Vacuum-ultraviolet absorption of hydrogenated and deuterated silanol groups and interstitial water molecules in amorphous SiO_2

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Vacuum-ultraviolet (VUV) absorption cross sections of hydrogenated and deuterated silanol groups (SiOX, where X=H or D) as well as interstitial water molecules (X_2O) in amorphous SiO_2 (a-SiO_2) were determined between photon energies of 7 and 8.2 eV. The absorption bands for the deuterated species are blueshifted compared to those for the hydrogenated ones by ~0.1 to 0.2 eV as a result of a decrease in the zero-point energy associated with the OX groups. The VUV absorption of interstitial X_2O below 8 eV is blueshifted with respect to that of X_2O trapped in rare-gas solids due to the contribution of hydrogen bonding, and is ~1 to 2 orders of magnitude stronger than that of SiOX groups.

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Hydrogen is the most common dopant or impurity in synthetic amorphous SiO_2 (a-SiO_2) which significantly modifies various properties of this material. Since a-SiO_2 is important practically as an optical material for the vacuum-ultraviolet (VUV, $\lambda \lesssim 190$ nm or $h\nu \gtrsim 6.5$ eV) spectral region, the influence of hydrogen on the VUV optical properties of a-SiO_2 has attracted considerable attention. The silanol group (SiOH), which is the dominant network-bound form of hydrogen, has an absorption band at $\gtrsim 7.3$ eV.[1–3] SiOH groups help to improve the radiation hardness of a-SiO_2 for <7 eV light by relaxing the glass structure. However, a photoexcitation in the SiOH VUV absorption band creates defects by dissociating the O-H bond.[4,5] Another form of hydrogen, the interstitial H_2 molecule, which is mobile in a-SiO_2 at room temperature, is often intentionally loaded in a-SiO_2 to terminate photoinduced paramagnetic color centers whose main absorption bands are located at ~4–7 eV. However, an excess H_2 loading enhances the formation of oxygen vacancies and macroscopic cracks in a-SiO_2 exposed to ArF ($\lambda = 193$ nm, $h\nu = 6.4$ eV) or F_2 (157 nm, 7.9 eV) laser light.[6] This is a possible indication that yet another type of hydrogenous species, the interstitial water molecule (H_2O),[7] is created by the photoreduction of the a-SiO_2 network with interstitial H_2, $\equiv$Si-O-Si$\equiv + H_2 \xrightarrow{h\nu} \equiv$Si-Si$\equiv + H_2O$, and that it stimulates crack formation by a mechanism analogous to stress corrosion.[8,9]

The participation of interstitial H_2O in photoinduced reactions in a-SiO_2 has been largely overlooked, despite the presence of an intense VUV absorption band for a free H_2O molecule,[10,11] whose O-H bonds are broken by VUV light to form reactive radical fragments.[12,13] In addition, a reaction involving interstitial H_2O, the hydrolysis of the network-bound chloride (SiCl) group generating a SiOH group and an interstitial HCl molecule, has been recently confirmed.[14] It is therefore necessary to investigate the properties of interstitial H_2O and its role in defect processes in a-SiO_2.

A crucial and still missing piece of fundamental data is the VUV absorption spectrum of interstitial H_2O. It may differ from that of a free H_2O molecule because of interactions with an a-SiO_2 network and with other interstitial species. The differences between the VUV absorption spectra of SiOH groups and interstitial H_2O may shed some light on the influence of adjacent atomic groups on the electronic transition associated with OH groups. The nature of the transition can be further examined using isotope exchange between H and D.

In this study, we identified VUV absorption bands of SiOD groups, interstitial H_2O, and D_2O in a-SiO_2. Further, we reevaluated that of SiOH groups to the higher energy side up to ~8.2 eV. Hereafter, X denotes either H or D.

Two types of synthetic a-SiO_2, "wet" (SiOH $\sim 1\times 10^{20}$ cm^{-3}, SiCl $\sim 5\times 10^{18}$ cm^{-3}) and fluorine-doped (SiOH $\lesssim 10^{17}$ cm^{-3}, SiF $\sim 4\times 10^{19}$ cm^{-3}), were used. The former is originally SiOH-rich, and the latter has a good VUV transparency,[15] which is beneficial in measuring VUV absorption bands of interstitial species. They were shaped into plates (area: 10×7 mm^2) of three different thicknesses: 0.16 or 2 mm for the fluorine-doped a-SiO_2, and 1 mm for the "wet" one. These plates denoted "ThinF," "ThickF," and "Wet," respectively, were carefully heat-treated to incorporate SiOX groups and interstitial X_2O of controlled concentrations.

