

OH and Interstitial-H₂ Concentration Dependence of Intensities of X-ray-Induced Absorption of Type-III Fused Silica

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Hydroxyl and interstitial-H₂ concentration dependence of X-ray-induced absorption of type-III fused silica up to an irradiation time of 6 h was studied. Induced absorption spectra in the fused silica irradiated with X-rays from a Rh target with a dosage of $2 \times 10^4 \text{ C kg}^{-1} \text{ h}^{-1}$ were reproduced by six Gaussian absorption bands at 3.8, 4.8, 5.0, 5.4, 5.8 and 6.5 eV. Intensities of these absorption bands increased with the power of the irradiation time. OH and interstitial-H₂ concentration dependence at 1 h and 6 h are similar in the doubly logarithmic plot. A linear relationship between the intensities of each absorption component and the H₂ concentration was observed, while no clear dependence of these intensities on the OH concentration was observed. Intensities of absorption bands decreased linearly as the H₂ concentration increased except for 5.0-eV band in which the intensity increased as the H₂ concentration increased.

1 . Introduction

Vitreous silica ($v\text{-SiO}_2$) has a high optical transmission from the vacuum ultraviolet to the near infrared [1]. Utilization of this optical property allows this material to be used in optical materials such as optical waveguides, lenses and prisms for ultraviolet (UV) light. $v\text{-SiO}_2$ can be divided into synthetic fused silica (SFS) synthesized from liquid silicon compounds and fused quartz (FQ) produced by melting natural quartz powder [1]. SFS can be further divided into several types [2]: type-III SFSs produced directly by flame hydrolysis of silicon compounds such as SiCl_4 , the soot-remelting method, the plasma chemical vapor deposition (CVD) method and the sol-gel method. Most optical SFSs are type-III SFS or soot-remelted silica produced by the vapor axial-phase deposition (VAD) method.

Type-III SFS contains $3 \times 10^{19} - 1 \times 10^{20} \text{ cm}^{-3}$ (400 - 1500 mass ppm) of OH. Most optical materials for KrF- and ArF-excimer lasers are type-III SFS because this material is resistant to UV irradiation [2]. Point defects might be induced by irradiating with excimer lasers [3,

4]. Point defects are unfavorable in practical applications in UV optical materials because they cause optical absorption in the UV region. Two effects on the suppression of the ArF- and KrF-excimer-laser-induced absorption have been proposed: one is the effect of Si-OH structure [5 - 7] and another is interstitial-hydrogen molecules [8, 9].

Point defects are also induced by irradiating with γ -rays and X-rays [3, 4]. A study of the irradiation time dependence of the absorption intensity of X-ray-induced absorption provides useful information to understand the characteristics of the radiation-induced point defects in SFSs. Nakamura et al. studied the effect of heat treatment on the X-ray induced absorption of type-III SFS [10, 11]. Kuzuu and Murahara studied the X-ray induced absorption of type-III SFS synthesized under reducing and oxidizing conditions [12]. They showed that the absorption spectra of SFS synthesized under reducing condition has a peak at 5.7 eV, and an SFS synthesized under an oxidizing condition has a peak at 5.7 eV, a shoulder at 4.8 eV and a slight peak at 2.0 eV. The characteristics of these absorption bands were discussed based on a model proposed for

describing the ArF-excimer-laser-induced absorption of the same kinds of SFSs [13, 14]. Kuzuu studied the OH concentration dependence of the X-ray-induced absorption of type-III SFSs synthesized under reducing conditions up to the irradiation time of 3 h [15]. The induced absorption spectra were reproduced by fitting five Gaussian absorption bands at 6.5, 5.8, 5.4, 5.0, 4.8 eV, respectively, and the origin of the OH concentration dependence was discussed. At that time, the author considered only the OH concentration dependence [15] but did not consider the effect of the interstitial-H₂ molecules. Based on the absorption bands proposed in Ref. [15], Kuzuu et al. analyzed X-ray- and ArF-laser-induced absorptions in type-III SFSs synthesized under reducing and oxidizing conditions [17]. The present authors studied the OH concentration dependence of X-ray-induced absorption of type-III and VAD SFSs that contain various amounts of OH up to the irradiation time of 6 h [16]. In addition to the absorption bands used in our foregoing studies [15, 17], an absorption band at 3.8-eV, which might be due to interstitial-Cl₂ molecules, appeared at long irradiation times. The intensity of each absorption component increases with the power of the irradiation time. At irradiation times shorter than 2 h, the intensities of the 5.8-, 5.4- and 5.0- eV bands decrease with increasing OH concentration. At irradiation times longer than 2 h, on the other hand, each of these intensities shows a minimum at an OH concentration of $\approx 5 \times 10^{18} \text{cm}^{-3}$. The power index of the time dependence also shows a minimum at an OH concentration of $\approx 5 \times 10^{17} \text{cm}^{-3}$.

This OH concentration dependence of the power index is the origin of the difference in the OH concentration dependence of the absorption component depending on the irradiation times.

As mentioned before, the characteristics of the excimer-laser-induced absorption in type-III SFSs depend both on OH and interstitial-H₂ concentrations. In a previous paper [15], however, we focused only on the OH concentration dependence in excimer-laser-induced absorption in type-III SFSs. The nature of the interstitial-H₂ concentration dependence in Ref. [15] is unknown because we did not measure the interstitial-H₂ concentration. Therefore, the change in OH concentration dependence might possibly be due to the effect of interstitial-H₂ molecules. We then studied OH and interstitial-H₂ concentration dependence of the X-ray-induced absorption using type-III SFSs containing various amounts of OH and interstitial-H₂.

2. Experimental procedure

Twelve samples (A - L) containing various amounts of OH and H₂ contents shown in Table 1 were used. All samples used are type-III SFSs. Samples were cut to a size of $1 \times 3 \times 1 \text{ cm}^3$, and two facing surfaces with a thickness of 1 cm were optically polished.

X-rays from a Rh target operated at 50 kV and 50 mA were utilized with a Rigaku System 3270 fluorescent X-ray analyzer. The dosage was $2 \times 10^4 \text{ C kg}^{-1} \text{ h}^{-1}$. X-ray exposure was up to 6 h ($1.2 \times 10^5 \text{ C kg}^{-1}$). Induced absorption spectra were measured with a Shimadzu

Table 1 Samples used in the present study

Sample	OH conc. (10^{19}cm^{-3})			H ₂ conc. (10^{18}cm^{-3})			Si-H conc. (10^{18}cm^{-3})	
	Before	After	Symbol ^{a)}	Before	After	Symbol ^{b)}	Before	After
A	11	11		0.09	<0.05		<0.05	<0.05
B	11	11		0.71	<0.05		<0.05	0.05
C	9.4	9.4		0.18	<0.05		<0.05	0.05
D	9.0	9.0		1.2	<0.05		<0.05	0.2
E	9.1	9.0		2.5	0.93		<0.05	0.8
F	7.8	7.8		0.16	<0.05		<0.05	<0.05
G	7.7	7.7		1.3	0.06		<0.05	0.3
H	7.6	7.5		3.1	1.4		<0.05	0.6
I	5.7	5.7		0.41	<0.05		<0.05	<0.05
J	5.4	5.3		1.2	<0.05		<0.05	<0.05
K	5.3	5.3		3.4	1.8		<0.05	0.6
L	4.0	4.0	x	10	8.0		0.3	2

a) Symbols are the same as used in Figs. 3 and 5.

b) Symbols are the same as used in Figs. 4 and 6.

