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Reflection spectra of dense amorphous SiO_2 in the vacuum-uv region

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Vacuum ultraviolet (vuv) reflection spectra have been measured from amorphous SiO_2(a-SiO_2) plates of varying densities. Two bands were observed at 10.3 and 11.4 eV in the vuv reflection spectra for as-received a-SiO_2. Upon densifying the a-SiO_2 with a multianvil-type high-pressure apparatus, both the strong band at 10.3 eV and the weaker shoulder at 11.4 eV were found to shift toward lower energies and to broaden. The shift of these bands during densification can be explained either by a unification of the extended point-dipole theory and harmonic oscillator model, or by the relationship between the band-gap energy and Si-O bond length. The broadening of the bands during densification, and thus the Si-O-Si bond-angle decrease, may be due to either the distortion of SiO_4 tetrahedra or a widening of the distribution of rotational arrangements between connected SiO_4 tetrahedra causing a distortion of the electronic structure. A shift of the band at 10.3 eV toward higher energy is observed upon cooling in undensified a-SiO_2, but this shift gradually disappears with increasing densification. Although the reason for the temperature dependence of band position for the undensified a-SiO_2 is not yet clear, it appears that the disappearance of this dependence with densification is related to an increase of the structural randomness of the glass.

I. INTRODUCTION

Amorphous silica (a-SiO_2) attracts many researchers who wish to understand the structure and properties of amorphous materials because of its simple compositions and its many polymorphous crystal phases compared with the amorphous state. Densification of the a-SiO_2 (Refs. 1–3) is an interesting phenomenon for understanding the amorphous structure. The structure of dense a-SiO_2 has been studied by infrared (ir) absorption and/or reflection,[4–8] Raman-scattering[7–12] spectra, and x-ray and/or neutron diffraction[13–16] measurements. In these studies, it was interpreted that the densification of the a-SiO_2 is due to a decrease in average Si–O–Si bond angle between connecting SiO_4 tetrahedra,[4–11,17–19] which form a random network of the a-SiO_2, or due to decreasing the mean number of members consisted of ring structure.[12,17,18] These suggestions of structural reformation are consistent with theoretical studies by molecular dynamics (MD) simulation.[16,20] The electronic structure of the undensified a-SiO_2 or crystalline SiO_2 was also investigated by reflectivity measurements in the vacuum ultraviolet (vuv) (Refs. 21–23) region, by photoluminescence and photoconductivity,[24,25] and by several simulation methods.[26–29] The two bands at 10.3 and 11.4 eV in the vuv reflection spectra have been attributed to the interband transition between the oxygen $2p$ and oxygen $3s$ orbitals from calculations of band structure.[26,28] These bands in the vuv spectra have also been assigned to excitonic resonances by using the tight-binding-method calculations.[27] This second assignment was supported by the shift of the band at 10.3 eV toward higher energy upon cooling[23] and by the measurements of photoconductivity at a photon energy below the peak position of the 10.3-eV band.[25] Little information on the influence of densification on the electronic structure, however, has been reported. The dependence of π bonding between Si and O and bond strain on density were discussed in terms of the molar polarizability of the Si—O bond using information derived from refractive index measurements.[30] Band structures of polymorphic crystalline SiO_2 such as quartz, cristbalite, coesite, etc., have been thoroughly investigated, and it was shown that the band-gap energy did not depend on the Si–O–Si bond angle but on the Si—O bond length among the series of the polymorphic crystals.[28] Recently Kitamura *et al.*[31] reported the dependence of the wavelength dispersion of refractive index on density. This dependence was explained by a model, which unifies the extended point dipole theory[32,33] and harmonic oscillator model. In this model, it is suggested that the two bands in the vuv region will shift toward lower energy with increasing density. This suggestion may be easily confirmed by measuring reflection spectra in the vuv region for densified and undensified a-SiO_2 specimens.

In this paper, synthetic a-SiO_2 has been densified by a multianvil-type high-pressure apparatus. Reflection spectra of the dense a-SiO_2 in the vuv region has been measured by using a synchrotron radiation source. The dependencies of the widths and positions of the bands at 10.3 and 11.4 on density are discussed in terms of the microscopic structure of the glass.

