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Coordination environment of silicon in silica glass up to 74 GPa: An x-ray Raman scattering study at the silicon *L* edge

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Near-edge x-ray Raman scattering (XRS) spectra of the silicon *L* edge have been obtained on SiO_2 glass under compression in a diamond anvil cell up to 74 GPa. Partial densities of states (DOS's) of electrons, which the spectra reflect, have been calculated. The spectra for the glass do not show significant variations with pressure, whereas distinct differences are observed between quartz and stishovite, providing clear evidence for the nonexistence of sixfold-coordinated silicon by oxygen, that is stishovitelike silicon, in silica glass up to 74 GPa. A post main-edge hump, which is not seen in the XRS spectra and DOS's of quartz and stishovite, and an edge energy shift suggest that the silicon is in a different coordination environment under pressure. A compression mechanism of SiO_2 glass which involves the formation of fivefold-coordinated silicon following the decrease in Si-O-Si angle is proposed to explain the observed changes up to 74 GPa.

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Silica (SiO_2) plays an important role both in mineralogy and condensed-matter physics.[1] As one of the most abundant minerals, the structure of silica glass under high pressure is of paramount importance for earth science as it provides the zeroth order model of silicate magma in the earth's interior. This glass is also of great technological interest. From the viewpoint of condensed-matter physics, silica glass is considered to show polyamorphism[2] and has been the subject of extensive structural and spectroscopic analysis.

Experimentally, silica glass is known to undergo structural changes by compression at room temperature. For example, a permanent densification occurs at around 10 GPa,[3] which is considered to be due to intermediate structural changes, with collapsing void space in the glass structure.[4,5] A drastic density change most likely involves local or short-range structural changes that result in changes in the coordination number. There have been some reports which suggest that the structural changes in the short-range order occur in silica glass at higher pressures.[6–8] Hemley *et al.* performed optical Raman measurements and suggested that irreversible changes involving ring statistics begin at around 8 GPa and that a gradual structural breakdown in the intermediate range, and perhaps short-range order occurs above 30 GPa.[6] Williams and Jeanloz discussed the compression mechanism of silica glass from their infrared absorption spectra and concluded that it involves three steps, which begin with the decrease in Si-O-Si angle below 10 GPa, then the distortion of SiO_4 tetrahedron as the onset of a coordination change above 10 GPa, and finally the coordination increase in silicon to sixfold above 20 GPa.[7] An *in situ* x-ray diffraction study[8] reported that the nearest Si-O distance increases gradually with pressure from 8 to 42 GPa, which was suggested to be due to the change of the nearest-neighbor geometry. There was another x-ray diffraction study showing that the short-range structure was mostly preserved up to 19.2 GPa.[5] Clearly, no consensus has yet been reached on the nature of the transition and the pressure at which this transition takes place.

X-ray absorption spectroscopy (XAS) is a powerful technique to obtain local structural information around a certain type of atom, and has been applied to GeO_2 under high-pressure conditions.[9,10] Unfortunately, this technique cannot be applied to SiO_2 because the photon energies to access the specific absorption edges of silicon and oxygen are too low to penetrate the materials surrounding the sample. X-ray Raman scattering (XRS) yields similar information to that of XAS with hard x-ray photons and therefore provides a viable alternative.[11,12] Recently, an XRS study at the oxygen *K* edge on silica glass reported that the electronic structure of oxygen changes from quartzlike to stishovitelike between 10 and 22 GPa and that the stishovitelike electronic structure persists up to 41 GPa.[13] Based on this study, it was deduced that the coordination number of silicon in silica glass changed from four to six in the pressure range between 10 to 20 GPa.[13] However, as we will show in this work, more direct information on the local structure around the silicon atoms can be obtained by XRS measurements at silicon edges, and in this case, the information obtained proves to be critical in determining the coordination change of silicon.

The XRS measurements on silica glass under high-pressure conditions were performed with respect to the silicon *L* edge in this work. We have chosen the Si *L* edge instead of the *K* edge since the *L*-edge jump is expected to give higher intensity in the XRS spectrum. We have also performed first-principles calculations of partial densities of states (DOS's) of electrons, which the XRS spectra reflect, in some crystalline silica polymorphs, and have successfully interpreted the structure of the experimental XRS spectra with respect to quartz- and stishovitelike components.