UV3100-type spectrophotometer within 5 min after each irradiation. The OH contents were determined by the peak intensity at 3650 cm⁻¹ with an extinction coefficient of 77.5 dm³ mol⁻¹ cm⁻¹ [18] using a Perkin Elmer System 2000 FT-IR spectrophotometer. Interstitial-H₂ and Si-H contents were measured with a Jasco NRS-2000 Raman spectrophotometer [19].

3 . Results

An example of the X-ray-induced absorption is shown in Fig.1. All absorption spectra were reproduced by six Gaussian bands at 3.8, 4.8, 5.0, 5.4, 5.8, and 6.5 eV, whose peaks and full widths at half maxima (FWHMs) are shown in Table 2. The irradiation time dependence of each absorption component is shown in Fig. 2. The curve of each component is linear in doubly logarithmic plot,

$$I \propto t^{\alpha}, \quad (1)$$

where I is the absorption intensity, t is the irradiation time, and α is a constant. Hereafter, we will refer to the “ power index ”. In a previous paper [16], however, the time dependence curve was convex in low-OH-containing VAD silicas. This could be due to the error in the measurement in large absorption at

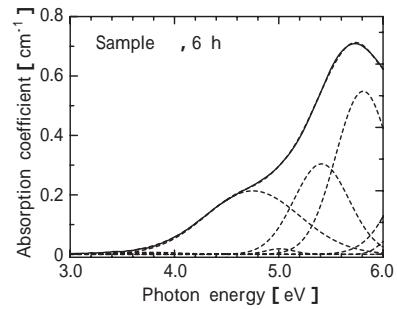


Fig. 1 An example of Gaussian peak decomposition of X-ray-induced absorption; — : observation, - - - : calculation

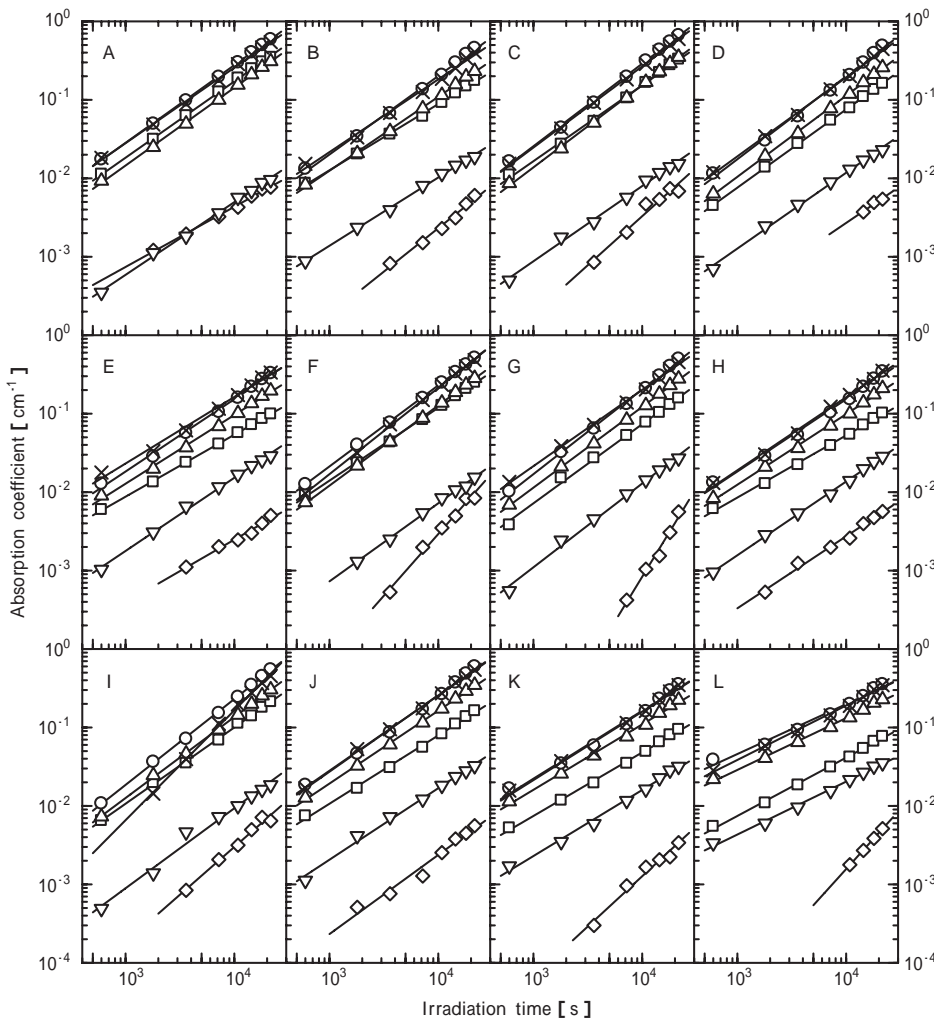


Fig. 2 Irradiation time dependence of each absorption components; × : 6.5 eV, o : 5.8 eV, Δ : 5.4 eV, □ : 5.0 eV, ▽ : 4.8 eV, ◇ : 3.8 eV

Table 2 Absorption components and their origins

Peak (eV)	FWHM (eV)	Defects	Structure	Absorption cross section ^{a)} (cm ²)	Oscillator Strength
3.77	0.69	Interstitial Cl ₂	Cl ₂	1 × 10 ⁻¹⁹	
3.77	0.69	POL	Si-O-O-Si		
4.75	1.06	NBOHC	Si-O•	2 × 10 ⁻¹⁷ b)	0.2
5.01	0.32	ODQ ()	Si•••Si	2 × 10 ⁻¹⁷	
5.41	0.62	E'	Si-H Si•	6 × 10 ⁻¹⁷ b)	0.4
5.81	0.62	E'	Si•	6 × 10 ⁻¹⁷ b)	0.4
6.50	0.74	Unknown			

a) The absorption cross sections are after those in Ref.4.

b) Calculated from the oscillator strength shown in this table.

long irradiation times, because part of the absorption spectra of these samples is truncated due to the value of absorption being beyond the measurement range. In the present samples, the intensities of absorption are

low enough to measure the absorption.

