

## Formation and decay mechanisms of electron–hole pairs in amorphous SiO<sub>2</sub>

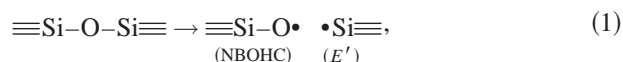
T. Uchino,<sup>a)</sup> M. Takahashi, and T. Yoko

*Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan*

(Received 23 August 2001; accepted for publication 30 November 2001)

We present theoretical evidence for the creation of an electron–hole pair at an edge-sharing SiO<sub>4</sub> site that is supposed to exist in *a*-SiO<sub>2</sub> as an intrinsic structural defect. The present electron–hole pair consists of a nonbridging oxygen hole center and an *E'* center, but these paramagnetic defects do not form a close pair but are separately located by over  $\sim 4$  Å. The subsequent decay mechanism along with the related radiolytic process is also discussed. © 2002 American Institute of Physics. [DOI: 10.1063/1.1448173]

The structure and formation mechanism of point defects in amorphous SiO<sub>2</sub> (*a*-SiO<sub>2</sub>) have been a subject of numerous studies since the advent of fiber optic communications and modern microelectronic devices.<sup>1,2</sup> In *a*-SiO<sub>2</sub>, pre-existing diamagnetic defects such as oxygen-deficiency-related centers are transformed into paramagnetic defects by dense electronic excitations or ionizing radiation.<sup>3</sup> It should be noted, however, that radiation-induced paramagnetic defects are also generated by the cleavage of Si–O–Si bridges,<sup>3</sup> which are not normally envisaged as defect sites. In such a case, an Si–O–Si bond scission is caused by a bound electron–hole pair that is created by the absorption of band edge light in *a*-SiO<sub>2</sub>, followed by the formation of a nonbridging oxygen hole center (NBOHC)–*E'* center defect pair.<sup>4,5</sup>



where “ $\equiv$ ” denotes the three Si–O bond and “ $\cdot$ ” the unpaired sign.

Owing to dipole–dipole interactions between the unpaired spins, the electron paramagnetic resonance (EPR) signal of a close NBOHC–*E'* pair shown in Eq. (1) should be unobservable.<sup>3,6</sup> In *a*-SiO<sub>2</sub>, however, the EPR signals associated with the NBOHC and *E'* center can be observed without showing any distinct broadening.<sup>6,7</sup> This indicates that a mechanism that separates the NBOHC and *E'* center exists in *a*-SiO<sub>2</sub>. Analogous EPR signals are not observed in crystalline SiO<sub>2</sub> (*c*-SiO<sub>2</sub>), implying that the stabilization of a NBOHC–*E'* pair is only possible in the amorphous structure. It should also be worth mentioning that densification of *a*-SiO<sub>2</sub> enhances correlated growth of the EPR signals ascribed to the NBOHC and *E'* center.<sup>7,8</sup> Although several models have been proposed to explain a related creation and its subsequent separation of the NBOHC and *E'* center in *a*-SiO<sub>2</sub>,<sup>3,6,9</sup> a detailed understanding of the mechanism is still lacking.

Devine<sup>7,10</sup> proposed that a possible precursor of a NBOHC–*E'* pair is a strained Si–O–Si linkage that may exist intrinsically in *a*-SiO<sub>2</sub>. The enhancement of its growth

rate by densification was interpreted in terms of an increase in the number of strained bonds having small Si–O–Si bond angles ( $<120^\circ$ ) since densification of *a*-SiO<sub>2</sub> is accompanied by a reduction in the ring size from major six-membered rings to smaller, for example, four- and/or three-membered ones.<sup>11</sup> Devine<sup>10</sup> also pointed out that even in densified *a*-SiO<sub>2</sub> the maximum numbers of the NBOHC and *E'* center created via the excitonic mechanism are  $\sim 10^{18}$  cm<sup>-3</sup>, which would correspond to  $\sim 10^{-4}$  of the total number of all Si–O–Si linkages. Thus it has been suggested that NBOHC–*E'* pairs are created only at special sites of the SiO<sub>2</sub> network;<sup>9,10</sup> that is, among other Si–O–Si bonds, a highly strained bond is responsible for cross-band-gap electron–hole excitation to form the NBOHC–*E'* pairs.

