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Mechanism of electron localization at edge-sharing units in amorphous SiO_2

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We have presented a model of the electron-trapping process at edge-sharing SiO_4 units that are supposed to exist as structural defects especially at the surface of silica-based materials. It has been shown that the edge-sharing SiO_4 dimer can trap an electron, giving rise to a paramagnetic threefold-coordinated silicon and a negatively charged nonbridging oxygen. The former Si-related paramagnetic center exhibits a characteristic of the so-called E' center. The electrical level of the related electron trapping center is ~ 2 eV below the conduction band.

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Radiation-induced point defects in amorphous SiO_2 (a-SiO_2) and related metal-oxide-semiconductor (MOS) devices have been extensively studied during the past decades.[1–3] The electronic excitation during ionizing radiation will produce primarily electrons, holes, and excitons, and the defect formation will be closely related to the subsequent self-trapping and/or decay processes of these radiation-induced particles. The principal tool for the identification of the microscopic structure of these defects is electron paramagnetic resonance (EPR) spectroscopy. As for silicon-based MOS devices, capacitance-voltage (C-V) techniques are also been used to determine the total electrical charge accumulated during ionizing radiation. Previous C-V measurements on various MOS devices have demonstrated that ionizing radiation certainly creates electron-trapping centers in a-SiO_2 layers,[4,5] and the resultant electron-trapping center is assumed to be paramagnetic. It is curious to note, however, that with the exception of a few impurity-related species,[3] there has been no report of the EPR signature of such electron-trapping centers.[6] In α-quartz, one of the E' variants called the E_4' center, which consists of a hydrogen atom substituting for an oxygen atom in α-quartz, is believed to behave as a deep electron trap,[7] but there has been no EPR evidence for a defect in a-SiO_2 of the E_4' type. Thus all the defects monitored by EPR so far in a-SiO_2 are either of the trapped-hole type or else result from self-trapping of excitons.[1–3]

From semiempirical molecular orbital calculations on a cluster of atoms modeling a neutral oxygen vacancy in α-quartz, Rudra and Fowler[8] proposed that this type of vacancy site will trap an electron and form a stable negatively charged center. They found that the s-spin density is delocalized on both silicon atoms in the defect site. The results of Rudra and Fowler[8] suggest that if such an electron-trapping site exists, the observed EPR signals will be characterized by two almost equally strong hyperfine interactions with ^{29}Si. As mentioned above, however, the corresponding defect has not been detected in a-SiO_2 by any EPR measurements. This appears to be incompatible with the results of C-V measurements, but there has been no accepted model that accounts for the seemingly enigmatic character related to the trapped electrons in SiO_2-based materials during ionizing radiation. In this Rapid Communication, we therefore present a possible model of the electron trapping process in a-SiO_2. We propose that an edge-sharing tetrahedral dimer, which has attracted renewed interest as a model of a strained silica surface,[9] is one of the probable candidates for an electron-trapping center at least near the surface of a-SiO_2.

Before going into details of the fate of the trapped electron at the edge-sharing tetrahedral site, we reexamine the electron-trapping process at a neutral oxygen vacancy, which has been regarded as a likely candidate of the negative-charge precursor. As mentioned earlier, Rudra and Fowler[8] calculated minimum-energy configurations of neutral and negatively charged oxygen vacancies starting from a defect model in α-quartz. However, the calculations were performed using a semiempirical molecular orbital method, which does not necessarily yield a quantitative picture for the relevant electronic processes of atoms or molecules of interest. In this work, we hence calculate the optimized geometry of a neutral oxygen vacancy using the *ab initio* molecular orbital method and investigate its possible relaxation process upon trapping an electron. Figure 1 shows a cluster of atoms used to model a neutral oxygen vacancy in the random SiO_2 network. The surface Si atoms in the cluster were saturated by H atoms. Such H termination is employed to suppress the ''surface'' effect arising from the dangling bonds of the outermost atoms and has been shown to be useful to eliminate the unsaturated bonds of clusters modeling the local structure of the corresponding amorphous system.[10] To begin with, we optimized the cluster in the neutral charge state [model 1; see Fig. 1(a)] without imposing any structural constraints. We then intentionally added one electron to model 1 to create a negatively charged cluster [model 2; see Fig. 1(b)], and its geometry was fully reoptimized using the optimized configuration of model 1 as an initial geometry. To take account of electron correlation effects in the electron trapping process,

