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Effect of Xe_2* light (7.2 eV) on the infrared and vacuum ultraviolet absorption properties of hydroxyl groups in silica glass

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Changes in the optical-absorption properties of hydroxyl group (≡SiOH) in silica glasses were studied to determine the specific form of ≡SiOH whose absorption takes place at around the intrinsic absorption edge of silica glass (~8 eV). In the experiments, four kinds of fused silica were irradiated with 7.2 eV light from a xenon dielectric-barrier discharge lamp or they were heated at 1273 K in vacuum. In addition to the near-edge absorption, changes in the intensity, peak position and the shape of the infrared absorption bands due to a bond-stretching mode of ≡SiOH s at 3673 cm^{-1} (2.72 μm) and the first overtone of these stretching vibrations at 7230 cm^{-1} (1.38 μm) were monitored. The results of absorption spectral observation after the irradiation are summarized as two points: (i) a blue shift of the effective absorption edge took place (increasing in the transmissivity); (ii) the 3673 cm^{-1} band broadened and shifted to the red for all the samples except the OH-free silicas, and similarly, the absorption intensity of the 7230 cm^{-1} band decreased and the band shifted to the red, too. It was found through analysis of these changes that the blue shift of the absorption edge corresponded with the decrement of a particular form of ≡SiOH and the red shift of the 3673 cm^{-1} band was caused by the decrement of the isolated ≡SiOH. The ≡SiOH absorption located at more than 7.4 eV region is tentatively ascribed to ≡SiOH existing as the isolated form in silica glass. It is argued that the isolated ≡SiOH was converted into the hydrogen bonded ≡SiOH by irradiation of the Xe_2* band emission.
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I. INTRODUCTION

Molecular water, molecular hydrogen, hydroxyl group (≡SiOH) [the notation of ≡SiOH means a hydroxyl group (OH) bonded to a silicon (Si) in the glass network, and ''≡'' presents three (3) bonds with other O's in the network], and silicon hydride give unique optical absorption bands due to vibrational modes in the infrared (ir) spectra of silica glass. Especially, ≡SiOH has been extensively studied so far because of a demand from developments of optical fiber manufacturing technique for telecommunication using ~1.3 μm light.[1,2] Some kinds of ≡SiOH species are generated through reaction of water with the silica glass network during various processing steps or atmosphere, i.e., diffusion of moisture into the silica fibers even at room temperature. In this issue, an absorption band at around 1.38 μm (7230 cm^{-1}), which is due to the first overtone of the fundamental vibrational band of ≡SiOH (at 3672 cm^{-1}),[3,4] had been studied and several different kinds of ≡SiOH species were distinguished by means of band separation method.[5,6] Davis and Tomozawa analyzed silica glass treated in a moist atmosphere and reported details of 3672 cm^{-1} ≡SiOH absorption band.[6] Walrafen proposed that two classes of ≡SiOH interactions are present among the ≡SiOH groups of silica glass on the basis of the polarized spectral measurements.[7]

On the other hand, the ≡SiOH group gives intense optical absorption in the vacuum ultraviolet (vuv) region near the absorption edge of the glass.[8–10] Although much effort has been made to determine specific forms of ≡SiOH in silica glass, it is still not known what particular kinds of ≡SiOH present in silica are responsible for the measured absorption of vuv light.

The present study focuses on clarifying the detailed form of the ≡SiOH absorbing vuv photons near the absorption edge in silica glass. As a hint for how to solve the problem, Shelby[11] reported that the 3672 cm^{-1} ≡SiOH band was shifted to smaller wave number resulting from the creation of a shoulder on the low-frequency side of this band by irradiation with gamma rays up to 10–100 MGy. On our first attempt, we selected xenon-excited-dimmer (Xe_2*) light (i.e., 7.2 eV) emitted from the Xe dielectric-barrier discharge lamp. This emission band originates from decay of the excited state of Xe_2*.[12] It was hoped that the band-edge absorption due to ≡SiOH would be excited by this irradiation and that consequent changes of the ≡SiOH absorption properties would be observed. By comparing the absorption property changes induced by vacuum heat treatment with those induced by the irradiation, we will discuss the origin of the ≡SiOH absorption in the vuv region of silica glass.

II. EXPERIMENTAL DETAILS

Four commercially available kinds of synthetic silica glass were used in this study: ES (Nippon Silica Glass Co., Ltd.) and Suprasil P20 (P20, Shinetsu Quartz Products Co., Ltd.) which were made by the direct method and, Suprasil F310 and Suprasil F300 (F310 and F300, Shinetsu Quartz Products Co., Ltd.) which were made by the vapor phase axis deposition (VAD) method. The ES, P20, and F310 samples contain 1200–1300, ~700, and ~300 weight (wt) ppm of