Recently, we have evaluated the strained energies of the *n*-membered ( $n=2,3,4$ ) silica rings on the basis of quantum-chemical calculations at the Hartree-Fock (HF) level using clusters of atoms.<sup>12</sup> We have shown that the strain energies of the four- and three-membered rings are estimated to be 0.02 and 0.26 eV, respectively. Hamann<sup>13</sup> also reported a similar value (0.25 eV) for the strain energy of the three-membered ring using continuous SiO<sub>2</sub> network models based on density functional calculations with the generalized-gradient approximation (GGA). These calculated results elucidate that the Si–O–Si bridges in the three- and four-membered silica rings do not store considerable strain energies and, therefore, will not behave as “precursors” of the NBOHC–*E'* pairs.

Another possible source of the intrinsic precursors may be a two-membered ring or an edge-sharing SiO<sub>4</sub> tetrahedral dimer. The strain energy of the two-membered ring has been estimated to be  $\sim 1.2$ – $1.8$  eV,<sup>12–14</sup> which are substantially larger than those obtained for the three- and four-membered rings. Indeed, the calculated Si–O–Si ( $\sim 90^\circ$ ) and O–Si–O ( $\sim 90^\circ$ ) bond angles<sup>12–14</sup> in the two-membered silica ring are appreciably smaller than the corresponding average values ( $\sim 145^\circ$  and  $\sim 110^\circ$ , respectively), suggesting that the edge-sharing structural unit is the cause of the severe strain stored in the siloxane bonds. It has generally been accepted that the random network of *a*-SiO<sub>2</sub> consists of the corner-sharing SiO<sub>4</sub> units. However, it is quite possible that the two-membered rings exist as structural “defects,” and these highly strained defect sites will play a vital role in the elec-

<sup>a)</sup>Author to whom correspondence should be addressed; electronic mail: uchino@scl.kyoto.u.ac.jp

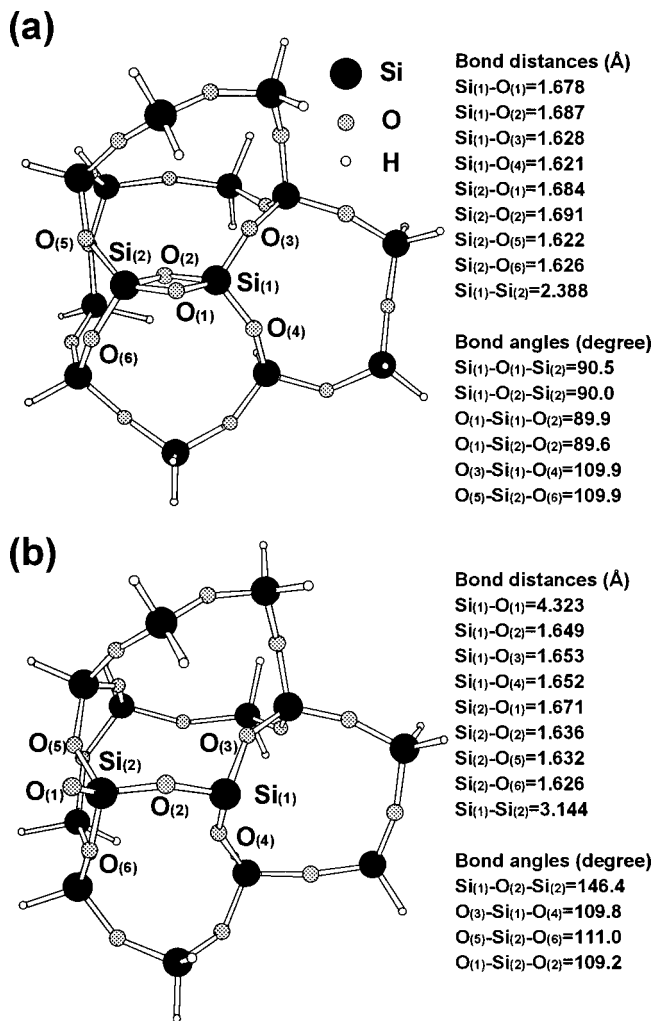


FIG. 1. Clusters of atoms ( $\text{Si}_{14}\text{O}_{19}\text{H}_{18}$ ) used to model (a) an edge-sharing  $\text{SiO}_4$  tetrahedral dimer in the random silica network, model 1, and (b) its corresponding triplet self-trapped exciton, model 2. Principal bond distances and bond angles are shown. The geometries of the clusters were optimized at the B3LYP/6-31G(d) level.

tronic excitation process especially in  $\alpha$ - $\text{SiO}_2$ . Thus, the aim of this letter is to investigate the electron-hole excitation at this particular “defect” site on the basis of quantum-chemical cluster calculations.

