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Model of oxygen-deficiency-related defects in SiO_2 glass

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We propose a model of the oxygen-deficiency-related defect in silica glass on the basis of the *ab initio* molecular-orbital calculations. This model can be regarded as an oxygen vacancy derived from the edge-sharing structural unit and will be inherent in glassy silica. Our calculations demonstrate that this defect can be transformed into the structurally stable hole trapping center whose calculated hyperfine parameters quantitatively reproduce the experimental hyperfine features observed for the E'_γ center in silica glass.

Understanding the structure and formation mechanism of defects in silica glass has been a subject of considerable interest since amorphous silicon dioxide is an indispensable material component of fiber optics technologies and metal-oxide-semiconductor devices. It has been demonstrated that irradiation by, for example, uv, x, or γ rays can induce point defects in silica glass resulting in various paramagnetic centers.[1,2] However, there have been no accepted models that explain all the experimental phenomena initiated by the creation of point defects on irradiation, and, therefore, the structure and optical properties of defects in silica glass are still challenging problems both in fundamental and technological aspects.

Among other radiation-induced defects in silica glass, the E'_γ center is a principal paramagnetic center, which is characterized by a large ^{29}Si hyperfine splitting A of $\sim$42 mT (Ref. 3) and yields an optical absorption band at $\sim$5.8 eV.[4] Our most detailed understanding of the E'_γ center in silica glass comes from the experimental and theoretical studies of the E'_1 species ($A\sim 40$ mT) in crystalline α-quartz.[5,6] The first model of the E'_1 center in α-quartz was proposed by Feigl, Fowler, and Yip,[7] who suggested the positively charged single-oxygen-vacancy model composed of a nearly planar $\equiv$Si$^+$ unit and a singly occupied dangling bond $\equiv$Si$^\bullet$, namely, $\equiv$Si$^+$ $^\bullet$Si$\equiv$. Subsequent works[8] suggested a further relaxation of this configuration, in which the positively charged Si atom moves through the plane of its three-neighboring oxygens into a puckered configuration.

Although the above defect models were originally proposed for α-quartz, it was assumed that a similar defect is responsible for the E'_γ center in silica glass.[9] That is, in silica glass it was suggested that the E'_γ center is formed according to the following photoionization reaction:[10]

$$\equiv\text{Si—Si}\equiv$$

and/or

$$\equiv\text{Si}\cdot\cdot\text{Si}\equiv + \hbar\omega \rightarrow \equiv\text{Si}^+ + {}^\bullet\text{Si}\equiv(E'_\gamma) + e^-, \qquad (1)$$

where $\equiv$Si—Si$\equiv$ and $\equiv$Si$\cdot\cdot$Si$\equiv$ mean the ''relaxed'' and ''unrelaxed'' oxygen monovacancies, respectively. It is believed that the former Si-Si distance is almost identical with that of H_3Si-SiH_3 ($\sim$2.3 Å), and the latter has a Si-Si distance similar to [$\sim$3.1 Å (Refs. 9 and 10)] or even longer [$\sim$4 Å (Ref. 11)] than that of regular Si—O—Si bonding. Imai *et al.*[10] proposed that the $\equiv$Si$\cdot\cdot$Si$\equiv$ bond is more easily converted to the E'_γ center than the $\equiv$Si—Si$\equiv$ bond, since the latter bond will require extra relaxation in the neighboring network configuration to produce the E'_γ center and its planar counterpart of $\equiv$Si$^+$.