Figure 3 shows the interstitial-H₂ concentration dependence of the absorption components at irradiation times of 1 h and 6 h. Interstitial-H₂ concentration

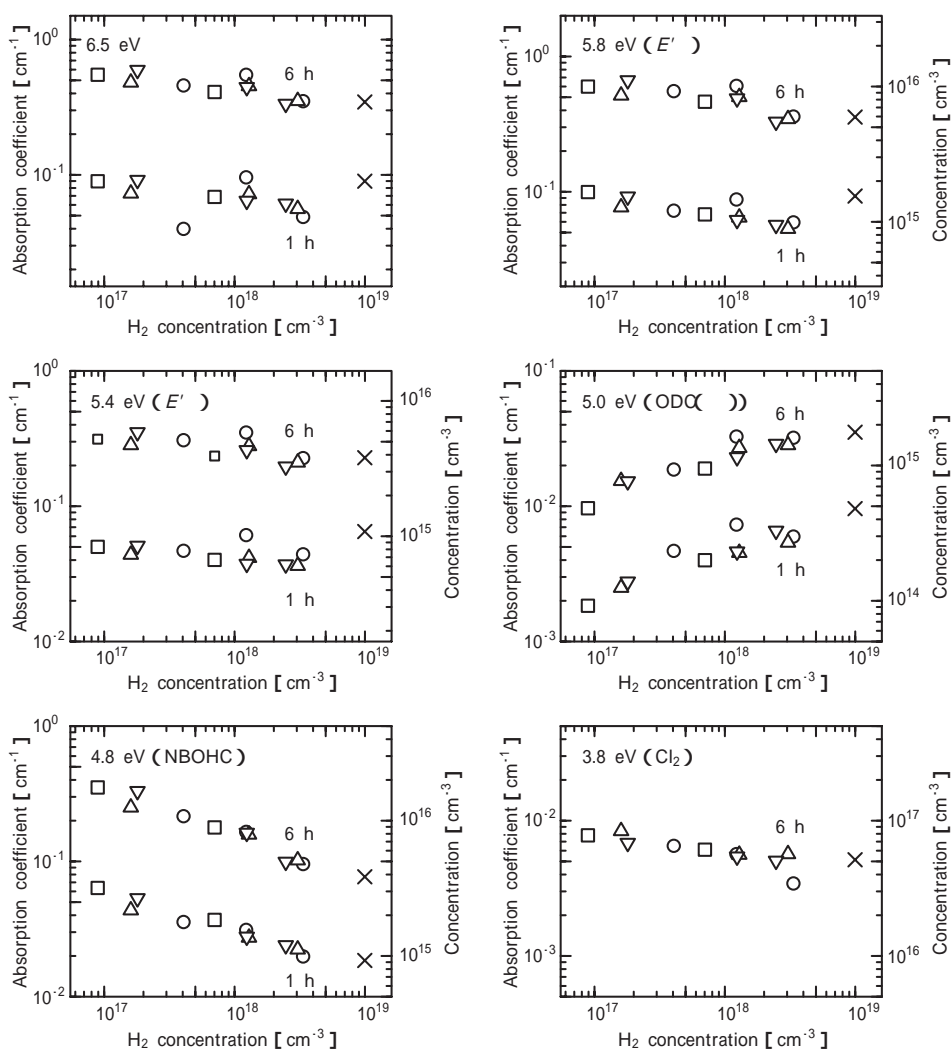


Fig. 3 Interstitial-H₂ concentration dependence of the intensities and corresponding defect concentrations at the irradiation times of 1 h and 6 h

The symbols indicate the range of the OH concentrations;

× : 4.0 × 10¹⁹cm⁻³, ◊ : 5.3 - 5.7 × 10¹⁹cm⁻³, ◑ : 7.6 - 7.8 × 10¹⁹cm⁻³,
 ◒ : 9.0 - 9.4 × 10¹⁹cm⁻³, ◓ : 11 × 10¹⁹cm⁻³

dependences at 1 h and 6 h are similar in the doubly logarithmic plot. Therefore, the interstitial-H₂ concentration dependence at any irradiation time must be similar at least between 1 h and 6 h. The intensity of each component falls on a curve irrespective of the OH concentration. The intensities of the 5.8-, 5.4-, 4.8- and 3.8- eV bands decrease with increasing H₂ concentration. The intensity of the 5.0-eV band, on the other hand, increases with increasing H₂ content.

Figure 4 shows the OH concentration dependence of absorption components at irradiation times of 1 h and 6 h. The OH concentration dependences at 1 h and 6 h are similar in the doubly logarithmic plot. Therefore, these data suggest that the OH concentration dependences at any irradiation time are similar at least between 1 h and 6 h. No apparent OH concentration

dependence was observed as in the case of interstitial-H₂ concentration dependence.

Figure 5 shows the interstitial-H₂ concentration dependence of the power indices. They decrease weakly with increasing H₂ concentration except for the 3.8 eV-band. The power indices for 3.8-eV components disperse over large amplitude compared to the other components. This could be due to the power index having greater errors because the intensity of the 3.8-eV components is very weak and exists in the tail of the absorption spectra.

The OH concentration dependence of the power index is shown in Fig. 6. The OH concentration dependences are similar among all absorption components except for the 3.8-eV band; the values are approximately constant (≈ 1) except at $[\text{OH}] = 4 \times 10^{19}$