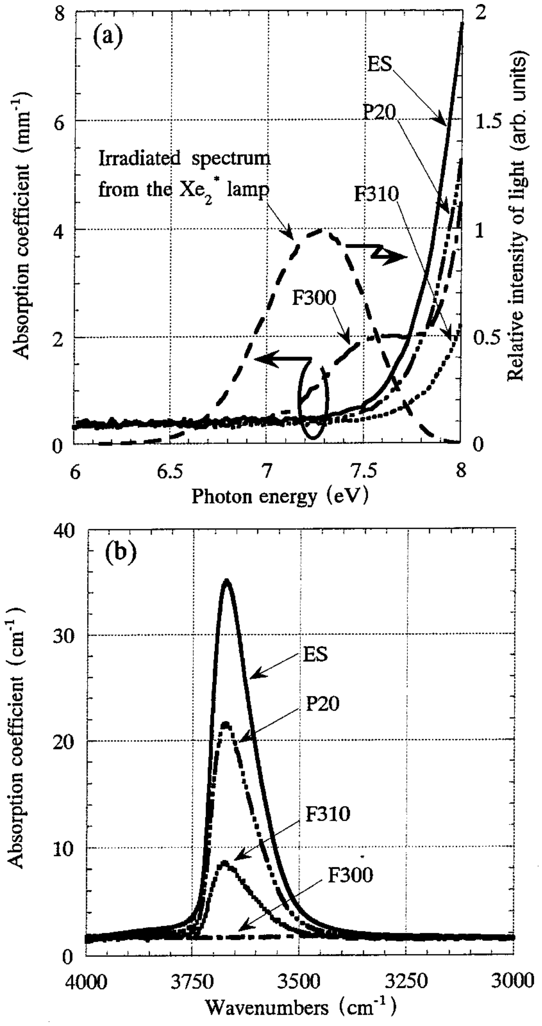

FIG. 1. The series of absorption spectra of as-received silica glass in (a) 6.0–8.0 eV vuv region; (b) 3000–4000 cm^{-1} ir region. Samples are selected to vary the absorption intensity in vuv absorption edge region and at 3673 cm^{-1} absorption band. The irradiated spectrum by the Xe dielectric barrier discharge lamp is also shown in (a).

≡SiOH, respectively, while the concentration of ≡SiOH of the F300 sample is less than 1 wt ppm, according to the manufacturer's catalog. These samples were selected to vary the absorption intensity in vuv absorption edge region and at 3673 cm^{-1} absorption band. In general, these materials include metallic impurities at levels below 0.1 wt ppm. Samples of $20\times10\times0.5\,\mathrm{mm}^3$ were prepared with optically polished two faces.

The samples were irradiated with the Xe dielectric-barrier discharge lamp (UEM20-172, Ushio, Inc.) under a nitrogen-flow atmosphere. The lamp emits relatively monochromatic light whose maximum intensity was located at 7.2 eV with an effective band width of 1.5 eV. The lamp spectrum is shown in Fig. 1. The irradiance at the place where the samples were mounted was measured to be $14\pm0.8\,\mathrm{mW\,cm}^{-2}$, and the temperature at the surface of the samples was $413\pm12\,\mathrm{K}$. All irradiations were performed continuously for a fixed duration: they were 25, 100, and 430 hours for all of the samples except for Suprasil F300 which was irradiated for 240 hours.

TABLE I. List of determined SiOH concentration in the samples.

Sample	As received (cm^{-3})	After heating (cm^{-3}) at 1273 K for 50 h
ES	1.24×10^{20}	7.5×10^{19}
Suprasil P20	7.4×10^{19}	5.3×10^{19}
Suprasil F310	2.5×10^{19}	2.1×10^{19}

Vuv-uv and ir absorption spectra were measured for all as-received and as-irradiated samples at room temperature. A vacuum ultraviolet spectrometer (Acton Research Corp. VM502) was utilized in the photon energy range from 4.0 to 8.0 eV with 0.035 eV resolution. The errors of the absorbance measured were ±1.5% and ±9.5% for photon energy (PE)<7.0 eV and PE>7.6 eV region, respectively. An ultraviolet-visible-near ir spectrophotometer (Shimazu UV-3100 PC) and FT-IR (Digilab FTS-40) were used in the range from 10 000 to 4000 cm^{-1} with 2.5 cm^{-1} resolution and from 4000 to 2000 cm^{-1} with 0.5 cm^{-1} resolution, respectively. To record the weak absorption band at 7230 cm^{-1}, the 3-mm-thick ES sample was irradiated for 330 hours. The errors of optical measurements were evaluated to be ±1.5% in both of uv-vis-nir and ir measurements by the multiple measurements.

Some samples of ES, P20, and F310 were heated in vacuum (at $\sim5\times10^{-6}$ Pa) at 1273 K for 50 hours in order to reduce the ≡SiOH amount.

III. RESULTS

Absorption spectra of as-received silica glass samples are shown in Figs. 1(a) and 1(b) for uv-vuv and ir regions, respectively. Notice here the remarkable differences in absorption coefficient near the absorption edge in the vuv region and at the 3673 cm^{-1} absorption band in the ir region which is due to ≡SiOH's.[13–15] Table I summarizes the concentration of ≡SiOH for each sample other than F300, estimated by using the following equation:

$$C_{\mathrm{OH}}=\frac{\Delta A}{\sigma_{\mathrm{OH}}t}, \qquad (1)$$

where C_{OH} is ≡SiOH concentration, σ is the cross section of ≡SiOH absorption at 3673 cm^{-1} which is $2.6\times10^{-19}\,\mathrm{cm}^2$,[15] t is the sample's thickness in cm, and ΔA is the absorbance in cm^{-1} at 3673 cm^{-1} obtained by subtracting the base line from the measured absorption intensity. The base line was assumed to be a line connecting the intensity at 4000 and 3000 cm^{-1}. Davis and Tomozawa reported that the absorption band due to asymmetric stretching of molecular water bound to silica network lies at 3425 cm^{-1} and first overtone of the 1611 cm^{-1} bending mode of molecular water lies at 3208 cm^{-1}.[6] Since no noticeable absorption at 3425 or 3208 cm^{-1} was resolved in our samples, the base line assumed should be valid in our experiment.