It should be noted, however, that recent theoretical calculations have raised some questions concerning the existence of the unrelaxed $\equiv$Si$\cdot\cdot$Si$\equiv$ bond in silica glass. Stefanov and Raghavachari[12] recently carried out theoretical calculations on several oxygen vacancy models in silica glass and concluded that ''a completely unrelaxed geometry with a Si-Si distance of 3.1 Å is not a stable arrangement and is unlikely for the ground state.'' Other theoretical calculations have shown that even a puckered unrelaxed oxygen vacancy proposed originally for α-quartz has a barrier of only $\sim$0.2–0.3 eV against the relaxation into the stable $\equiv$Si—Si$\equiv$ bond.[13,14] Such a small barrier may be too small to explain the thermal stability of the relevant defect in silica glass. Furthermore, *ab initio* calculations by Pacchioni and Ieranò[11] have shown that the unrelaxed oxygen vacancy will yield the $S_0\rightarrow S_1$ and $S_0\rightarrow S_2$ transition bands at 3.3 and 5.3 eV, respectively. Pacchioni and Ierano[11] originally suggested that the $S_0\rightarrow S_2$ transition is responsible for the observed so-called ''B_2'' photoabsorption band at $\sim$5.0 eV. However, Skuja[2] recently pointed out that ''the B_2 band is quite surely due to the excitation to the first excited singlet state,'' and that ''the calculation[11] may provide the first theoretical evidence that the energy of the excited states of the unrelaxed oxygen vacancy may be too small to be responsible for the B_2 band.'' It should also be worth mentioning that the unrelaxed geometry would give rise to a high biradical character since the wave function at long distance should be of a covalent type; however, such a biradical character has not been reported for unirradiated silica glass. Taking these things mentioned above into account, we suggest that the oxygen monovacancy will tend to be relaxed in the glass network. In other words, the unrelaxed oxygen vacancy is quite difficult to exist even metastably in silica glass. For these reasons, another plausible defect model will be welcomed to explain the formation mechanism of the E'_γ center along with the origin of the B_2 band in silica glass.

In this paper, we, therefore, propose a model of oxygen monovacancy on the basis of the *ab initio* molecular orbital (MO) calculations. As mentioned above, all the previous

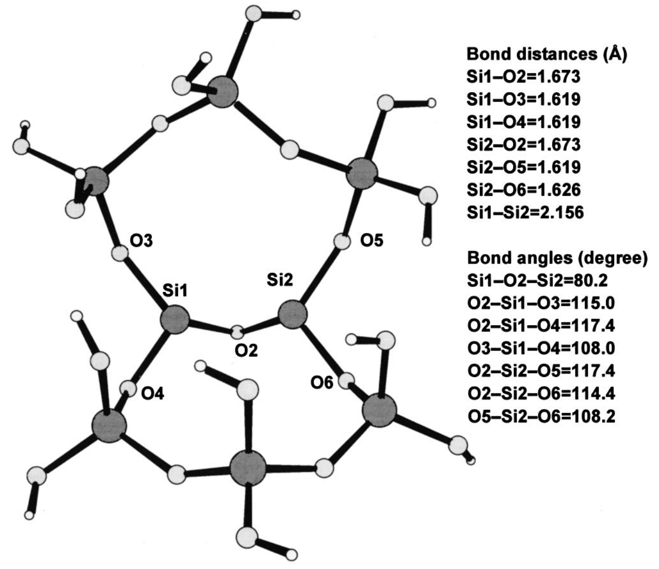
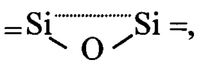


FIG. 1. The $Si_8O_2H_{12}$ cluster modeling TODC (model 1). The geometry was optimized at the HF/6-31$G(d)$ level.

models on oxygen-deficiency-related defects in silica glass are based on the assumption that a corner-sharing oxygen in the glass network is missing, forming $\equiv$Si$\cdot\cdot$Si$\equiv$ bonds. It is well accepted that the structure of silica glass is dominated by the corner-sharing SiO_2 tetrahedra that link together to form a three-dimensional random network. However, this does not necessarily rule out the existence of an edge-sharing unit as an intrinsic ''defect'' in the random glass network. Previous molecular-dynamics simulations on silica glass indeed demonstrated that a very small amount (less than 0.5%) of two-membered rings, namely, edge-sharing units can be found in the glass structure.[15] Recently, we carried out *ab initio* MO calculations on several clusters consisting of n-membered ($n=2-6$) silica rings, and the strained energy of the two membered ring was estimated to be ~1.8 eV.[16] This calculated strain energy is far smaller than the formation energies of the other point defects in SiO_2 glass such as oxygen vacancies [~7–8 eV (Ref. 17)] and Frenkel defects [~8 eV (Ref. 17)], implying that an edge-sharing ''defect'' is possible to exist in the actual glass network. It is reasonable to expect that the oxygen atom in such a strained edge-sharing unit will be removed rather easily as compared with that in a normal corner-sharing bond. We, therefore, consider that the defect in which one of the two edge-sharing oxygens is removed,



