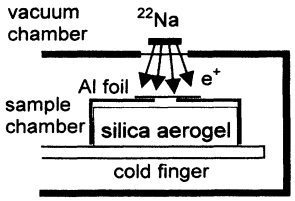

FIG. 1. Schematic diagram around the sample and positron source for the ACAR measurement. The thermal radiation shield between the sample cell and the vacuum chamber is not shown.

strong positron irradiation at low temperatures and that they are annealed out at room temperature.

The average diameter of the grains of the silica-aerogel sample was 4 nm. The typical distance across the space between the grains was ~100 nm. The density of the aerogel was 0.1 g/cm^3.

The ACAR apparatus used in this study has been described elsewhere.[24] The momentum resolution was adjusted to 0.36×10^{-3} mc (0.049 a.u.). The dimensions of the silica-aerogel sample were $30\times30\times6$ mm^3. It was contained in a sample cell (Fig. 1) with a hole of 1 cmϕ covered by 10 μm thick Al foil. The hole limits the area of the sample irradiated by the positrons. The sample cell was attached on a cold finger of a closed-cycle helium refrigerator, surrounded by a thermal radiation shield, and kept in a vacuum chamber. The pressure inside the chamber was $\sim10^{-7}$ torr. The inside of the cell was evacuated through openings along the bottom edges. A positron source of ~25 mCi was attached outside the vacuum chamber, ~10 mm apart from the sample.

The observed ACAR curves are shown in Fig. 2. The open circles represent the data at 295 K and the closed circles represent those at 13 K. The counts, which were obtained by summing 20 scans of 8 h duration each, have been normalized to the number of incident positrons. The central part of the ACAR curve for the first scan at 13 K was observed to have increased significantly. A separate measurement to monitor the early change in the peak count showed that it took several hours before the change almost saturated. In contrast, the ACAR curve at 295 K showed no time dependence. It was not affected by the foregoing measurement temperatures either.

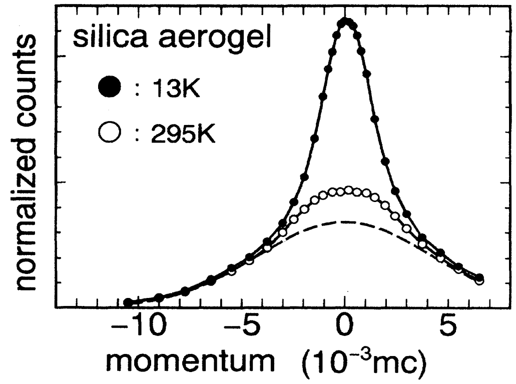

FIG. 2. ACAR curves for silica aerogel without magnetic field at 295 K (○) and at 13 K (●).

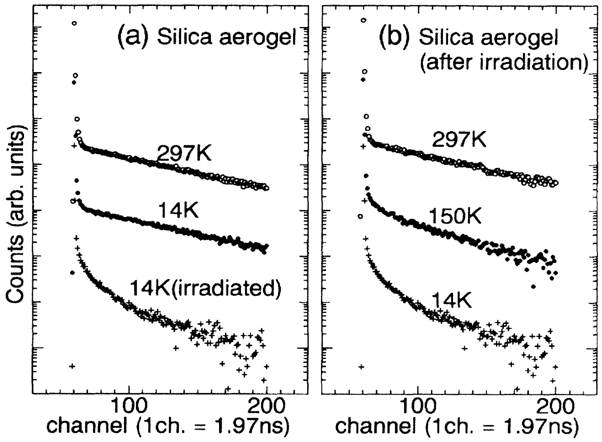

FIG. 3. (a) Positron-lifetime spectra for silica aerogel at 295 K (○), at 14 K before irradiation (●), and at 14 K after (+) irradiation for 720 min. (b) Spectra for silica aerogel during heating up after irradiation.

Positron-lifetime spectra were obtained with an ordinary fast-fast lifetime spectrometer with BaF$_2$ scintillators.[25] The same sample, sample cell, and vacuum chamber as in the ACAR measurements (Fig. 1) were used. The 6 μCi positron source for the lifetime measurements was kept between the sample and Al foil of the sample cell. Temperature was controlled by the same refrigerator as in the ACAR measurements. To irradiate the sample, the 25 mCi positron source was attached at intervals between the measurements.