Figure 2(a) shows the difference spectra in vuv region obtained by subtracting spectra of as-received samples from the ones of samples irradiated for 100 hours for the ES, P20, and F310 samples and 240 hours for F300 sample. By Xe_2* light irradiation, a decrease in absorption from 7.4 eV up to

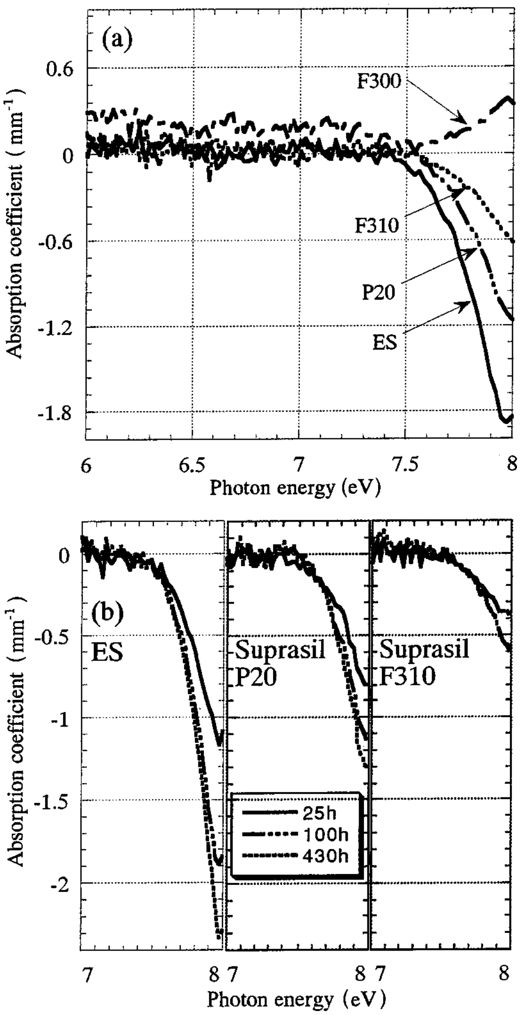

FIG. 2. (a) The difference spectra in 6.0–8.0 eV region obtained by subtracting spectra of as-received samples from the ones of samples irradiated for 100 hours for the ES, P20, and F310 samples and 240 hours for F300 sample. This negative change in absorption by Xe_2* irradiation in the ES, P20, and F310 sample is, hereafter, called ''beta absorption.'' (b) Change in absorption grew with the irradiation time. The more the ≡SiOH content was in the sample, the larger the intensities of the beta absorption grew up.

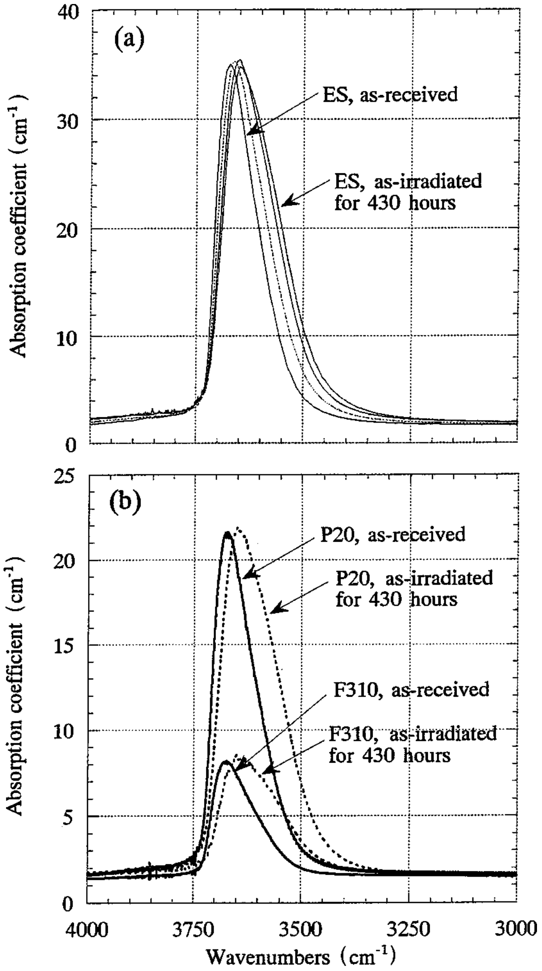

FIG. 3. Changes in the band shape of ≡SiOH group for (a) ES at 0, 25, 100, and 430 hours irradiation, and (b) P20 and F310 samples of the initial and irradiated for 430 hours, respectively.

8.0 eV (upper limit of the measurement) was observed for the ES, P20, and F310 samples. Only the F300 sample, which does not contain ≡SiOH as low as the detection limit, did not show any decrement in the absorption at all, or even an increase. Figure 2(b) shows the decrement of absorption for ES, P20, and F310 samples with the irradiation time, where one notes that the longer the time, the greater the decrement of absorption. This negative change in vuv absorption induced by the Xe_2* irradiation is, hereafter, called ''beta absorption.''

