

First-principles calculations for charged states of hydrogen atoms in SiO₂

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Charged states of H atoms in defect-free SiO₂ have been proposed from first-principles total-energy band-structure calculations within a framework of the local-density approximation. The polarities of the charged states are determined depending on the position of the Fermi level. A positively charged state forms an Si-(OH⁺)-Si complex, while a negatively charged state forms an Si-H⁻ bond. Calculated vibrational frequencies of newly formed O-H⁺ and Si-H⁻ bonds for each charge state are found to be lower than those for neutral O-H and Si-H bonds, so the H-originated charge traps are expected to be distinguishable by either Raman or infrared spectroscopies. [S0163-1829(97)02120-6]

I. INTRODUCTION

Recent progress in large-scale integrated circuits requires downsizing of metal-oxide-semiconductor (MOS) devices, in which the thickness of gate silicon dioxide (SiO₂) films should be less than 100 Å. The dielectric reliability of such thin SiO₂ films is a crucial issue. Charge traps in SiO₂ films and the Si/SiO₂ interface states are known to degrade the dielectric reliability of the films and the device performance. Microscopic origins of the charge traps have attracted great interest from both technological and scientific viewpoints. *E'* centers (possibly O vacancies) have been identified by electron-spin resonance,¹ while structural distortions in the SiO₂ bond network have been found to generate self-trapped holes.² Both are expected to play some roles in degrading the dielectric reliability of the SiO₂ films.

In the semiconductor industry, annealing of the SiO₂ films in hydrogen ambient has been used as a standard technique to reduce the defects in SiO₂ films and interface states. However, hydrogen in SiO₂ films has been reported to affect the generation of the charge traps in the films. Nissan-Cohen and Gorczyca observed that negatively charged traps are generated by high-temperature (900 °C) annealing in a hydrogen ambient following charge injection into the SiO₂ films.³ This is explained as that hydrogen makes precursors of electron traps. Even without the hydrogen annealing, hydrogen is inevitably introduced into SiO₂ films during the silicon oxidation process, and fabrication of overlayer films, such as polycrystalline silicon. Some of these H atoms are found to form Si-OH and Si-H bonds by measuring their vibrational frequencies.⁴ When hot carriers are injected in the SiO₂ films of the MOS devices, the positive charge traps near the Si/SiO₂ interface increase.⁵⁻⁸ This phenomenon is expected to be caused by hydrogen released from the Si-OH and Si-H bonds in the SiO₂ film due to hot carriers. The behavior of hydrogen in generating charge traps in SiO₂ films is thus complex, as mentioned above, and is affected by the processing conditions in sample preparation.

We consider a simple model of the behavior of H atoms

in SiO₂, in which excess H atoms in a defect-free SiO₂ film change themselves to trap centers. In order to examine this idea, we compare the stability of either positively or negatively charged states of a H atom with that of a neutral one in a defect-free SiO₂ crystal. First-principles total-energy band-structure calculations have been performed, in which the density-functional theory within the framework of the local-density approximation has been employed as well as pseudo-potentials. From the present calculations, we propose that H atoms in the defect-free SiO₂ crystal are stabilized, being charged states whose polarities depend on the position of the Fermi level (E_F).

When the system captures a positive charge, a H atom bonds to a bridging O atom in a Si-O-Si bond, and forms a Si-(OH⁺)-Si complex. On the other hand, when the system is negatively charged, a H atom forms a Si-H⁻ bond in the film. From the present calculations, atomic structures and charge-density distributions of the H-incorporated SiO₂ system strongly depend on the polarity of the charge states. Moreover, to examine the characteristics of the newly formed Si-(OH⁺)-Si and Si-H⁻ bonds in the charged system, we calculated the vibrational frequencies of these bonds. The calculated frequencies are found to be lower by at least 500 cm⁻¹ than the frequencies of neutral Si-OH and Si-H bonds in SiO₂ measured by infrared (IR)-absorption method. This difference in the frequencies suggests that careful measurement enables us to distinguish the atomic configurations of the charged states of H atoms from those of the neutral states in the real Si/SiO₂ systems.

In this paper, details of the present calculations are shown in Sec. II. The stable geometries and relative total energies of H atoms in SiO₂ for neutral and charged states are presented in Sec. III as well as calculated local vibrational frequencies of H atoms. The conclusions are given in Sec. IV.