Figure 1(a) shows a cluster of atoms, termed model 1, that models the edge-sharing tetrahedral unit embedded in the random silica network. The “surface” silicon atoms of the model cluster were terminated by hydrogen atoms to saturate the dangling bonds. We optimized the total energy of model 1 in the singlet state at the density functional theory (DFT) levels with the 6-31G(d) basis set.<sup>15</sup> For the DFT calculations, we used the B3LYP exchange-correlation functional consisting of the Lee–Yang–Parr correlation functional<sup>16</sup> in conjunction with a hybrid exchange functional proposed by Becke.<sup>17</sup> We further optimized the geometry of the cluster in the triplet state, termed model 2 [see Fig. 1(b)], without imposing any structural constraints as in the case of model 1. Such a triplet state would be a model of the electron-hole pair formed at this strained edge-sharing  $\text{SiO}_4$  tetrahedral dimer. All the *ab initio* quantum chemical calculations in this work were performed using the GAUSSIAN 98 program<sup>18</sup> on a supercomputer CRAY T94/4128.

We see from Fig. 1(a) that both the Si–O–Si and

TABLE I. Mulliken atomic charges  $q$  and spin densities  $\rho$  for the O and Si atoms in the defect site of the present model clusters.

	Model 1	Model 2		Model 3
	$q$	$q$	$\rho$	$q$
Si(1)	1.175	0.915	0.844	1.275
Si(2)	1.188	1.157	-0.018	1.063
O(1)	-0.610	-0.313	0.958	-0.568
O(2)	-0.693	-0.604	0.044	-0.639

O–Si–O bond angles of the edge-sharing tetrahedral site in model 1 are calculated to be  $\sim 90^\circ$  to form a planar regular structure, in agreement with previous calculations using GGA<sup>13</sup> and HF<sup>12</sup> methods. This suggests that when the edge-sharing unit is formed in  $\alpha$ - $\text{SiO}_2$ , this strained site always retains such a regular configuration even in the random Si–O–Si network. On the other hand, the configuration of the triplet state (model 2) is substantially different from the single state (model 1). In model 2, one Si–O bond in the edge-sharing unit in model 1 (Si(1)–O(1) in Fig. 1) is broken, and, accordingly, one nonbridging O (O(1)) and one three-coordinated Si (Si(1)) atoms are generated. Consequently, the bond angle of the remaining Si–O–Si bridge (Si(1)–O(2)–Si(2)) in the defect site increases from  $90.0^\circ$  (in model 1) to  $146.4^\circ$  (in model 2). Furthermore, it has been found that the spin density of O(1) and Si(1) are 0.958 and 0.844, respectively (see Table I). This indicates that the hole and the electron are almost localized, respectively, on the paramagnetic O (O(1)) and Si (Si(1)) atoms, showing a characteristic of the NBOHC– $E'$  pair. It should also be noted that the resultant electron and hole components are geometrically wide apart, yielding the large interatomic distance  $R$  between Si(1) and O(1) (4.323 Å). This indicates that the electron part becomes separated from the hole counterpart by over  $R=4$  Å upon electronic excitation at the edge-sharing site. Thus, the cross-band-gap electron-hole excitation and its subsequent bond-breaking mechanism at the edge-sharing site probably explains the reason why dipole–dipole interactions, which decrease with  $R^{-3}$ , are not observed in the EPR

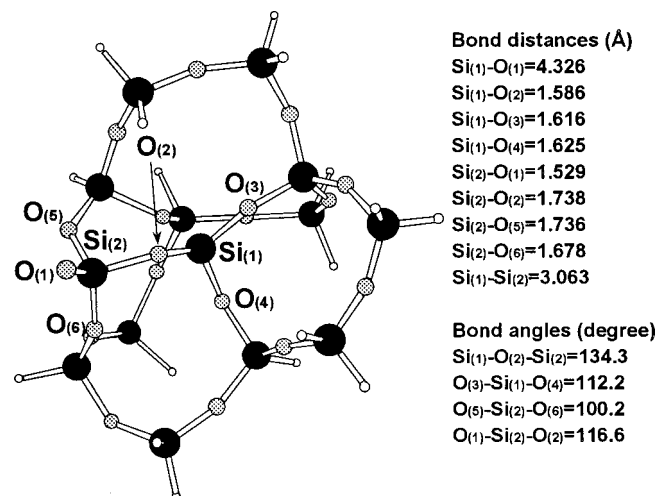


FIG. 2. A metastable configuration of the singlet  $\text{Si}_{14}\text{O}_{19}\text{H}_{18}$  cluster, model 3, obtained from a recombination process of the self-trapped exciton shown in Fig. 1(b). The geometry of the cluster was optimized at the B3LYP/6-31G(d) level.

