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# A QUANTUM MECHANICAL INVESTIGATION OF POSITIVELY CHARGED DEFECTS IN $SiO_2$ THIN FILM DEVICES

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## ABSTRACT

*Ab initio* Hartree-Fock and second-order Möller-Plesset theory calculations have been performed to investigate the stability of triply-coordinated $O^+$ centers in the Si-O-Si network of amorphous $SiO_2$. The calculations reveal that the $H^+$ ion binds with a bridging O center to form a very stable ($D_e > 6$ eV) trivalent O complex. Capture of an electron by the positively charged protonated complex, however, is predicted to immediately lead to the dissociation of the O-H bond. A relatively weaker, but stable bond is also formed between the bridging O atom and a $^+SiH_3$ ion.

## INTRODUCTION

Radiation-induced positively charged defects in metal-oxide-semiconductor (MOS) devices have been the subject of numerous studies since the late 1960.[1] These defects often have an unpaired electron and can, thus, be characterized by electron paramagnetic resonance (EPR) spectroscopy.[1] Even though EPR has been a powerful characterization tool, there is evidence that some positively charged defects generated in the oxide layer of MOS devices are diamagnetic, i.e., EPR-inactive.[2-6] Thus, characterization of the microscopic structure and properties of these defects based on experimental techniques alone presents a great challenge. In such cases, it is anticipated that quantum mechanical calculations may be useful to gain insight into the microscopic nature of these defects. In this paper, we present an *ab initio* quantum mechanical investigation of such a diamagnetic defect center, which has been suggested to be involved during the post-irradiation cracking of $H_2$ in an oxide layer[2] or, when thin $SiO_2$ films on Si are annealed in H-containing ambient at $T > 500°C$.[3-5] Stahlbush et al.[2] have proposed that $H^+$ ions generated in an irradiated oxide layer can bind with a bridging O atom, resulting in a triply-coordinated, positively charged, diamagnetic O atom. Warren et al.[5] have also attributed the positive charging of $Si/SiO_2$ structures by high-temperature annealing in a hydrogen containing ambient to the formation of triply-coordinated $O^+$ centers. In view of these experimental observations and interest in these positively charged over-coordinated

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oxygen atoms in $SiO_2$, we have performed calculations to evaluate the binding energy of $Si^+$, $H^+$ and $H^0$ with a bridging O atom in the Si-O-Si network.

Previous calculations of positively charged trivalent-O atoms include a tight-binding calculation by O'Reilly and Robertson,[6] semiempirical modified intermediate neglect of differential overlap (MINDO) calculations by Edwards and Germann[7] and Edwards et al.,[8] and an *ab initio* Hartree-Fock (HF) calculation by Edwards.[9] O'Reilly and Robertson[6] found from their tight-binding calculation that a trivalent positively charged O center bonded to three Si atoms results in a shallow defect near the conduction band edge in $SiO_2$. Furthermore, their calculations also indicated that all trivalent-O defects can be characterized with a shallow state approximately 1 - 2 eV below the conduction-band minimum in $SiO_2$. Edwards and Germann[7] performed a series of MINDO/3 calculations on neutral, trivalent-O atom bonded to two Si atoms and to atomic H ($H^0$). These calculations yielded a binding energy which ranged from 0 eV to -0.26 eV, depending upon the degree of relaxation of the hydrogenated complex. In all cases, however, the MINDO/3 calculations yielded a deep potential minimum at R(O-H) ~1.0 Å, where R is the distance between O and H. More recent *ab initio* HF calculations[9] utilizing a 6-31G** basis set, have examined the nature of positively charged trivalent oxygen atoms bonded to two Si atoms and to a proton ($H^+$). These results obtained a binding energy of 1.2 eV for the O-$H^+$ bond resulting from the interaction of a $H^+$ ion with the bridging O atom.

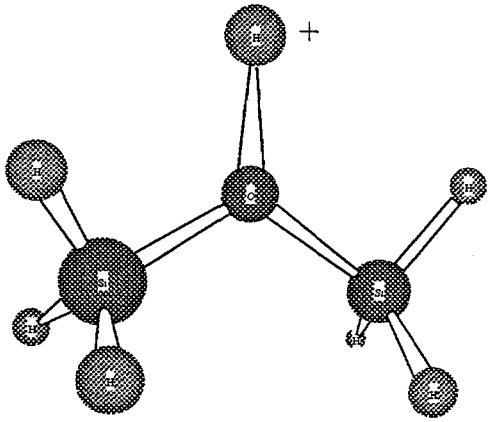
In this study, we further examine the stability of the triply-coordinated O center in which the O is bonded to two Si atoms and to either $H^+$, $Si^+$ or $H^o$ ions. Our calculations are performed on a $SiO_2$ cluster which is the same size as that used by Edwards and Germann[7] and another somewhat smaller cluster. Our results yield a binding energy for the $H^+$ ion at the bridging O, which is greater than 5.5 eV and an equilibrium R(O-$H^+$) ~ 1.0 Å. For a $Si^+$ ion interacting with a bridging O atom, our calculation gives a shallow potential minimum, with a binding energy ~0.3 eV and an equilibrium R(O-$Si^+$), which is twice the normal R(Si-O) distance in *a*-$SiO_2$. The interaction of a neutral H atom with the bridging O is calculated to be strongly repulsive.

