PHYSICAL REVIEW B VOLUME 35, NUMBER 2 15 JANUARY 1987-I

Oxygen-diffusion kinetics in densified, amorphous SiO_2

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(Received 8 October 1986)

The dynamics of intrinsic defect creation and annealing have been studied in dry, amorphous SiO_2 subjected to a hydrostatic pressure of 5 GPa at 600 °C. The compaction produced does not in itself result in the creation of significant numbers of paramagnetic defects but it does greatly enhance their creation efficiency when samples are subjected to subsequent γ irradiation. Annealing after irradiation results in a growth in the number of peroxy-radical defects and a correlated decrease in the number of oxygen-vacancy defects. The higher temperatures needed for annealing with respect to the case of undensified, amorphous SiO_2 lead us to conclude that interstitial molecular-oxygen diffusion is severely inhibited in the compacted samples.

It is well known that under certain conditions of temperature and pressure a densification of amorphous silica (a-SiO_2) occurs which remains when the compressed sample is returned to ambiant conditions. Such a permanent densification may be induced at room temperature using hydrostatic pressures ~ 17 GPa,[1] whereas at higher temperatures the required pressures are lower.[2] For example, a pressure of 4 GPa at 600 °C is adequate to produce a densification $\sim 16\%$. The relative ease with which a-SiO_2 can be induced to densify may be related to the flexibility of the structure resulting from the rather small variations in bond energy required to cause significant Si—O—Si bond angle variations[3] (0.17 eV/molecule for a $\pm 25°$ angle variation about the mean of 144°). Alternatively, the densification might arise through the creation of large numbers of broken bond defects.[1] Detailed physical information on the densified material is, however, lacking. On a macroscopic scale, measurements[2] indicate that the refractive index and density of a-SiO_2 follow the simple Lorentz-Lorenz relationship[4] with a curve which fits almost identically that found[2] for crystalline SiO_2 polymorphs. Although macroscopic, this result suggests that for the greater part,[5] refractive index variations arise from volume changes in the network rather than bond-length—induced charge transfer, etc.

In interpreting the Brillouin frequency shift and Raman spectra of room-temperature compacted a-SiO_2, it has been suggested[1] that the compaction may proceed either by a process of collapse of large network ring structures[6] into smaller ones, or by a process of bond breaking leaving nonbridging oxygen defects.[7] In uncompacted a-SiO_2 three intrinsic paramagnetic structural defects have been identified and well characterized both experimentally[8] and theoretically.[9] They are the oxygen vacancy or E_1' center ($\equiv Si^{+}\,{}^{\cdot}Si\equiv$), the nonbridging oxygen-hole center (NBOHC) ($\equiv$Si—O$^{\cdot}$) and the peroxy radical ($\equiv$Si—O—O$^{\cdot}$), the latter being suggested[10] to be the natural partner of the oxygen vacancy center. The creation efficiency, annealing dynamics, and symmetry of these defects have revealed significant information on the basic SiO_4 tetrahedron and the environment around the defect and upon various physical properties of the network such as gaseous diffusion.[11,12] The present work presents the results of a study of these same defects in compacted a-SiO_2, undertaken with the aim of exploring the microscopic properties of the compressed phase.

Samples of Heraeus Suprasil W1 (dry silica, <10 ppm OH) were cut from commercial 4-mm diam rod in 6-mm lengths and compressed in a belt apparatus[13] to a pressure of 5 GPa at a temperature of 600 °C for 20 min. Al_2O_3 was used as the pressure-transmitting medium. After crushing, samples were irradiated with 115 Mrad of ^{60}Co γ rays at room temperature. A series of compacted samples were then given 10-min anneals in flowing Ar gas at temperatures up to 525 °C. Uncompacted bulk samples were given identical irradiation and annealing treatment for comparative purposes. Electron-spin resonance (ESR) measurements were carried out using a Bruker ER 200 D spectrometer operating in the region of 9.23 GHz. Oxygen-vacancy centers were studied at room temperature while peroxy-radical and NBOHC resonances were studied at -120 °C. All measurements were made using nonsaturating microwave power levels and nondistorting field modulation levels.