The starting material was reagent quartz glass, which was confirmed to be pure SiO_2 by electron microprobe. The glass was ground with an agate mortar and loaded into a sample chamber with a diameter of 150 microns. No contamination from the mortar was observed by optical Raman spectroscopy. The high-pressure generating device was a so-called clock type diamond anvil cell.[14] The gasket material was rhenium metal precompressed to 80 microns. Pairs of diamonds with a 1.0-mm thickness were used as anvils. The culet size was 350 and 200 microns for 40 GPa and below and for 60 GPa and above, respectively. A few chips of ruby

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were loaded with the sample for pressure estimation.[15] A piece of the glass was also prepared for measurement at the ambient condition. We also measured two of the crystalline silica polymorphs, quartz and stishovite, at the ambient condition for comparison. The details of the crystalline sample preparation is described elsewhere.[16]

XRS measurements were carried out on the Taiwan inelastic x-ray scattering beamline, BL12XU at SPring-8.[17] The synchrotron radiation from an undulator was monochromatized by a Si(111) double-crystal monochromator (DCM). The scattered x rays were monochromatized to 13.3 keV using a Ge(777) bent analyzer (40 GPa and below) or 13.8 keV using a Si (777) bent analyzer (60 and 74 GPa) and were detected by a Si diode. A *K-B* mirror focusing system[18] was used for high-pressure experiment. The inelastic spectra were obtained by scanning the energy of incident x ray. The incident x ray was introduced to the sample through one of the diamond anvils and the scattered x ray was detected through the same diamond. The scattering angle was 140 degrees. X rays with energy more than 13.3 keV and a scattering angle of 140 degrees are required to reduce the Compton background from diamonds on the silicon *L* edge. For measurements of the crystalline polymorphs at the ambient conditions, the scattered x rays were monochromatized to 9.89 keV with Si(555) reflection at two scattering angles of 20 and 145 degrees. All measurements were performed at 300 K. The energy resolution for silica glass and crystalline polymorphs was 2.0 and 0.3 eV, respectively. Due to the *K* absorption edge of Ge (11.1 keV), the spectra obtained with the Ge analyzer were noisy. In comparison, those obtained with the Si analyzer have relatively better S/N ratio in spite of the smaller scattering volume.

We also performed conventional optical Raman spectroscopy on the silica glass at the ambient and high-pressure conditions. The spectral shapes were consistent with previous results.[6] The polycrystalline samples were also measured by optical Raman spectroscopy before and after x-ray exposure to confirm that no phase transition had occurred during the measurements.

Figure 1(a) shows the obtained XRS spectra of the silicon *L* edge for the SiO$_2$ crystalline polymorphs with a scattering angle of 20 degrees. They were normalized to the same pre-edge background level. Clear difference appears at the very near-edge region of the XRS spectra. The spectrum of quartz has a peak of 108.7 eV (peak q−1) with a shoulder at 106.5 eV (peak q−2). The spectrum of stishovite shows a strong sharp peak at 107.2 eV (peak s−1) and a small peak at 110.0 eV (peak s−2). Some difference is also seen at around 115 eV. The spectrum of quartz has a peak at 115.7 eV (peak q−3) and that of stishovite at 114.0 eV (peak s−3). These features are generally consistent with the spectra of XAS (Ref. 19) and electron-energy-loss spectroscopy (EELS) (Ref. 20) for each polymorph.

The spectra obtained at the scattering angle of 145 degrees are shown in Fig. 1(b). The spectra show similar features to those at 20 degrees, although the shape of the XRS band, which indicates the transition probability of the inner-shell electron, depends on the momentum transfer (or more precisely, the value of qr, where q is the momentum transfer of photon and r is the radius of a classic electron orbital).[21] At large momentum transfer, nondipole-allowed transition can be excited, whereas at low-momentum transfer, the spectrum is dominated by dipole-allowed transitions as is in XAS. The comparison between Figs. 1(a) and 1(b) indicates that the main characteristic features are independent of the scattering angle though the intensity changes. The higher background is mainly due to Compton scattering. As a result, the peaks around 115 eV become difficult to distinguish. Because the momentum transfer for silica glass measurement with 13.8 keV at 140 degrees is not so much different from that with 9.89 keV at 145 degrees, a similar spectral shape corresponding to its short-range structure is expected and has been obtained in the XRS measurement on silica glass.

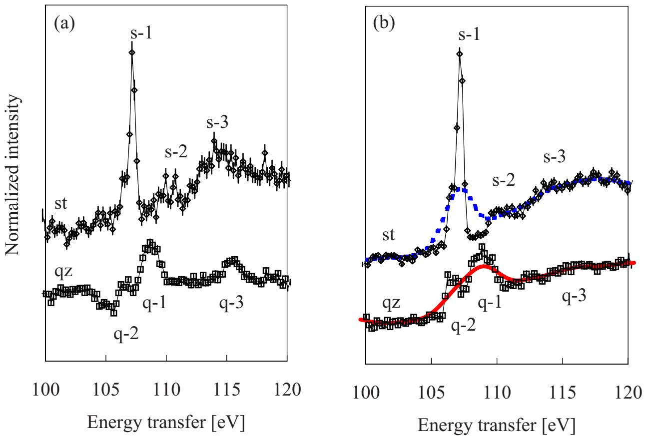

FIG. 1. (Color online) XRS spectra of silicon *L* edge for quartz (open squares) and stishovite (open diamonds) obtained at the ambient condition with a scattering angle of (a) 20 degrees and (b) 145 degrees. The edge features are independent of the scattering angle. The thin lines are guides for the eyes. The thick lines shown with the spectra of quartz (solid) and stishovite (dotted) at 145 degrees are convoluted ones with the 2.0-eV resolution function. See text for the labels on the peaks.