Two Wet plates, which initially had equal SiOH concentrations, were used to prepare a pair of samples with equal SiOH and SiOD concentrations. One of them was completely deuterated in D_2 (~3 atm) at 900 °C for 96 h. Since this treatment caused a considerable (~20%) loss of SiOH groups by thermal dehydroxylation, the other plate was similarly treated in H_2 to equalize the final SiOX concentrations between these samples. Another pair of samples with equal SiOH and SiOD concentrations was made from the ThinF plates by three-step thermal annealings: first in humid air

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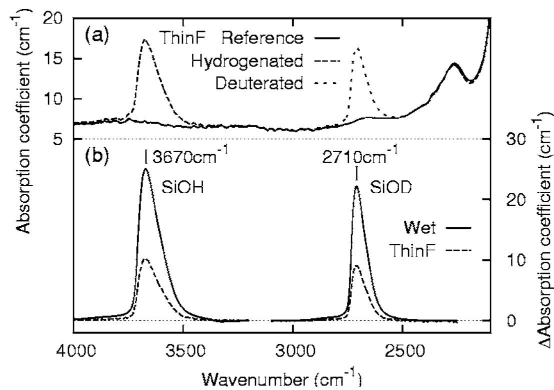

FIG. 1. (a) IR absorption spectra for the ThinF set. (b) IR absorption spectra of SiOH and SiOD groups measured for the Wet and ThinF sets. The detailed procedure used to derive the spectra is described in the text.

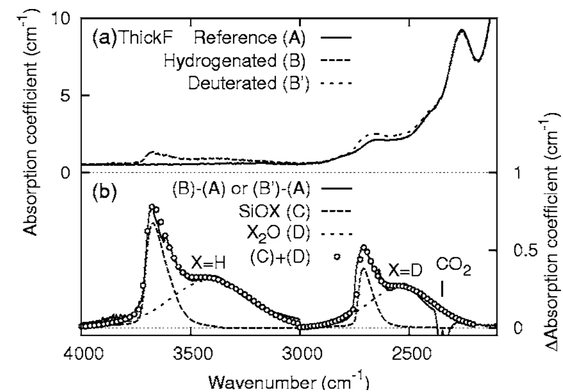

FIG. 2. (a) IR absorption spectra for the ThickF set: reference (A), H_2O- (B), and D_2O-loaded (B′) samples. (b) Induced IR absorption spectra, (B)-(A) and (B′)-(A), and their decompositions into absorption bands of SiOX groups (C) and interstitial X_2O (D). The band shapes for SiOX groups were taken from Fig. 1, and those for interstitial X_2O were assumed to be Gaussian-shaped.

(H_2O partial pressure ~7 atm) for 48 h at 900 °C to embed SiOH groups by hydrolyzing the a-SiO_2 network, second in vacuum for 48 h at 900 °C to desorb the unreacted interstitial H_2O, and finally, in H_2 or D_2 (~3 atm) at 900 °C for 24 h to exchange hydrogen. The use of the ThinF sample (0.16-mm-thick fluorine-doped a-SiO_2) of a reduced fundamental absorption expanded the viable measurement range of absorption spectra of SiOX groups to energies of >8 eV.[16] The ThickF plates were used to prepare samples containing measurable amounts of interstitial X_2O: they were treated in X_2O vapor-saturated air for 720 h at a relatively low temperature, 170 °C,[17] to slow down the hydrolysis of an a-SiO_2 network.[18]

The absorption spectra were measured both by VUV (VU-201M, Bunkou-Keiki) and by Fourier-transform IR (Spectrum One, Perkin Elmer) spectrometers at 6.5–8.2 eV and 2100–4000 cm^{-1}, respectively. The IR and VUV absorptions due to SiOX groups and interstitial X_2O in the ThinF and ThickF sets were extracted by subtracting background spectra, measured on SiOX- and X_2O-free reference samples. The ThinF reference was prepared by thermally annealing a pristine plate for 48 h at 900 °C in vacuum to account for the variation in the fundamental absorption due to the thermally induced structural relaxation.[19,20] The ThickF reference was a pristine plate with no additional annealing, because the structural relaxation at the X_2O loading temperature (170 °C) was negligible. The background for the Wet set, whose SiOX-free reference was not available, was derived as follows. The background in the IR region was assembled from the spectral segments of the hydrogenated sample outside the SiOH band and the deuterated sample outside the SiOD band. The SiOX absorption in this synthesized background was negligible. In the VUV region at <8 eV, the reflection loss calculated from the reported refractive index spectrum[21] was used as the background, assuming that the fundamental absorption of a-SiO_2 at this spectral region is sufficiently weak (~1 cm^{-1} at 8 eV[16]).