The conditions of time, temperature, and pressure used to compress our samples lead[2] to a densification $\sim 16\%$. In "as-compacted" samples (nonirradiated) we found no evidence for the production of measurable numbers of any of the three intrinsic, paramagnetic defects. After subsequent irradiation with 115 Mrad of ^{60}Co γ rays, defects

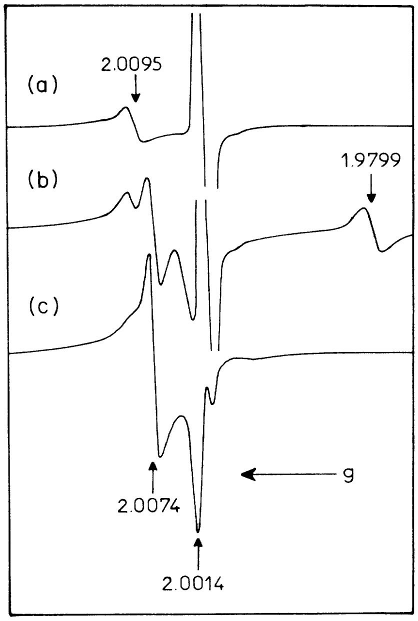

FIG. 1. Observed experimental ESR spectra at $-120\,^{\circ}\mathrm{C}$ in samples of Suprasil W1 after irradiation with 115 Mrads of ^{60}Co γ rays: (a) sample compacted at 600 °C under a pressure of 5 GPa, (b) uncompacted sample, and (c) the compacted sample shown in (a) having been annealed for 10 min at 525 °C in Ar post irradiation. The resonance at $g = 1.9799$ is due to a Cr in MgO marker. The large resonance shown off scale in (a) and (b) is the E'_1 resonance.

TABLE I. Relative efficiency of creation of the three intrinsic paramagnetic defects by ^{60}Co γ rays in dry Suprasil W1.

Defect	Ratio of concentrations (compacted to uncompacted)
E'_1	110
NBOHC	>17
Peroxy radical	$>43^{a}$

^{a}After irradiation plus 10 min at 525 °C.

were revealed as demonstrated in the typical resonance spectrum taken at $-120\,^{\circ}\mathrm{C}$ and shown in Figs. 1(a) and 1(b). The intense central resonance is the E'_1 vacancy center while the curve to the left centered upon a g factor ~ 2.0095 is part of the NBOHC resonance[8] [Fig. 1(a)], the remaining downward peak is masked by the large E'_1 resonance. Figure 1(b) shows the result obtained at $-120\,^{\circ}\mathrm{C}$ for an identically irradiated, uncompacted sample of Suprasil W1. Noticeably, the peaks associated with the peroxy radical resonance ($g = 2.0074$ and 2.0014) now present, were absent in the irradiated, compacted sample [Fig. 1(a)]. Finally, in Fig. 1(c) we show the resonance spectrum for an irradiated, compacted sample after subsequent anneal at 525 °C in flowing Ar gas for 10 min. We note that the E'_1 resonance has almost completely disappeared and that the previously absent peroxy resonance has now appeared.

Prior to the annealing studies we estimated the comparative yields of the different defects in dry a-SiO$_2$ as a function of compaction. These results are shown in Table I. For the E'_1 resonance, minor differences in line shape were found between the compacted and uncompacted states so that numerical integration was performed in order to extract reasonably accurate defect density ratios. Analysis of the line shapes using computer fitting suggested that the differences arose from small variations in the linewidth and g factor distribution widths;[11] they disappeared upon annealing suggesting that they were induced by strain and defect density effects. The differences were not consistent with those expected if other forms of the basic E'_1 defect were present. For the other resonances (peroxy and NBOHC) the either incomplete nature of the observed spectrum [e.g., Fig. 1(a)] or the superposition of spectra lead to inherent inaccuracy in determining the defect density ratios. In all cases, however, we note that the three defects are much more readily created by radiation in the compacted a-SiO$_2$ than in the uncompacted. Most striking is the result for the oxygen vacancy center where the process is 2 orders of magnitude more efficient. Note that the peroxy comparison required studies on annealed samples since this resonance was not observed in the irradiated "as-compacted" case. The figure quoted for the ratio of compacted to uncompacted defect densities was therefore that obtained after annealing.

The annealing dynamics of E'_1 centers and peroxy radicals in irradiated compacted Suprasil W1 were measured following 10-min anneals; the results are presented in Figs. 2(a) and 2(b). The solid curve in Fig. 2(a) shows the annealing of E'_1 defects in irradiated, uncompacted Suprasil W1 while the solid triangles show the results obtained for the compacted samples. For simplicity we have normalized our signal amplitudes to unity (corrected for line shape variation) corresponding to 4.7×10^{17} E'_1 defects per cm^3 for the compacted samples and 4.3×10^{15} E'_1 defects per cm^3 for uncompacted samples. The precision in the absolute value determination is $\lesssim 50\%$. The peroxy-radical signal amplitude in compacted Suprasil W1 is shown by the solid circles in Figs. 2(b) while uncompacted results, taken from Ref. 14, are shown by the solid stars.

