Bi-self-trapped-exciton model for Frenkel defect formation in amorphous SiO_2 by proton irradiation

Noriaki Matsunami*
Energy Engineering and Science, School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

Hideo Hosono
Materials and Structures Laboratory, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226-8503, Japan
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The observed depth profile of the concentrations of the Frenkel defect (Si-Si bonds, E' centers or peroxy radicals) in amorphous SiO_2 irradiated by high-energy H^+ ions is shown to be close to the calculated depth profile of O 2*s*-shell ionization as well as that of the electronic energy deposition (EED). A new model, namely, bi-STE model is proposed: the Frenkel defect is created by nonradiative decay of two neighboring self-trapped excitons generated through O 2*s*-shell ionization followed by an Auger decay process. This model can explain the observed linear dependence of the Frenkel defect formation on the EED, in contrast to the superlinear EED dependence expected for dense electronic excitation as for focused ArF excimer-laser irradiation. [S0163-1829(99)10339-4]

Formation of the intrinsic defects in SiO_2 (Refs. 1 and 2) has been extensively studied under irradiation of various ionizing radiations [ultraviolet (UV) photons,[3–5] x rays,[6,7] γ rays,[8,9] electrons,[10–13] and high-energy ions[14,15]]. Degradation of optical and electrical properties of amorphous (a-)SiO_2 by such radiations has considerable interest in view of fundamental aspects of the defect-formation mechanism as well as of applications in lens materials for UV optics and insulators in Si electronic devices. Hobbs and Pascucci,[10] Pfeffer,[12] and Devine[3] showed that the number of radiation-induced defects such as E' centers ($\equiv$Si•, where • and —, respectively, mean an unpaired electron and a Si-O bond) is nearly proportional to either the ionization cross section or the electronic energy deposition (EED) or the electronic energy loss,[16] and that the defects are created by EED but not by knock-on processes due to the nuclear energy deposition. Furthermore, measurements were carried out on the complementary defects such as the Si-Si bonds (oxygen vacancies) and the peroxy radicals (POR's, i.e., Si-O-O •) or the interstitial O_2 molecules in order to identify the radiation-induced Frenkel defects (vacancy and interstitial pairs), eliminating E' centers created from the pre-existing defects.[4] Nonaka *et al.*[13] observed the oxygen vacancies created by irradiation with low-energy electrons (0.3–10 keV). Tsai and Griscom[5] reported that POR's are created through the reaction of radiation-induced O_2 with E' centers in wet a-SiO_2 (OH content $>1\times10^{19}/cm^3$) as the dominant oxygen-related center (OHC) instead of NBOHC (nonbridging-oxygen hole center, i.e., $\equiv$Si-O•) by irradiation of focused ArF excimer laser-pulse (193 nm). Formation of POR's was also observed for irradiation of x rays[6,7] and γ rays.[9] All of these results confirm that formation of the Frenkel defects is due to EED but not due to knock-on. For high-energy H^+-ion irradiation,[14,15] Si-Si bonds, E' centers, POR's and the interstitial O_2 molecules are confirmed as the Frenkel defects created by EED in wet a-SiO_2 (the OH content is $3\times10^{19}/cm^3$).

It is known that in alkali halides,[17] the excitons or electron-hole (e-h) pairs are generated by ionizing radiation (Fig. 1) and the self-trapped excitons (STE's) are created via relaxation of excitons.[18,19] It has been suggested that the Frenkel defect in a-SiO_2 is formed through nonradiative decay of a single STE [Fig. 2(a)] and the subsequent rotation of the Si-O bond.[20] This model predicts the linear EED dependence of the defect formation that the concentration of the radiation-induced defects is proportional to the STE concentration or the EED, and can explain most of the observations mentioned above, except for the report by Tsai and Griscom.[5] They found that the POR concentration depends superlinearly on the STE concentration for focused ArF excimer laser-pulse irradiation, and suggested that O_2 molecule formation, resulting in POR's, is greatly enhanced by dense electronic excitation[21] or a biexciton mechanism. The observed results of high-energy proton irradiation do not show a superlinear EED dependence of the Frenkel defect formation but a linear EED dependence,[14,15] contrary to the predic-

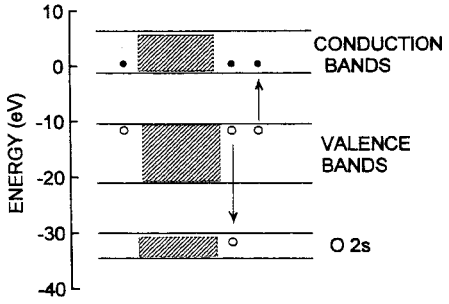

FIG. 1. Energy-band diagram for SiO_2 according to Ref. 2 and the schematic excitation diagram. The vacuum level is taken as the origin of the energy scale. Open and closed circles denote holes and electrons. The left-hand side shows an electron-hole pair excitation (exciton). The right-hand side shows Auger decay of a single O 2*s* hole, creating two electron-hole pairs in the valence bands (two excitons).