is not far from realistic and can be employed as an alternative model of the oxygen-deficiency-related defect in silica glass. In what follows, we refer to this defect as a triangular-oxygen-deficiency center (TODC) from its geometrical configuration.

In order to investigate the geometry and electronic structure of TODC we used the clusters shown in Fig. 1 (model 1). The dangling bonds of surface oxygen atoms in the cluster were saturated by H atoms. The geometry of the cluster was fully optimized at the Hartree-Fock (HF) level using the 6-31$G(d)$ basis set.[18] All *ab initio* MO calculations in this work have been performed with the GAUSSIAN-98 program.[19]

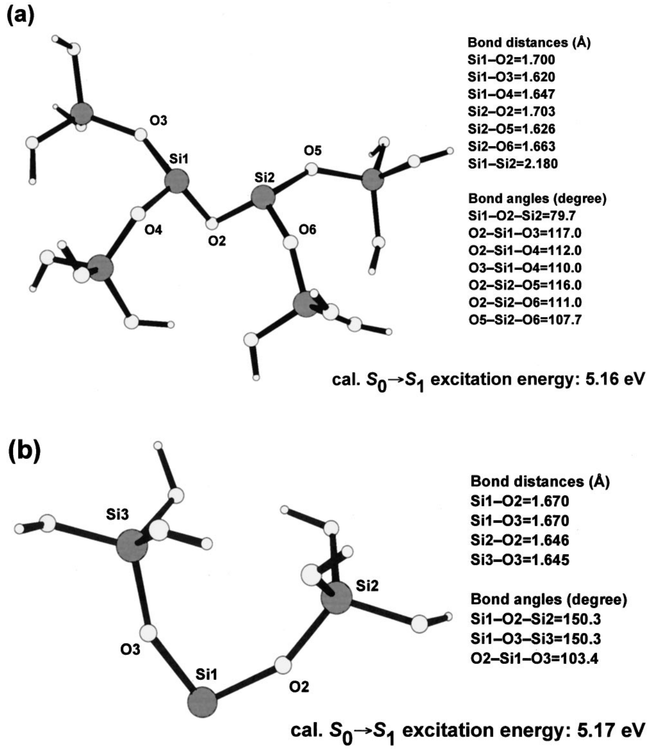


FIG. 2. The clusters of atoms used for the calculations of excitation energies: (a) the $Si_6O_{17}H_{12}$ cluster modeling TODC (model 1′) and (b) the $Si_3O_8H_6$ cluster modeling a divalent Si defect (model 2). The geometries were optimized at the B3LYP/6-31$G(d)$ level. The calculated $S_0 \rightarrow S_1$ excitation energies at the TD-B3LYP/6-31 $+G(d)$ level are shown.

As a result of the geometry optimization, we have found that in model 1 the neighboring Si atoms in the TODC site come together to form a substantial Si—Si bond ($d_{\mathrm{Si—Si}} = 2.156$ Å). However, this does not simply mean that this Si—Si bond has a strong covalent nature, because in model 1 the bonding orbitals of the neighboring SiO_3 units cannot satisfactorily be overlapped to each other because of the intervening oxygen atom. On the other hand, the Si—O—Si bond angle of the TODC site in model 1 is rather small (~80°) as compared with a normal Si—O—Si bond angle (~140°), indicating that the Si—Si chemical bond in TODC is formed at the expense of the Si—O—Si bond angle. In other words, the oxygen vacancy in model 1 keeps a balance of the Si—Si bond distance and Si—O—Si bond angle, forming a rather stable defect configuration on the short-range length scale.