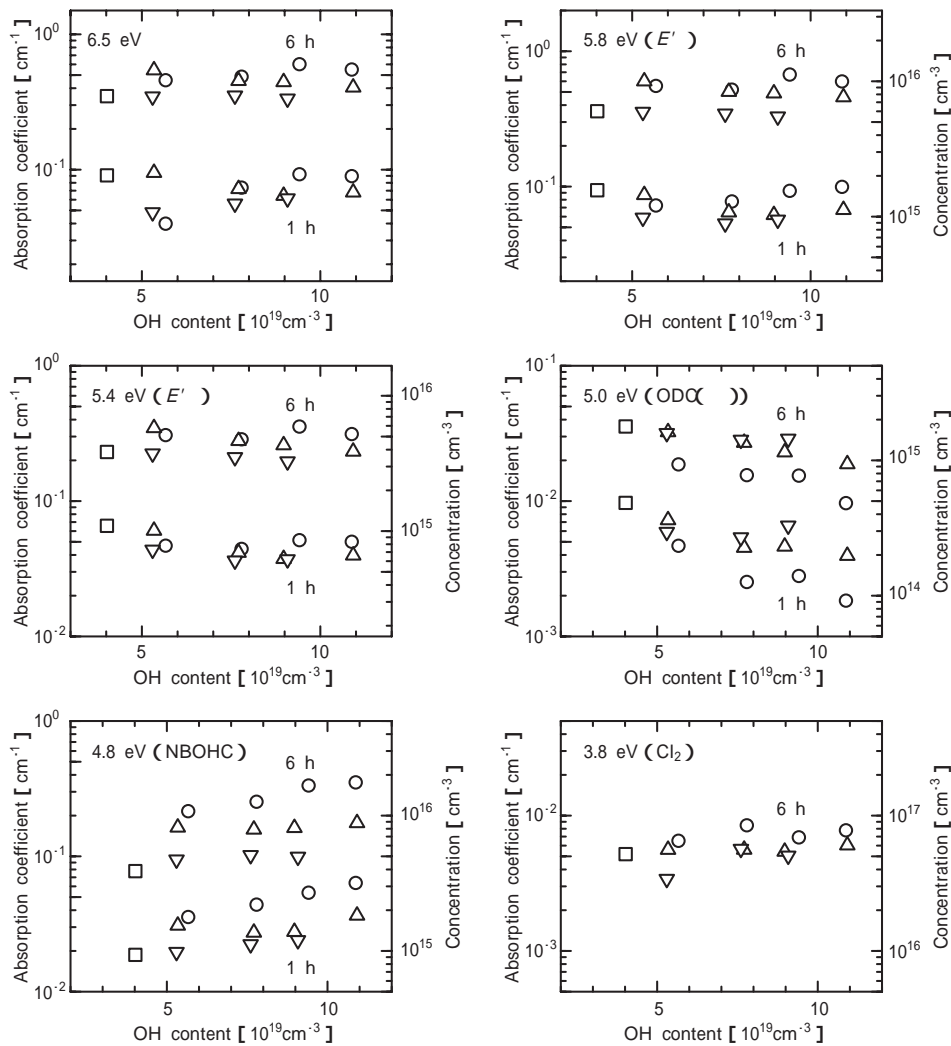


Fig. 4 OH concentration dependence of the intensities and corresponding defect concentrations of each absorption components at the irradiation times of 1 h and 6 h
 The symbols indicate the range of the interstitial-H₂ concentrations;
 □ : $0.09 - 0.41 \times 10^{18} \text{ cm}^{-3}$, △ : $0.7 - 1.3 \times 10^{18} \text{ cm}^{-3}$, ◇ : $2.5 - 3.4 \times 10^{18} \text{ cm}^{-3}$,
 ○ : $10 \times 10^{18} \text{ cm}^{-3}$

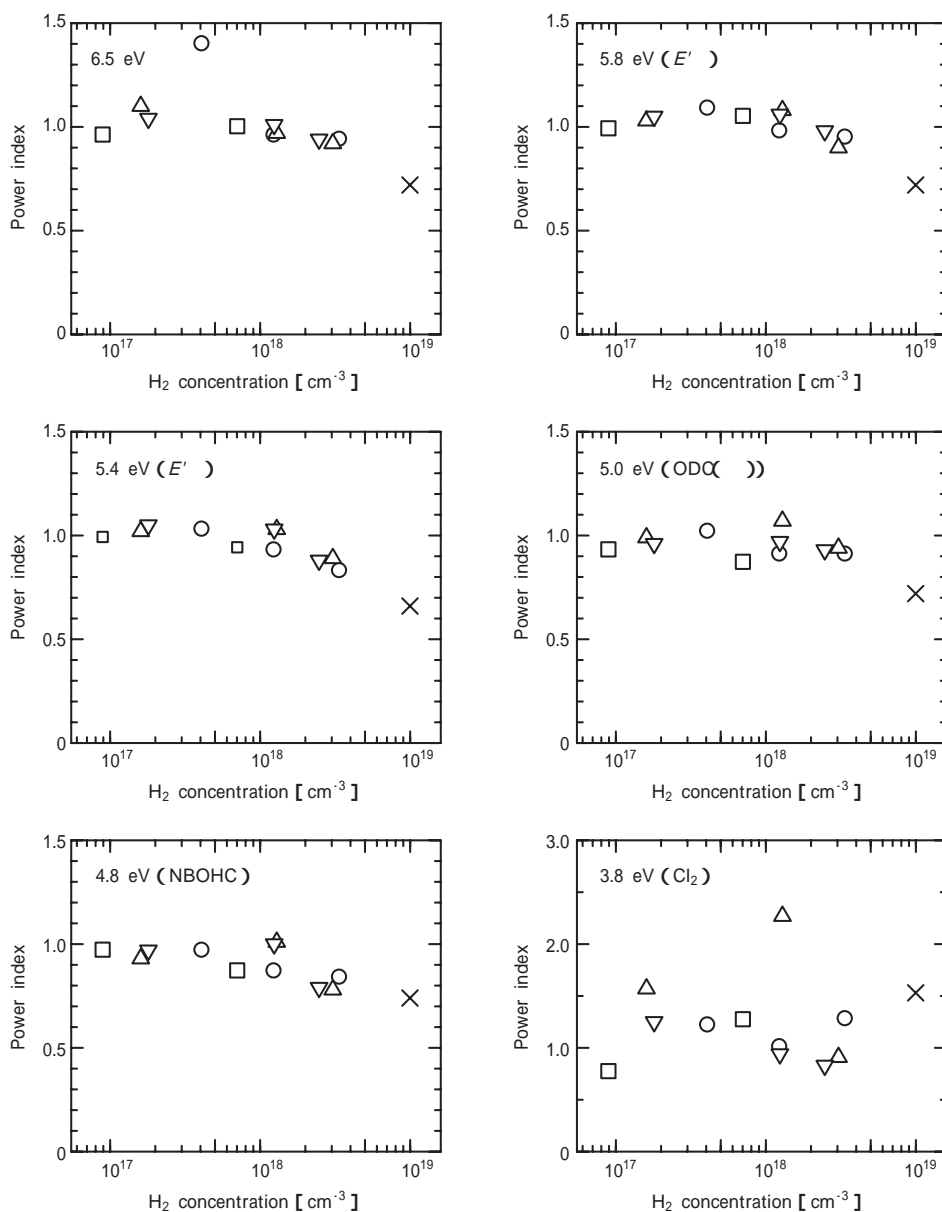


Fig. 5 Interstitial- H_2 concentration dependence of the power index of the irradiation time
 The symbols indicate the range of the OH concentrations;
 \times : $4.0 \times 10^{19} \text{cm}^{-3}$, \square : $5.3 - 5.7 \times 10^{19} \text{cm}^{-3}$, \circ : $7.6 - 7.8 \times 10^{19} \text{cm}^{-3}$,
 \triangle : $9.0 - 9.4 \times 10^{19} \text{cm}^{-3}$, ∇ : $11 \times 10^{19} \text{cm}^{-3}$

cm^{-3} which was less than those at higher OH concentration. The OH concentration dependence of the power index for the 3.8-eV band is complicated as in the case of the interstitial- H_2 concentration dependence.

4 . Discussion

[1] Origin of the absorption components

One of the present authors and colleagues showed that X-ray- [15 - 17], γ -ray- [20] and excimer-laser- [17, 21] induced absorption spectra can be reproduced

by five Gaussian absorption bands at 6.5, 5.8, 5.4, 5.0 and 4.8 eV, respectively. The absorption bands used in this paper include the absorption bands used in these papers. In addition to these absorption bands, an absorption band at 3.8 eV is assumed in the previous [16] and the present papers. The peaks and full width at half maxima (FWHMs) shown in Table 2 are the same as in Ref. [16].