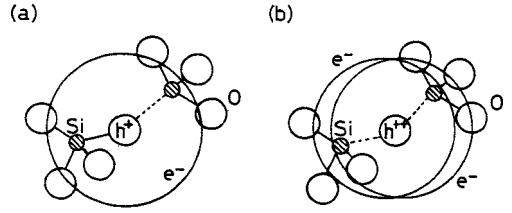

FIG. 2. Schematic illustrations in SiO_2: (a) single STE (self-trapped exciton) according to Ref. 18 and (b) bi-STE's generated from two electron-hole pairs as shown on the right-hand side of Fig. 1. Solid and dashed lines denote a normal Si-O bond and an elongated (due to an additional hole) Si-O bond, respectively. Large circles with e^- indicate schematic orbits of electrons trapped by a hole (h^+) or double holes (h^{2+}).

tion due to the high-density electronic excitation for proton irradiation.

In the present paper, we report that the linear EED dependence of the Frenkel defect formation observed for H^+ irradiation[14,15] can be explained by a bi-STE model, i.e., nonradiative decay of two neighboring STE's created by O $2s$-shell ionization followed by Auger decay process, leading to the Frenkel defect formation in a-SiO_2. The above controversy can be reconciled by the present model, provided that (i) the O $2s$-shell ionization probability is comparable to the valence-band excitation probability or reasonably large for ion irradiation, and (ii) the bi-STE's are more efficient than the single STE for the Frenkel defect formation. One should notice that the bi-STE model has not been established yet but is considered to be a reasonable extension of the single-STE model.

Now we discuss the EED density. For conventional laser-pulse irradiation [fluence of 30 mJ/cm^2 and a pulse duration of 20 ns (Ref. 5)], the energy density per pulse is estimated to be roughly 4×10^{-6} eV/nm^3, using the absorption coefficient of 0.02/cm at 193 nm.[22] On the other hand, for 10-MeV H^+ in a-SiO_2, more than 90% of the electronic energy is calculated to be deposited within the adiabatic radius $R_{ad}=hv/2\pi I$ of 1.4 nm.[23] Here h is the Planck constant, v the H^+ velocity, and I the mean ionization potential, taken as 20 eV for valence electrons, i.e., approximately twice the band gap. Then an EED of $\sim$10 eV/nm per H^+ ion of 10 MeV in SiO_2 (Ref. 24) [see Fig. 3(a)] corresponds to approximately 1 eV/nm^3. The number of the valence electrons (O $2p^4$ and Si $3s^2p^2$) is 12/30 of the total electrons, and the EED per electron is nearly independent of the electron shell for high-energy ions,[23] and hence the valence electron contribution to the EED is reduced to $\sim$0.4 eV/nm^3. Both the laser-pulse duration (20 ns) and the time for ion stopping ($R_p/v\sim10^{-11}$ s, R_p being the projected range of H^+ ion[24]) are much shorter than the lifetime of a STE ($\sim$10 ms),[25] which is of primary importance for the defect formation. Accordingly, the above calculated energy densities may represent the electronic excitation densities, provided that the conversion efficiency from EED to STE's is the same for both laser-pulse and ion irradiation. Hence the energy density by H^+ irradiation is far larger than that by conventional laser-pulse irradiation.

We examine two conditions mentioned above. For ion irradiation, the ionization probability of the O $2s$ shell is estimated to be the same order of magnitude as those of the