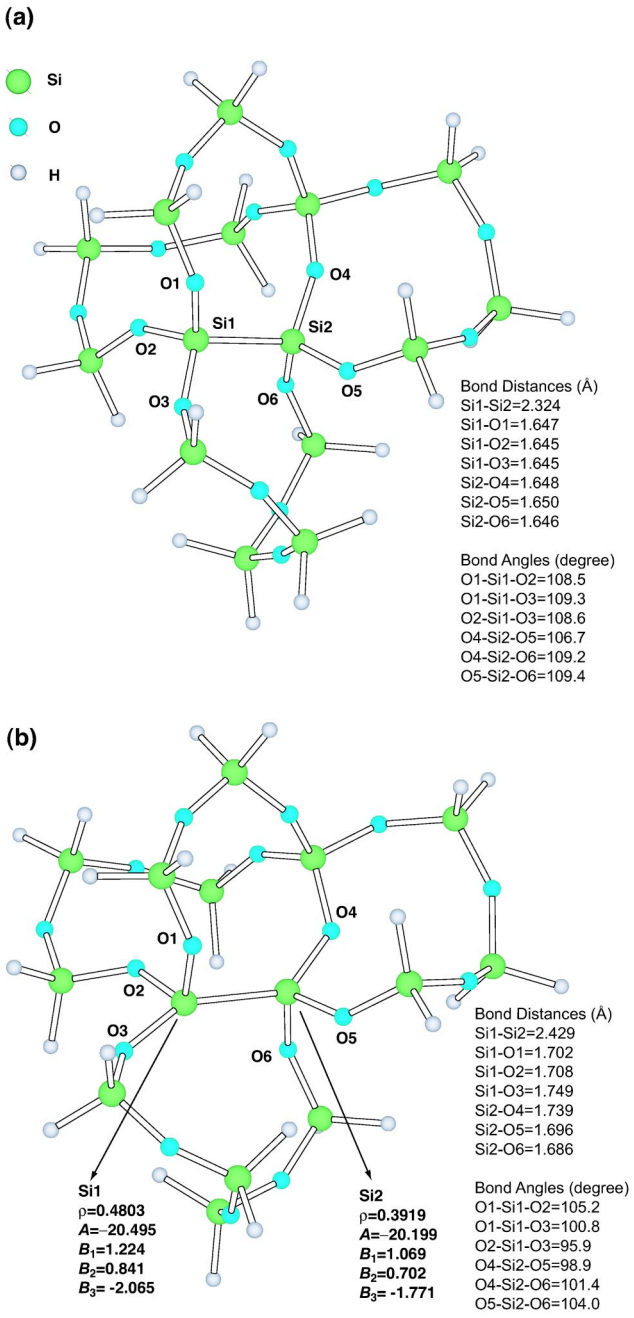

FIG. 1. $Si_{15}O_{17}H_{24}$ cluster models of (a) a neutral oxygen vacancy (model 1) and (b) a negatively charged oxygen vacancy (model 2). The geometries of the clusters were fully optimized at the B3LYP/6-31G(d) level. Principal optimized structural parameters, spin densities ρ, and isotropic A, and anisotropic B hyperfine coupling constants (in mT) are also shown.

geometry optimizations of the above neutrally and negatively charged clusters were performed at the density functional theory (DFT) levels with the 6-31G(d) basis set.[11] For the DFT calculations, we used the B3LYP exchange-correlation functional consisting of the Lee-Yang-Parr correlation functional[12] in conjunction with a hybrid exchange functional proposed by Becke.[13] All the *ab initio* quantum-chemical calculations in this work were performed using the GAUSSIAN 98 program.[14]