The contour of the 3673 cm^{-1} absorption band of ≡SiOH was also deformed by the irradiation. Figure 3 shows the changes in the absorption band shape for the ES, P20, and F310 samples, respectively. For each sample, the wave number of the absorption maximum shifted to lower wave number side and the bandwidth became broader with increasing irradiation time. For example, the wave number of the absorption maximum and the full width at half maximum of the band were 3673 and 119 cm^{-1} before irradiation for the ES sample, while they were measured to be 3647 and 161 cm^{-1}, respectively, after 430 hours irradiation. The magnitude of the peak shift was smaller for the band with initial peak position at high wave number. Almost same results were obtained for the P20 and F310 samples. As seen in Fig. 3, the absorption intensities at the absorption maximum were, on the other hand, almost unchanged by the irradiation for each sample containing ≡SiOH. The absorption band located at 7230 cm^{-1} should be altered because this is the overtone spectra of the ≡SiOH absorption. Figure 4 shows the alteration of the absorption properties for the ES sample ($t = 3$ mm), as-received and as-irradiated for 330 hours. The molar extinction coefficient of this band was reported by several authors.[2,16] However, it is now seen that this band cannot be used to determine the total amount of ≡SiOH, because the decrease in absorbance by the Xe_2* light irradiation takes place even though the total amount of ≡SiOH remains what it was.

After the samples containing ≡SiOH (ES, P20, and F310) were heated at 1273 K for 50 hours in vacuum, a decrease in absorbance was also detected in the region above 7.4 eV; Fig. 5 shows the difference spectra obtained by subtracting spectra of as-received samples from those of heat treated samples. The largest decrement was observed in ES, the highest ≡SiOH contents among them. The ≡SiOH

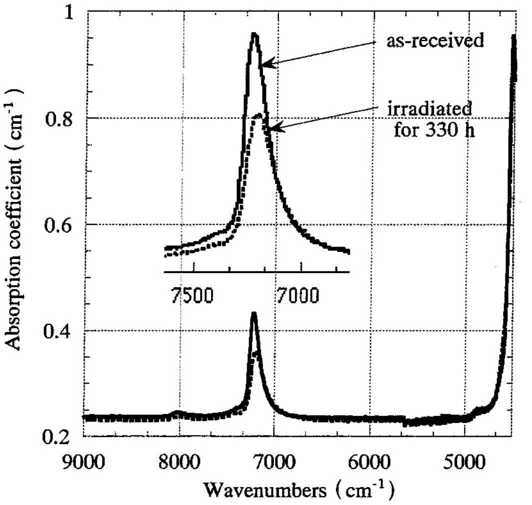

FIG. 4. The overtone spectra of ≡SiOH absorption recorded before and after irradiation (330 hours). The sample is the ES of the 3 mm thickness. The inset is an enlarged overtone band.

amounts of the samples were diminished after the heat treatment, and are summarized in Table 1. The shape and peak position of the absorption band, which are controlled by the relative intensities of several components of ≡SiOH bands, were not changed by the simple heat treatment in vacuum at all. The difference spectra were calculated between the spectra taken after and before heat treatment, and it was confirmed that the simple, proper multiplication of the difference spectra in the range 3800–3400 cm^{-1} led to almost the same absorption spectra as the ones recorded before and after heat treatment.

IV. DISCUSSION

The induction of beta absorption by Xe_2* light irradiation was accompanied by the broadening and the peak shift of the 3673 cm^{-1} absorption band of ≡SiOH. In the complementary experiment, in which the samples were heated at 1273 K for about one hour in air, it was observed that all the alterations which took place in the absorption spectra were identical in peak position, shape, and width to those of as-received samples. These results suggest that the Xe_2* light induced blue shift of the vuv absorption edge might not be due to a decrease in the total amount of ≡SiOH contained in the sample silica glasses. Another thing we would like to mention here is that neither the beta absorption nor the deformation of the 3673 cm^{-1} ≡SiOH band was observed when the silica glasses were irradiated with light from high pressure Xe arc plasma.[17] In this section, the relation between the beta absorption and ≡SiOH is discussed.

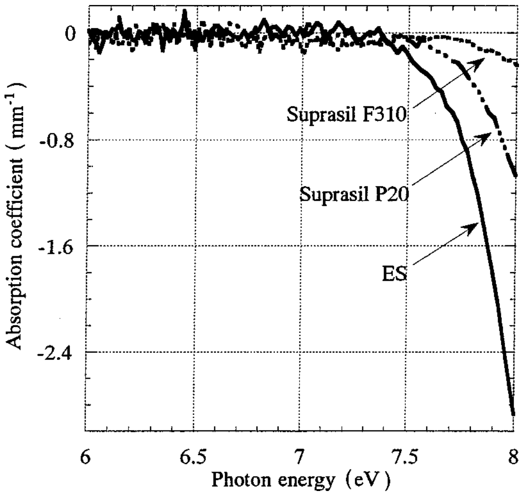

FIG. 5. Difference spectra of the ES, P20, and F310 sample obtained by subtracting spectra of as-received one from the spectra of samples heated in vacuum for 50 hours. The largest decrease in the vuv absorption was observed for ES in which the highest amount of ≡SiOH is contained.