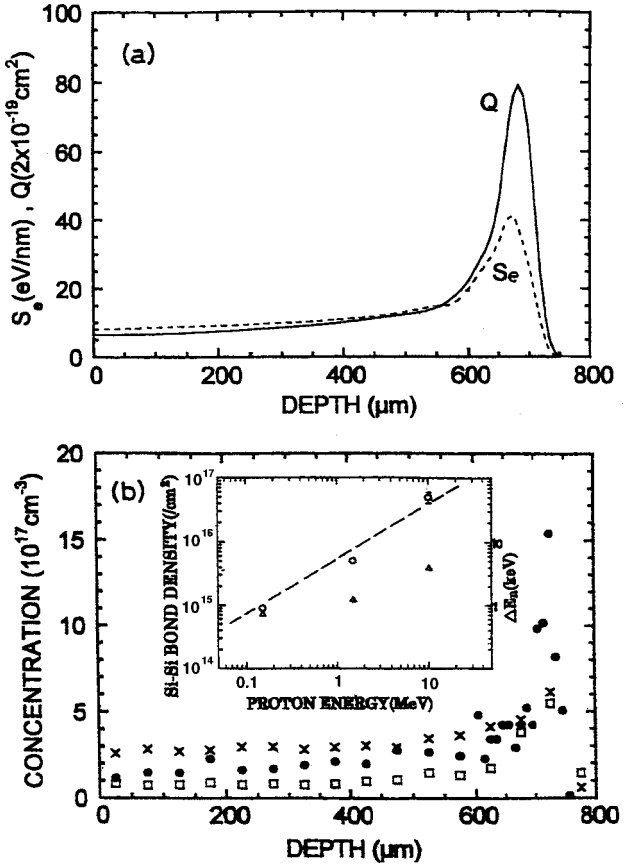

FIG. 3. (a) The calculated energy dependence of EED per unit length S_e (dashed line) and ionization cross section Q (solid line) of the O $2s$ shell for 10-MeV H^+ irradiation in a-SiO_2. (b) Depth profiles of the concentrations of Si-Si bonds (●), POR's (X) and E' centers (□) in a-SiO_2 for 10-MeV H^+ irradiation with total dose of 10^{16}/cm^2 according to Ref. 14. Note that the POR concentration is multiplied by a factor of 5. Open circles in the inset show the H^+ energy dependence of the Si-Si bond density for the H^+ fluence of 10^{16}/cm^2, taken after Ref. 15, illustrating the linear EED dependence of the Si-Si bond density (more than 99% of the incident energy of H^+ being deposited into EED). Open triangles show the nuclear energy deposition (ΔE_n) calculated by TRIM (Ref. 24).

valence bands, because the ionization probability is roughly proportional to the inverse of the binding energy[26] (30 eV for the O $2s$ shell and 10–20 eV for the valence bands[2,27]). Furthermore, the depth profile of the O $2s$ shell ionization is found to be close to that of the defect concentration and that of the EED [see Figs. 3(a) and 3(b)]. Hence condition (i) is justified. Once a hole is created in the O $2s$ shell by ion irradiation, Auger decay is possible, and results in the generation of two holes in the valence bands, since the energy difference of 20 eV between the O $2s$ level and the top of the valence bands is larger than twice the energy gap (9 eV) between the conduction and valence bands as seen in the right-hand side of Fig. 1. In this situation, bi-STE's can be created via relaxation of two neighboring excitons [Fig. 2(b)]. The probability would be fairly high that two holes occupy the valence orbital of an oxygen atom. We assume that fast lattice relaxation and two e-h pairs go immediately into bi-STE's with the certain efficiency, as in alkali halides.[17] The bi-STE model does not require rotation of the Si-O bond to create Frenkel defects, and an oxygen with two

holes in the bi-STE's would have more energy available for the formation of an oxygen interstitial than a single STE. Thus condition (ii) is reasonable. Enhancement of the defect formation by focused ArF laser-pulse irradiation[5] can be explained in terms of bi-STE's generated by collisions of excitons at high density due to valence-band excitations, which predicts naturally the superlinear EED dependence of the defect formation. There is a probability that two *e-h* pairs are created in one or two neighboring tetrahedral (t-) SiO_4 units (resulting in bi-STE's) due to high-density excitation of the valence electrons by ion irradiation, leading to a linear EED dependence of the defect formation. This will be discussed later in more detail.