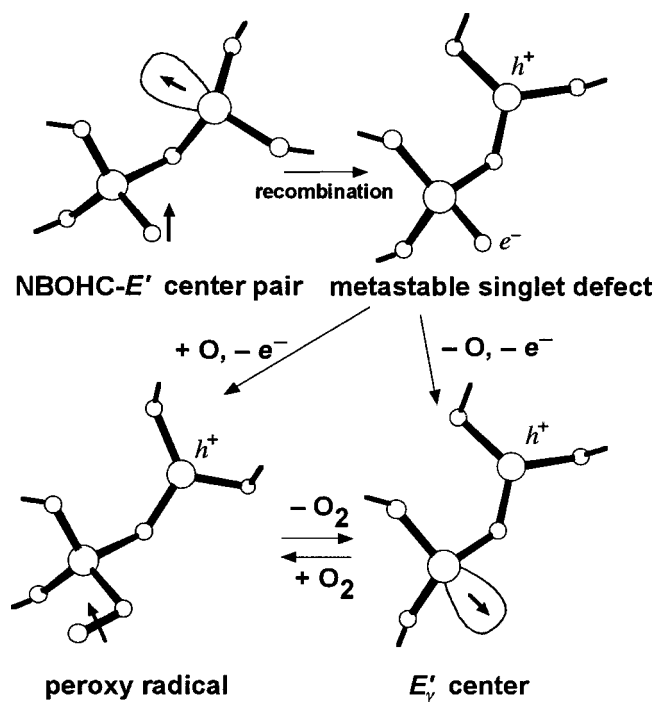


FIG. 3. Possible radiolytic mechanisms of the NBOHC- $E'$  pair generating the  $E'_\gamma$  center and the peroxy radical via the metastable single defect. Microscopic models for the  $E'_\gamma$  center and the peroxy radical are from Refs. 22 and 23.

signals for the resultant NBOHC- $E'$  pair in irradiated  $\alpha$ -SiO<sub>2</sub>.

We next turn to recombination of the present NBOHC- $E'$  pair. To investigate the triplet-to-singlet recombination process, we reoptimized the structure of model 2 by assuming that its total charge and multiplicity are 0 and 1, respectively. The resulting optimized geometry of the cluster, termed model 3, is shown in Fig. 2. One sees from Fig. 2 that model 3 still retains the basic configuration of model 2; that is, the broken bond between O<sub>(1)</sub> and Si<sub>(1)</sub> remains to be reformed. Thus, in the above recombination process diamagnetic O<sup>-</sup>(O<sub>(1)</sub>) and Si<sup>+</sup>(Si<sub>(1)</sub>) atoms are formed, but these charged atoms do not come together to relax to the original edge-sharing structure. Since the total energy of model 3 is higher than that of model 1 by 2.13 eV, the defect configuration shown in model 3 corresponds to a transient state. In the corner-sharing Si-O-Si configurations, such a metastable state will not exist but will reform easily because of the strong Coulomb interaction between the O<sup>-</sup> and Si<sup>+</sup> atoms facing each other.

We suggest that this metastable singlet defect plays a role in the radiolytic generation of  $E'$  centers and peroxy radicals. Tsai and Griscom<sup>19</sup> found that when highly focused 6.4 eV excimer laser beams are used, peroxy radicals (PORs) along with  $E'_\gamma$  centers, which are the major paramagnetic centers among the  $E'$  center variations in  $\alpha$ -SiO<sub>2</sub>, are formed instead of NBOHC- $E'$  pairs. They interpreted that this is evidence for radiolytic displacement of oxygens initiated by intense laser beams. Such radiolytic processes have also been found to occur by various forms of energetic radiation including ions<sup>20</sup> and electrons.<sup>21</sup> According to the present scheme, generation of  $E'_\gamma$  centers and PORs can be inter-

preted in terms of release and capture of oxygen by the transient singlet defect (see also Fig. 3). Note also that the structures of the  $E'_\gamma$  center and POR depicted in Fig. 3 are identical to those proposed recently by the present authors.<sup>22,23</sup> It is hence quite likely that these recently proposed Si-related paramagnetic centers give a renewed insight into the radiolytic generation of stable paramagnetic defects in  $\alpha$ -SiO<sub>2</sub> as well as the formation of the NBOHC- $E'$  pairs.

