Si—O bond-length modification in pressure-densified amorphous SiO2

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(Received 2 April 1987)

The hyperfine splitting of the oxygen-vacancy center resonance in amorphous SiO2 has been measured as a function of density in samples densified under pressure at high temperature. Densification of ~24% is found to produce an increase in the isotropic hyperfine coupling constant of 11.5%, which is interpreted as resulting from a reduction in the mean O—Si—O tetrahedral bond angle of the three Si—O backbonds from 108.3° to 107.2°. This reduction corresponds to an increase in mean Si—O bond length from 1.618 to 1.623 Å and to a reduction in the mean Si—O—Si bond angle associated with the defect back bonds and adjacent SiO4 tetrahedra of 5.1°. This reduction is in excellent agreement with that estimated from x-ray scattering and nuclear magnetic resonance studies on the densified SiO2 network.

Among the diverse range of amorphous materials known to solid-state physics, amorphous SiO2 remains undeniably one of the most interesting of the species. Apart from its interest concerning a vast range of technological applications, the fundamental physics of the structure of amorphous SiO2 in its normal and densified states remains somewhat of a mystery.[1-3] The major problem in elucidating this mystery is in finding an appropriate experimental technique which will probe the short-range structure of the amorphous network. Such methods as x-ray scattering[4,5] and nuclear magnetic resonance[6,7] have been used, but fail to give detailed insight into the structure and the subtle changes which may occur under, say, densification. In particular, although densification is found to result in a reduction in the mean Si—O—Si bridging bond angle between adjacent SiO4 tetrahedra, we do not know how this reduction in angle comes about in terms of modification of the internal structure of the SiO2. We do know that the bond energy per molecule is a relatively insensitive function[8,9] of the bond angle in the range 120° to 180° and that, consequently, densification via bond-angle reduction should not be too costly energywise. How the internal ring structure accommodates angular variation, whether by puckering (presumably elastic) or subdivision of large rings into smaller ones (pseudoplastic), remains to be demonstrated.

Since the different vibrations of the SiO2 network are intimately related to the bond angles and elastic constants, considerable effort has been expended in understanding the origin[1-3,10-12] of the different peaks observed in the Raman spectra of undensified and densified amorphous SiO2. For example, peaks at 495 and 606 cm^{-1}, originally thought to be due to defects, have now been assigned to puckered four-member and planar three-member rings, respectively.[13] It has been remarked that under pressure the Si-O stretching modes at 1060 and 1200 cm^{-1} shift to lower energy[8,10,14] and that this is consistent with a reduction in the mean Si—O—Si bond angle. The Raman frequency for these modes is determined from the central-force model to be[15]

$$\omega^2 = \frac{\alpha}{m_O}(1-\cos\theta) + \frac{4}{3}\frac{\alpha}{m_{Si}}, \quad (1)$$

where α is a central-force constant, θ is the Si—O—Si bond angle, and m_O and m_{Si} the masses of the oxygen and silicon atoms, respectively. Differentiation yields

$$\frac{d\omega}{\omega} = \frac{\frac{1}{2}\sin\theta d\theta}{(1-\cos\theta)+(4m_O/3m_{Si})} + \frac{d\alpha}{2\alpha}. \quad (2)$$

If the densification is carried out at room temperature, then for a reversible densification[16] of ~22% one measures[3] a fractional shift of −0.0076 in the nominal 1060-cm^{-1} peak. Under irreversible conditions[17] the same densification produces a shift of 0.039. Insertion of these values into Eq. (2) and neglecting terms in $d\alpha$ leads to a value of $d\theta$ in the correct sense but more than an order of magnitude smaller than that found by x-ray scattering[5] or nuclear magnetic resonance.[6] One is lead to the conclusion that large competing changes must be occurring in the force constants and this appears to be born out experimentally.[16,18] Consequently, and unfortunately, the Raman approach would appear to be unsuitable for quantitative analysis of structural variations in amorphous SiO2.