II. METHODS OF CALCULATIONS

Though the gate oxides in the MOS devices are known to be amorphous SiO₂, it has been reported that the oxides

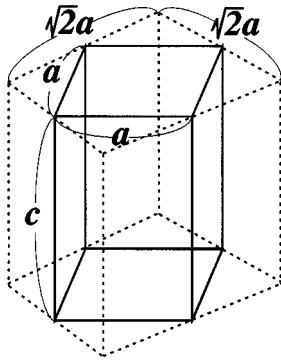


FIG. 1. Shapes of the single-sized (solid lines) and double sized (dotted lines) unit cells of the α cristobalite. These cells share a common c axis.

include the structures of crystal SiO_2 such as α quartz and α cristobalite,⁹ and that the local network has a form of tetragonal SiO_4 structure. In the present calculations, the structure of the SiO_2 film is assumed to be that of α cristobalite with periodic boundary conditions. We investigate the size effect of the unit cell by comparing the results obtained by using two different unit cells. One has the same size as that of the primitive cell of the α cristobalite containing four SiO_2 units. The other has twice as many as the former one, containing eight SiO_2 units. Hereafter, we call the former (smaller) one a single-sized unit cell and the latter a double-sized unit cell, respectively. Figures 1 and 2 show corresponding shapes of the unit cells and the first Brillouin zones for each of the single- and double-sized unit cells. The calculated relaxed geometries, band structures, and relative total energies are compared between these two unit cells for the different charged states, i.e., H^0 , H^+ , and H^- .

For dealing with the influence of core electrons, norm-conserving pseudopotentials for Si, O, and H atoms are generated by using a scheme given by Troullier and Martins.¹⁰ For a H atom, only local pseudopotentials are adopted. The plane-wave basis sets with the cut off energy of 60 Ry are used to express wave functions. Hellmann-Feynman forces are calculated to perform the geometry optimizations. Calculations of the single-sized unit cell are performed using four special k points¹¹ for the momentum-space integration, while calculations of the double-sized unit cell are performed using only the Γ point. In the calculation for the charged system, a

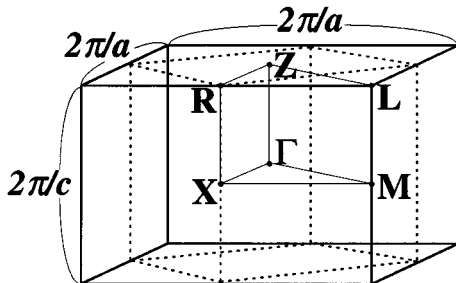


FIG. 2. Shapes of the first Brillouin zones of the single-sized (solid lines) and double-sized (dotted lines) unit cells of the α cristobalite. These Brillouin zones share a common Γ -Z axis. Other symmetric points in this momentum space are also shown.

TABLE I. Structural parameters on α -cristobalite, obtained in previous theories (Refs. 12 and 13), present calculations, and experiment (Ref. 14).

		Previous	Present	
		(Refs. 12 and 13)	Expt.	(Ref. 14)
Lattice constants (\AA)	a	4.973	4.968	4.957
	c	6.926	6.891	6.890
Si-O length (\AA)		1.594	1.620	1.610

uniform background charge with opposite polarity is adopted to keep the neutrality of the whole system, which prevents the divergence in the calculated total energies.

The lattice parameters for the α cristobalite are optimized so as to minimize the total energy of the single-sized unit cell. The calculated lattice parameters are listed in Table I, and it is confirmed that the obtained values agree well with other theoretical^{12,13} and experimental results.¹⁴ Furthermore the band structure along the symmetry axes of the Brillouin zone for α cristobalite is found to reproduce previous theoretical works.^{12,13} (The present result is shown in Fig. 3.) This demonstrates that qualitatively reliable results are obtained by the present calculations.

III. RESULTS

A. Atomic and electronic structures of neutral and charged H atoms in SiO_2

The equilibrium position of a neutral H atom in the single-sized unit cell of α cristobalite is determined by the geometry optimizations with different initial positions of the H atom. From the present calculations, all systems with several different initial positions of the H atom have been found to reach the same relaxed structure. The same structure is confirmed to be at a local minimum of the total-energy surface when we perform a calculation using the double-sized unit cell. The structural deviations in the SiO_2 host induced by a neutral H atom are very small as seen in Fig. 4(a), which corresponds to the case of the double-sized unit cell.