## CALCULATIONS

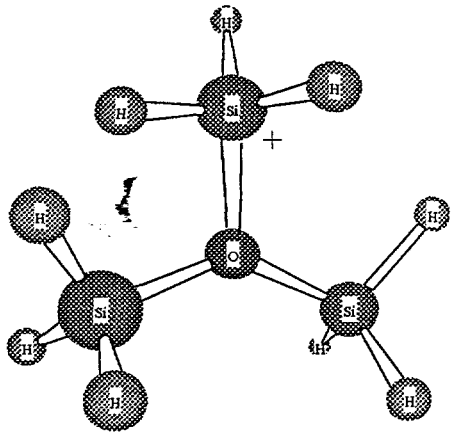
Calculations were performed on two precursor clusters. A small precursor (Structure I and II) was used to calculate the interaction potential of the $H^+$ and $Si^+$ ions with the bridging O atom. In the case of the $Si^+$, the three valences of the Si atom were neutralized by H atoms. Next, the interaction potentials of $H^+$ and $H^0$ were calculated with a larger precursor (Structure III) as schematically shown below.

Calculations on all three clusters were performed using an *ab initio* HF method. For the larger cluster, calculations were also performed by using an *ab initio* second-order Möller-Plesset method. The geometry of the precursors were optimized by *ab initio* HF calculations. The geometry for the $^+SiH_3$ ion was taken from the literature. In the calculations only the distance between the interacting centers (bridging O atom and the $H^+/H^o$ /$^+SiH_3$) was varied in the Si-O-Si plane. The rest of the geometry was fixed

throughout the calculation. In all calculations, a double-zeta plus polarization (DZP) basis set[11] was used. *Ab initio* HF and MP/2 calculations were performed utilizing the HONDO-8 electronic structure code.[12]



Structure I



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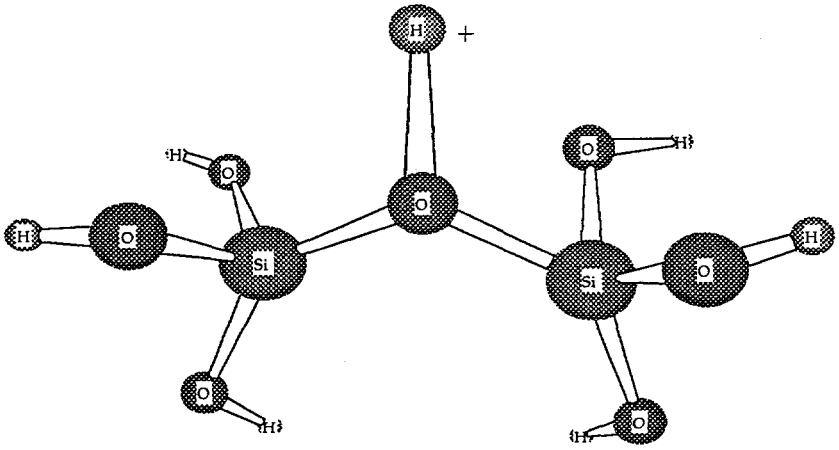

Structure III

## RESULTS

The calculated bond distance and bond angles for the precursor molecules,

$H_3Si\text{-}O\text{-}SiH_3$ and $(OH)_3Si\text{-}O\text{-}Si(OH)_3$ are listed in Table 1.

Table 1. *Ab initio* Hartree-Fock optimized geometry of the various precursor molecules.

| Molecule | $H_3Si\text{-}O_c\text{-}SiH_3$ | $(OH)_3Si\text{-}O_c\text{-}Si(OH)_3$ |
|---|---|---|
| $R_{Si\text{-}Oc}$ (Å) | 1.633 (1.62)[a] | 1.617 (1.62)[a] |
| $R_{Si\text{-}O}$ (Å) | - | 1.625 (1.62)[a] |
| $R_{Si\text{-}H}$ (Å) | 1.474 | - |
| $R_{O\text{-}H}$ (Å) | - | 0.941 |
| $<SiO_cSi$ (°) | 150 (~152)[a] | 174 (~152)[a] |
| <HSiO/<OSiO | ~110 | ~110 |

[a]Experimental values cited in ref. 13.

Also listed in Table I (inside the parentheses) are the experimental values[13] of the bond-distance and bond angles in $\alpha$-$SiO_2$. The bridging O center interacting with $H^+$, $H^0$ and $^+SiH_3$ is labeled as $O_c$. We note that the calculated bond distance and angles are close to the bulk values. A larger value of $<SiO_cSi$ bond angle is calculated in the larger cluster. However, the calculated bond angle is within the observed range[13] of 128 - 180°.

