Experimental Evidence for Frenkel Defect Formation in Amorphous SiO_2 by Electronic Excitation

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Concentrations of defects in amorphous SiO_2 created by implantation of 10 MeV protons were examined. The depth profile of Si-Si bonds, E' centers, or peroxy radicals (PORs) was close to that of electronic energy loss. Interstitial O_2 molecules were identified and their concentration was larger than that of PORs. The total concentration of the Si-Si bonds and E' centers was comparable to that of the interstitial O_2 and PORs. These results provide experimental evidence that Frenkel defect formation of an oxygen occurs in amorphous SiO_2 by dense electronic excitation. The efficiency of the Frenkel defect formation was estimated as $\sim 5 \times 10^{-7}$ eV^{-1}. [S0031-9007(97)04997-1]

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Defects in amorphous SiO_2 have been extensively studied to date [1] since the discovery of E' centers by Weeks [2] in 1956. Defect formation may be classified as extrinsic type and intrinsic type depending upon whether the defect is derived from a precursor or not. Amorphous (a-)SiO_2 is the key material in lenses for UV optics, optical fibers, and insulating oxide films in metal-oxide semiconductors, and defect formation by ionizing radiation gives degradation of its material functions. Intrinsic defect formation in a-SiO_2 by electronic excitation has attracted much interest so far because understanding of its mechanism is one of the most important issues in the science of amorphous solids.

In 1979, Griscom [3] strongly suggested the transient formation of E' centers and perhaps oxygen vacancy through observation of the transient absorption spectra following irradiation by a 500 eV electron pulse. In 1983, Hobbs and Pascucci [4] found that amorphization of α-quartz occurs by irradiation of a focused low energy electron beam, indicating that intrinsic defect formation occurs by dense electronic excitation. Devine [5] clarified that E' centers are created by energy deposited into ionization processes and not into atomic displacement. Tanimura *et al.* [6] proved the quasistable Frenkel defect formation by measuring transient volume change induced with an electron pulse. Although the dominant oxygen-related center (OHC) is a nonbriding oxygen hole center (NBOHC, $\equiv$Si—O$\cdot$, where — and $\cdot$ denote an Si-O bond and an unpaired electron, respectively) for *wet* SiO_2 glasses (type III, prepared by flame hydrolysis, OH content $\gtrsim 1 \times 10^{19}$ cm^{-3}) irradiated by X, γ, or unfocused excimer laser light [7], Tsai and Griscom [8] found that peroxy radicals (PORs, $\equiv$Si—O—O$\cdot$) are created as the dominant OHCs instead of NBOHCs in *wet* SiO_2 glasses by irradiation with focused ArF laser light. They suggested that O_2 molecules are created through the biexciton process as a consequence of dense electronic excitation. Schluger and Stefanovich [9] proposed on the theoretical calculation that peroxylinkages ($\equiv$Si—O—O—Si$\equiv$) and oxygen vacancies are created as a consequence of relaxation of a self-trapped exciton. Although these works suggest the formation of a Frenkel defect in a-SiO_2 by dense electronic excitation, the information reported so far has been restricted to a specific defect species.

Here, we report complementary evidence for Frenkel defect formation of interstitial oxygens by dense electronic excitation of a-SiO_2 for the first time. Centers relevant to the Frenkel defect are Si-Si bonds, E' centers, PORs, interstitial O_2 molecules, and peroxylinkages. The concentrations of E' centers and PORs can be measured by EPR, and the Si-Si bond concentration may be evaluated from the intensity of the 7.6-eV band in the vacuum UV absorption spectra using the reported absorption cross section [10]. According to a recent Letter by Skuja and Guttler [11], the identification and concentration evaluation of interstitial O_2 molecules in a-SiO_2 are also possible by a photoluminescence band, corresponding to the forbidden transition $a\ {}^1\Delta_g(\nu' = 0) \rightarrow X\ {}^3\sum_g (\nu'' = 0)$, at 1272 nm upon excitation with 1064 nm light from a Nd:YAG laser.

A high energy proton beam was employed as the excitation tool to examine defect formation by dense electronic excitation because most of the kinetic energy of energetic light ions accelerated by high voltages dissipates through electronic excitation (ionization) processes.

The specimens are synthetic *wet* SiO_2 glass (Nippon Silica Glass Co., type III, OH content; $\sim 3 \times 10^{19}$ cm^{-3}) plates having a size of $20 \times 20 \times 1.2$ mm. Protons were implanted at an energy of 10 MeV to fluences of $1 \times 10^{13} \sim 1 \times 10^{16}$ cm^{-2} using a cyclotron accelerator at Takasaki of JAERI TIARA, Japan. Dose rates were $\sim$10 nA cm^{-2} and the maximum temperature rise, monitored by attaching a thermocouple to the sample during bombardment, was $\sim$70 °C.