We then used the time-dependent density-functional response theory[20] (TD-DFRT) to calculate excitation energies of the model clusters employed. It has been demonstrated that the average absolute error of the TD-DFRT is closer to that of the more costly correlated *ab initio* methods such as configuration interaction (CI) methods.[20] However, since model 1 is still too large to perform the TD-DFRT calculations, we employed a smaller cluster [model 1′, see Fig. 2(a)] as another model of TODC. In addition, we calculated the TD-DFRT excitation energies for the cluster modeling a divalent Si defect (=Si:) in silica glass [model 2, see Fig. 2(b)], which has been suggested as an alternative candidate for the B_2 absorption band.[2] The TD-DFRT excitation ener-

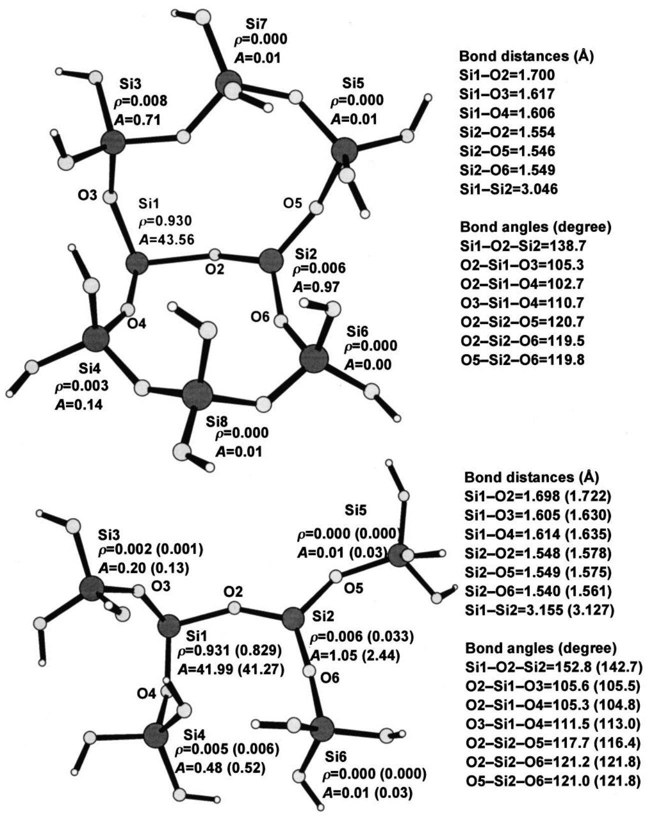


FIG. 3. Lower-energy configurations of the positively charged $(\mathrm{Si_8O_{21}H_{21}})^+$ (model 3, upper) and $(\mathrm{Si_6O_{17}H_{12}})^+$ (model 3′, lower) clusters optimized at the UHF/6-31$G(d)$ level. Principal bond distances (in Å), bond angles (in degrees), spin densities, ρ, and ^{29}Si isotropic hyperfine coupling constants A (in mT), calculated at the UHF/6-31$G(d)$ are also shown. Values in parentheses for model 3′ indicate the results calculated at the B3LYP/6-31$G(d)$ level.

gies were calculated at the Becke's 1993 hybrid exchange functional with the Lee-Yang-Parr correlation energy functional[21] (B3LYP) level with the 6-31$G(d)$ basis set augmented by two sets of diffuse s and p functions[12] on the Si atom(s) in the respective defect sites using the B3LYP/6-31$G(d)$ geometries.