Pressure variation of the XRS spectra of the silicon *L* edge on silica glass is shown in Fig. 2. At the ambient condition for the bare glass sample, the near-edge structure has the same features as those of quartz although the energy resolution was poorer. For a direct comparison, the XRS spectra of quartz and stishovite in Fig. 1(b) are convoluted with a Gaussian function with full width at half maximum (FWHM) of 2.0 eV (the thick curves) and are superimposed on the spectra taken from the glass in Fig. 2. A peak corresponding to the s−1 peak for stishovite did not appear by compression up to 74 GPa. This indicates that the electronic structure and hence the coordination environment of silicon in the glass is not stishovitelike even at 74 GPa, in sharp contrast with the results obtained at the oxygen *K* edge.[13] Furthermore, the XRS edge position is almost pressure independent up to 60 GPa, where the spectrum begins to show qualitative differences. At 74 GPa the XRS edge shifts to a higher energy by ca. 1.3 eV. The intensity in the postedge region around 113 eV is also found to be stronger in the spectra at 60 and 74 GPa than that at the ambient condition. Although the spectra at 23 and 40 GPa may show the intensity around 113 eV, it is difficult to conclude due to the poorer statistics. Note that the intensity from 112 to 115 eV

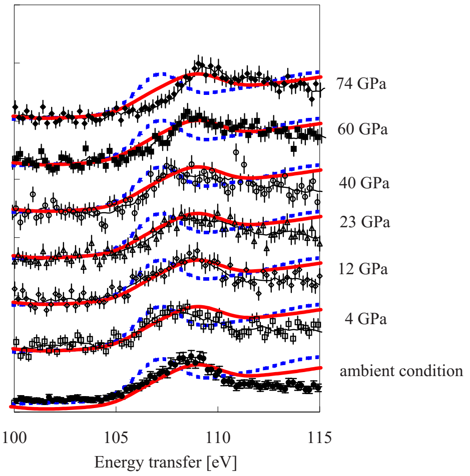

FIG. 2. (Color online) Silicon *L*-edge XRS spectra on silica glass at the ambient condition (solid circle), 4 GPa (open squares), 12 GPa (open diamonds), 23 GPa (open triangles), 40 GPa (open circles), 60 GPa (solid squares), and 74 GPa (solid diamonds). The thin lines are smoothed curves of the raw data by moving average to guide the eyes. The intensities are normalized by the peak height. The convoluted XRS spectra of quartz (red/solid) and stishovite (blue/dotted) shown in Fig. 1(b) are also shown by thick lines with each spectrum for comparison.

in the spectra of quartz and stishovite is mostly due to Compton scattering. Therefore, some qualitative changes of the glass structure probably occur above 12 GPa, which may be accompanied with the formation of fivefold-coordinated silicon.

Partial DOS's for electrons have been calculated with density functional theory using the WIEN2K program package[22] in order to interpret the XRS spectra of silica glass under high-pressure conditions. A series of calculations was conducted with the core-hole effect being taken into account. Each calculation was performed with a supercell that consists of ca. 100 atoms. The details of the calculations are described elsewhere.[16] The calculated partial DOS's for quartz and stishovite are shown in Fig. 3. These DOS's successfully reproduce the structures of the experimental XRS spectra, indicating that the adopted parameters were appropriate. We also calculated the DOS of high-pressure cristobalite (hp-cristobalite)[23,24] and penta-SiO_2.[25] Hp-cristobalite is formed from cristobalite under less hydrostatic pressure conditions.[23] A recent theoretical study[24] proposed the detail of the crystal structure, which is very similar to that of cristobalite and has fourfold silicon, twofold oxygen, and an Si-O-Si angle of 135.07 degrees. Penta-SiO_2 was theoretically predicted to appear under a deviatoric stress condition and has six fivefold silicon atoms, six threefold oxygen atoms (O1), and six twofold oxygen atoms (O2) in its unit cell. The Si-O2-Si angle is 117.97 degrees.[25] Therefore, these polymorphs can be good models of the silica glass structure at high-pressure conditions. We used the crystallographic parameters proposed by the calculated results in Refs. 24 and 25 for our calculations. The calculated DOS's are shown in Fig. 3. DOS's where inner-core electrons are excited by dipole transitions mostly reflect the shape of XRS spectra although nondipole-allowed transitions can occur in XRS processes.[16,26] The obtained *p*-electron DOS's of oxygen for hp-cristobalite and penta-SiO_2 shown in Fig. 3(b) are similar to that of stishovite rather than quartz. On the other hand, the *s*- and *d*-electron DOS's of silicon are different from the other ones as shown in Fig. 3(a). However, they do not produce a sharp peak at the edge like in stishovite.