EPR spectra were measured at 300 or 77 K using a Brucker 300E spectrometer. Spin concentrations were evaluated by double integration of first-derivative spectra using a $CuSO_4 \cdot 5H_2O$ reference crystal of a known weight.

Vacuum ultraviolet absorption (VUV) spectra were measured using a VUV single beam spectrophotometer (JASCO, model VUV-200, light source; D_2 discharge lamp). High voltages applied to the phototube were varied at each sampling wavelength so as to keep the sensitivity of the system constant. The drift of the base line in the transmittance was within $\pm 1\%$ in the wavelength region 140–220 nm by this procedure. Photoluminescence (PL)-Raman spectra were measured with a Fourier-transform Raman spectrometer (JASCO, RFT-800) equipped with a cw YAG:Nd laser. The measurement was made by irradiating a 1064 nm laser beam (~300 μm diameter) to an optically polished cross section of implanted samples.

The depth concentrations of induced defects were examined by repeating mechanical thinning and spectral measurements. Attention was given to the choice of a glue to fix the sample to the support for the thinning. A glue which softens at ~70 °C was used so as to avoid the thermal bleaching of created defects (E' centers begin to decay at ~150 °C). The range, range straggling, and energy deposition were calculated with the TRIM-92 code [12].

Figure 1 shows VUV-UV absorption and EPR signals in SiO_2 glasses induced by the implantation. Two absorption bands peaking at ~7.6 and ~5.8 eV are seen in the absorption spectra. In the EPR spectra, NBOHC, E' centers, and PORs were observed. Two structural models have been proposed for the 7.6-eV band; one is the POR [13], which is paramagnetic and may be regarded as an oxygen-interstitial-type defect. Another is the Si-Si bond [10], which is diamagnetic and an oxygen-vacancy-type defect. They may be discriminated from each other by the experiment using the observation that although PORs are bleached by 5-eV light illumination [14], Si-Si bonds remain unchanged [15]. The figure shows that the EPR signal of PORs is fairly bleached, while the intensity of the 7.6-eV band remains unchanged. Thus, it can be concluded that the 7.6-eV band in the present sample is due entirely to the Si-Si bond. The bond concentrations were evaluated using the absorption cross section of 7.5×10^{-17} cm^2 [10] and were plotted in the inset in Fig. 2(a) as a function of fluence [16]. It is evident from the figure that the Si-Si bond concentrations linearly increase with fluence in the log-log plot (slope; ~0.65)

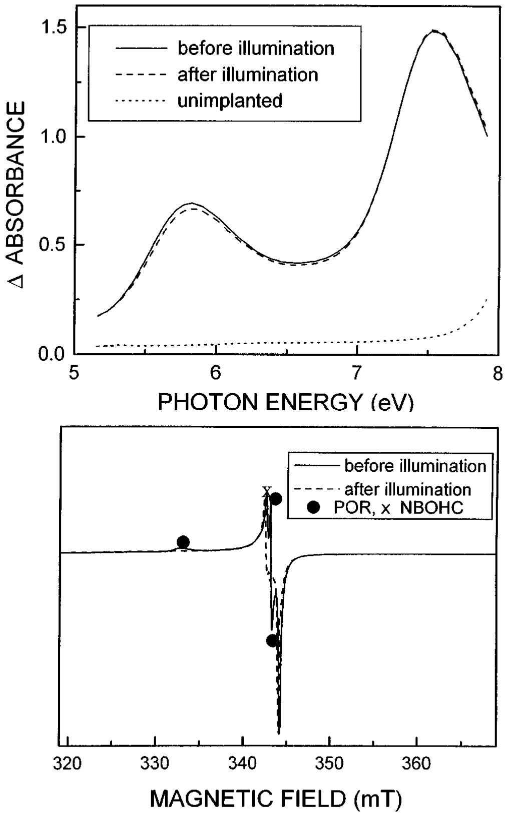

FIG. 1. Induced VUV-UV absorption (top) and EPR (bottom) spectra by 10 MeV proton implantation. Fluence; 1×10^{16} cm^{-2}. EPR spectra were measured at 77 K. Solid and broken curves indicate traces before and after illumination with 5 eV light, respectively. Filled circles in the bottom denote features of POR signals.