Figure 1(a) shows the IR absorption spectra for the ThinF sample and reference plates, and Fig. 1(b) shows IR absorption due to the SiOX groups, obtained as the difference spectra from the sets of ThinF and Wet samples, whose degrees of isotope exchange[22] were ~98% and ~99.5%, respectively. The absorption maxima of the SiOH and SiOD groups[23–26] were located at ~3670 and 2710 cm^{-1}, respectively. The observed ratio between the peak wave numbers (~1.35) agrees well with the square root of the reduced mass ratio between the OH and OD groups (1.37). The peak and integrated intensity ratios between the 3670 and 2710 cm^{-1} bands were ~1.13 (Ref. 27) and ~1.7 (Ref. 28), respectively. Using the peak intensity [Fig. 1(b)] and the reported peak absorption cross section [2.7×10^{-19} cm^2 (Ref. 3)] of the 3670 cm^{-1} band, the SiOX concentrations in the Wet and F-doped samples were calculated to be ~9.3×10^{19} and ~3.8×10^{19} cm^{-3}, respectively.[29]

Figures 2(a) and 2(b) show the IR absorption spectra and the absorption induced by the X_2O loading at 170 °C for the ThickF set, respectively. A broad band due to interstitial X_2O (Ref. 7) is seen at the lower energy side of the SiOX band. The induced absorption was decomposed using the spectral shape determined in Fig. 1(b) for the SiOX groups, and postulating a single Gaussian peak for interstitial X_2O. Assuming that the integrated absorption coefficient of interstitial X_2O is equal to that of liquid X_2O,[30–32] the concentrations of interstitial H_2O and D_2O were both calculated to be ~1.0×10^{18} cm^{-3}, respectively.[32,33] The concentrations of the SiOH and SiOD groups, formed simultaneously with the X_2O loading, were ~2.5×10^{18} and 1.6×10^{18} cm^{-3}, respectively.[29] The larger SiOX/X_2O ratio in the case of hydrogenation (X=H) as compared to the deuteration (X=D) suggests a presence of the kinetic isotope effect: the slower hydrolysis of a-SiO_2 with D_2O than with H_2O.

Figure 3 shows the VUV absorption spectra of the ThinF, Wet, and ThickF sets. Using the concentrations of the SiOX groups and interstitial X_2O measured in these samples (Figs. 1 and 2), the respective spectra of the VUV absorption cross sections, σ, were obtained (Fig. 4). The σ values of the SiOX groups between 7.5 and 8 eV, determined in this way both from the Wet and ThinF sets, agree well.[34] Further, they are consistent with one[3] of the two available σ data.[2,3] This consistency may indicate that the σ values obtained for the

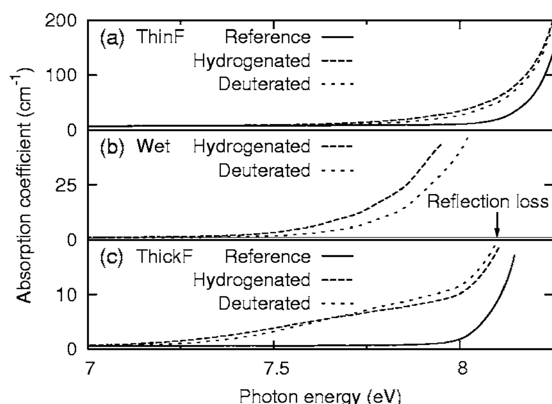

FIG. 3. VUV absorption spectra for the ThinF (a), Wet (b), and ThickF (c) sets. The thin solid line in panel (b) denotes the losses due to surface reflection calculated from the refractive index spectrum of a-SiO_2 reported in Ref. 21.

SiOX groups are reliable and can be used for the background subtraction to extract σ for interstitial H_2O from the VUV absorption data of Fig. 3(c). The absorption of interstitial X_2O was found to be prominent at $\gtrsim 7$ eV, and σ was ~ 1 to 2 orders of magnitude larger than that of the SiOX groups at <8 eV (Fig. 4, inset), indicating that interstitial X_2O is a potential origin of VUV photoinduced phenomena in a-SiO_2. The VUV absorptions of deuterated species are weaker than those of the hydrogenated ones, except for photon energies $\gtrsim 7.7$ eV for X_2O.

Next, we consider the origin of the blueshift in the VUV absorption with deuteration. Photoexcitation of the lowest absorption bands of X_2O and SiOX groups results in an efficient cleavage of O-X bonds,[4,5,12,13] indicating that the potential energy curve of the excited state is repulsive with respect to the elongation of the O-X bonds. The energy of the repulsive state, which does not couple to any vibrational modes, is not influenced by isotope exchange. Hence the observed blueshift is due to the deuteration-induced energy decrease in the ground vibronic states of the OX group, which downshifts the zeroth vibrational level (zero point energy) by ~ 0.06 eV. Additionally, the deuterated species have steeper VUV absorption edges, making the blueshift as large as $\sim 0.1-0.2$ eV (Fig. 4). The change in the absorption edge slope is likely due to a shrinking of the wave function in the zeroth vibrational level that accompanies its energy decrease. An increase in the absorption edge slope results in a larger peak σ if the integrated transition probability remains constant. This is actually observed for interstitial X_2O (Fig. 4). The modification of the VUV absorption of CH_3OH by deuteration has been interpreted in a similar way.[35]