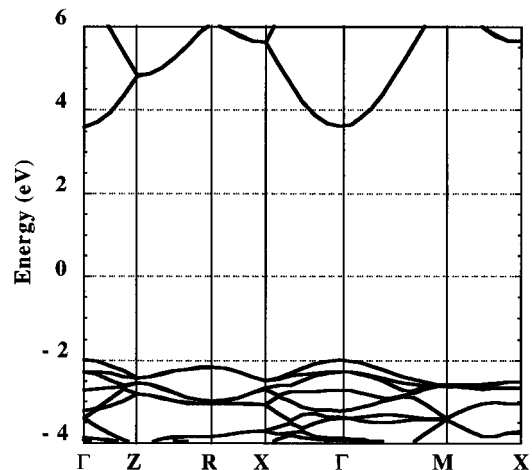


FIG. 3. Band structure of the α cristobalite obtained by the present calculation. Notations of the symmetric points in the momentum space are same as those in Refs. 12 and 13, and those in Fig. 2.

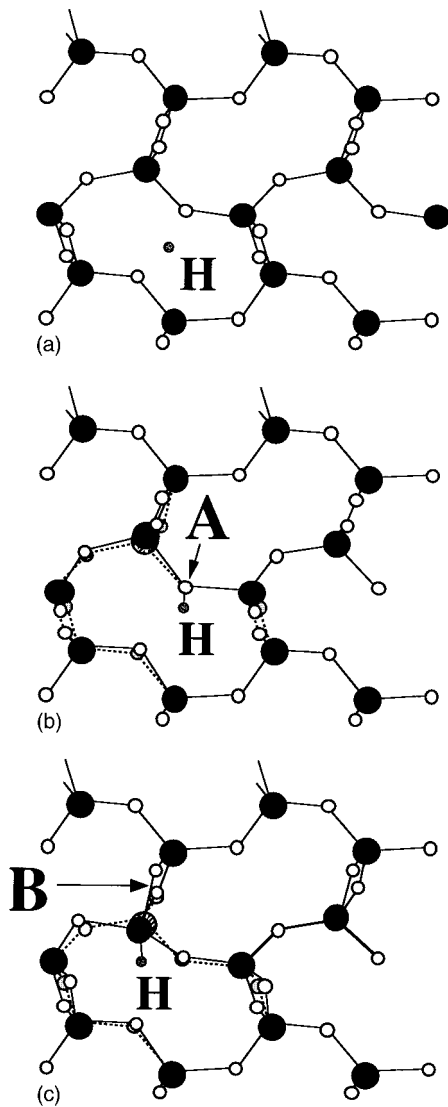


FIG. 4. The optimized structures of the α cristobalite with a H atom in three different charged states, (a) neutral, (b) positively charged, and (c) negatively charged by using the double-sized unit cell (see text). Larger shaded and solid circles denote Si atoms in SiO_2 without and with a H atom, respectively. While smaller shaded and open circles denote O atoms without and with a H atom, and the smallest circles denote the H atoms. Atomic bonds without H atoms are also shown by dotted lines for comparison. In this figure, a part of a repeated pattern of the double-sized unit cell is displayed.

The calculated electronic structure is shown in Fig. 5(a). Due to the assumed periodicity, the electronic level structure has a dispersion with respect to the k vectors in this calculation. The state originated from the H atom is indicated by an arrow in Fig. 5(a). The obtained electronic structure corresponds to a superposition of those of the α cristobalite and the H atom, i.e., there is no orbital hybridization between a H atom and the SiO_2 host.

Next, the charged states of the H atoms in the SiO_2 host are investigated. The equilibrium position of the H atom for each charged system is determined in the same manner as in the case of the neutral state. When the H^+ atom is incorporated in the system, the H^+ atom favors the position near the