The absorption bands near 5 eV are called the B_2 bands. At least two kinds of B_2 bands, a B_2 band with a peak at 5.02 eV and an FWHM of 0.32 eV and a B_2 band with a peak at 5.15 eV and an FWHM of 0.42 eV,

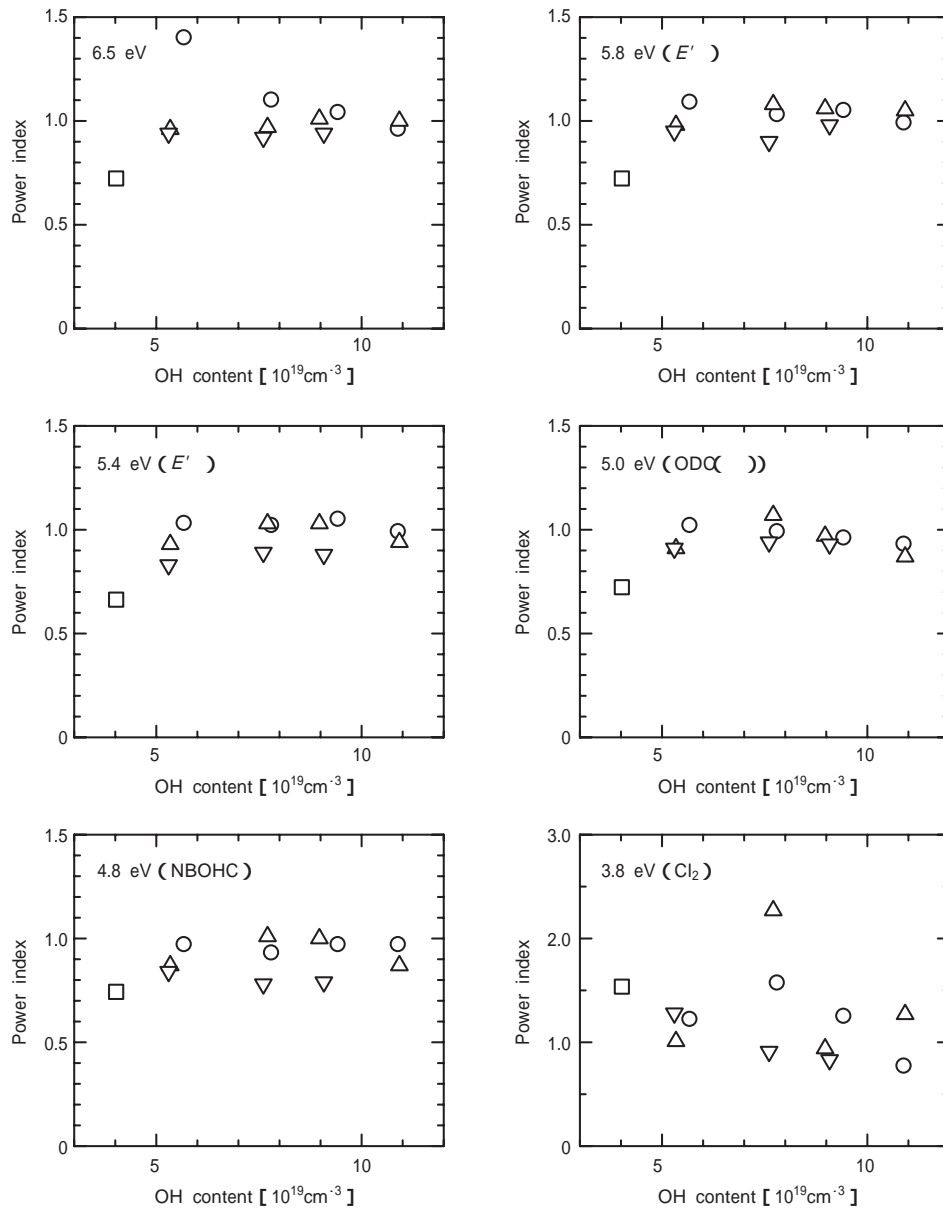


Fig. 6 OH concentration dependence of the power index to time dependence of each absorption component
 The symbols indicate the range of the interstitial- H_2 concentrations;
 \square : $0.09 - 0.41 \times 10^{18} \text{cm}^{-3}$, \diamond : $0.7 - 1.3 \times 10^{18} \text{cm}^{-3}$, \triangle : $2.5 - 3.4 \times 10^{18} \text{cm}^{-3}$,
 \circ : $10 \times 10^{18} \text{cm}^{-3}$

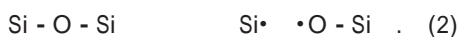
exist [4, 22]. The origin of the B_2 band is an unrelaxed oxygen vacancy $\text{Si}\cdots\text{Si}$ called ODC(II) [4]. Here, “ ” represents covalent bonds to three oxygen atoms, and “ \cdots ” represents a vacancy at which an oxygen atom is removed from an $\text{Si}-\text{O}-\text{Si}$ structure. ODC(II) was named by Imai et al. [23] as distinct from the $\text{Si}-\text{Si}$ structure called ODC(I), in both of which ODC stands for “oxygen deficient center”. ODC(I) causes an absorption band at 7.6 eV.

The origin of the 5.8-eV band is the E center ($\text{Si}\cdot$), where “ \cdot ” represents an unpaired electron. The 5.4-eV band may be caused by the E' center [4],

which is related to hydrogen. A possible structure is $\text{Si}-\text{H}-\text{Si}\cdot$. The absorption bands due to two kinds of E' centers, at 5.4 and 5.8 eV, respectively, have the same value of FWHM, 0.62 eV. Some reports assume that the FWHM of the E' centers is 0.8 eV [4]. In previous papers, we also used 0.8 eV as the FWHM of the 5.8-eV bands induced by irradiating with X-rays [15, 17], an ArF-excimer-laser [17, 21], and γ -rays [20]. However, KrF-excimer-laser-induced absorption cannot be reproduced if we assume the FWHM of the 5.8-eV band to be 0.8 eV [7]. If we assume the FWHM of the 5.8- and 5.4-eV bands to be 0.62 eV, the

absorption spectra for various types of SFSs irradiated with X-rays, γ -rays and excimer-lasers can be reproduced [19]. The origin of the 6.5-eV band is unknown. This absorption component is used to reproduce the effects of absorption at the energy higher than 6.2 eV.