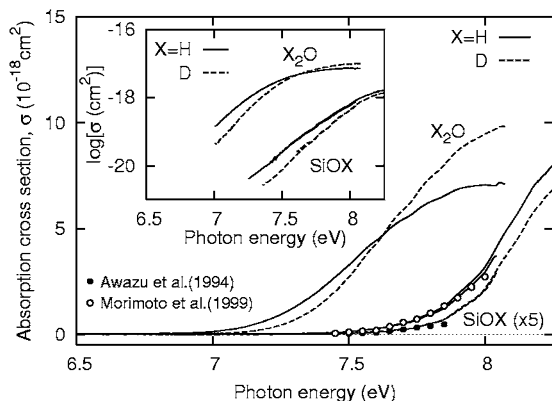

FIG. 4. Absorption cross-section spectra of SiOX (X=H or D) groups and interstitial X_2O in a-SiO_2 determined in this study. The data on SiOX groups obtained from the Wet (low-energy part) and ThinF sets (high-energy part) closely overlap between 7.5 and 8 eV. Closed and open circles denote data on SiOH groups taken from Refs. 2 and 3. The insets show semilogarithmic plots of data shown in the main panel.

Interactions that dominantly influence the VUV absorption of molecules trapped in solid matrices include the London dispersion interaction (attractive force between two induced dipoles[36]), electron-electron Coulomb repulsion, and hydrogen bonding. In systems where hydrogen bonding is absent, for example, O_2 in solid rare gases or a-SiO_2, the energy of VUV absorption is determined only by the London interaction and the Coulomb repulsion, which usually cause redshift and blueshift in the absorption band, respectively. Here, the energy of absorption of O_2 decreases in the order of $Ne > Ar > Kr > Xe > a$-SiO_2, as the Coulomb repulsion becomes weak due to an expansion of the lattice interstices, and as the London interaction becomes strong due to an increase in the polarizability.[37,38] However, this order is not the same as that for H_2O, where the absorption of H_2O in a-SiO_2 (Fig. 4) is significantly blueshifted with respect to those in rare gas solids: a-$SiO_2 \sim Ar > Kr$.[39] This change likely results from the hydrogen bonding because it easily aggregates H_2O molecules, and analogous blueshifts are seen for hydrogen-bonded H_2O (Refs. 10, 40, and 41) and SiOH groups.[3,42] It seems likely that interstitial H_2O is hydrogen bonded with oxygen atoms in the a-SiO_2 network, other interstitial H_2O molecules, and SiOH groups created by the hydrolysis of the network. However, aggregation of interstitial H_2O molecules by hydrogen bonding would be largely restricted in the direction along the channels connecting the voids, due to the relatively small diameter of the voids ($\sim 0.1-0.3$ nm[43]) compared to that of an H_2O molecule (~ 0.3 nm).

The vacuum-ultraviolet (VUV) optical absorption of silanol groups (SiOX, where X=D or H) and interstitial water molecules (X_2O) in amorphous SiO_2 (a-SiO_2) was studied. The finding of an intense absorption band of interstitial X_2O at photon energies >7 eV demonstrates that interstitial water is a possible origin of photoinduced phenomena in a-SiO_2. However, the VUV absorption band of X_2O in a-SiO_2 is shifted to the higher-energy side with respect to its positions in rare gas matrices, suggesting the hydrogen bonding of interstitial X_2O with oxygen atoms of a-SiO_2, other X_2O molecules, and SiOX groups. The deuteration lowers the vibrational levels in the ground electronic state associated with OX groups. This results in a high-energy shift in the VUV absorption bands of interstitial X_2O and SiOX groups, accompanied by an increase in the slope of the absorption edge.

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[33] The uncertainty, which was mostly due to the inaccuracy in the absorption coefficient of interstitial X_2O, was $\sim 10^{\pm 0.5}$.
[34] It is possible to estimate the upper limit of σ of SiCl groups in a-SiO_2, from the good coincidence of the σ data of the SiOX groups between ThinF and Wet samples (Fig. 4), calculated from the absorption spectra shown in Fig. 3. This agreement indicates that the absorption of $\sim 5\times 10^{18}\ cm^{-3}$ of SiCl groups, additionally present in the Wet sample, is less significant than the estimated systematic error of the absorption measurements ($\lesssim 5\%$). Hence σ for the SiCl groups is $< 4\times 10^{-19}\ cm^2$ at 8 eV, consistent with the value ($1.14\times 10^{-20}\ cm^2$ at 7.77 eV) reported in Ref. 47.
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