In Fig. 3(a), dots represent the positron-lifetime spectrum at 14 K. This spectrum is quite similar to that at 295 K represented by open circles; a long lifetime component due to o-Ps atom sin the space between the grains annihilating into 3γ is clearly seen. After taking the spectrum at 14 K we irradiated the sample with the 25 mCi source. The spectrum after the irradiation for 720 min is shown by crosses in Fig. 3(a). The irradiation resulted in drastic shortening of the longer lifetime. The sample was then warmed up to room temperature in steps of ~50 K. The lifetime spectrum was measured at each temperature for 4 h. Some of the obtained spectra are shown in Fig. 3(b). The spectrum at room temperature was identical to that before irradiation.

The Doppler-broadening measurements were performed with the same setup of the sample and positron source as the lifetime measurements. The spectra measured at 295 K and at 14 K showed no difference. When the sample was irradiated sufficiently at low temperatures, Doppler-broadening spectra showed remarkable increase in the counts in the central part. When the sample temperature was elevated to room temperature, the spectrum recovered to that before irradiation.

All these data show that irradiation by a 25 mCi positron source at low temperature causes considerable changes in the Ps state. The fact that the positron-lifetime spectrum does not change when the sample was cooled before the sufficient irradiation shows that the variation of sample temperature itself or gas adsorption during the sample cooling does not have appreciable effect. It was shown in a separate lifetime measurement lasting for a week that the irradiation by the 6 μCi positron source, whose intensity was $\frac{1}{4000}$ of that for

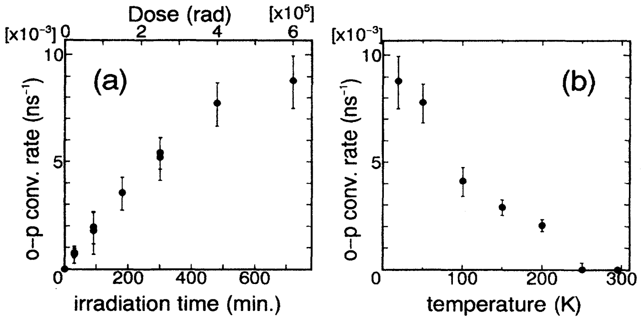

FIG. 4. (a) Ortho-para conversion rate vs irradiation time (dose) in silica aerogel at 14 K. (b) Ortho-para conversion rate vs temperature in silica aerogel during heating up after irradiation. The measurement at each temperature took 4 h.

ACAR measurement, gave no effect.

The ACAR curve at 295 K (Fig. 2) can be resolved into two components.[26] The broad component having a full width at half maximum (FWHM) of $\sim 10\times 10^{-3}$ mc (represented by the dashed curve in Fig. 2) is mainly due to the positrons annihilating with electrons bound in SiO_2. Pickoff annihilation of a Ps atom, in which the positron in the Ps annihilates with an electron in a-SiO_2, also contributes to this component. The narrower component having a FWHM of $\sim 5\times 10^{-3}$ mc is due to p-Ps atoms in the free space between the grains.[26] The increase in the count rate on cooling the sample is prominent in the narrower component; the broad component is almost unchanged. The change is similar to that due to ortho-para conversion observed when O_2 is introduced in silica aerogel.[19] This shows that at 13 K o-Ps atoms convert into p-Ps which annihilates into 2γ and contribute to the ACAR curve, while at 295 K they mainly annihilate into 3γ and do not contribute to the ACAR curve. It also shows that the change in the pickoff annihilation rate of o-Ps on cooling is very small. Therefore the drastic decrease of long lifetime of o-Ps after irradiation at 14 K [Fig. 3(a)] is not due to pickoff annihilation but to ortho-para conversion of Ps atoms.

The origin of the ortho-para conversion must be spin-exchange collision between Ps atoms and paramagnetic centers induced by irradiation, as in powdered Al_2O_3 (Ref. 20) and MgO (Ref. 21). The disappearance of this effect at room temperature is due to thermal annealing of these centers.