The 4.8-eV band is an oxygen-related center. Several origins have been proposed [3, 4]; non-bridging oxygen hole center (NBOHC [$\text{Si} - \text{O} \cdot$]), peroxy radical (POR [$\text{Si} - \text{O} - \text{O} \cdot$]) and interstitial- O_3 molecule. The FWHM of the 4.8-eV band due to POR is 0.8 eV, while that of the others is 1.05 eV [4]. NBOHC can be produced by bond breakage, as follows :



The same amount of E' center as NBOHC is also produced in this process. In a previous paper [16] on X-ray-induced absorption of various kinds of SFSs, we assumed that the main process of the 4.8-eV band is NBOHC, because the estimated values of E' centers and NBOHCs in samples containing OH at greater than $4 \times 10^{18} \text{ cm}^{-3}$ are of the same order. In the present paper, these amounts are also of the same order in the sample with the interstitial- H_2 contents of $0.09 - 0.41 \times 10^{18} \text{ cm}^{-3}$ (Symbol \square in Fig. 4). The NBOHCs in the other samples are less than that of the E' centers which may be due to the effect of interstitial H_2 -molecules to suppress the creation of the NBOHC. In our previous papers on X-ray- and ArF-laser-induced absorption of type-III silicas, we assumed that the 4.8-eV band was due to interstitial-ozone [12 - 14, 17]. In these papers, the 4.8-eV band is apparent only in samples synthesized under oxidizing conditions [12, 14, 17] in which oxygen molecules could dissolve into the glass network during the glass formation process, because an excess amount of oxygen molecules exists in the flame used for the hydrolysis. The intensities of the 4.8-eV band in fused silicas produced under reducing conditions are not so strong [12, 13, 20]. The present samples are also type-III silicas produced under a reducing condition. In these samples, the 4.8-eV band might be due to NBOHC because an excess amount of hydrogen molecules exists in the flame and an oxygen molecule can hardly be dissolved during the glass formation process.

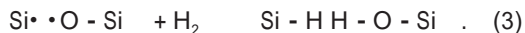
In our previous papers except for Ref. [16], we did

not assume the 3.8-eV band [15, 17]. Because the maximum irradiation time in these papers was 3 h [12, 15, 17], the intensity of the 3.8-eV band was still weak compared to the other absorption components. In fact, the 3.8-eV band intensity in the present study at an irradiation time of 3 h, $\approx 10^{-3} \text{ cm}^{-3}$, is two orders less than those of the 5.8- and 5.4-eV bands. Nishikawa et al. proposed that the 3.8-eV band is due to a peroxy linkage (POL [$\text{Si} - \text{O} - \text{O} - \text{Si}$]) [24]. Awazu et al. [25] showed that the 3.8-eV band was induced in VAD silica vitrified in an ambient mixture of Cl_2 and He gas and that the intensity of this band increased with increasing Cl_2 concentration in the ambient atmosphere during the vitrification process. Based on this experimental evidence, they proposed that the 3.8-eV band is due to the interstitial- Cl_2 . In a previous paper [16], we discussed whether the origin of the 3.8-eV band is POL or the interstitial- Cl_2 . POL could be formed by the reaction of ODC(II) and an interstitial- O_2 molecule. Because the POL will be changed into a pair of NBOHC or a peroxy radical (POR) and an E' center by the irradiation, the intensity of the 3.8-eV band must be saturated or decreased due to the destruction of the POL. Therefore, the interstitial- Cl_2 is a more probable candidate for the origin of the 3.8 eV-band. In Figs. 3 and 4, the concentration of Cl_2 is tentatively indicated.

[2] Effects of $\text{Si} - \text{OH}$ and interstitial- H_2 molecules on the defects creation

Hydroxyl groups and interstitial- H_2 molecules are considered to suppress the increment in the excimer-laser-induced absorption of $\nu\text{-SiO}_2$. One of the present authors and coworkers studied the hydroxyl-content-dependence of ArF- and KrF-excimer-laser-induced absorption and showed that the absorption intensities decreased with increasing hydroxyl content [5 - 7]. The authors considered that the OH group makes the glass network softer and prevents bond breakage upon irradiation. Yamagata showed that the interstitial- H_2 molecules make the SFS resistant to the excimer-laser irradiation [8]. The interstitial- H_2 molecules react with the dangling bonds formed by the irradiation through the process of Eq. (2), and the defect structure becomes optically inactive. The E' centers and NBOHCs on the right side in Eq. (2) react with the H_2

molecule as



Through this reaction, creation of optical absorption due to *E* centers and NBOHCs is suppressed.

X-ray-induced absorption in SFSs was characteristics similar to the case of excimer-laser-induced absorption. The absorption intensity of X-ray-induced absorption and the probability of bond breakage are greater than those in excimer-laser-induced irradiation. The feature of the absorption peak intensity can be described by that of the 5.8-eV band, because this band is dominant among all absorption components. In a previous paper [16], we showed that the induced absorption intensity decreases with increasing OH content at irradiation times shorter than 2 h among SFSs containing more than $5 \times 10^{17} \text{ cm}^{-3}$ of OH. At irradiation times longer than 2 h, on the other hand, the induced absorption intensity increased with increasing OH concentration. The change in the sign of the slope of the OH concentration dependence of the absorption intensity is due to the increment in the power index with the increment in OH concentration. In a previous study [16], we used VAD silicas and a type-III silica. In the present study, on the other hand, only type-III silicas are used. In type-III silicas, no strong dependency on OH concentration is observed, as shown in Fig. 4. The absorption intensity decreased with increasing interstitial- H_2 concentration except for the 5.0-eV band as shown in Fig. 3. Only the intensity of 5.0-eV band increases with increasing H_2 concentration. However, almost no contribution of the increment in the 5.0-eV band intensity to the peak intensities of the induced absorption is seen, because the intensity of this band is quite small compared to the other components. The increment in the 5.0-eV band, however, must be an important phenomenon with respect to understanding the defect creation mechanism. The intensity of the 4.8-eV band decreases with increasing interstitial- H_2 concentration. The origins of the 5.0- and 4.8-eV bands must be due to ODC(II) and NBOHC, respectively. Interstitial- H_2 concentration dependence on the population of these defects at irradiation times of 1 h and 6 h is shown in Fig. 7. At each irradiation time, the H_2 concentration dependence of every defect concentration is similar, i.e., the slope is the same in the doubly logarithmic plot.

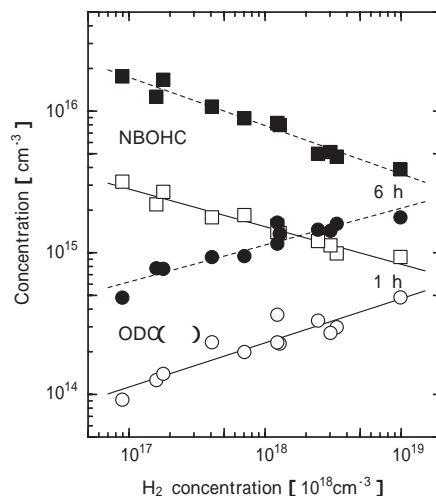


Fig. 7 Interstitial- H_2 concentration dependence of the concentration of NBOHC and ODC(II) at the irradiation times of 1 h and 6 h;
 : NBOHC 1 h, : NBOHC 6 h,
 : ODC(II) 1 h, : ODC(II) 6 h

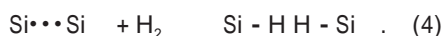
The slopes of the ODC(II) and NBOHC concentrations versus interstitial- H_2 concentration, respectively, are the same in absolute value and opposite in sign. This fact indicates that the product of the ODC(II) and NBOHC concentration, $[\text{ODC(II)}][\text{NBOHC}]$, is constant at each irradiation time. In fact, the product is $3.6 \pm 0.8 \times 10^{29} \text{ cm}^{-6}$ at irradiation time of 1 h and $0.92 \pm 0.20 \times 10^{31} \text{ cm}^{-6}$ at that of 6 h.