As shown in Fig. 1, it has been found that when an electron is added to the neutral cluster, the electron is trapped at the oxygen vacancy, showing a slight elongation of the Si-Si and Si-O distances in the defect site. The spin densities of Si1 and Si2 in model 2 are calculated to be 0.48 and 0.38, respectively. This indicates that the trapped electron is delocalized over the two silicon atoms in the defect site, in agreement with the results obtained previously by Rudra and Fowler.[8] It has also been found that the two paramagnetic Si atoms have rather large hyperfine couplings ($\sim$20 mT) [see Fig. 1(b)] although, as has been pointed out repeatedly in this paper, such hyperfine interactions have not been detected by previous EPR measurements. We further calculated the electrical level position of the negatively charged state using the definition of Rudra and Fowler[8]: $E(n/(n+1))=E_{\mathrm{tot}}(V_{\mathrm{O}}^{n})-E_{\mathrm{tot}}(V_{\mathrm{O}}^{n+1})-E_{\mathrm{CBM}}$, where $E_{\mathrm{tot}}(V_{\mathrm{O}}^{n})$ is the total energy of the O vacancy with net charge n and E_{CBM} is the energy of the conduction-band minimum with respect to vacuum (~ -0.9 eV). The addition of the term E_{CBM} hence moves the reference energy from the vacuum level to the bottom of the conduction band. In the present model clusters, $E_{\mathrm{tot}}(\mathrm{model\ 2})-E_{\mathrm{tot}}(\mathrm{model\ 1})$ was calculated to be 0.01 eV. Thus the electrical level of the present negatively charged state, $E(-/0)$, is estimated to be $\sim$0.91 eV. We should note, however, that in the real dielectric continuum, the long-range polarization effects, which are neglected in our cluster models, are likely to exist, causing a downward shift in the total energy of the negatively charged state.[15] In this work, the energy shift due to the electronic polarization E_p was evaluated by a classical non-self-consistent model,[16,17] which assumes that the cluster is a cavity of the same dielectric as the solid with a point charge at its center. According to this model, the polarization energy is given by $E_p=-Q^2/2R(1-1/\varepsilon)$, where R is the radius of the cavity, which can be regarded as the radius of the cluster, Q is the net charge, and ε is the static dielectric constant in a-SiO_2. By assuming $R=6$ Å in model 2, we have $E_p\approx 0.91$ eV. That is, the corrected electrical level $E(-/0)^{\mathrm{corr}}$ of the present negatively charged oxygen vacancy is $\sim$0 eV, indicating that the electrical level of this charged defect center is comparable to the band edge of the conduction band. This result strongly suggests that, in contrast to the previous semiempirical calculations reported by Rudra and Fowler,[8] the neutral oxygen vacancy behaves only as a ''shallow'' electron trap. In irradiated a-SiO_2, however, ''deeper'' trapped electrons, which are stable even at room temperature, are reported to exist.

It is hence most likely that another form of defects is responsible for deep electron traps in a-SiO_2. The random network of a-SiO_2 consists mostly of the corner-sharing SiO_4 units. However, it is quite probable that the ''edge-sharing'' SiO_4 tetrahedral dimer or a two-membered silica ring exists as a structural ''defect.'' We should note that the strain energy of the edge-sharing unit is estimated to be $\sim$1.2 to $\sim$1.8 eV (Refs. 9 and 18), which is far smaller than the formation energy of an neutral oxygen vacancy [$\sim$6 to $\sim$10 eV (Ref. 19)]. Indeed, recent studies[9,20] have provided plenty of evidence demonstrating that edge-sharing units ex-

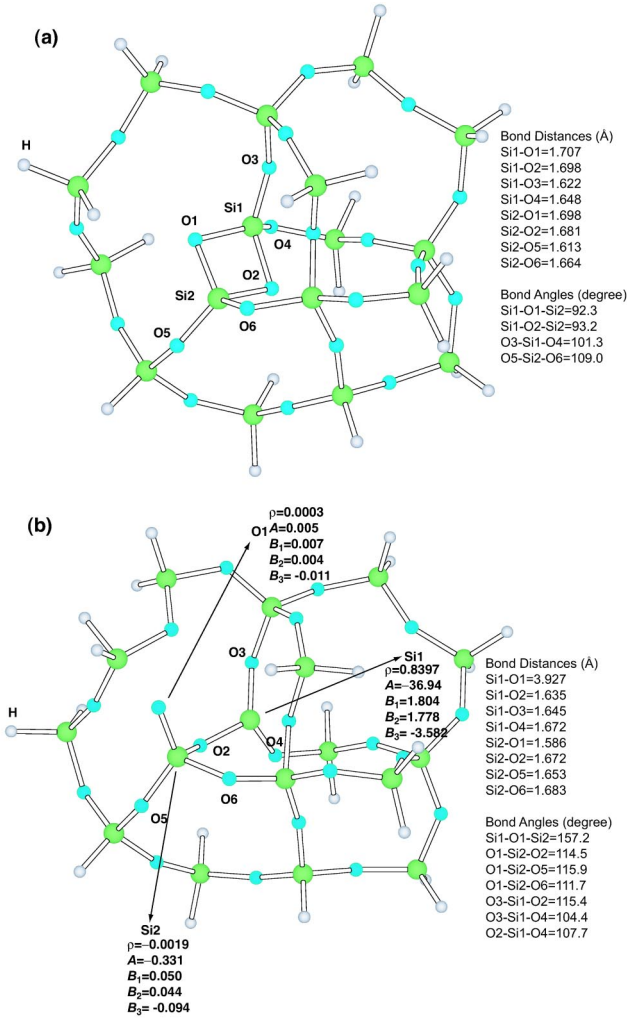

FIG. 2. Optimized geometries of (a) the neutral $Si_{17}O_{23}H_{22}$ cluster having an edge-sharing SiO_4 dimer and (b) the corresponding negatively chargedcluster. The geometries were fully optimized at the B3LYP/6-31G(d) level. Principal optimized structural parameters, spin densities ρ, and isotropic A, and anisotropic B hyperfine coupling constants are also shown.