In a recent publication[19] we endeavored to examine pressure-induced structural variations in amorphous SiO2 through an electron-spin-resonance study of intrinsic defects revealed by γ irradiation after the process of densification. However, since the spins are highly localized on the defects such as the oxygen-vacancy (E'_1) center[20] a straightforward study revealed no clear information on the environment around the defect, but it did yield information on annealing kinetics and hence molecular diffusion in densified SiO2. In the present Rapid Communication we report the results of a study of the hyperfine splitting of the E'_1 electron-spin-resonance spectrum produced at defects involving the weakly abundant

^{29}Si (4.7 at.%) nuclei. We demonstrate that through measurement of the hyperfine parameters, one can gain some insight into microstructural changes induced by densification.

Samples used in the experiments were in the form of cylinders cut initially from commercially available Suprasil I and Suprasil W1 silica rod (Heraeus GmbH). Densification of the samples was performed as previously described,[21] the density being ascertained by the flotation method. After densification, samples were γ irradiated at room temperature using a ^{60}Co source at a rate of 0.8 Mrad/h up to a total accumulated dose of 76 Mrad. Electron-spin-resonance measurements were carried out at room temperature using an X-band Bruker spectrometer in the first- and second-harmonic detection modes.[22] In the latter case, the possibility of using high microwave power levels ($\sim$5 mW) enabled us to obtain satisfactory

signal-to-noise ratios with a single magnetic field sweep. The experimental second-harmonic spectra observed in five samples of Suprasil I having different densities are shown in Fig. 1. We verified by studies on Suprasil W1 samples that for a given densification, the spectrum did not depend upon the type of Suprasil (within the range of experimental error). It was also verified that the separation in field of the maxima of the two second-harmonic hyperfine lines was indeed equal to the separation in field of the hyperfine lines observed in the first-harmonic detection mode. In Fig. 2 we plot the measured fractional increase in the separation of the hyperfine constant with respect to the undensified value (410 G) as a function of densification; a result for a sample of Suprasil W1 is included to demonstrate the insensitivity to silica type.

The magnetic field for resonance in the presence of a hyperfine interaction is calculated from the formula

$$H(m_I,\theta)=\frac{h\nu_0}{g\beta}\left[\frac{K}{g\beta}\right]m_I-\frac{A_\perp^2}{4g\beta h\nu_0}\left[\frac{A_\parallel^2+K^2}{K^2}\right][I(I+1)-m_I^2]-(2g\beta h\nu_0)^{-1}\left[\frac{A_\parallel^2-A_\perp^2}{K}\right]^2\left[\frac{g_\parallel g_\perp}{g^2}\right]^2\sin^2\theta\cos^2\theta m_I^2 ,$$

$$(3)$$

with

$$g^2=g_\parallel^2\cos^2\theta+g_\perp^2\sin^2\theta ,$$

$$K^2=(A_\parallel^2 g_\parallel^2\cos^2\theta+A_\perp^2 g_\perp^2\sin^2\theta)/g^2 ;$$

θ is the angle between the applied magnetic field and the principal axes of the SiO$_4$ tetrahedron and ν_0 is the resonance frequency. The parallel and perpendicular hyperfine constants $A_\parallel$ and $A_\perp$ are related to the isotropic (A_{iso}) and anisotropic (A_{anis}) parts of the hyperfine constant through $A_{anis}=(A_\parallel-A_\perp)/3$ and $A_{iso}=(A_\parallel+2A_\perp)/3$. Following other authors[20,23] we assume that

the 3s plus 3p electron spin density in the defect orbital is constant and equal to 0.85, so that if the wave function is written

$$\psi=a_s|3s\rangle+a_p|3p\rangle+a_0|\text{other}\rangle ,$$

then $a_s^2+a_p^2=0.85$. Assuming the hyperfine field contributions from the 3s plus 3p characters of the defect electron are given by $a_s^2 A_s$ and $a_p^2 A_p$, we may write