By using both the data of the changes in the absorption in the region PE>7.4 eV and changes in the intensity of the 3673 cm^{-1} band induced by vacuum heat treatment, the absorption cross section of ≡SiOH, σ_{OH}, in vuv region was calculated to compare the spectrum with the beta absorption. The following equation gives a relation between the measured intensity of the transmitted light, I, and the concentration of the absorbers, C:

$$\frac{I}{I_0}=(1-R)^2\exp^{-t(\sigma_{\mathrm{OH}}C_{\mathrm{OH}}+\Sigma_{i=1}^{n}\sigma_i C_i)}, \qquad (2)$$

where I_0 is the intensity of the impinging light, C_{OH} is calculated from Eq. (1), R is the reflectance, and σ_i and C_i are the absorption cross sections and the concentrations of absorbers other than ≡SiOH. Assuming that only the concentration of ≡SiOH is decreased by the vacuum heat treatment, σ_{OH} should be related to the measurement results, as

$$\sigma_{\mathrm{OH}}=\frac{\ln(I_{ah}/I_0)-\ln(I/I_0)}{t(C_{\mathrm{OH}}-C_{ah})}, \qquad (3)$$

where the subscript ''ah'' connotes the values taken in the heat treated sample. The cross section can be estimated from the vuv transmission spectra and the absolute concentration of the absorbing species determined from the intensity of the 3673 cm^{-1}. Although impurities like a chloride might be contained as minor species and contribute to the absorption in the region >7.4 eV, for present purposes the changes were assumed to be due only to ≡SiOH, and also the refractive index changes were neglected. Figure 6 shows the obtained absorption cross section for ≡SiOH in the range from 7.2 to 8.0 eV. The data reported by Awazu and co-workers[9,10] are also plotted as a comparison and it is found that the obtained values in this study are in good agreement with their data. They obtained the σ_{OH} values by means of the ir and vuv transmission measurement technique and the samples examined were three kinds of silica glasses. One was prepared by direct method (type III silica glass, contains ~10^{20} of ≡SiOH cm^{-3}) and the other two samples were fabricated with the vapor phase axial deposition (VAD) technique by different condition to vary the ≡SiOH concentration, which were measured to be 9.5×10^{17} and 7.8×10^{18} of SiOH cm^{-3}, respectively. The reason for the good fit is presumed to be due not only to the major part of the decreased species in our samples being ≡SiOH but also to the same existing ratios of different types of ≡SiOH species in our samples as in the sample studied by Awazu and co-worker.[9,10]

Hereafter, the origin of the beta absorption is considered. The beta absorptions obtained by 430 hours irradiation were

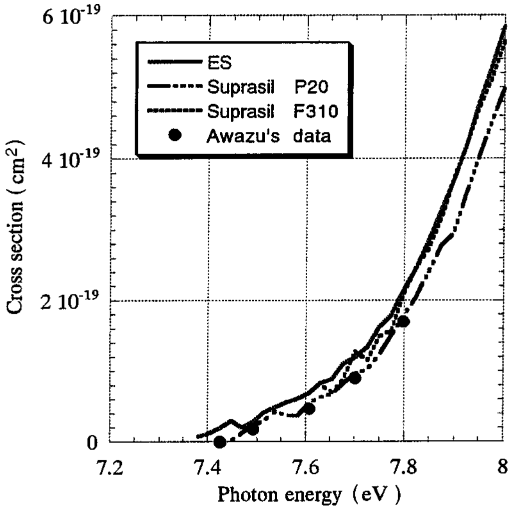

FIG. 6. Evaluated absorption cross section of ≡SiOH in silica glass in the vuv range (7.2–8.0 eV). Data on the ES, P20, and F310 samples were plotted along with data reported by Awazu.[9,10] The absorption apparently started at 7.4 eV and increased with photon energy. The error in the cross section was ±9.5% in this region.

well fit to the spectrum which was calculated by using the ≡SiOH cross-section spectrum, on the assumption of the 40% decrement from the total amount of ≡SiOH for the ES, 42% for the P20, and 24% for the F310 samples, respectively. Stated early in this section as complemental results, it is assumed that total number of the ≡SiOH's did not change by the irradiation, because it was observed that the heat treatment annealed all the alterations which took place in the absorption spectra after irradiation and any hydrogen and water, the reaction products of dissociated ≡SiOH's, are less likely to released out from the samples at the irradiation temperature of 413 K than during heating at 1273 K. Considered together with this assumption, it is supposed that a part of ≡SiOH's taking a particular form in the silica glass is responsible for the beta absorption.

Figure 7 shows the difference spectra of the ES, P20, and F310 samples at around 3673 cm^{-1} ≡SiOH absorption band obtained by subtracting the spectrum prior to irradiation from those recorded after 25, 100, and 430 hours irradiation. It is clearly seen that the absorption intensity was decreased by the irradiation in the higher wave-number side and increased in the lower wave-number side, while the area of the positive part was larger than that of the negative part. As also seen in the figure, both the positive and negative changes grew up with irradiation time and the degrees of these changes were more in the samples containing more ≡SiOH. The wave numbers at the minimum of the negative part were located at between 3694 and 3698 cm^{-1} for the three samples and for each irradiation time, and the location did not move at all within the errors of the measurements. The wave numbers at the maximum of the positive part in the difference spectra were, however, shifted to the lower side with the time of irradiation; it was at 3596 and 3576 cm^{-1} for each kind of sample irradiated for 25 hours and 100 hours, respectively. In addition, as described in Results section, the features of the ‘‘3673-cm^{-1} band’’ shape and peak position changed in almost the same way for each of the samples, therefore, the process of the ≡SiOH band changes did not depend upon the ≡SiOH concentration.