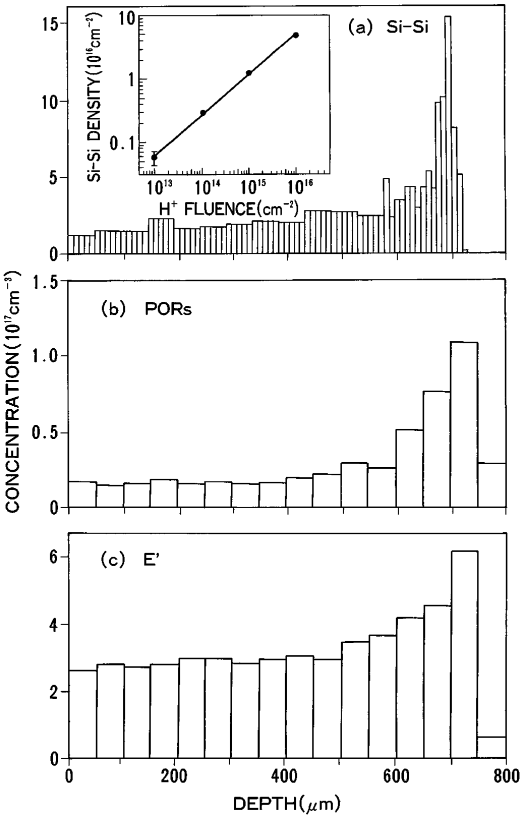

FIG. 2. Depth concentrations of Si-Si bonds (a), PORs (b), and E' centers (c). Inset in (a) shows the concentration of Si-Si bonds as a function of fluence.

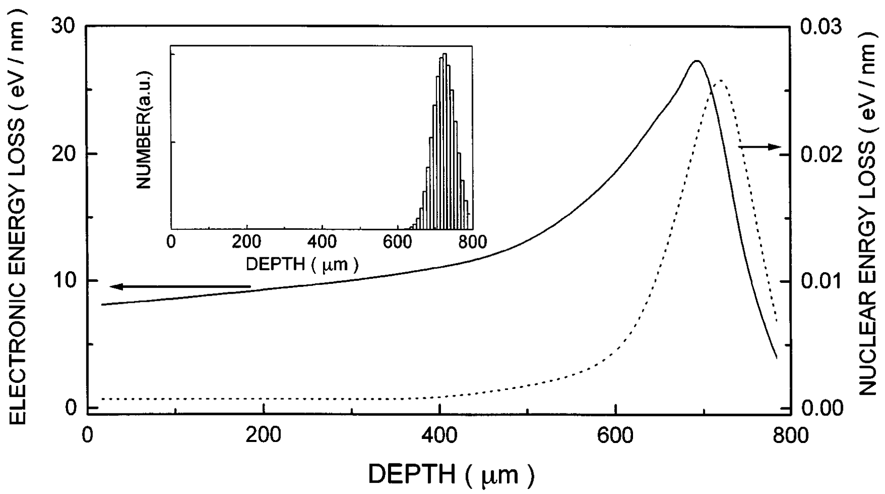

FIG. 3. Energy depositions and ion range of 10 MeV H^+ calculated with the TRIM-92 code.

without a significant saturation behavior in the range examined here.

Figure 2(a) shows the depth concentrations of the Si-Si bonds from the implanted surface. The concentration is almost constant ($2 \sim 3 \times 10^{17}$ cm^{-3}) from the surface to ~600 μm, increases with depth, reaches the maximum (~10×10^{17} cm^{-3}) at ~700 μm, and then rapidly decreases down to zero at ~750 μm. Figures 2(b) and 2(c) show the depth concentrations of E' centers and PORs [17], respectively. Both profiles are similar to the depth profile of the Si-Si bond, and the average concentration of E' centers is comparable to that of the Si-Si bonds, but is larger by a factor of 6 than that of PORs.

Figure 3 depicts the depth profile of energy depositions and ion ranges calculated with the TRIM-code. The ion range and range straggling are calculated as ~700 μm and ~90 μm, respectively. The magnitude of electronic energy loss (EEL) has an almost constant value of ~10 eV nm^{-1} ion^{-1} from the top surface to ~500 μm, increases distinctly with depth, reaches the maximum at ~700 μm, and then decreases monotonically down to zero. On the other hand, the magnitude of nuclear energy loss (NEL) is very small (~0.001 eV nm^{-1} ion^{-1}). Even compared at the peak position of NEL, the magnitude of NEL is ~0.2% as large as that of EEL. It is evident from a comparison of the depth profiles (a), (b), and (c) with those of energy depositions that the Si-Si bonds, E' centers, and PORs are created primarily by electronic energy depositions.