It has been suggested[11] that peroxy radicals might form by the trapping of diffusing, molecular oxygen at E'_1 centers, thereby annihilating them. Results previously obtained in uncompacted Suprasil W1 support this tendency, but we believe that the results on compacted Suprasil W1 shown in Figs. 2(a) and 2(b) confirm this hypothesis beyond reasonable doubt. Furthermore, when one estimates the peroxy-radial density at saturation in the compacted samples one obtains the figure of 3.3×10^{17} peroxy radicals per cm^3 as compared to an E'_1 density prior to annealing of 4.7×10^{17} per cm^3. Given the anticipated inaccuracy in absolute-value determination previously mentioned, we consider the agreement between these two numbers to be better than satisfactory. The annealing re-

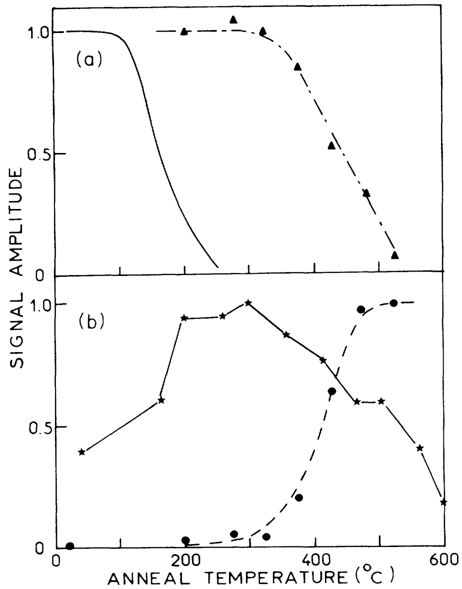

FIG. 2. Results of isochronal annealing in compacted and uncompacted a-SiO$_2$ samples: (a) solid line, E_1' defects in uncompacted Suprasil W1; solid triangles, E_1' defects in Suprasil W1 compacted by 16% and (b) sold stars peroxy-radical defects in uncompacted Suprasil W1 (Ref. 14); solid circles, peroxy-radical defects in Suprasil W1 compacted by 16%.

sults [Figs. 2(a) and 2(b)] and the results for the initial defect creation by room-temperature irriadation then confirm the hypothesis that peroxy-radical defects form by the transformation of E_1' defects by the trapping of diffusing O$_2$. The results further suggest, by comparison with the behavior observed in uncompacted Suprasil W1, that the diffusion of O$_2$ in compacted silica is severely inhibited as compared to the uncompacted case. Within the framework of the Waite model[15] for correlated defect or interstitial annealing one can demonstrate that the results shown in Fig. 2(a) suggest that the diffusion coefficient of O$_2$ in our compacted silica is between 10^7 and 10^9 times smaller at 450 °C than in uncompacted silica. Assuming a constant diffusion coefficient preexponential factor this suggests that the activation energy in compacted silica must increase from the uncompacted value[16] of 1.17 eV to $2\text{ eV} < E_A < 2.4\text{ eV}$. Such a reduction in diffusion related to compaction is consistent with a reduction found in crystalline polymorphs. In α quartz,[17] whose density is approximately that of our compacted samples, the diffusion coefficients at 600 °C is between 10^4 and 10^7 times less than that in uncompacted a-SiO$_2$.

The restriction in the ease with which gas molecules diffuse through compacted silica is consistent with the picture of a network composed of a distribution of interstitial sizes,[18] themselves resulting from a multiple ring structure in the amorphous lattice.[6,19] Compression of the structure should lead to a reduced "pore" size (via reduction in the mean Si—O—Si bond angle) which would certainly account for a decreased diffusion. Such a modification may indeed have been confirmed by recent Raman spectroscopy studies[20] on a-SiO$_2$ at high pressure which have been interpreted as suggesting that both the width of the bond angle distribution and its mean value decrease under applied pressure.

The present results clearly demonstrate the validity of the anticipated E_1'—peroxy-radical interelationship and underline the important role of oxygen diffusion in the creation of peroxy radicals even at room temperature. These results undermine the idea that the peroxy radicals originate from intrinsic peroxyl bridges (Si—O—O—Si) which open under irradiation. The effect of limited O$_2$ diffusion in densified a-SiO$_2$ on the creation of peroxy radicals may hold the key to the lack of observation of this defect in crystalline quartz, and this suggests that a search for the defect in damaged quartz after high-temperature annealing might be instructive.

Finally, it should be added that the observation of enhanced radiation sensitivity in compacted a-SiO$_2$ may be relevant in the area of device technology. Various authors[21,22] have identified the presence of radiation-induced oxygen-vacancy centers in the Si-SiO$_2$ interfacial region, and their importance in the degradation of devices has been underlined.[22] The possibility that oxides of Si may grow with large residual stress[23] indicates that they may be significantly more radiation sensitive than unstressed forms so that care must be exercised to minimize the appearance of possible sources of stress.

ACKNOWLEDGMENT

The Laboratoire de Cristallographie is associe au Centre National de la Recherche Scientifique.

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