$$\frac{A_{anis}}{A_p}+\frac{A_{iso}}{A_s}=0.85 ,$$

$$(4)$$

where A_p and A_s are the hyperfine coupling constants for the Si 3p and 3s orbital electrons. We approximate[23] $A_s=1710$ G and $A_p=34$ G. Assuming a Gaussian distri-
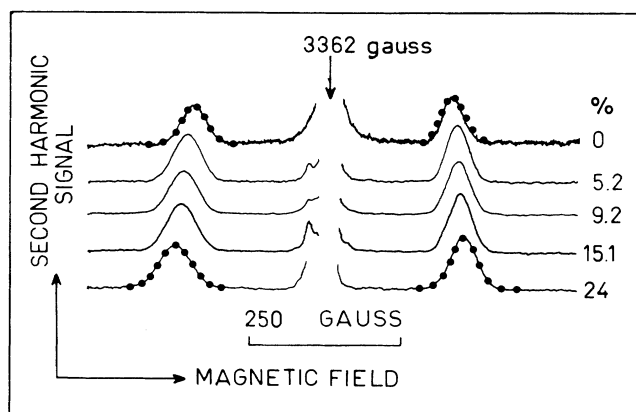

FIG. 1. Experimentally observed electron-spin-resonance spectra of oxygen vacancy (E_1') centers in densified Suprasil I samples subjected to 76 Mrad of ^{60}Co γ radiation after densification. The second harmonic detection mode was used. The central peak, largely offscale, corresponds to the E_1' spectrum with no hyperfine splitting, and the smaller peaks are the hyperfine lines due to defects having ^{29}Si nuclei. The dots on the 0% and 24% curves are the fits obtained as discussed in the text.
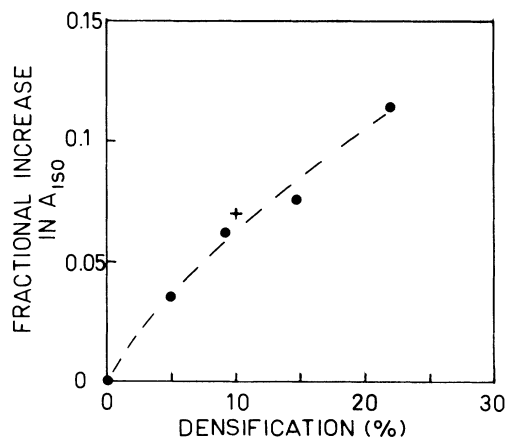

FIG. 2. Fractional increase of the isotropic hyperfine constant extracted from fits to the experimental hyperfine spectra shown in Fig. 1 as a function of densification of the sample. The increase is referred to the value of 410 G found in undensified Suprasil I. The cross refers to a Suprasil W1 sample and is included to demonstrate that the type of silica does not play a role.

bution in A_{iso} together with Eq. (4) and averaging over all possible field orientations (θ), we have calculated best fit theoretical line shapes to the experimental results shown in Fig. 1. Values for $g_{\parallel}$ and $g_{\perp}$ were taken from our previous line-shape fits[19] to E_1' results in the absence of hyperfine splitting (^{28}Si nuclei). For simplicity we assumed $g_{\perp} = (g_2 + g_3)/2$, a minor approximation given the width of the hyperfine lines (Fig. 1) as compared to the difference in g_2 and g_3 factors. Fits obtained to undensified and 24%-densified Suprasil I are shown by the dots in Fig. 1. Appropriate values of A_{iso} were 410 G (31 G) for the undensified sample and 457 G (85 G) for the 24%-densified sample; the values in parentheses are the full widths of the Gaussian distribution at 0.606 of the maximum height. The A_{iso} distributions corresponding to the two cases cited are shown in Fig. 3(a). From the A_{iso} distribution it is possible to calculate[23] the distribution of defect tetrahedral bond angles, ρ (the angle between the lone electron orbital and one of the Si—O backbonds in the defect tetrahedron). Assuming[24]

$$\tan\rho = -\left[2\left(1 + \frac{A_{anis}}{A_p}\frac{A_s}{A_{iso}}\right)\right]^{1/2} \quad (5)$$

and using Eq. (4), we obtain the distributions shown in Fig. 3(a). We note that ρ increases by approximately $1.1°$ due to the densification of 24%. We also note that

even in the undensified case, ρ is already increased by $\sim 1°$ with respect to the ideal tetrahedral angle ($109.47°$).

