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Vacuum ultraviolet optical absorption band of non-bridging oxygen hole centers in SiO_2 glass

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Abstract

An intense broad vacuum ultraviolet (VUV) optical absorption band with peak at 6.8 eV and halfwidth ≈ 1.7 eV is identified in irradiated glassy SiO_2 and assigned to dangling oxygen bonds (non-bridging oxygen hole centers, NBOHC). It was selectively created by photolysis of silanol (SiO–H) groups by 7.9 eV photons of F_2 excimer laser at low temperature. Subsequent analysis by VUV absorption, time-resolved luminescence, and electron paramagnetic resonance spectroscopies during thermal annealing showed an exact correlation to the well-known 4.8 and 2 eV absorption and 1.9 eV luminescence bands of NBOHC. The estimated oscillator strength of the 6.8 eV band is $f \approx 0.05$. This band may be one of the dominant causes of VUV optical absorption induced by excimer-laser irradiation of silica. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Information on VUV optical absorption of color centers in SiO_2 glass is important for rapidly growing demand of optical elements for vacuum and deep UV optics. Optical elements (lenses and mask blanks) for F_2-laser lithography aiming a minimum feature size of 100–70 nm [1–3] and optical fibers [4] for deep UV light are representative applications. While the visible and UV parts of the absorption spectrum of SiO_2 have been extensively studied, [5,6], the vacuum ultraviolet (VUV) region has received relatively little attention, evidently due to its location in the spectral range, inaccessible by conventional spectrophotometers. There are two identified VUV optical absorptions in SiO_2 glass: the band peaking at 7.6 eV [7] due to Si–Si bonds, and absorption at >7.4 eV [8] arising from silanol groups Si–OH. Irradiation by F_2 laser pulses induces pairs of oxygen dangling bonds (non-bridging oxygen hole centers, NBOHC) and E' centers by excitation of heavily strained Si–O–Si bonds [9]:

$$\equiv\text{Si–O–Si}\equiv(\text{strained}) \rightarrow \equiv\text{Si}^{\cdot}(E') + {}^{\cdot}\,\text{O–Si}\equiv\text{NBOHC} \qquad (1)$$

NBOHC is one of the fundamental defects in amorphous SiO_2, which contributes to visible/UV absorption spectrum and gives rise to characteristic photoluminescence (PL) peak at 1.9 eV [10–12]. It is established that the NBOHC has two absorption bands at 1.97 and 4.8 eV. The spectral characteristics of these bands are quite different [13,14]: the 1.97 eV band is weak and narrow, while the 4.8 eV band is broad and intense (Table 1). Both bands serve as excitation bands to the 1.9 eV PL band. While it is known that this PL band can be excited in the VUV region as well, no distinct optical band of the NBOHCs in VUV region has been reported so far. This situation is caused by the overlap of

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Table 1
Summary of optical absorption bands due to NBOHCs in SiO_2 glass

Band	I[a]	II[b]	III[c]
Peak position (eV)	1.97	4.8	6.8
FWHM (eV)	0.17	1.07	1.76
Oscillator strength	1.5×10^{-4}	0.05	0.05

[a] Ref. [13].
[b] Refs. [13,14].
[c] Present work.

several broad absorption bands, typically taking place in the 6–8 eV spectral region.

However, contributions by different centers can be separated if they can be created *selectively*. It was recently reported that F_2 laser irradiation destroys bound hydroxyl (silanol) groups in silica, which have absorption at energies higher than 7.4 eV. It is anticipated that NBOHCs in this case are created not by the rupture of strained Si–O–Si bonds, but rather by an extrinsic mechanism, by photolysis of silanol groups [15,16]:

$$\equiv\text{Si–O–H} \rightarrow \equiv\text{Si–O}^{\cdot} + {}^{\cdot}\text{H}, \qquad (2)$$

where $H^{\cdot}$ denotes atomic hydrogen, H^0. Since H^0 is reactive and highly mobile at the room temperature, the decay of NBOHCs and formation of other color centers occurs as a secondary reaction [17]. Thus, in order to maximize the formation of NBOHC and suppress the secondary reactions, irradiation by F_2 laser pulses at low temperature is desirable.