Figure 3(a) shows the depth profiles of the calculated EED or the electronic energy loss per unit path length (S_e) and the ionization cross section Q of the O $2s$ shell for 10-MeV H^+-ion irradiation. The calculation is based on the TRIM simulation code (1992 version)[24] with a concentration of a-SiO_2 of $2.2\times10^{22}/cm^3$, and the Bragg additive rule is applied. Firstly, the energy E of H^+ ions is calculated as a function of depth z. For depths smaller than the projected range (<600 μm), Q and S_e are given by $Q(E)$ and $S_e(E)$[24] at $E(z)$, because the energy straggling (fluctuation) is small. $Q(E)$ is calculated using the binary encounter approximation[26] with a binding energy of 30 eV for the O $2s$ shell.[2,27] For depths near the projected range (600–800 μm), Q and S_e are given as the convolution of $Q(E)$ and $S_e(E)$ with a Gaussian distribution $\{(2\pi)^{-1/2}/\sigma\}\exp\{-[E-E(z)]^2/2\sigma^2\}$, by taking the energy straggling σ into account. For 10-MeV H^+, σ is estimated to be approximately 900 keV using the derivative of $E(z)$, 90 keV/μm (nearly equal to the maximum S_e of 120 keV/μm at $E\sim80$ keV) and a range straggling of 10 μm. The depth profile of S_e obtained with the above method is shown in Fig. 3(a), which reproduces well the S_e obtained directly by the TRIM. Figure 3(b) shows the depth profile of the defect concentration and the relation between the total density of Si-Si bonds and the incident energy of protons which are reproduced according to Refs. 14 and 15, noticing that more than 99% of the incident energy is deposited into EED for H^+ irradiation, and probable errors of the defect concentration were estimated as 20%. As mentioned before, we see that the depth profile of the defect concentration is close to that of Q as well as S_e. The defect formation efficiency is estimated to be $\sim0.7\times10^{-5}$ oxygen vacancies per O $2s$-shell ionization by taking the ratio of the defect concentration per ion over the O $2s$-shell ionization cross section from Fig. 3(a). The observed linear EED dependence of the Frenkel defect formation for H^+ irradiation reveals that the superlinear EED dependence process, i.e., creation of bi-STE's by valence-band excitations, is effectively suppressed. For H^+ irradiation, the valence-band excitation is so dense and nonuniform that the number of bi-STE's could be reduced by collisions with excitons and STE's, as observed in alkali halides,[28] and by their diffusion out from the ion-track region. These are plausible reasons for the suppression.

It is important to discuss the possibility whether the energy deposition is sufficient to create two *e-h* pairs in one or two neighboring t-SiO_4 units by valence-band excitations for energetic ion irradiation. A part of EED is due to generation of delta rays (high-energy secondary electrons generated by incident ion). The EED density $D(r)$ due to δ rays,[29,30] which contributes approximately half of the total EED, is integrated from the ion track center to a radius r. It is found that for $r<0.4$ nm (chosen as twice the Si-O bond length), the total deposited energy $\ll10$ eV, and is much smaller than 40 eV, viz., twice the mean excitation energy, indicating that two excitons are not created sufficiently in one or two neighboring t-SiO_4 units. Here the range of electrons, which is required to evaluate $D(r)$, is calculated using the data from Refs. 31 and 32. The rest of half the energy deposition density can be estimated using the dipole approximation.[23] Assuming that the mean excitation energy is 20 eV as before, more than 80–90 % of the total EED is calculated to be within the adiabatic radius R_{ad} of 0.14–1.4 nm for 0.1–10-MeV H^+. Thus the integrated energy over one or two neighboring t-SiO_4 units is found to be much smaller than 40 eV, indicating that two excitons in one or two t-SiO_4 units are unlikely to be created by valence-band excitations. Notice that all discussions so far are based on the mean values of the energy-deposition distribution, discarding the fluctuation effect of the energy deposition due to its statistical nature.[33]

It should be pointed out that for electron irradiation, the bi-STE could play a role in the Frenkel defect formation in a-SiO_2, because the ratio of O $2s$-shell ionization over valence excitation is roughly the same for both high-energy ion and electron irradiation,[33] and also because the electron irradiation has effects quite similar to ion irradiation [e.g., the maximum EED is $\sim$40 eV/nm at an electron energy of $\sim$100 eV (Ref. 30)]. This is supported by the observations of the oxygen-vacancy formation by electron irradiation.[13] Similarly, the bi-STE model is effective for x- and γ-ray irradiation, as observed.[6,7,9]

In conclusion, we have demonstrated that the linear EED dependence of the Frenkel defects created by high-energy H^+ irradiation in a-SiO_2 can be explained by the bi-STE model, where a bi-STE is created via Auger decay of a hole generated by O $2s$-shell ionization. This model may provide some clues in understanding the observed linear EED dependence of defect formation for high-energy H^+-ion irradiation, contrary to the predicted superlinear EED dependence due to high-density electronic excitation, and can also be applicable to the Frenkel defect formation in a-SiO_2 by irradiation with other ionizing radiations such as x rays, γ rays, and electrons.[34]

*Author to whom correspondence should be addressed. FAX: +81-52-789-3847.

Electronic address: n-matsunami@nucl.nagoya-u.ac.jp

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