From the analysis of a very large number of silica polymorphs it has been suggested[9] that the length of the Si—O bond is related to the average value of the three common O—Si—O backbonds in the SiO_4 tetrahedron [$\angle$(O—Si—O)] through the linear relationship

$$d(\text{Si—O}) = 2.17 - 0.0051[\angle(\text{O—Si—O})] . \quad (6)$$

We convert the distribution in ρ into a distribution in d(O—Si—O) and then use this equation to deduce the distribution of d(Si—O) lengths of the Si—O backbonds associated with the defect site. The distributions obtained are shown in Fig. 3(b). From these results we observe that densification of the silica by 24% has produced an *increase* in the length of the backbonds associated with the oxygen vacancy defect of the order of 0.36%. One can go a little further with this type of reasoning bearing in mind that it has been demonstrated[25] that there appears to be a solid relationship between variations in d(Si—O) and the bridging Si—O—Si bond angle. From a study using 161 data sets it has been shown[25] that to a very good approximation

$$\log_{10}[2d(\text{Si—O})] = 0.504$$
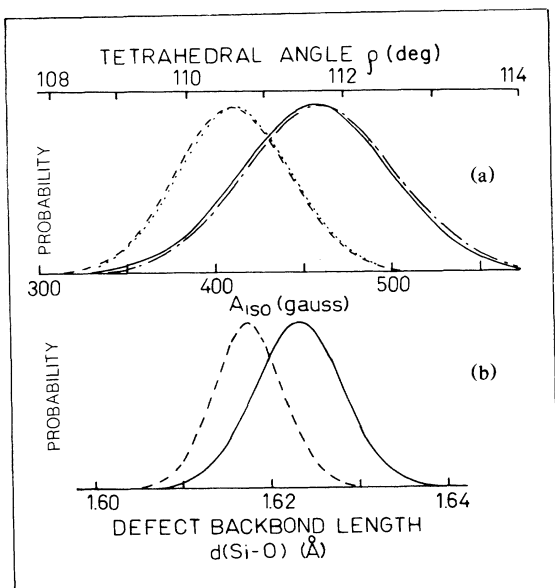$$-0.212\log_{10}\sin\left[\frac{\angle(\text{Si—O—Si})}{2}\right] .$$

FIG. 3. (a) The probability distribution of isotropic hyperfine constants (A_{iso}) in undensified (dashed line) and 24%-densified (solid line) samples as deduced from the experimental spectra using Eq. (3). The dotted line, barely visible from the dashed one, and the dot-dashed line are the distributions of tetrahedral bond angles, ρ, deduced from the A_{iso} distribution using Eq. (5). (b) The probability distribution of defect Si—O backbond lengths [d(Si—O)] obtained from the bond angle distribution together with Eq. (6).

Using values of d(Si—O) obtained from Eq. (6) for the defect backbonds, one deduces that in the undensified state, the backbonds are linked to other SiO_4 tetrahedra with a mean bridging angle of $139.6°$ (as opposed to $144°$ in undensified silica ignoring the role of the defect). In 24%-densified SiO_2 we find that the mean backbond bridging angle decreases to $134.5°$, suggesting that densification has produced, at the defect site, a reduction in mean bridging bond angle of the defect backbonds of $5.1°$. This figure is essentially identical to that found in x-ray scattering[15] and nuclear-magnetic-resonance[6] studies on 16%-densified silica. We underline the fact that one might expect a larger variation in 24%-densified material but, as shown in Fig. 2, the hyperfine splitting does not increase linearly with densification, so the similarity of the two figures is not unreasonable, particularly given the assumptions made.

Contrary to initial expectation, it would appear that the hyperfine data from electron-spin-resonance studies on densified silica do reveal some information on the variations produced in the microstructure. Bearing in mind the various approximations made throughout this work it seems that densification produces a reduction in bridging Si—O—Si bond angle and a coincident increase, albeit small, in the Si—O bond length. This increase in bond length, at a defect site, results in a decrease in tetrahedral O—Si—O bond angle on the defect. Variation of this angle induces a change in the relative $3s$ and $3p$ character density of the localized electron on the defect site. It is

this variation that the hyperfine splitting measurement has sensed.

The results of the studies presented demonstrate that there is much more direct sensitivity of the hyperfine spectrum to environmental changes than in the unsplit spectrum. Raman studies on samples subjected to equivalent densification but under reversible or irreversible regimes[3] clearly suggest significant differences between the structural variations induced. It would be interesting to pursue these points using spin resonance methods if the non-negligible problem of *in situ* high-pressure measurement could be resolved.

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