In a previous paper [15], the intensities of the 5.4- and 5.0-eV bands in type-III SFSs decreased almost linearly with increasing OH content. The intensity of the 5.8-eV band decreased with increasing OH content at an irradiation time shorter than 2 h. At an irradiation time longer than 3 h, on the other hand, the 5.8-eV band intensity increased with increasing OH concentration up to $6 \times 10^{19} \text{ cm}^{-3}$ of OH and saturated at higher OH concentration. The intensity of the 4.8-eV band increased almost linearly with increasing OH concentration at all irradiation times measured. We assumed that the FWHMs of 6.5-, 5.8-, 5.4-, 5.0- and 4.8-eV bands are 0.74, 0.80, 0.61, 0.31 and 1.12 eV, respectively. The FWHM of 5.8-eV band (0.80 eV) was larger than that used in the present study (0.62 eV). The reason for the different value of the FWHM used is described in Sec. 4. [1]. Although the values of FWHMs between the previous and the present studies are different, the feature of the OH concentration dependence of each absorption component must not be so different. In a previous study [15], we did not focus

on the effects of interstitial-H₂ molecules. Therefore, the intensity of the absorption components could be affected by interstitial hydrogen; a possibility is that the interstitial-H₂ concentration increased with increasing OH content. In that paper [15], we used samples containing 3.8, 5.4, 6.0 and 8.7 × 10¹⁹ cm⁻³ of OH. A slight inversion of the order of the intensity was observed between the samples with 5.4 and 6.0 × 10¹⁹ cm⁻³ OH. This inversion could be due to the effect of H₂ molecules. However, we cannot confirm that now, because we cannot obtain the same samples.

[3] Changes in interstitial-H₂ and Si - H concentrations upon irradiation

Interstitial-H₂ molecules may form Si - OH and Si - H by reaction with defect structures. In addition to the reaction expressed in Eq. (3), the following process must be considered.



Imai et al. [23] showed that the Si - H structures are created by heating a ODC(II)-containing SFS with ambient H₂. Each sample used in this study contains the Si - OH structure whose concentration is more than an order greater than that of interstitial-H₂ except for Sample L. Therefore, the OH concentrations of these samples before and after X-ray irradiation are constant within experimental accuracy as shown in Table 1. Hydride concentrations, on the other hand, change. The concentration of Si - H induced by irradiation must increase with increasing interstitial-H₂ concentration. In fact, a linear relationship is observed

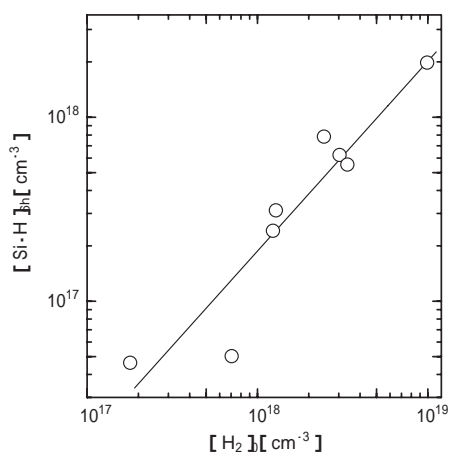


Fig. 8 Relation between the change of the interstitial-H₂ concentration before the irradiation [H₂]₀ and the Si - H concentration after irradiation for 6 h [Si - H]_{6h}

between the Si - H content after irradiation with X-rays for 6 h and the H₂ content before irradiation as shown in Fig. 8. The line drawn in Fig. 8 represents

$$[\text{Si} - \text{H}]_{6\text{h}} = 0.20[\text{H}_2]_0, \quad (5)$$

where [Si - H]_{6h} represents the Si - H concentration after irradiation for 6 h and [H₂]₀ represents the interstitial hydrogen concentration before irradiation. This relation shows that the Si - H content after irradiation is equal to the 20% of the initial H₂ content. Therefore 10% of the H atoms, i.e. 10% of the H₂ molecules, before irradiation becomes Si - H structure after irradiation of 6 h.

Figure 9 shows the increment in Si - H concentration versus the decrement in H₂ content upon irradiation for 6 h. Although the maximum value of [H₂]₀ before irradiation is 1 × 10¹⁹ cm⁻³, the maximum value of the change in [H₂], - [H₂], remains 2 × 10¹⁸ cm⁻³, which corresponds to the relation of Eq. (5); the change is about 20% of the amount of initial H₂ concentration. When the increment in H₂, - [H₂], is less than 1 × 10¹⁸ cm⁻³, almost no Si - H is induced. When - [H₂] is greater than 1 × 10¹⁸ cm⁻³, [Si - H] increases steeply with increasing - [H₂].

[4] Interstitial-H₂ concentration dependence of intensities of absorption components

We studied in a previous paper [16] the irradiation time dependence of X-ray-induced absorption of type-III and VAD SFSs. In that paper, only one kind of type-III silica, corresponding to Sample G in the present paper, was used. The amounts of E centers (5.8- and

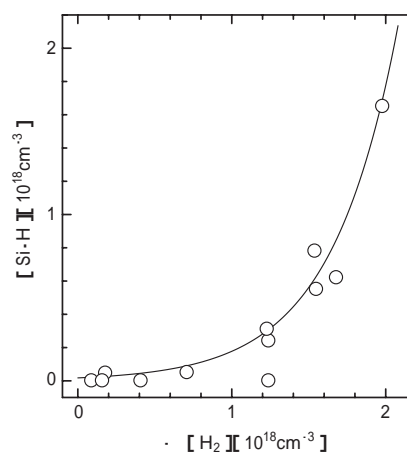


Fig. 9 Relation between the change of the interstitial-H₂ concentration and the Si - H concentration before and after irradiation for 6 h

5.4-eV bands) and ODC(II) (5.0-eV band) decrease with increasing OH concentration. As for the 4.8-eV band, on the other hand, the difference among samples is quite small compared to the 5.8-, 5.4- and 5.0-eV bands. This fact suggests that the NBOHCs are produced through the bond breakage expressed in Eq. (2). The interstitial-H₂ concentration of the VAD silicas in a previous paper [16] was less than the detection limit, $5 \times 10^{16} \text{ cm}^{-3}$, except for a VAD-silica which contained $8 \times 10^{16} \text{ cm}^{-3}$ of interstitial-H₂. This concentration is slightly greater than the detection limit of interstitial-H₂, $5 \times 10^{16} \text{ cm}^{-3}$. Anyway, the H₂ concentrations of VAD silicas are quite small compared to that of type-III silicas; the H₂ concentration of the type-III silica in that paper [16] was $1.3 \times 10^{18} \text{ cm}^{-3}$. Therefore, H₂ will not function in the creation of NBOHC in VAD silicas. NBOHC in type-III silica must be created through the process of Eq. (2), and Si-H and Si-OH are further produced by reacting with the interstitial-H₂ molecule from the process of Eq. (3).