Here we report an intense optical absorption band of NBOHC at 6.8 eV, which may be one of the major causes of VUV optical absorption of irradiated silica.

2. Experimental

Samples used here were SiO_2 glasses prepared by flame hydrolysis of $SiCl_4$. The SiOH content evaluated from the intensity of infrared absorption band at $3670\ \text{cm}^{-1}$ was $1 \times 10^{20}\ \text{cm}^{-3}$. The sample size was $20 \times 20 \times 1\ \text{mm}^3$. The samples were placed in cryostat with CaF_2 windows and were irradiated in vacuum by 7200 pulses of an F_2 excimer laser (Lambda Physik, Compex 102) delivered at 20 Hz, pulse width 10 ns, power density $\sim 2.5\ \text{mJ cm}^{-2}$. The cold finger of cryostat was kept at 77 K. It was estimated that the sample temperature during irradiation was below 95 K. The VUV and UV–visible absorption spectra and electron paramagnetic resonance (EPR) were measured at 77 K without an intervening warm-up. Time-resolved luminescence was measured with gated multichannel detector using excitation by F_2 (7.9 eV) or ArF (6.4 eV) excimer lasers, or fourth harmonics (4.7 eV) from a Q-switched Nd/YAG laser. EPR spectra were recorded by Bruker E580 spectrometer.

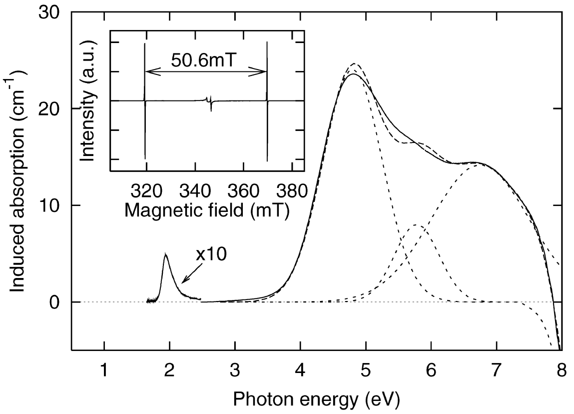

Fig. 1. Optical absorption induced by F_2 laser irradiation at temperature below 95 K. Inset shows the F_2-laser-induced EPR signals. Both spectra were measured at 77 K. Deconvoluted and synthesized spectra are also shown. The negative induced component at >7.4 eV is due to photo-modification of SiOH as described [[8,15,18]]. A doublet with a separation of 50.6 mT is due to the hyperfine structure of atomic hydrogen and the signal appearing in the central region is due to NBOHC and E' centers.

3. Results and discussion

Fig. 1 shows the VUV–UV–visible absorption induced in wet-SiO_2 glass by low-temperature F_2 laser-irradiation. Three peaks are evident: the most intense peak at 4.8 eV, a medium intensity peak at ~6.8 eV, and a low-intensity peak at ~2 eV. Inset shows EPR signals induced by F_2-laser irradiation. A doublet with a separation of 50.6 mT is undoubtedly identified as the hyperfine structure of atomic hydrogen [18]. This signal disappeared after the as-irradiated specimen was briefly warmed to 150 K. The broad signals appearing in the central region are primarily due to NBOHC and a trace of E' center. The concentrations of atomic hydrogen, E', and NBOHC were evaluated from the areal intensity of each EPR signal measured under an appropriate microwave power level (~1 μW for H or E' and 30 mW for NBOHC). The evaluated concentration of NBOHC is comparable to that of atomic hydrogen, and the E' concentration is ~1/10 of NBOHC. These results demonstrate that reaction (2) selectively occurs under the experimental conditions. Since atomic hydrogen has no optical bands in the visible–VUV range, the induced optical bands of Fig. 1 can be primarily attributed to NBOHC.

The negative-going component in the 7.5–8 eV region in induced absorption spectra indicates the VUV irradiation-induced modification of silanol groups in silica [8], which have optical absorption in this region.