II. EXPERIMENT

A fused silica synthesized directly by hydrogen-oxygen flame hydrolysis was used as the starting material. The OH content of this glass was about 1200 wt. ppm, which was estimated from the ir absorption of X-OH (X is Si or H) at 3650 cm^{-1}.[34] The samples used were in the form of

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small cylindrical plates 6 mm in diameter and 2 mm in length. The densification was carried out with a 6–8 multianvil-type high-pressure apparatus[35] by using the high-pressure cell as shown in Fig. 1(a). The glass sample was covered by a platinum foil and then embedded in a container of boron nitride. Graphite was used as the heater. The temperature was measured by a chromel-alumel thermocouple was in contact with the sample as shown in Fig. 1(b). The samples were gradually submitted to high pressures of 2 and 6 GPa at room temperature. Then, they were heated up to 700 °C (2 GPa) and 500 °C (6 GPa) within 10 min and were kept at these temperatures for 1 min. After these processes, the temperatures were let down to below 100 °C within 1 min, then the pressures were released. The densities of the dense and undensified a-SiO_2 were measured by Archimedes' method with distilled water. To measure the optical properties of the glass plates, both surfaces were polished to an optical grade. The vacuum ultraviolet (vuv) reflectance spectra were measured at the beam line BL7B of the UVSOR facility in the Institute for Molecular Science in Okazaki, Japan. A lithium fluoride single crystal was used for the relative calibration of photon energy. The measurement was performed at 300 and 105 K in the 8–12 eV region with a resolution of about 0.03 eV.

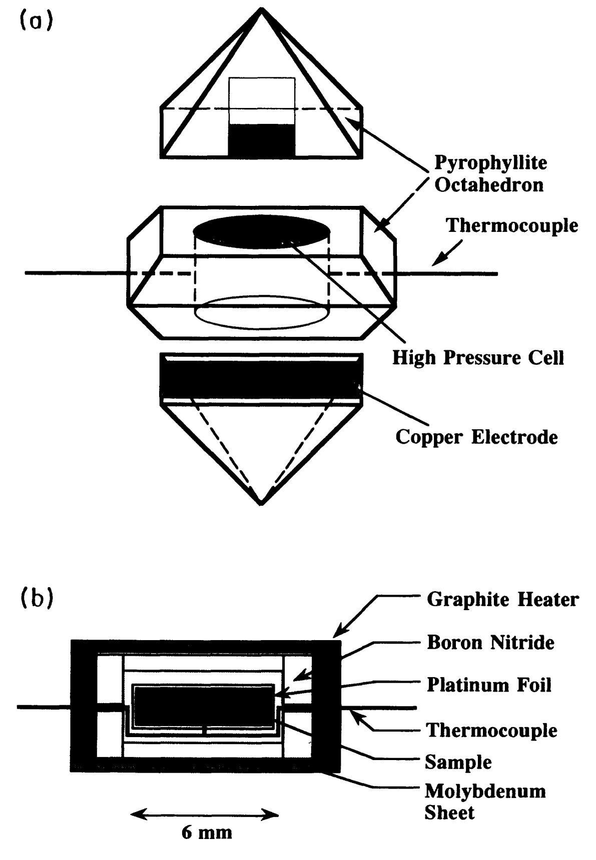

FIG. 1. Sample assembly within (a) the pyrophyllite octahedron and (b) the high-pressure cell for a 6–8-type high-pressure apparatus.

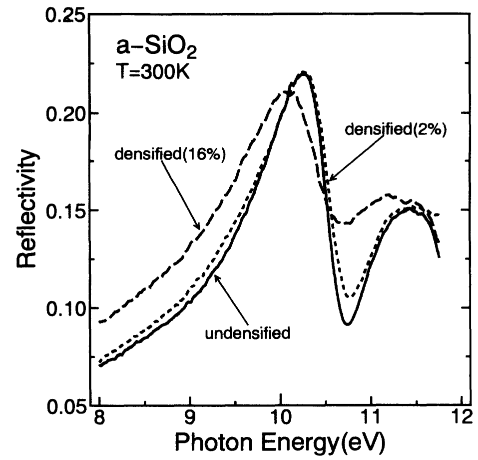

FIG. 2. Reflectivity at 300 K in the vacuum ultraviolet region of both undensified and densified (2% and 16%) a-SiO_2.