In conclusion, we have presented theoretical evidence that an electron-hole excitation can occur at the edge-sharing SiO<sub>4</sub> site, breaking one Si-O bond to form a pair of NBOHC and  $E'$  centers that are geometrically separated by over 4 Å. We have also shown that recombination of the present electron-hole pair results in a metastable single state, in which the diamagnetic O<sup>-</sup> and Si<sup>+</sup> atoms remain to be reformed. Furthermore, the present models sheds a microscopic insight into radiolytic processes in  $\alpha$ -SiO<sub>2</sub> in the course of electronic excitations.

The authors would like to thank the Supercomputer Laboratory, Institute for Chemical Research, Kyoto University, for providing the computer time. This work was supported in part by Grant-in-Aid (Nos. 12CE2005 and 12750742) from the Ministry of Education, Science, Sports and Culture, Japan.

<sup>1</sup>The Physics and Technology of Amorphous SiO<sub>2</sub>, edited by R. A. B. Devine (Plenum, New York, 1988).

<sup>2</sup>Structure and Imperfections in Amorphous and Crystalline Silicon Dioxide, edited by R. A. B. Devine, J.-P. Duraud, and E. Dooryhée (Wiley, Chichester, 2000).

<sup>3</sup>D. L. Griscom, J. Ceram. Soc. Jpn. **99**, 923 (1991).

<sup>4</sup>C. Itoh, T. Suzuki, and N. Itoh, Phys. Rev. B **41**, 3794 (1990).

<sup>5</sup>P. N. Saeta and B. I. Greene, Phys. Rev. Lett. **70**, 3588 (1993).

<sup>6</sup>H. Imai, K. Arai, J. Isoya, H. Hosono, Y. Abe, and H. Imagawa, Phys. Rev. B **48**, 3116 (1993).

<sup>7</sup>R. A. B. Devine and J. Arndt, Phys. Rev. B **39**, 5132 (1989).

<sup>8</sup>R. A. B. Devine, Phys. Rev. B **35**, 9783 (1987).

<sup>9</sup>N. Itoh, A. M. Stoneham, and K. Tanimura, 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), p. 330.

<sup>10</sup>R. A. B. Devine, Nucl. Instrum. Methods Phys. Res. B **46**, 244 (1990).

<sup>11</sup>R. J. Hemley, H. K. Mao, P. M. Bell, and B. O. Mysen, Phys. Rev. Lett. **57**, 747 (1986).

<sup>12</sup>T. Uchino, Y. Kitagawa, and T. Yoko, Phys. Rev. B **61**, 234 (2000).

<sup>13</sup>D. R. Hamann, Phys. Rev. B **55**, 14784 (1997).

<sup>14</sup>M. O'Keefe and G. V. Gibbs, J. Phys. Chem. **89**, 4574 (1985).

<sup>15</sup>M. S. Gordon, Chem. Phys. Lett. **76**, 163 (1980) and references therein.

<sup>16</sup>C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).

<sup>17</sup>A. D. Becke, J. Chem. Phys. **88**, 1053 (1988).

<sup>18</sup>M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Milliam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Menonucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Lahama, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Jonson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian 98, Revision A7 (Gaussian, Inc., Pittsburgh, PA, 1998).

<sup>19</sup>T. E. Tsai and D. L. Griscom, Phys. Rev. Lett. **67**, 2517 (1991).

<sup>20</sup>H. Hosono, H. Kawazoe, and N. Matsunami, Phys. Rev. Lett. **80**, 317 (1998).

<sup>21</sup>M. A. Stevens-Kalceff, Phys. Rev. Lett. **84**, 3137 (2000).

<sup>22</sup>T. Uchino, M. Takahashi, and T. Yoko, Phys. Rev. B **62**, 2983 (2000); Phys. Rev. Lett. **86**, 5522 (2001).

<sup>23</sup>T. Uchino, M. Takahashi, and T. Yoko, Phys. Rev. Lett. **86**, 4560 (2001).