Formation of Intrinsic Point Defects in Fluorine-doped Synthetic SiO_2 Glass by ^{60}Co γ-ray Irradiation

Koichi Kajihara,[1] Masahiro Hirano,[1] Linards Skuja,[1,2] and Hideo Hosono[1,3]
[1] *Transparent Electro-Active Materials Project, ERATO-SORST, Japan Science and Technology Agency,*
Mail Box S2-13, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503
[2] *Institute of Solid State Physics, University of Latvia, Latvia*
[3] *Frontier Collaborative Research Center, Tokyo Institute of Technology*

(Received November 28, 2006; CL-061405; E-mail: kaji2@lucid.msl.titech.ac.jp)

Intrinsic point defect formation in a fluorine-doped synthetic silica (SiO_2) glass by ^{60}Co γ-ray irradiation was examined. The most abundantly formed defects are oxygen vacancies (Si–Si bonds). The concentrations of Si–Si bonds and interstitial oxygen molecules increase almost linearly with the γ-ray dose. These observations indicate that the primarily intrinsic defect process in SiO_2 glass irradiated with ^{60}Co γ-rays is the Frenkel pair formation, rather than a simple cleavage of an Si–O bond into a pair of silicon and oxygen dangling bonds.

Silica (SiO_2) glass is the most radiation-resistant amorphous material for optical application and is widely used under intense ionizing radiation, such as X- and γ-rays. However, the ionizing radiation still induces some point defects that degrade optical properties of SiO_2 glass. These point defects are generated by impurity-related reactions as well as by intrinsic processes, i.e., radiation-induced decomposition of Si–O network. Since the currently available synthetic SiO_2 glasses contain little impurities, it becomes increasingly important to understand the intrinsic defect processes in SiO_2 glass. To date, two intrinsic mechanisms have been found. One is the cleavage of Si–O bond into a pair of the silicon and oxygen dangling bonds (E' center, $\equiv$Si$^\bullet$ and non-bridging oxygen hole center, NBOHC, $\equiv$SiO$^\bullet$),[1–5]

$$\equiv\text{Si–O–Si}\equiv \quad\longrightarrow\quad \equiv\text{Si}^\bullet + {}^\bullet\text{OSi}\equiv. \tag{1}$$

The other mechanism is the generation of oxygen vacancy (Si–Si bond) and interstitial oxygen atom (O^0),

$$\equiv\text{Si–O–Si}\equiv \quad\longrightarrow\quad \equiv\text{Si–Si}\equiv + \text{O}^0, \tag{2}$$

followed by the dimerization of O^0 into interstitial oxygen molecules (O_2).[6–9] Reaction eq 2 is due to the radiation-induced displacement of the bridging oxygen atom into interstitial position in the glass network and may be regarded as "Frenkel defect process" in SiO_2 glass. However, it has been unclear which mechanism (eqs 1 or 2) is dominant as the intrinsic defect formation process in SiO_2 glass.

In the present study, formation of E' centers, NBOHCs, Si–Si bonds, and interstitial O_2 was simultaneously measured with an aim to evaluate which of the reactions eqs 1 and 2 is more efficient. However, extrinsic processes, typically the radiolysis of common network modifiers in synthetic SiO_2 glass (SiH, SiOH, and SiCl groups), also yields NBOHC and E' centers,[10–12] and they hamper the evaluation of the efficiency of eq 1. We therefore chose fluorine-doped SiO_2 glass on the bases of following reasons. Fluorine atoms in SiO_2 glass hardly participate in radiation-induced defect processes[3,13] because they form Si–F bonds that are stronger than Si–O bonds. Furthermore, fluorine doping largely decreases the concentrations of SiH, SiOH, and SiCl groups. γ-rays (^{60}Co source) were employed as an excitation source to focus on the effects of the ionizing radiation and to avoid the nuclear displacement damage.

Fluorine-doped SiO_2 glass plates (SiF, ca. $4 \times 10^{19}\,\text{cm}^{-3}$; SiOH, SiCl, H_2 $\lesssim 10^{17}\,\text{cm}^{-3}$; 2-mm thick) were exposed to ^{60}Co γ-rays up to an absorbed dose ca. 4×10^6 Gy (SiO_2 equivalent) at a rate ca. $1 \times 10^3\,\text{Gy}\,\text{h}^{-1}$. The γ-ray-induced Si–Si bonds, NBOHC, and E' centers were observed by optical absorption using visible to ultraviolet (U-4000, Hitachi) and vacuum-ultraviolet (VU-201M, Bunkou-Keiki) spectrometers. Interstitial O_2 was detected utilizing the characteristic infrared (IR) photoluminescence (PL) band at 1272 nm (7860 cm^{-1}) under excitation at 765 nm with a continuous-wave titanium sapphire laser.[8,14,15] The PL spectra were recorded by a Fourier-transform IR Raman spectrometer (Model 960, Nicolet).