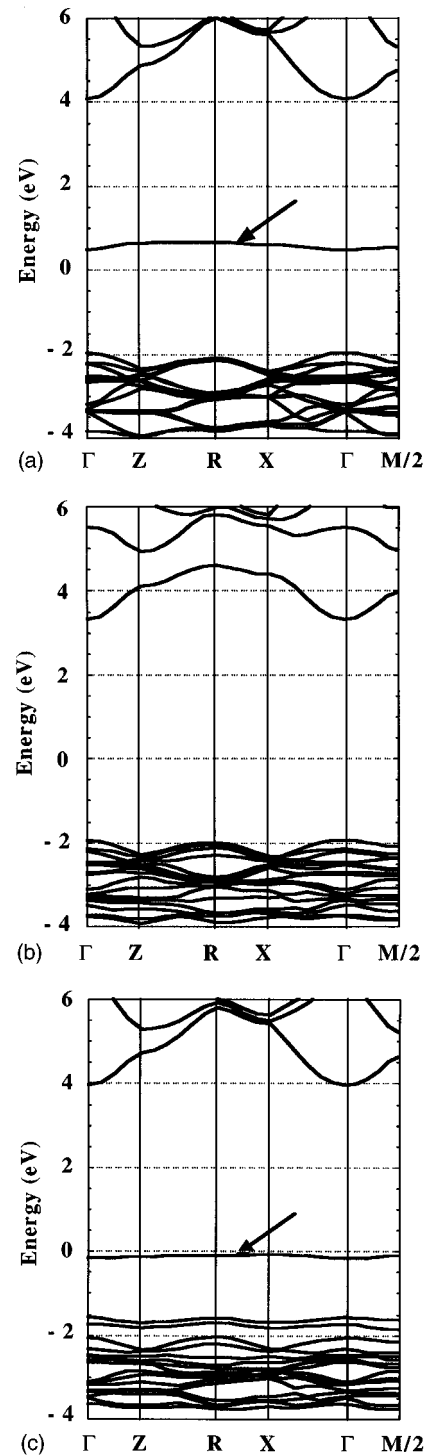


FIG. 5. The calculated band structures of α cristobalite with a H atom in the three different charged states, (a) neutral, (b) positively charged, and (c) negatively charged by using the double-sized unit cell. The indicated energy levels are raw data of the band-structure calculations. The H-induced gap states are denoted by arrows. Because of the usage of the double-sized cell, folded band structures of the α cristobalite are seen.

O atom, as seen in Fig. 4(b). The distance between the H^+ and O atoms [label A in Fig. 4(b)] is about 1.02 Å, and this is a little longer than that of the neutral O-H bond length of 0.95 Å. Meanwhile, the length of the Si-O bond near the H^+ atom shows remarkable elongation from 1.62 to 1.75 Å.

The result suggests that the H^+ atom weakens the neighboring Si-O bond to form an O- H^+ bond.

The calculated electronic structure of the system with the H^+ atom is shown in Fig. 5(b). The H-originated gap state, seen in Fig. 5(a), disappears here. An orbital character analysis has been performed to search for states having considerable weight on the H atom. Three states far below the valence top are found to be localized around the H atom and the neighboring O atom. The three levels have been found to have a bonding character between O and H atoms, suggesting a covalency of the O- H^+ bond. If the trapped positive charge is completely localized on the H atom, which corresponds to the naked proton, there should be no orbitals localized on the H site in the occupied levels. Therefore, we conclude that the trapped positive charge should be distributed to the H and neighboring O atoms.

When the H^- atom is incorporated, the H^- atom bonds to one of the Si atoms with a larger structural variation compared to the case of H^+ atom; see Fig. 4(c). The formation of the Si- H^- bond yields the elongation of the Si-O bonds, labeled B in Fig. 4(c). The bond length of the newly formed Si- H^- bond is about 1.54 Å, and this is longer than the neutral Si-H bond (1.48 Å). The corresponding electronic structure is shown in Fig. 5(c). The highest occupied state, which is associated with the trapped negative charge, is dominated by the H $1s$ orbital. We have found that this state also has considerable weight on the d orbital of the neighboring Si atom, and receives a minor contribution from the Si $3s$ orbitals. This indicates that the newly formed Si- H^- bond becomes stable because of covalency originating from the H $1s$ and Si $3d$ orbitals, rather than purely ionic interaction between H^- atom and the neighboring Si atom.