The $S_0 \rightarrow S_1$ excitation energy of model 2 was calculated to be 5.17 eV, which agrees well with the previously reported CI excitation energies (~5.2 eV) of $=$Si:[22,23] indicating that, as has been proposed previously,[20,24] the TD-DFRT method yields an excitation energy close to the CI value. On the other hand, the calculated $S_0 \rightarrow S_1$ excitation energy of model 1′ was 5.16 eV. This excitation energy is only slightly smaller than the $S_0 \rightarrow S_1$ excitation energy calculated for model 2. This suggests that the $=$Si: and TODC accidentally yield similar excitation energies at ~5 eV, and both these centers will contribute to the observed B_2-photoabsorption band in silica glass. Indeed, it has been demonstrated experimentally that there exists more than one species of oxygen-deficiency-centers that contribute to the ~5 eV photoabsorption band and subsequently affect the photobleaching of the absorption band in silica glass.[25]

We next investigate a possible change in geometry of TODC during a photoionization process. For that purpose, we reoptimized the geometry of model 1 (or model 1′) by assuming total charge of +1 at the unrestricted open HF (UHF) and/or B3LYP levels using the 6-31$G(d)$ basis set. Consequently, we found that there exist two different optimized configurations which are separated by ~0.60 eV in total energy. The higher-energy one retains the basic geometry of the neutral TODC in model 1 (or model 1′), and the charge density of the unpaired electron in TODC is almost equally distributed between the two constituent Si atoms. On the other hand, the lower-energy one is characterized by a highly asymmetric configuration with respect to the vacancy. The optimized geometry of the lower energy form, which will be referred to as model 3 (or model 3′), is shown in Fig. 3.

TABLE I. ^{29}Si isotropic hyperfine coupling constants, in mT, calculated for the positively charged TODC and unrelaxed oxygen vacancy models along with the experimental value obtained for the E'_γ center in silica glass.

Model		
Charged unrelaxed oxygen vacancy[b]	Charged TODC[c]	Experiment[a]
36.4	43.6[d] (model 3) 42.0[d] (model 3′) 41.3[e] (model 3′)	~42

[a] Reference 3.

[b] Reference 26.

[c] ^{29}Si isotropic hyperfine splittings calculated for Si1 in models 3 and 3′.

[d] Calculations were performed at the HF/6-31$G(d)$ level using the HF/6-31$G(d)$ geometry.

[e] Calculations were performed at the B3LYP/6-31$G(d)$ level using the B3LYP/6-31$G(d)$ geometry.

We see from Fig. 3 that in model 3 (or model 3′), which is expected to be a major component as a hole trapping TODC, one of the Si atoms in the vacancy site, Si2, moves close to the plane of its three neighboring oxygens, resulting in the planar $\equiv\mathrm{Si}^+$ structural unit having rather short Si—O bond distances (~1.55–1.57 Å). The unpaired electron is localized mainly on Si1 in the $(\mathrm{Si1})\mathrm{O_3}$ unit, and, such an electronic state of the unpaired electron in an Si dangling bond is characteristic of E' centers. As mentioned earlier, the electron-spin-resonance spectra of irradiated silica glass show the ''strong ($A_{\mathrm{obs}} \sim 42$ mT)'' hyperfine splitting due to the E'_γ center.[3] Table I shows that the observed hyperfine structure is quantitatively reproduced by the present calculations irrespective of the clusters chosen and the calculated levels of theory, indicating that the present model is quite reasonable as a model of the paramagnetic center of interest in silica glass. The ''strong'' feature was also predicted by the previous HF/6-31G cluster calculations based on the conventional unrelaxed oxygen vacancy model,[26] but the correspondence between the theoretical and experimental values is not so excellent as compared with the present case (see, also, Table I).

In conclusion, we have presented a model of a neutral oxygen-deficiency defect, TODC, which will be inherent in silica glass is most likely responsible (partially) for the observed 5-eV band. We have demonstrated that TODC can be transformed into the structurally stable hole trapping center without violating the neighboring network topology (see Fig. 3). Furthermore, the proposed models quantitatively reproduce the experimental 42-mT hyperfine splitting observed for the E'_γ center in silica glass. We hence believe that TODC has a reasonable advantage over the unrelaxed oxygen vacancy model in that the present models consistently reproduce the fundamental experimental features reported for the oxygen-deficiency-related defect in silica glass.

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