Figure 1 shows optical absorption spectra induced by exposure to γ-rays. As shown in the inset, the induced absorption below 6 eV was deconvoluted into three bands associated with NBOHC (4.8 eV), divalent Si (5.0 eV), and E' center (5.8 eV). The induced absorption above ca. 7 eV was mainly due to Si–Si bond (7.6 eV). The origins of the induced absorption between 6 and 7 eV were unclear because several absorption bands over-

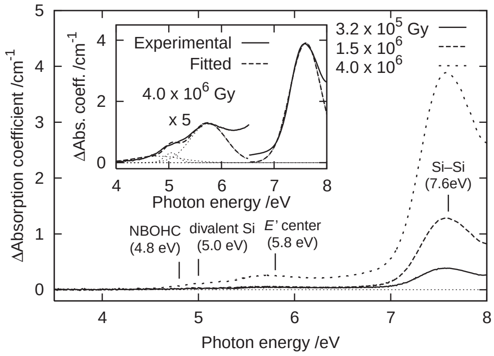

Figure 1. Optical absorption spectra (resolution 1 nm) of point defects induced in fluorine-doped SiO_2 glass by exposure to three different doses of γ-rays. Absorption of unirradiated sample was subtracted. The inset shows a peak deconvolution of the induced absorption at 4.0×10^6 Gy into components of NBOHC (peak at 4.8 eV, full-width at half-maximum 1.07 eV), divalent Si (5.0 eV, 0.3 eV), E' center (5.8 eV, 0.8 eV), and Si–Si bond (7.6 eV, 0.7 eV) by least squares fitting. These peaks were assumed to be Gaussian-shaped and the peak parameters were taken from Ref. 11.

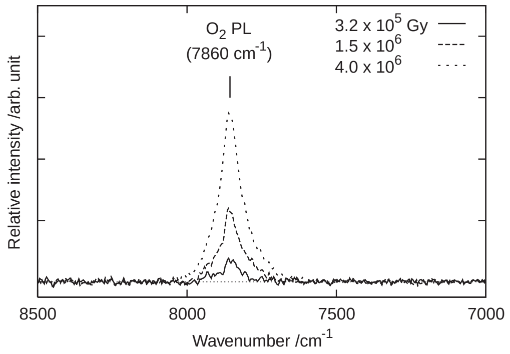

Figure 2. Photoluminescence (PL) spectra (resolution $8\,cm^{-1}$) of interstitial O_2 generated by exposure to three different doses of γ-rays. The PL band was excited at 765 nm.

lap in this spectral region and their peak parameters are highly uncertain. The concentrations of NBOHC, E' center, and Si–Si bond were calculated using the peak absorption cross sections reported for these absorption bands; NBOHC, $5.3 \times 10^{-18}\,cm^2$ at 4.8 eV; E' center, $2.5 \times 10^{-17}\,cm^2$ at 5.8 eV; Si–Si bond, $7.5 \times 10^{-17}\,cm^2$ at 7.6 eV.[11] Figure 2 shows PL spectra of interstitial O_2, whose intensity increased monotonically with the γ-ray dose. The concentrations of interstitial O_2 were determined from the PL intensity ratios between the irradiated samples and a reference O_2-rich SiO_2 glass with a known O_2 content.[16,17]

The concentration changes in Si–Si bond, NBOHC, E' center, and interstitial O_2 with the absorbed γ-ray dose, D, are summarized in Figure 3. Si–Si bond was the most abundant defect. The concentrations of Si–Si bond and interstitial O_2 increased almost proportionally to D. The concentrations of E' center and NBOHC were nearly equal and it is consistent with the formation mechanism eq 1. However, their concentrations were smaller than the concentration of Si–Si bonds and were not proportional to D. These observations indicate that the Frenkel process (eq 2) is dominant over the cleavage of Si–O bonds (eq 1) in high-purity SiO_2 glasses exposed to γ-rays. The concentration of O^0 forming interstitial O_2 (twice the O_2 concentration) was comparable to that of E' centers and NBOHC, but was smaller than the Si–Si concentration. It is probably because only a minor portion of the radiation-induced O^0 turns into interstitial O_2, and the rest of O^0 is stabilized in the glass network by forming Si–O–O–Si bonds (peroxy linkage).[18–21]