Figure 4 shows PL-Raman spectra of implanted and unimplanted cross sections of the specimen. The band at 1272.2 nm (apparent Raman shift; ~1540 cm^{-1}) is significantly observed only for the implanted portion. This band agrees well with that due to interstitial O_2 molecules in SiO_2 glasses reported by Skuja and Guttler [11]. The concentration of interstitial O_2 molecules, which was estimated from a comparison in relative intensities of the PL band to the fundamental Raman band with data by Skuja and Guttler, was ~10^{17} cm^{-3} [18]. This concentration is larger by a factor of ~4 than that of PORs. Interstitial O_2 molecules are formed by the reaction between two interstitial oxygen atoms created from intrinsic Si-O-Si bonds, while a POR is formed from an interstitial oxygen atom reacting with an NBOHC or an interstitial O_2 molecule reacting with an E' center. Thus, the dominant defect species relevant to oxygens is not a POR but an interstitial O_2 molecule. Table I summarizes defect species and their concentrations observed here, along with techniques used for the concentration determination.

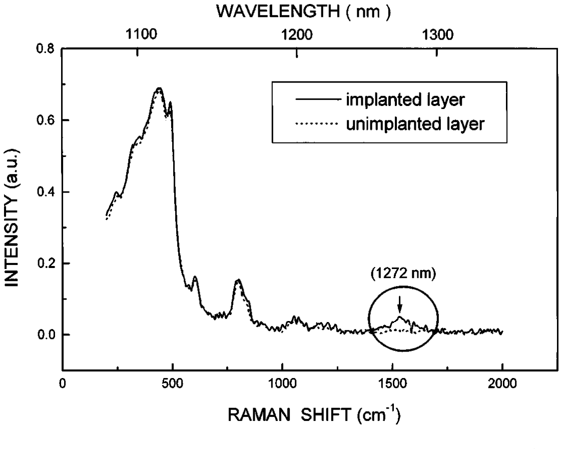

FIG. 4. Photoluminescence and Raman spectra of SiO_2 glasses. Excitation source: ND:YAG laser light (beam diameter ~300 μm). Solid and broken traces are spectra for implanted and unimplanted cross sections, respectively. The laser beam was positioned at ~300 μm from the implanted surface to measure the implanted cross section. Each spectrum was obtained by accumulation of 50 times. Spectral intensity was normalized by the peak intensity of the silica network Raman band at ~440 cm^{-1} for comparison.

TABLE I. Defect species and concentrations in wet SiO_2 glasses implanted with H^+ ions at 10 MeV to a fluence of 1×10^{16} cm^{-2} at room temperature.

Defects	Areal concentrations (10^{16} cm^{-2})	Methods
$\equiv$Si—Si$\equiv$	4	Vacuum UV absorption band peaking at 7.6 eV[a]
E' centers	2	EPR (300 K)
PORs	0.4	EPR (77 K)
O_2 molecules	$1 \sim 2$	PL band excited with 1064 nm light[b]

[a] The absorption cross section of 7.5×10^{-17} cm^2 [10] was used.

[b] The relative intensity of the PL band to the network Raman band in the spectrum of Suprasil W reported by Skuja and Guttler [11] was used as the concentration standard.

It is now evident that the Si-Si bonds, E' centers, PORs, and interstitial O_2 molecules are created by electronic excitation of SiO_2 glasses, and the concentrations of the Si-Si bonds + E' centers are comparable to those of the PORs + O_2 molecules. These results lead to the conclusion that the Frenkel defect pair of an oxygen vacancy and interstitial is created by an electronic excitation process of amorphous SiO_2. Provided that an E' center is created from an oxygen vacancy, the efficiency of Frenkel defect pair formation may be estimated as $\sim 5 \times 10^{-7}$ eV^{-1} by the total concentrations of the Si-Si bond and E' centers and the magnitude of EEL.

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[16] Two types of neutral oxygen vacancy occur in a-SiO_2, i.e., a relaxed and an unrelaxed type [H. Imai *et al.*, Phys. Rev. B **38**, 12 772 (1988)]. The former and the latter give optical absorption bands at ~7.6 and 5 eV, respectively, and the oscillator strength of the former is several times as large as that of the latter. However, the apparent intensity at 5 eV in the induced absorption is $\sim\frac{1}{10}$ as large as that at 7.5 eV. In addition, PORs also give a band at ~5 eV [14]. Therefore, the contribution of the unrelaxed oxygen vacancy to the total oxygen vacancy concentration can be neglected as a first approximation.

[17] NBOHCs are created from the Si-OH precursor by X, γ-ray, or unfocused ArF laser irradiation. Recently, it was suggested [11] that NBOHCs are created by the reaction of E' centers with an interstitial oxygen atom created from the intrinsic structure. Here, we did not regard a NBOHC as an oxygen interstitial. However, this difference in choice does not bring about a significant influence in the following discussion and conclusion because the concentration ratio of NBOHCs to POR is ~1.

[18] The variation in the PL intensity relative to the Raman band with depth could not be measured because of the large probe beam diameter (~300 μm) relative to the implanted layer thickness (~700 μm).