In the present samples, the intensities of the 5.8-, 5.4-, 4.8- and 3.8-eV bands decrease with increasing H₂ concentration (Fig. 3). A probable origin of the decrement in the amounts of E centers, 5.8- and 5.4-eV bands, is the process of Eq. (3); the probability for the reaction of Eq. (3) to proceed is increased with increasing interstitial-H₂ concentration. The effect of the interstitial-H₂ on the suppression of the 4.8-eV band creation is greater than that on the other components; the absolute value of the slope of the intensity versus interstitial-H₂ concentration is greater than that of the other absorption components. This fact seems to contradict the hypothesis that NBOHCs are created through the process of Eq. (2), because E centers produced from the process of Eq. (2) must cause the Si-H structure through the process of Eq. (3). A probable mechanism to explain this contradiction is as follows: If the interstitial-H₂ molecule reacts with NBOHCs and E centers produced by the process of Eq. (2), the same amounts of Si-OH and Si-H are produced by the process of Eq. (3). Some of the Si-H bonds can be broken by X-ray irradiation by the reaction



and E centers are produced again. Some of the Si-OHs produced by this mechanism might also change

into NBOHCs by X-ray irradiation. However, the Si-OH structures are stabler than Si-H under X-ray irradiation. Therefore, the difference in the stability on X-ray irradiation between Si-H and Si-OH causes the difference in the H₂ content dependence of the intensities between E centers and NBOHCs.

The intensity of the 5.0-eV band increased with increasing interstitial-H₂ concentration, which is opposite to the other components. From ODC(II), E centers must be produced by the process of



where Si⁺ represents a planar-three-fold-oxygen coordinated structure [4]. Because the ODC(II) concentration increases with increasing interstitial-H₂ concentration, the amount of E centers increases with increasing interstitial-H₂ content. This process also contributes the difference in H₂ content dependence between the amounts of E centers and NBOHCs.

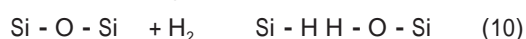
ODC(II) can be created by the knock-on process of strained Si-O-Si bond as



ODC(II)s can also be created by the reaction of interstitial-H₂ molecules with strained Si-O-Si bonds as



This reaction must be the origin of the H₂ concentration dependence of the intensity of the 5.0-eV band. By the reaction between interstitial-H₂ molecules and Si-O-Si bonds, the process



can also proceed. The criterion regarding whether the process of (9) or (10) occurs must depend both on the magnitude of the stress on the Si-O-Si bond and the probability of an encounter between a strained Si-O-Si bond and an H₂. Anyway, the process of Eq. (9) must be promoted by the existence of interstitial-H₂ molecules.

The intensity of 3.8-eV band at an irradiation time 6 h decreases with increasing interstitial-H₂ concentration as shown in Fig. 3. The data fall on a master curve irrespective of OH concentration. As discussed in Sec. 4. [1], we ascribe the Cl₂ to be the origin of the 3.8-eV band. The H₂ concentration dependence of the intensity of the 3.8-eV band can be explained as follows: The intensity must decrease with increasing interstitial-H₂ molecules because HCl

molecules are formed by the reaction between Cl_2 and H_2 . Therefore, the 3.8-eV band intensity decreases with increasing interstitial- H_2 molecules.

[5] Power indices of absorption components

In a previous paper [16], the power index shows a minimum at an OH concentration of $5 \times 10^{17} \text{ cm}^{-3}$ and increased almost linearly with increasing OH concentration at concentrations greater than $5 \times 10^{17} \text{ cm}^{-3}$. These samples were both VAD and type-III silicas. The power indices of the present samples are almost constant except at the lowest OH concentration as shown in Fig. 6 (Symbol). As for the 3.8-eV band, however, the dispersion of the data is larger than those of the other components because the intensity of the 3.8-eV band is quite weak and is located at the tail of the absorption spectra. In a previous paper [16], the power index of the 3.8-eV band was almost three times those of the other components. Although the power indices for the 3.8-eV band in the present study are also greater than those of the other components, the value of the power indices of the 3.8-eV band is less than three times of that of the other components.

As shown in Fig. 5, the power indices for all absorption components decrease with increasing interstitial- H_2 concentration except for the 3.8-eV band. This indicates the effect of interstitial- H_2 on the suppression of the X-ray-induced absorption.

Similar suppression effects of the interstitial- H_2 molecules on the intensities of KrF- and ArF- excimer-laser-induced absorption have been proposed [8, 9]. One of the present authors insisted that the Si-OH suppresses the excimer-laser-induced absorption [5-7]. However, in these papers, no interstitial- H_2 effect was considered. Therefore, we cannot deny the possibility that only interstitial- H_2 contributes the suppression of the induced absorption; the higher OH containing sample contains a higher content of interstitial- H_2 molecules. Further study must be required to examine this possibility.

5 . Summary and Conclusion

Hydroxyl and interstitial- H_2 concentration dependence of X-ray-induced absorption in type-III fused silica was studied. X-ray from a Rh target at a

dosage of $2 \times 10^4 \text{ C kg}^{-1}$ were utilized. Induced absorption spectra were reproduced by six Gaussian absorption bands at 3.8, 4.8, 5.0, 5.4, 5.8 and 6.5 eV. Hydroxyl and interstitial-hydrogen-molecule concentration dependences at irradiation times of 1 h and 6 h of each absorption component were proportional to each other in a doubly logarithmic plot. Apparent interstitial- H_2 concentration dependence was observed at each irradiation time. OH concentration dependence, on the other hand, was not as clear as in the case of H_2 concentration dependence. Absorption intensities decrease with increasing H_2 concentration except for the 5.0-eV band. The intensity of the 5.0-eV band, on the other hand, increases with increasing H_2 concentration. The results indicate that interstitial- H_2 molecules affect the characteristics of X-ray-induced absorption. The effect of the hydroxyl structure on the induced absorption is not apparent as in the case of interstitial- H_2 . This fact suggests a possibility that excimer-laser-induced absorption is also affected only by the interstitial- H_2 in spite of the apparent effect of Si-OH on the suppression of the excimer-laser-induced absorption.

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