III. RESULTS

The density of the glass increased by 2% and 16% after the treatment under the pressures of 2 GPa and 6 GPa, respectively. The reflection spectra of one undensified and the two densified a-SiO_2 samples at 300 K are shown in Fig. 2. A strong reflection band at 10.3 eV and a weak band at 11.4 eV are observed. Line widths of the both bands broaden with increasing density. The peak positions of the strong and the weak bands shift toward lower energy by about 0.2 eV after the 16% densification. Reflection spectra of these a-SiO_2 at 105 K are shown by dotted lines in Fig. 3. The peak position of the strong band shifted toward higher energy by about 0.05 eV and almost 0 eV in the 2% and 16% densified a-SiO_2 upon cooling, respectively, while it shifted by about

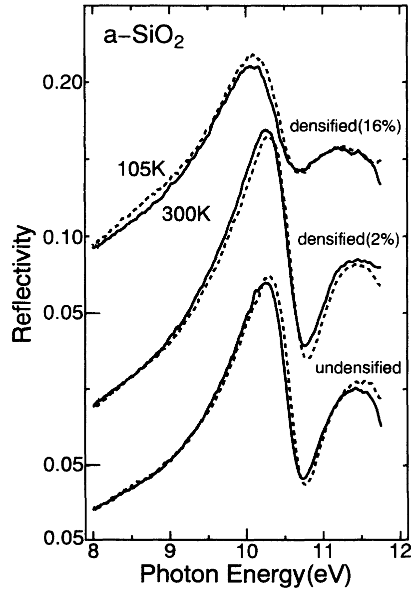

FIG. 3. Shift toward the high-energy side upon cooling for a-SiO_2 with various densities. Solid and broken lines are for spectra at 300 K and 105 K, respectively.

0.1 eV in the undensified one. Thus, the shift upon cooling disappears gradually with increasing density.

IV. DISCUSSION

Three interesting phenomena were found in the vuv reflection spectra of the dense a-SiO_2. They are the shifts of the strong band at 10.3 eV and the weak band at 11.4 eV toward lower energy with increasing density, the broadening of both bands upon densification and the disappearance of the temperature dependence of the peak shift of the strong band with increasing densification.

First, the shift of both bands toward lower energy with increasing density is in agreement with an empirical model proposed by Kitamura *et al.*[31] The model was derived from a unification of the extended point dipole theory and the harmonic oscillator model. This model suggests that the two bands at 10.2 and 16.6 eV shift toward lower energy with increasing density because of an increasing number of oscillators per unit volume. The resonance energy at 10.2 eV in the model corresponds to the strong band in the vuv spectra. The model also predicts the magnitude of the shift. In the case of 16% densification, the lower-energy shift of the band at 10.2 eV estimated from the model is about 0.05 eV. The estimated value is smaller than the value (0.2 eV) of the shift observed in the vuv reflection spectra. This difference between the estimated and observed values is probably due to a change in band-gap energy, since a change in the electronic structure during densification is not taken into account in the model. More accurate approaches were made by Wemple and DiDomenico[36] or by Levine[37] using the dielectric property of materials. Their models would explain the magnitude of the shift, if they are combined with appropriate assumptions expressing the dependence of the dielectric properties on density. However, experimental data of optical properties for densified a-SiO_2 are not sufficient in the vacuum or extreme uv region. Therefore, we have explained the lower-energy shift of the two bands qualitatively by using the model in Ref. 31 as mentioned above. Next, we shall discuss to the origin of the shift in terms of structural change during densification. Narrowing of the mean bond angle between SiO_4 tetrahedra(Si-O-Si) and slight elongation of the mean Si—O bond length on densification were deduced from Raman scattering and ir absorption spectra.[4–12,38] Xu *et al.* pointed out, through the calculations on the series of polymorphs of crystalline SiO_2, that there is no relationship between the Si-O-Si bond angle and the band gap energy, while the band gap widens with a decrease of the Si—O bond length. Since the length increases slightly with increasing density, the band-gap energy decreases to some extent by densification resulting in the shift of the bands toward lower energy in the vuv region.