ist at the surface of a-SiO_2. Thus it is interesting to investigate a possible electron-trapping process at edge-sharing SiO_4 tetrahedral units in terms of the structure and energetics especially of the irradiated silica surface. Furthermore, although we do not have a detailed microscopic understanding of the structure of the interface in $Si/SiO_2/Si$ layers, such an edge-sharing dimer as seen at the silica surface may provide an alternative candidate of the reported negative-charge precursor at the Si/SiO_2 interface.[21]

We thus investigate a possible electron trapping process at an edge-sharing SiO_4 tetrahedral dimer on the basis of quantum-chemical cluster calculations. In our recent paper,[22] we have already shown that the edge-sharing dimer can capture an exciton, leading to structural reorganizations that are different from those of the corner-sharing ones. Figure 2 shows the cluster of atoms used to model an edge-sharing SiO_4 tetrahedral dimer embedded in the corner-sharing SiO_4 network. The geometry of the neutrally charged cluster [model 3; see Fig. 2(a)] was fully optimized at the B3LYP/6-31G(d) level. To simulate an electron trapping process at the ''defect'' site in model 3, the geometry was then fully reoptimized at the same level of theory by assuming the total charge of -1 [model 4; see Fig. 2(b)].

One sees from Figs. 2(a) and 2(b) that the structural relaxation after trapping an electron at the edge-sharing SiO_4 tetrahedral site is substantially different from that seen at the oxygen vacancy site. That is, when an electron is trapped at the edge-sharing site, one of the four Si-O bonds in the two-membered ring is broken to form a threefold-coordinated silicon atom (Si1 in model 4) and a nonbridging oxygen atom (O1 in model 4). The added electron is mainly localized at the nonbridging oxygen atom, yielding a negatively charged center. The spin density ρ and the hyperfine coupling constant A of O1 are calculated to be 0.0003 and 0.005 mT, respectively, showing an almost diamagnetic nature of the nonbridging oxygen atom. On the other hand, the threefold-coordinated Si atom (Si1) has an unpaired spin that is located mainly at its dangling tetrahedral orbital ($\rho_{Si1}=0.8397$, $A=36.9$ mT). The resultant paramagnetic center in model 4 is hence quite analogous to the E' center, in which an unpaired spin is localized in a dangling tetrahedral orbital of a threefold-coordinated silicon atom. The observed hyperfine coupling observed for the localized E' center (42 mT, Ref. 3) is in reasonable agreement with the value calculated for Si1 in model 4. It should also be worth mentioning that the total energy of model 4 is lower than that of model 3 by 2.27 eV and the corrected electrical level $E(-/0)^{corr}$ of the defect in model 4 is calculated to be ~ -2.3 eV. This large negative electrical level, as compared with the one calculated for the oxygen vacancy center, suggests that the edge-sharing tetrahedral site can behave as a ''deep'' electron trap. Thus the edge-sharing structure contrasts sharply with the oxygen vacancy in terms of the electron-trapping process and its subsequent structural relaxation. The edge-sharing structure induces dissociative electron capture at one of the Si-O bonds in the ''defect'' site, resulting an almost diamagnetic negatively charged nonbridging oxygen and a paramagnetic threefold-coordinated silicon center. Consequently, the resultant paramagnetic defect will not be identified as an electron trap, but as a conventional E'-like defect by EPR. This scheme is hence reconcilable with the observed experiments that no paramagnetic defect associated with ''trapped electrons'' has been observed in a-SiO_2.

In conclusion, previously unidentified electron trapping centers in a-SiO_2 have been associated with the defects resulting from the electron-trapping process at the edge-sharing SiO_4 sites. This process leads to the generation of the

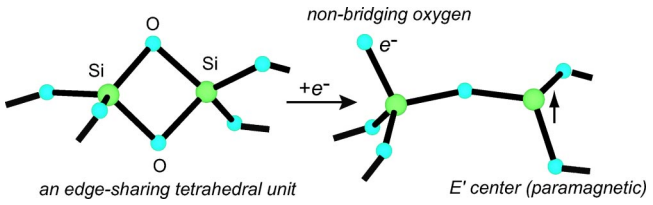

FIG. 3. Proposed electron-trapping mechanism of the edge-sharing SiO_4 dimer and the accompanying defect formation.

neutral E'-like center, whereas the trapped electron is localized at a nonbridging oxygen site (see also, Fig. 3). The trapping of electrons at the edge-sharing SiO_4 sites will hence account for the underlying experimental features of radiation-induced phenomena peculiar to a-SiO_2.