The ortho-para conversion rates deduced from the lifetime data are shown in Fig. 4. Since the sample is not uniformly irradiated by the positrons, along the depth in particular, ortho-para conversion rate due to the paramagnetic centers on the grain surfaces is not uniform in the sample. We obtained the averaged conversion rate for each spectrum by using multicomponent fitting to the data between 20 and 280 ns after the prompt peak. Since the sample-source configuration was not the usual sandwich type, half of the positrons did not annihilate in the aerogel sample. They contribute only to the prompt peak and do not have effects on this analysis. The result is plotted against the irradiation time in Fig. 4(a). The ortho-para conversion rate is nearly proportional to the irradiation time. Averaged irradiation dose estimated within a factor of less than 3 is shown at the top of the figure. The ortho-para conversion rate while heating up is plotted in Fig. 4(b).

There have been reported several ESR studies of paramagnetic centers in a-SiO_2 with high-surface area, created by fracture, plasma enhancement, or γ irradiation. The situation is less complicated in the case of defects created by fracture studied by Hochstrasser and Antonini[15] and those created by plasma enhancement studied by Meyer *et al.*[5] and W. Wintruff *et al.*,[6] because the number of the paramagnetic centers in the bulk region may be neglected. These authors observed the change of ESR spectra on introducing the gases and concluded that the observed paramagnetic centers are located on the surfaces.

When paramagnetic centers are produced by γ irradiation, the situation is very complex and a variety of results and interpretations are reported.[7–14] In these studies, changes in ESR spectra after introduction of gases are usually considered to be the evidence for the localization of the paramagnetic centers on the surfaces. However, a variety of additional processes, adsorption of gases on diamagnetic centers, formation of paramagnetic species, diffusion of gases, and the reaction in the subsurface layer make it difficult to study surface paramagnetic centers separately.

Since the Ps atoms in the intergrain space interact with the surface directly and exclusively, it is unambiguous that the centers they interact with are on the surfaces. The kinetic energy of the Ps atoms determined initially by the negative of the Ps work function (estimated to be -0.8 eV for silica aerogel[26,27]) reaches almost the thermal value within ~ 10 ns.[28] All the p-Ps atoms annihilate in this time range. After that, only the o-Ps atoms remain repeating collisions against a-SiO_2 grains till they annihilate into γ rays. Their penetration depth is very small.[29] It is thus certain that the observed ortho-para conversion is due to spin-unpaired electrons on the very surfaces of the a-SiO_2 grains.

Although the structure of the surface paramagnetic center observed here cannot be determined by positronium measurement alone, the most probable center is NBOHC (Si-O $\cdot$). The surfaces of silica grains are usually covered by OH species. Thus NBOHC can be formed on the surfaces through the reaction[8,12,30,31]

$$\text{Si-OH}\rightarrow \text{Si-O}\,\cdot + \text{H}\,\cdot . \qquad (1)$$

The mobility of the atomic hydrogen is high even at low temperatures. The reverse reaction of Eq. (1) and the following reactions:

$$2\text{H}\,\cdot \rightarrow \text{H}_2, \quad \text{Si-O}\,\cdot + \text{H}_2 \rightarrow \text{Si-OH} + \text{H}\,\cdot \qquad (2)$$

are observed above ~ 100 K.[8,12,30,31] The coincidence of the annealing temperature with our data [Fig. 4(b)] supports this interpretation. Atomic hydrogen is also paramagnetic, but it is not likely to be localized on the surfaces because of its high mobility.

Dauwe and Mbungu-Tsumbu[20] attribute the surface paramagnetic centers in powered Al_2O_3 to Al atoms which diffuse to and accumulate on the surfaces. In the case of a-SiO_2, the corresponding process is knockon displacement followed by the diffusion of a Si atom to the surface and the formation of an E' center (-Si $\cdot$). This process is not, however, likely to be the cause of the surface paramagnetic centers observed here. It is known that the electronic effect, such as excitation and band abscission, is a main factor of formation of paramagnetic centers in bulk a-SiO$_2$. Furthermore, the observed surface paramagnetic center is unstable at room temperature. This is not consistent with the results of Hochstrasser and Antonini[15] that show stable surface E' centers are formed by crushing at room temperature.

In conclusion, we measured ACAR, positron-lifetime, and Doppler-broadening spectra in silica aerogel at various temperatures below 295 K. The positron-lifetime and Doppler-broadening spectra were measured changing the irradiation condition. We found, by observing the spin conversion of Ps, that paramagnetic centers are induced on the first layer of the surfaces of the a-SiO$_2$ grains when they are irradiated sufficiently at low temperatures. These centers are unstable above 150 K and are likely due to nonbridging oxygen-hole center.

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