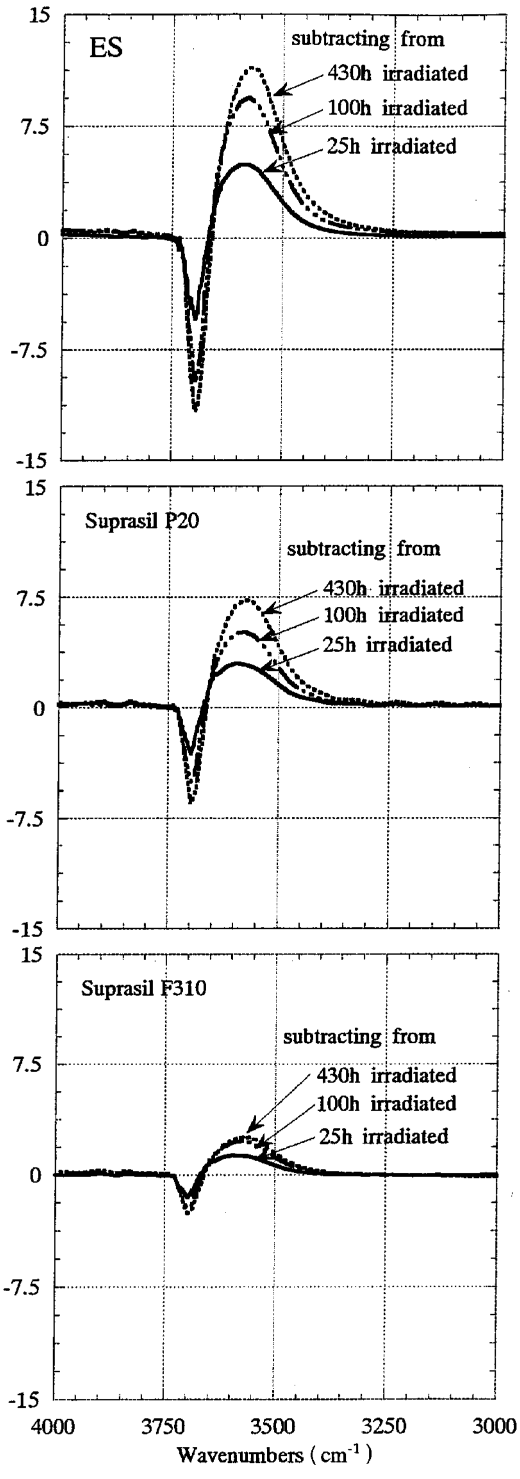

FIG. 7. Difference spectrum of the ES, P20, or F310 samples at around 3673 cm^{-1} ≡SiOH absorption band obtained by subtracting the spectrum prior to irradiation from that after 25, 100, or 430 hours irradiation. The wave numbers at the minimum of the negative part were located at between 3694 and 3698 cm^{-1} for each spectrum. However, the wave numbers at the maximum of the positive part in the difference spectra were shifted to lower side with the irradiation time; it was at 3596 and 3576 cm^{-1} for each kind of sample irradiated for 25 and 100 hours, respectively.

In Fig. 8 the intensity changes at 3694 cm^{-1} by the irradiation are plotted as a function of the negative intensity

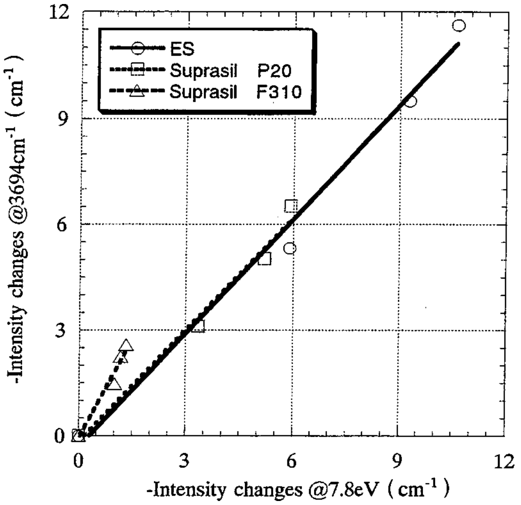

FIG. 8. Correlation between absorption change in $\equiv$SiOH vibration band at 3694 cm^{-1} and intensity changes in beta absorption at 7.8 eV upon irradiation with the Xe_2* lamp. The lines in figure were obtained by the regression fit to the each plot of the data. The errors were ±1.5% and ±9.5% in the intensity at 3694 cm^{-1} and at 7.8 eV, respectively.

changes at 7.8 eV in the beta absorption for samples ES, P20, and F310 (values taken from Figs. 2 and 7). Obviously linear relations were obtained for each sample, with the lines for ES and P20 samples coinciding with each other, while a steeper line was gotten for F310 sample. The lines in Fig. 8 were obtained by regression fits to each data set. The steep line for F310 resulted from a less negative rate of intensity change at 7.8 eV compared with the ES and P20 samples, which could, in turn, be caused by a slight red shift of the band edge for the F310 material in addition to the beta absorption. The latter effect is speculated to be due to radiation damage. From these plots in Fig. 8, it is supposed that the changes in the absorption intensity of 3694 cm^{-1} band and of the beta absorption spectra correlate as a linear function. Moreover, since the 3694 cm^{-1} band is a specific part of the complex $\equiv$SiOH's 3673 cm^{-1} bands, the beta absorption is closely correlated with a particular form of $\equiv$SiOH whose absorption band is located at around 3694 cm^{-1} in ir region.