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[1] E. Dooryhée, J.-P. Duraud, and R. A. B. Devine, in *Structure and Imperfections in Amorphous and Crystalline Silicon Dioxide*, edited by R. A. B. Devine, J.-P. Duraud, and E. Dooryhée (Wiley, Chichester, 2000), pp. 349–421.

[2] P. Paillet, J. L. Leray, and H. J. von Bardeleben, in *Structure and Imperfections in Amorphous and Crystalline Silicon Dioxide*, edited by R. A. B. Devine, J.-P. Duraud, and E. Dooryhée (Wiley, Chichester, 2000), pp. 293–328.

[3] D. L. Griscom, in *Glass-Science and Technology*, edited by D. R. Uhlmann and N. J. Kreidl (Academic, San Diego, 1990), Vol. 4B, pp. 151–251.

[4] P. Paillet, D. Hervé, J. L. Leray, and R. A. B. Devine, Appl. Phys. Lett. **63**, 2088 (1993).

[5] R. E. Stahlbush, G. J. Campisi, J. B. McKitterick, W. P. Maszara, P. Roitman, and G. A. Brown, IEEE Trans. Nucl. Sci. **NS-39**, 2086 (1992).

[6] R. A. B. Devine, Nucl. Instrum. Methods Phys. Res. B **91**, 378 (1994).

[7] P. E. Blöchl and J. H. Stathis, Phys. Rev. Lett. **83**, 372 (1999).

[8] J. K. Rudra and W. B. Fowler, Phys. Rev. B **35**, 8223 (1987).

[9] D. Cerasoli, M. Bernasconi, S. Iarlori, M. Parrinello, and E. Tosatti, Phys. Rev. Lett. **84**, 3887 (2000); S. T. Bromley, M. A. Zwijnenburg, and Th. Maschmeyer, *ibid.* **90**, 035502 (2003).

[10] G. Pacchioni, in *Defects in SiO_2 and Related Dielectrics: Science and Technology*, edited by G. Pacchioni, L. Skuja, and D. L. Griscom, Vol. 2 of *NATO Science Series II: Mathematics, Physics and Chemistry* (Kluwer, Dordrecht, 2000); T. Uchino, Curr. Opin. Solid State Mater. Sci. **5**, 517 (2001).

[11] M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees, and J. A. Pople, J. Chem. Phys. **77**, 3654 (1982).

[12] C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).

[13] A. D. Becke, J. Chem. Phys. **98**, 1372 (1993).

[14] M. J. Frisch *et al.*, computer code GAUSSIAN 98, revision A7, Gaussian Inc., Pittsburgh, 1998.

[15] G. Pacchioni and C. Mazzeo, Phys. Rev. B **62**, 5452 (2000).

[16] W. Jost, J. Chem. Phys. **1**, 466 (1933).

[17] A. H. Edwards, W. M. Shedd, and R. D. Pugh, J. Non-Cryst. Solids **289**, 42 (2001).

[18] D. R. Hamann, Phys. Rev. B **55**, 14 784 (1997); B. C. Chakoumakos, R. J. Hill, and G. V. Gibbs, Am. Mineral. **66**, 1237 (1981); T. Uchino, Y. Kitagawa, and T. Yoko, Phys. Rev. B **61**, 234 (2000).

[19] G. Boureau, S. Carniato, N. Capron, J. Garapon, and B. Poumellec, J. Appl. Phys. **89**, 165 (2001) and references therein.

[20] B. C. Bunker, D. A. Haaland, K. J. Ward, T. A. Michalske, J. S. Binkley, C. F. Melius, and C. A. Balfe, Surf. Sci. **210**, 406 (1989); C.-M. Chiang, B. R. Zegarski, and L. H. Dubois, J. Phys. Chem. **97**, 6948 (1993).

[21] It has been reported in a recent first-principles study of silica by Pacchioni and Mazzeo (Ref. 15) that a corner-sharing fourfold-coordinated Si center in a-SiO_2 cannot act as an electron trap since the attempt to add one electron to this type of Si center leads to an unstable system.

[22] T. Uchino, M. Takahashi, and T. Yoko, Appl. Phys. Lett. **80**, 1147 (2002).