B. Comparison of stability of neutral and charged H atoms

We examine which is the most stable state of the H atom among these neutral and charged states based on the obtained total energies. When a system contains an excess charge q , the stability of the system compared to the neutral one should be evaluated by the difference between $E_{\text{tot}}(q)$ and $E_{\text{tot}}(0) - \mu q$. Here $E_{\text{tot}}(q)$ and $E_{\text{tot}}(0)$ are the total energies of the charged and neutral states, and μ is the electron's chemical potential, i.e., E_F . The relative total energies are therefore given as functions of E_F . In the present calculations, we adopted the periodic boundary conditions and background charge to neutralize the system as mentioned in Sec. II. Therefore, $E_{\text{tot}}(q)$ is underestimated because of fictitious attractive interaction between the background charge and the excess charge q . To reduce this underestimation, we estimated the total energy of the charged states according to the Slater's argument.¹⁵ When two systems with the same atomic geometry have charged states 0 and -1 , the total energy difference between them is given as the highest occupied level ϵ of a system having half-negative charge with the same atomic geometry. In order to obtain the relative total energy of a H^- charged state having a different atomic geometry from the neutral one, we first calculate ϵ of the negative-half state, and $E_{\text{tot}}(-1)'$ of the H^- state, keeping atomic geometries the same as of the neutral one. The total-energy difference $E_{\text{tot}}(-1)' - E_{\text{tot}}(0)$ is then replaced by ϵ . Meanwhile, the total-energy lowering dE (positive defi-

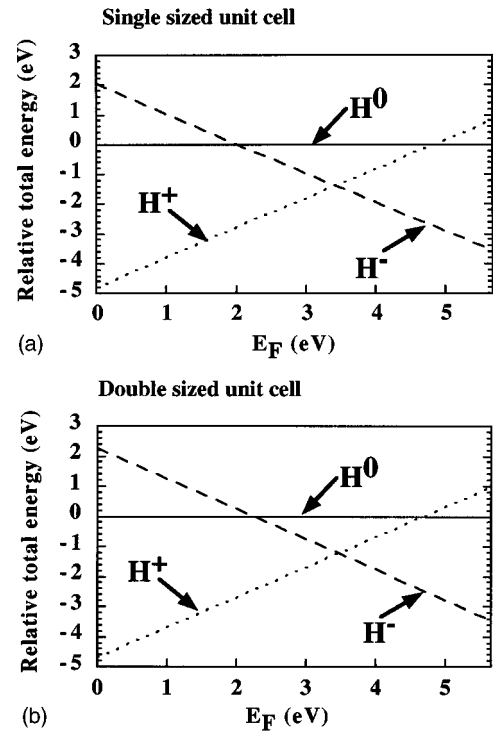


FIG. 6. The relative total energies of the three charged states, H^0 (neutral), H^+ (positively charged), and H^- (negatively charged), as a function of the Fermi level, in cases of (a) a single-sized unit cell and (b) a double-sized unit cell, respectively. The total energy of the neutral state is set to 0 in each unit cell.

nit), after optimizing the atomic geometry of the H^- state, is obtained by $E_{\text{tot}}(-1)' - E_{\text{tot}}(-1)$. [Here $E_{\text{tot}}(-1)$ is a total energy of the -1 charged state after the geometry optimization.] Therefore, the relative total energy of the geometry-optimized H^- state compared to the neutral one, $E_{\text{tot}}(-1)' - E_{\text{tot}}(0)$, is evaluated as $\epsilon - dE$. The stability of the positive charged state H^+ is also evaluated in the same manner.

Figures 6(a) and 6(b) show the obtained total-energy diagrams for the cases using the single- and double-sized unit cells. In these diagrams, E_F is set to zero at the top of the valence band of the α cristobalite, and E_F changes within the calculated band-gap energy. These diagrams are found to be almost the same, suggesting the calculation by using the double-sized unit cell to give numerically converged results. This is because the structural variations among different charged states are restricted in a range corresponding to the single-sized unit cell. The obtained diagrams show that either positively or negatively charged state for the H atom in SiO_2 is stable compared to the neutral one for whole range of E_F , and that the H atom behaves a strong negative- U center. Neugebauer and Van de Walle proposed that H atoms in semiconductors generally form negative- U centers.¹⁶ The present results suggest that their idea can be generalized in cases of H atoms in insulators. In the case of Ref. 16, the host material is GaN, which is a polarized semiconductor. In the present case, SiO_2 is also a polarized host. It is expected to be a common trend that the charged H atom tends to bond to an atom with an opposite polarity in a polarized, host and that the charged H atom is more stable than the neutral one.

A question can be raised, in the case of SiO_2 , as to whether the atomic geometries containing H^+ (or H^-) remain or change into other kinds of atomic geometries such as well-known E' centers. This question should be solved by further calculations including the effect of kinetics of the reaction of H atoms in the SiO_2 films.