Figure 3 indicates that the formation efficiency of Si–Si bonds and interstitial O_2 is nearly constant up to ca. 4×10^6 Gy. The efficiency (number of defects created per an electron–hole pair, Φ) may be expressed by the concentrations of defects, C, divided by the number of electron–hole pairs generated in SiO_2 glass, N: $\Phi = C/N = C/(D\rho/W)$, where ρ is the density of SiO_2 glass ($\rho \simeq 2.2\,g\,cm^{-3}$) and W is the energy necessary to create an electron–hole pair. Using the C/D ratio evaluated from Figure 3 (Si–Si bond, ca. $1.3 \times 10^{10}\,cm^{-3}\,Gy^{-1}$; interstitial O_2, ca. $1.0 \times 10^{9}\,cm^{-3}\,Gy^{-1}$) and provided that $W \simeq 18\,eV$,[22] Φ was calculated to be ca. 2×10^{-5} for Si–Si bonds and ca. 1×10^{-6} for interstitial O_2. The formation efficiency of Si–Si bonds agrees well with that reported for an SiO_2 glass implanted with 10 MeV protons (ca. 1×10^{-5} at $W = 18\,eV$).[7]

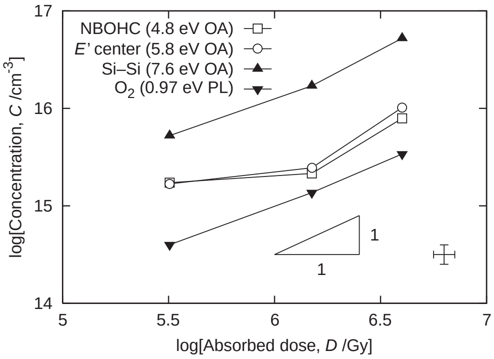

Figure 3. Dependence of the concentrations of Si–Si bond, E' center, NBOHC, and interstitial O_2 on the absorbed γ-ray dose. The error bars represent the experimental uncertainties.

We wish to thank Dr. Isao Yoda of Division of Radioisotope Research, Center of Biological Resouces and Informatics Tokyo Institute of Technology for the assistance with ^{60}Co γ-ray irradiation.

References

1 R. A. B. Devine, J. Arndt, *Phys. Rev. B* **1989**, *39*, 5132.
2 R. A. B. Devine, J. Arndt, *Phys. Rev. B* **1990**, *42*, 2617.
3 K. Arai, H. Imai, J. Isoya, H. Hosono, Y. Abe, H. Imagawa, *Phys. Rev. B* **1992**, *45*, 10818.
4 F. L. Galeener, D. B. Kerwin, A. J. Miller, J. C. Mikkelsen, Jr., *Phys. Rev. B* **1993**, *47*, 7760.
5 H. Hosono, Y. Ikuta, T. Kinoshita, K. Kajihara, M. Hirano, *Phys. Rev. Lett.* **2001**, *87*, 175501.
6 T. E. Tsai, D. L. Griscom, *Phys. Rev. Lett.* **1991**, *67*, 2517.
7 H. Hosono, H. Kawazoe, N. Matsunami, *Phys. Rev. Lett.* **1998**, *80*, 317.
8 L. Skuja, B. Güttler, D. Schiel, A. R. Silin, *Phys. Rev. B* **1998**, *58*, 14296.
9 M. A. Stevens-Kalceff, *Phys. Rev. Lett.* **2000**, *84*, 3137.
10 D. L. Griscom, *J. Ceram. Soc. Jpn.* **1991**, *99*, 923.
11 L. Skuja, H. Hosono, M. Hirano, *Proc. SPIE-Int. Soc. Opt. Eng.* **2001**, *4347*, 155.
12 K. Kajihara, *J. Ceram. Soc. Jpn.*, in press.
13 K. Kajihara, M. Hirano, L. Skuja, H. Hosono, *J. Non-Cryst. Solids*, in press.
14 K. Kajihara, T. Miura, H. Kamioka, M. Hirano, L. Skuja, H. Hosono, *J. Ceram. Soc. Jpn.* **2004**, *112*, 559.
15 K. Kajihara, H. Kamioka, M. Hirano, T. Miura, L. Skuja, H. Hosono, *J. Appl. Phys.* **2005**, *98*, 013529.
16 L. Skuja, B. Güttler, D. Schiel, A. R. Silin, *J. Appl. Phys.* **1998**, *83*, 6106.
17 K. Kajihara, M. Hirano, M. Uramoto, Y. Morimoto, L. Skuja, H. Hosono, *J. Appl. Phys.* **2005**, *98*, 013527.
18 G. Pacchioni, G. Ieranó, *Phys. Rev. B* **1997**, *56*, 7304.
19 D. R. Hamann, *Phys. Rev. Lett.* **1998**, *81*, 3447.
20 M. A. Szymanski, A. L. Shluger, A. M. Stoneham, *Phys. Rev. B* **2001**, *63*, 224207.
21 L. Skuja, K. Kajihara, T. Kinoshita, M. Hirano, H. Hosono, *Nucl. Instrum. Methods Phys. Res., Sect. B* **2002**, *191*, 127.
22 G. A. Ausman, Jr., F. B. McLean, *Appl. Phys. Lett.* **1975**, *26*, 173.