The induced absorption was deconvoluted into 3-Gaussian bands on the basis of the induced EPR centers, i.e. a band peaking at 4.8 eV with the FWHM of 1.1 eV due to NBOHC [19], a band at 5.8 eV with the FWHM of 0.8 eV due to E' center [6], and a band at ~6.8 eV in

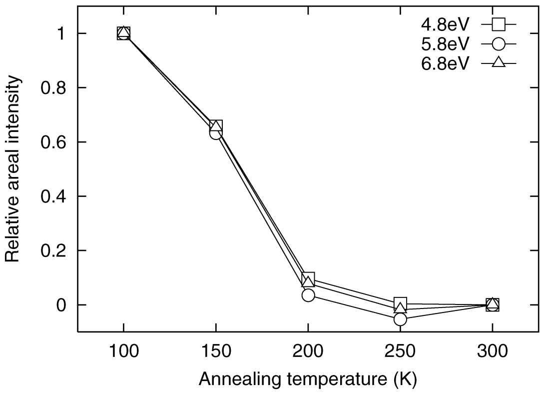

Fig. 2. Variation in the intensity of 4.8, 5.8, and 6.8 eV absorption bands destroyed by isochronal annealing of the specimen irradiated at $T < 95$ K. Annealing time was ≈ 10 min at each temperature. All the optical measurements were carried out at 77 K.

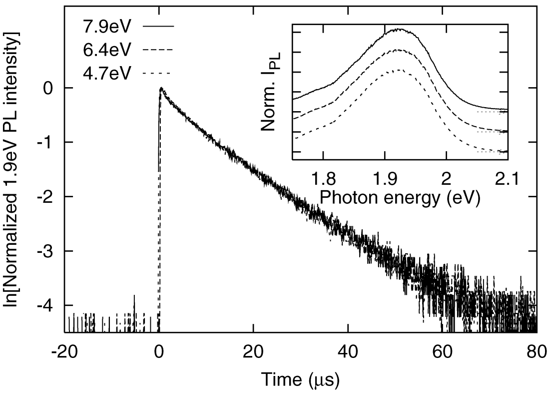

Fig. 3. PL spectra F_2 laser irradiated silica and PL decay kinetics recorded at excitation by 7.9, 6.4, and 4.7 eV photons.

question. To account for irradiation-induced change in SiOH absorption, the shape of the optical absorption spectrum of silanol groups [8] was approximated by a polynomial and added to the fitting function. In the deconvolution procedure, only the peak position and FWHM of the 6.8 eV band were allowed to vary, the shapes of other three fitting components were kept constant, only their amplitudes were changed. As shown in Fig. 1, a satisfactory agreement was obtained between the observed and synthesized shapes.

When the as-irradiated specimen was annealed at temperatures between 100 and 300 K, part of the induced absorption diminished. All the difference spectra between the 77 K-irradiated and annealed specimen were successfully decomposed into the same 3 Gaussian bands keeping constant peak positions and widths. Fig. 2 shows the variation of the normalized intensities of these bands with thermal annealing. All the three bands decayed almost simultaneously in the range 100–300 K.

The simultaneous decay of the 5.8 eV band due to E'-centers and that of the 6.8 eV band could link the latter band to E'-centers. However, this possibility can be discounted because of the excessive magnitude of the 6.8 eV band: with the oscillator strength of 5.8 eV band of $f = 0.15$–0.20 [6], the estimated oscillator strength of 6.8 eV band then would reach an unrealistic value of $f = 2.2$. On the other band, if the 6.8 eV band is assigned to NBOHC, the evaluated oscillator strength has a reasonable value of $f \approx 0.05$. We suggest that 6.8 eV absorption band is due to transitions to higher-energy excited state of NBOHC.

To prove the assignment of the 6.8 eV band, the PL measurements at different excitation photon energies (7.9, 6.4, and 4.7 eV) were performed (Fig. 3). A characteristic red PL band at 1.93 eV (645 nm) was observed in all cases, PL spectra and their time decay curves were identical within the experimental uncertainty at all excitation energies. The peak position and the lifetime (15–20 μs at 295 K) observed here agree with those of PL band upon excitation of the 2 eV band of NBOHC [10]. The 4.7 eV photons excite the 4.8 eV band of NBOHC while 6.4 eV photons excite the 6.8 eV band. These observations further support the assignment of the 6.8 eV band to NBOHC.