At least two $\equiv$SiOH classes have been proposed; one is essentially gaslike or isolated $\equiv$SiOH, whose absorption is located at 3690 cm^{-1}, while the tail (~3620 cm^{-1}) is due to weakly interacting $\equiv$SiOH groups.[7] In order to obtain a more detailed understanding of the origin of the absorption band at around 3694 cm^{-1}, band separations in the 3200–4000 cm^{-1} region were performed for the spectra obtained for the ES sample. Davis and Tomozawa[6] reported a band separation technique using a Pearson VII band expressed as

$$I(\nu)=I_{\max}[1+K^2(\nu_{\max}-\nu)^2]^{-N}, \qquad (4)$$

where K is a scaling factor given by

$$K=(2^{1/N}-1)^{1/2}/B. \qquad (5)$$

$I(\nu)$ is the band intensity as a function of wave number ν, $I_{\max}$ is the maximum intensity, $\nu_{\max}$ is the wave number at the maximum of the band, B is the half width at half maximum, and N is a constant between 1 and 10, where 1 gives a Lorentzian profile and 10 gives approximately a Gaussian profile. By following the Pearson VII method, the features shown in Fig. 9 were calculated; the six component bands used are listed in Table II. These six bands were also cited in the paper by Davis and Tomozawa;[6] i.e., band No. 1 at 3426 cm^{-1} assigned to asymmetric stretching of molecular water bound to the silica network and symmetric stretching of free/hydrogen bonded (H bonded) molecular water inside the glass, band No. 2 at 3551 cm^{-1}, band No. 3 at 3612 cm^{-1} due to OH stretching of $\equiv$SiOH's which are H bonded to the oxygen of neighboring $\equiv$SiOH, band No. 4 at 3661 cm^{-1}, band No. 5 at 3694 cm^{-1} due to OH stretching of $\equiv$SiOH, and band No. 6 at 3810 cm^{-1}, possibly arising from combination torsion and OH stretching of $\equiv$SiOH. It is seen in Fig. 9 that the species decreased by irradiation were the elements No. 4 and No. 5, and the increased ones were the Nos. 1, 2, and 3 bands, respectively. The beta absorption generated by 430 hours irradiation corresponded to the 40% of the total amount of $\equiv$SiOH for the ES sample. On the other hand, for the sum of the intensities of the 3694 and 3661 cm^{-1} $\equiv$SiOH band elements, the percentage of the absorption intensity diminished by irradiation relative to that before irradiation was also 40%. As a matter of fact, two of the ratios were strikingly coincident with each other, as in the

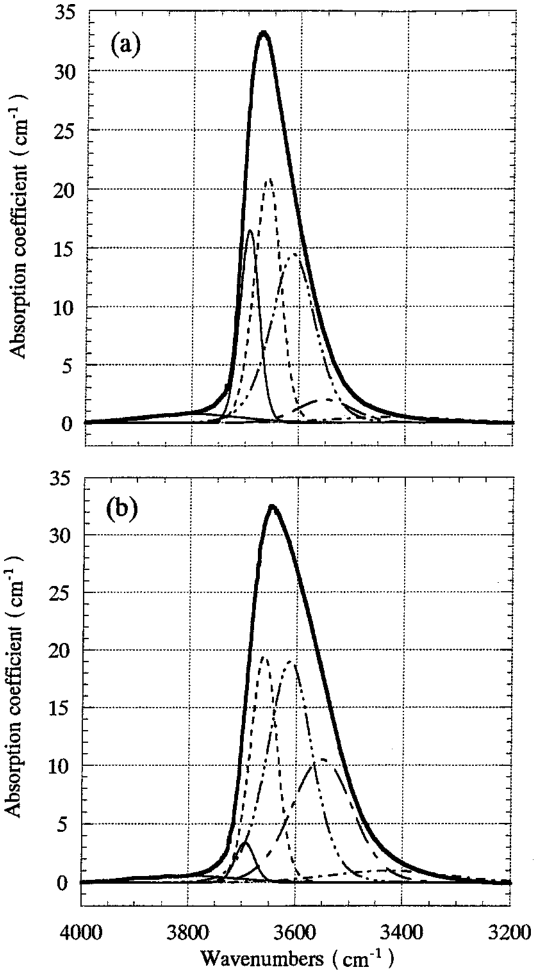

FIG. 9. Results of the Pearson VII band separation method adapted for the ES sample: (a) as-received and (b) as-irradiated for 430 hours. The six component bands used for this separation are listed in Table II.

TABLE II. List of parameters for adapted Pearson VII bands.

Band position[a] $\nu_{\max}$(cm^{-1})	FWHM, B (cm^{-1})	Exponent, N
No. 1 3426	130	10
No. 2 3551	67	10
No. 3 3612	49	4.5
No. 4 3661	29	8.7
No. 5 3694	21.1	10
No. 6 3810	114	7.15

[a] Band assignments by K. M. Davis and M. Tomozawa: (Ref. 6): 3426 cm^{-1}: asymmetric stretching of molecular water bound to silica network and symmetric stretching of free/H bonded molecular water inside the glass. 3551 and 3612 cm^{-1}: OH stretching of SiOH's which are H bonded to the oxygen of neighboring SiOH. 3661 and 3694 cm^{-1}: OH stretching of SiOH (two independent SiOH). 3810 cm^{-1}: Possibly combination torsion and OH stretching of SiOH.

case of the P20 and F310 samples, as well.