Secondly, the broadening of the strong and weak bands is probably due to an increase in the randomness of the microscopic structure because the band width of a-SiO_2 in the vuv reflection spectrum is wider than that of crystalline SiO_2. The increase in the randomness is not due to Si-O-Si linkages. This idea is supported by the fact that widths of spectral bands, which are attributed to Si-O-Si vibration modes, show narrowing with the decrease of Si-O-Si bond angle in the ir absorption or Raman scattering spectra.[5,39] In other words, the distribution of the bond angle is narrower in the dense a-SiO_2 than in the undensified one. Additionally, the band-gap energy does not obey the bond angle as mentioned above.[28] One possible origin is in rotational arrangements between connected SiO_4 tetrahedra. The radial distribution functions obtained from x-ray and neutron diffraction measurements[13–15] show broadening of a band attributed to the second-nearest Si-O length with increasing density. The broadening of distribution on the second nearest Si-O length by densification suggests that the rotational arrangement between two SiO_4 tetrahedra have diversity as compared with the undensified state. Another possible reason of the broadening is a distortion of the SiO_4 tetrahedra. Levien, Prewitt, and Weidner[40] observed an increase in distortion of the SiO_4 tetrahedra for single-crystal quartz under high pressures. In a-SiO_2 the tetrahedral distortion should also occur under high pressures. Susman *et al.*[16] and Tse, Klug, and Page[41] predicted a broadening of O-Si-O bond angle distribution of the glass during densification by using MD simulation methods. Since the O—Si—O bond is in the tetrahedron, broadening of the distribution is a decrease of symmetry in the SiO_4 tetrahedra, which should correspond to the broadening of the two bands at 10.3 and 11.4 eV.

Thirdly, the disappearance of the shift toward the higher energy for the strong band upon cooling may be due to the broadening of the band, i.e., distortion of SiO_4 tetrahedron during densification, although the reason for the higher-energy shift for the undensified a-SiO_2 itself is not entirely clear yet. Breaking of symmetry of SiO_4 tetrahedron not only increases ambiguity of the interband transition energy but also probably causes a loss of some selection rules for interband transitions coupled with lattice vibrations. Mott[42] assigned this reflection band at 10.4 eV to Frenkel excitons on oxygen sites in a review article. Laughlin[27] explained that the band is independent of the network as long as the integrity of the basic SiO_4 tetrahedron is preserved. The small limit of the exciton mean free path is consistent with the independence of the Si—O—Si bond angle on the band-gap energy. Thus this excitonic character localizes in the SiO_4 tetrahedron. Therefore, the temperature dependence of this excitonic band will be weakened becuase loss of symmetry of the SiO_4 tetrahedron breaks the $k=0$ selection rule.[23] This might be the reason for the disappearance of temperature dependence in the dense a-SiO_2.

V. CONCLUSIONS

In summary, a-SiO_2 increases its density by reducing the Si-O-Si bond angle between two SiO_4 tetrahedra in the glass network. Increasing the number of dipoles per unit volume and elongation of Si—O bond length by the densification cause the lower energy shift of the reflection bands at 10.3 and 11.4 eV. Either a distortion of the SiO_4 tetrahedron or a diversification of the rotational arrangements between tetrahedra during reduction of the Si—O—Si bond angle can explain the broadening of the two bands. It seems likely that the disappearance of the higher-energy shift upon cooling for the dense a-SiO_2 relates to loss of tetrahedral symmetry, although the reason of the shift for the undensified a-SiO_2 is not clear yet.

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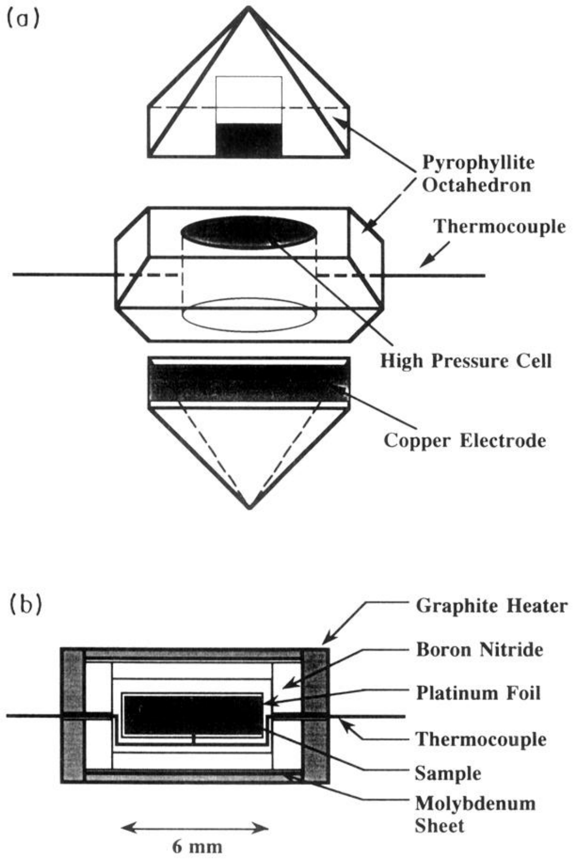

FIG. 1. Sample assembly within (a) the pyrophyllite octahedron and (b) the high-pressure cell for a 6–8-type high-pressure apparatus.