Table 1 summarizes the optical absorption bands of NBOHC in SiO_2 glass. The values of f and FWHM of the newly identified 6.8 eV are quite similar to those of the 4.8 eV, in contrast to the 2 eV band, which has much smaller f and FWHM. Although the theoretical calculations of optical properties of NBOHC are reported by several groups [20–23], the character of the optical transitions is still controversial. The present finding of the 6.8 eV band provides an additional clue to theoretical understanding of NBOHC in SiO_2 glass. Furthermore, this finding is important for practical applications of SiO_2 glasses for VUV and deep UV optics. The 6.8 eV band of the NBOHC has relatively large oscillator strength and halfwidth (1.75 eV). It appears to be a major cause of absorption at ArF (6.4 eV) and F_2 (7.9 eV) laser photon energies. Evidently, the suppression of NBOHC formation is an important issue to improve the quality of the SiO_2 glasses for excimer-laser applications.

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References

[1] T.M. Bloomstein, M.W. Horn, M. Rothschild, R.R. Kunz, S.T. Palmacci, R.B. Goodman, J. Vac. Sci. Technol., B 15 (1997) 2112.
[2] H. Hosono, M. Mizuguchi, H. Kawazoe, T. Ogawa, Appl. Phys. Lett. 74 (1999) 2755.
[3] Y. Ikuta, S. Kikugawa, M. Hirano, H. Hosono, J. Vac. Soc. Technol., B 18 (2000) 2891.

[4] M. Oto, S. Kikugawa, N. Sarukura, M. Hirano, H. Hosono, IEEE Photo. Technol. Lett. 13 (2001) 978.
[5] D.L. Griscom, J. Ceram. Soc. Jpn 99 (1991) 923.
[6] L. Skuja, J. Non-Cryst. Solids 239 (1998) 16.
[7] H. Hosono, Y. Abe, H. Imagawa, H. Imai, K. Arai, Phys. Rev. B 44 (1991) 12043.
[8] Y. Morimoto, S. Nozawa, H. Hosono, Phys. Rev. B 59 (1999) 4066.
[9] H. Hosono, Y. Ikuta, T. Kinoshita, K. Kajihara, M. Hirano, Phys. Rev. Lett. 87 (2001) 175501.
[10] L. Skuja, J. Non-Cryst. Solids 179 (1994) 51.
[11] G.H. Sigel, J. Non-Cryst. Solids 13 (1973/74) 372.
[12] P. Kaiser, J. Opt. Soc. Am. 64 (1974) 475.
[13] L. Skuja, in: G. Pacchioni, L. Skuja, D.L. Griscom (Eds.), Defects in SiO_2 and Related Dielectrics: Science and Technology, Kluwer Academic Publishers, Dordrecht, 2001, pp. 73–116.
[14] A.A. Bobyshev, V.A. Radtsig, Sov. Phys. Chem. Glasses 14 (1988) 501.
[15] K. Kajihara, L. Skuja, M. Hirano, H. Hosono, Appl. Phys. Lett. 79 (2001) 1757.
[16] K. Kajihara, Y. Ikuta, M. Hirano, T. Ichimura, H. Hosono, J. Chem. Phys. 115 (2001) 9473.
[17] D.L. Griscom, J. Non-Cryst. Solids 73 (1985) 51.
[18] R.A. Weeks, M.M. Abraham, J. Chem. Phys. 42 (1965) 68.
[19] L. Skuja, K. Tanimura, N. Itoh, J. Appl. Phys. 80 (1996) 3518.
[20] E. O'Reilly, J. Robertson, Phys. Rev. B 27 (1983) 3780.
[21] Z. Hajnal, P. Deak, Th. Köhler, R. Kaschner, T. Frauenheim, Solid State Commun. 108 (1998) 93.
[22] G. Pacchioni, D. Erbetta, Phys. Rev. B 60 (1999) 12617.
[23] V.A. Radzig, in: G. Pacchioni, L. Skuja, D.L. Griscom (Eds.), Defects in SiO_2 and Related Dielectrics: Science and Technology, Kluwer Academic Publishers, Dordrecht, 2000, pp. 339–370.