The equilibria shown in Fig. 10 are proposed as a molecular level model for the processes described. Here, the photo chemical reaction is shifted to the right side by irradiation with the Xe_2* light, which changes the isolated form of ≡SiOH to the H bonded one. In the drawing, the dotted line indicates H bonding between H and O atoms. Therefore, according to the band assignment, it is natural to consider that the number of H bonded ≡SiOH is increased at the expense of a decrease of the same number of isolated ≡SiOH by 7.2 eV band light irradiation. The degree of the H bonding is affected by the electronic states of O^- and H^+,[18,19] which might result from electronic defect generation. It has been also reported that the vibrational frequency of ≡SiOH decreases and the bandwidth becomes broader as the degree of H bonding increases.[20–22] Therefore, the absorption cross sections of species #1 through #3 of the H bonded ≡SiOH could be larger than those of Nos. 4 and 5, the isolated ≡SiOH in silica glass, and which is responsible for the broadening of 3673 cm^{-1} absorption band (see Figs. 3, 7, and/or 9). On the other hand, there was no increase in the absortion intensity in the vuv region, despite the increase of the number of the H bonded ≡SiOH. Therefore, it is supposed that the absorption due to the H bonded OH groups must be located at higher energy portion than the absorption edge of silica glass.

The radiation induced shift of the 3673 cm^{-1} ≡SiOH band indicates the ongoing process of these electronic state changes. There was no data available for the defects generation during Xe_2* light irradiation at the present time, however, only the speculation of photo physical and/or chemical processes can be done on the basis of the band assignments of ≡SiOH in the ir region as follows. The photon energy of Xe_2* emission (7.2 eV) is ~2 eV below the conduction band of silica glass and is absorbed by exciting a transition of the OH group. The dissociations of the H atom from the isolated ≡SiOH occurred as a result and the H atoms move freely through the glass network. By the way, since the band of Xe_2* emission spread up to the band edge of the glass (Fig. 1), the bond cleavage occurs and the paramagnetic defects, e.g., E' center and nonbridging oxygen hole center (NBOHC), should be generated during irradiation. The dissociated H atoms react with the electronic defects, at which the H bonding occurs and then gives rise to Nos. 2 and 3 OH absorption bands in the ir region. A molecular water may be produced by the reaction between the H atom and the abundant oxygen or other −OH group (No. 1 band). There is another possibility of the ≡SiOH-form conversion. Assuming that the distribution of ≡SiOH is homogeneous, the distance between two −OH is about 2 nm for the concentration of 10^{20} OH cm^{-3}. Thus, in the homogeneous distribution scenario, two of the −OH would not affect each other. Therefore, the ≡SiOH's transformed to the other form might exist as more like a pair originally and give some different degree of H bonding in silica glass.

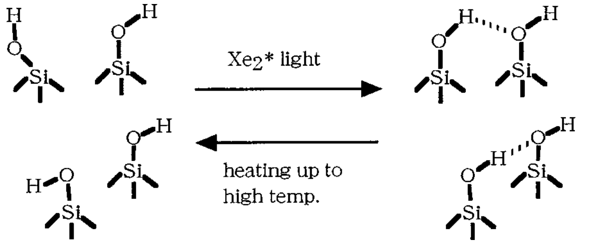

FIG. 10. The speculated equilibria showing the photo chemical reaction of the ≡SiOH contained in silica glass. Which is shifted to right side by the irradiation with the Xe_2* light by the changes of isolated form ≡SiOH to the H bonded one. Here in the reaction the dotted line indicates the H bonding between H and O atoms.

The experimental results in the literature[23] suggest that the isolated form of ≡SiOH is stable at high temperature; the H bonded ≡SiOH is decreased by heating to form the isolated ≡SiOH and some H may be released out. The experiment by Davis and Tomozawa[6] showed that heating silica glass at lower temperature introduces the H bonded ≡SiOH, but high-temperature heating makes smaller amounts of the H bonded ≡SiOH. The present experiment has shown that relatively low-temperature (413 ± 12 K) exposure to 7.2 eV light favors the production of ≡SiOH in H bonded form, and which could be a kind of new method to convert the isolated ≡SiOH to the H bonded ≡SiOH without any concentration changes of ≡SiOH in silica glass.

V. SUMMARY

The optical absorption due to ≡SiOH groups in silica in PE>7.4 eV up to the absorption edge is primarily controlled by isolated ≡SiOH form. (The absorption due to the H bonded ≡SiOH must be located at higher energy portion than the absorption edge in the vuv region.)

This conclusion was substantiated by the following three pieces of evidence:

(1) The negative changes in vuv absorption spectra (PE>7.4 eV) induced by Xe_2* lamp irradiation were essentially the same as the spectrum change caused by the reduction of ≡SiOH amount in silica glass upon heating in vacuum.

(2) The fraction of the isolated ≡SiOH was diminished and that of the H bonded one was increased by Xe_2* irradiation without any change of the total amount of ≡SiOH contained. Therefore, the Xe_2* light irradiation appears to induce conversion of the isolated ≡SiOH into the H bonded

≡SiOH in silica glass. The magnitude of negative changes in vuv absorption spectra ($PE > 7.4$ eV) was linearly proportional to those of the infrared absorption due to the isolated ≡SiOH absorption.

(3) Supposing that the isolated ≡SiOH absorption band at 3694 cm^{-1} consisted mainly of the 3694 and 3661 cm^{-1} bands, the ratio of the diminished isolated ≡SiOH was the same as the ratio of the decrease in intensity of vuv absorption spectra ($PE > 7.4$ eV).

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