C. Local vibrational frequencies of charged H atoms in SiO_2

As obtained in the present calculations, the stable states for H atoms in defect-free SiO_2 are charged states, and both states have closed-shell structures in electronic configurations. This suggests that these structures will not be detected by the electron-spin resonance (ESR) measurement. In the charged systems, either an O-H^+ or a Si-H^- bond is generated. The bond length and bonding characteristics of O-H^+ and Si-H^- bonds differ from those of the neutral O-H and Si-H bonds, respectively. It is expected that observing the vibrational frequencies of the newly formed O-H^+ or Si-H^- bonds will be good proof of the H-originated charge traps. We have calculated the vibrational frequencies of the O-H^+ and Si-H^- bonds to investigate whether the frequencies are good fingerprints.

The vibrational frequencies are deduced from the force constants. The force constants are estimated from the calculated Hellmann-Feynman forces obtained by replacing the H atoms by 0.02 a.u. away from their equilibrium positions for each direction of the Cartesian coordinates. In the present calculations of force constants, a single-sized unit cell for each charged state is used. We checked that the present calculation condition gives a proper value of the vibrational frequency for the stretching mode of a neutral Si-H bond by performing the following procedures: First, one O atom in α cristobalite is removed, and the two neighboring Si dangling bonds are terminated by two H atoms. Second, the obtained structure is relaxed toward the total-energy minimum. Finally, the force constants for the Si-H bonds are obtained in the manner mentioned above, and the vibrational frequencies for several modes of the Si-H bonds are obtained. The stretching mode of the neutral Si-H bond is found to have a frequency of 2278 cm^{-1} , which agrees well with the value of the stretching modes of the Si-H bonds in amorphous SiO_2 [2280 cm^{-1} Ref. 17]. This indicates that we can obtain quantitatively reliable frequencies with the present calculation condition.

The frequencies of the H stretching modes for O-H^+ and Si-H^- are calculated to be about 2950 and 1763 cm^{-1} , respectively. These frequencies are lower than those of the stretching modes for neutral O-H ($3600\sim 3650\text{ cm}^{-1}$) (Ref. 18) and Si-H (2280 cm^{-1}).¹⁷ These lower frequencies are due to weaker strengths of the O-H^+ and Si-H^- bonds than those of the neutral O-H and Si-H bonds, respectively. The O-H^+ bond is likely covalent, but the O atom is coordinated by three neighboring atoms, i.e., two Si atoms and one H atom. This may be the reason of the weakness of the

O-H^+ bond compared to the neutral O-H bond. On the other hand, the Si-H^- bond consists of H $1s$ and Si $3d$ orbitals. The Si $3d$ orbitals are rather extended compared to Si $3p$ orbitals constructing the neutral Si-H bond with H $1s$ orbitals. The rather extended feature of the $3d$ orbitals may be the reason of weaker Si-H^- bond than neutral Si-H bond.

Because of the differences in the vibrational frequencies, the O-H^+ and Si-H^- bonds in the charged systems may be distinguishable from neutral O-H and Si-H bonds in SiO_2 in observing the vibrational frequencies by means of Raman or IR spectroscopies. One of the practical problems here is that the typical density of the charge traps is around 10^{12} cm^{-2} , which is very low for frequency measurements. Technical progress for higher sensitivity, or an artificial increase in the trap density, are therefore required. Another problem is that the frequencies of 2950 and 1763 cm^{-1} are close to those of carbon hybrids contaminants,¹⁹ so the frequency measurements should be done with samples free from these contaminants.

IV. CONCLUSIONS

It is demonstrated from first-principles total-energy calculations that H atoms can form charge traps in the defect-free SiO_2 film. Either positively or negatively charged traps appear depending on the position of E_F . The stable position of the H atom in the SiO_2 film depends on the polarity of the system. When the system is positively charged, the H atom forms $\text{Si}(\text{OH}^+)$ -Si complex, while it forms a Si-H^- bond when the system is negatively charged. As expected from the obtained electronic structures, the H-originated charge traps obtained in the present calculation are not detectable by electron-spin resonance, which widely used for the investigation of the charge trap centers having dangling bonds, such as the E' center. It is, however, found from our calculations that the vibrational frequencies of the newly formed $\text{Si}(\text{OH}^+)$ -Si and Si-H^- bonds are lower than those of the neutral Si-OH and Si-H bonds, respectively. This suggests the possibility of detecting these charged states by either Raman or IR spectroscopy.

Note added. Recently, charged states of a H atom have also been obtained in α quartz by the first-principles calculations.²⁰ We believe that this is a strong indication of a universality of the charged states of H atoms in SiO_2 .

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