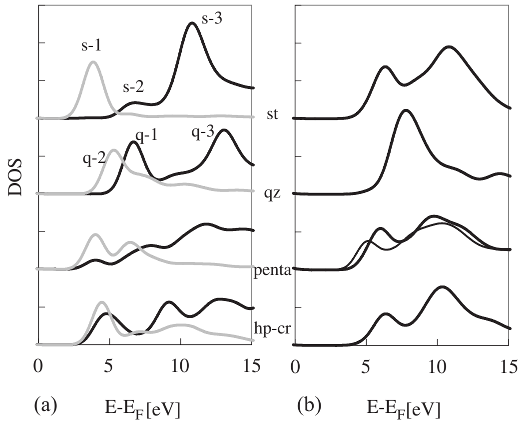

FIG. 3. Calculated partial DOS's for electron of stishovite (st), quartz (qz), penta-SiO_2 (penta), and hp-cristobalite (hp-cr) from above. The horizontal axes are with respect to the Fermi level. (a) *s*- and *d*-DOS's of silicon are shown by black and gray lines, respectively. (b) *p*-DOS of oxygen. The thick and thin lines for penta-SiO_2 indicate DOS of oxygen 1 and 2, respectively. The peaks correspond to those in Fig. 1 with the same labels. The characteristic features of oxygen *p*-DOS for stishovite are also found in those of hp-cristobalite and penta-SiO_2. The strong peak of stishovite does not appear in other silicon *s*-DOS, indicating that this peak is a good indicator of sixfold silicon. Note: The calculated silicon *s*- and *d*-DOS's of hp-cristobalite or penta-SiO_2 are difficult to compare directly with experimental Si *L*-edge XRS spectra because this calculation does not provide the core-level energy shift as the reference energy for comparison.

The calculated DOS's suggest two conclusions. The first is that the Si *L*-edge XRS from sixfold silicon should produce a unique (the $s-1$) feature. The second is that oxygen *K*-edge XRS is not sensitive to changes in the coordination number. Observation from the perspective of both silicon and oxygen is thus essential for a reliable analysis of the local structure of SiO_2 glass.

Therefore, we conclude that the electronic structure of silicon in silica glass has not yet become sixfold-coordinated (stishovitelike) at pressures up to 74 GPa although the electronic structure of oxygen, which is not always related to the coordination number as shown above, was changed from quartzlike to stishovitelike.[13] It may be surprising that stishovitelike silicon has not been formed in silica glass up to 74 GPa because crystalline stishovite would be formed below 7 GPa at room temperature (see, Ref. 27) and because sixfold silicon was theoretically predicted to be formed from around 15 GPa in silica glass.[28] The high-pressure structure of silica glass above 10 GPa seems so stable as Inamura *et al.* shows that the intermediate structure is not thermally relaxed.[5] However, besides changes in spectral features of the XRS spectrum, a shift in energy of the edge position can also be expected in the event of a coordination change as our experimental data have indicated. Unfortunately, the method adopted in this study cannot accurately calculate the core-level energy or chemical shift of Si *L*-edge energy. The *L*-edge XRS features of fivefold silicon could be obtained with a crystalline polymorph consisting of fivefold silicon or by the advanced calculation of core-level energy shift including core-hole effects.

A compression mechanism proposed previously[1,29] is that the coordination number of silicon changes to six only when the Si-O-Si angle gets smaller (to ca. 100 degrees), following the progressive decrease in the Si-O-Si angles between corner-shared SiO_4 tetrahedra. There is probably not enough space for all of the silicon atoms in fourfold form even before the Si-O-Si angle becomes ca. 100 degrees. It seems plausible that some silicon atoms are in fivefold coordination, the sign of which could be the intensity appearing around 113 eV and the edge shift to higher energy transfer in silicon *L*-edge XRS spectra of the present study. The Si-O bond length elongation and the peak shift of the bending vibrational mode to higher energy do not always require the existence of sixfold silicon.[8,30] The compression mechanism involving a decreasing Si-O-Si angle and the formation of fivefold silicon explains the experimental results not only by XRS but also by the other techniques. However, the observation of sixfold silicon in silica glass may be expected with further compression above 74 GPa.

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