Figures 1 and 2 show the calculated potential energy curves as a function of O-X ($X = H^+, {}^+SiH_3$) bond length for the interaction $H_3Si\text{-}O_c\text{-}SiH_3 + H^+$ and $H_3Si\text{-}O_c\text{-}SiH_3 + {}^+SiH_3$, respectively. It is evident from the figures that the $H^+$ interaction with the bridging O atom leads to a very stable bonding, with a dissociation energy close to 6.8 eV. The equilibrium $O\text{-}H^+$ distance in the case of the protonated complex (1Å) is about the same as calculated earlier by Edwards and Germann.[7] The corresponding energy for the $O\text{-}{}^+SiH_3$ is much smaller.

The HF and MP/2 potential energy curves for the $H^+/H^\circ$ interaction with the larger cluster $((OH)_3Si)_2O$ are shown in Figs. 3 and 4, respectively. As can be noted, the results for the interaction of $H^+$ are reproduced by the larger cluster calculations. Quantitatively, the dissociation energy of the $O\text{-}H^+$ bond is calculated to be slightly smaller. For the larger clusters, inclusion of electron correlation (MP/2) gives slightly larger values for the dissociation energy ($D_e$) as well as the equilibrium distance ($R_e$), as expected, than the HF values. It is also noted that both HF and MP/2 calculations yield a repulsive potential energy curve for the interaction of neutral $H^\circ$ with the bridging oxygen. An implication of this result is that capture of an electron by the protonated trivalent-O complex will result in the dissociation of the O-H bond. Examining the molecular orbitals of the unhydrogenated $[(OH)_3Si]_2O$ helps to understand this result. It reveals that the lowest unoccupied molecular orbital is a strongly antibonding $\pi^*$-type orbital.[6] One can,

therefore, expect that trapping an electron in this orbital is energetically unfavorable and causes the strong repulsion.

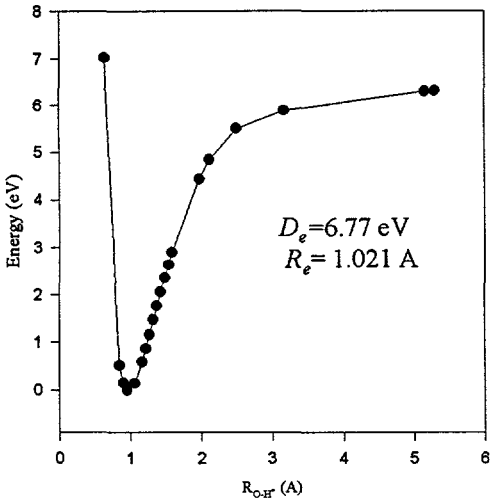


Figure 1, Potential energy curve for $(H_3Si)_2O\text{-}H^+$ interaction

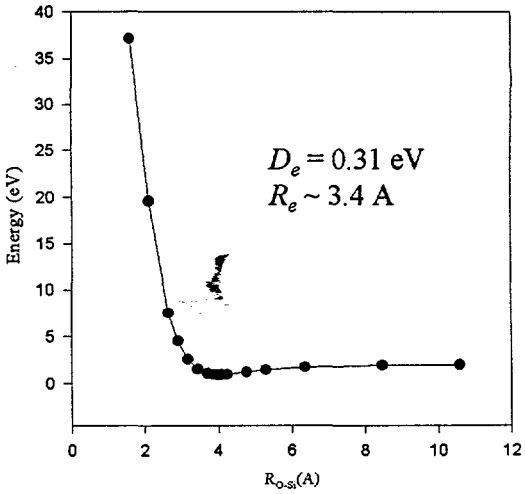


Figure 2. Potential energy curve for $(H_3Si)_2O\text{-}SiH_3^+$ interaction

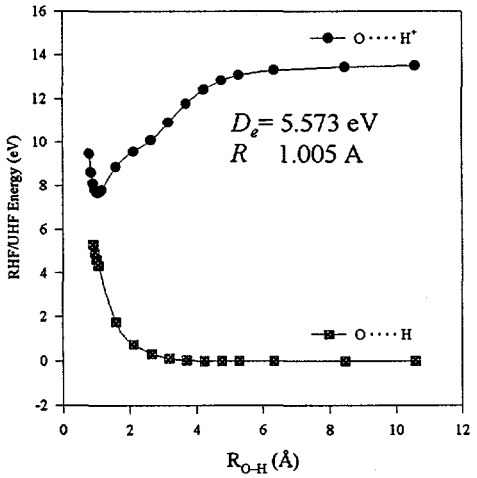


Figure 3. Potential energy curve for $((HO)_3Si)_2O\text{-}H^+/H^0$ interaction

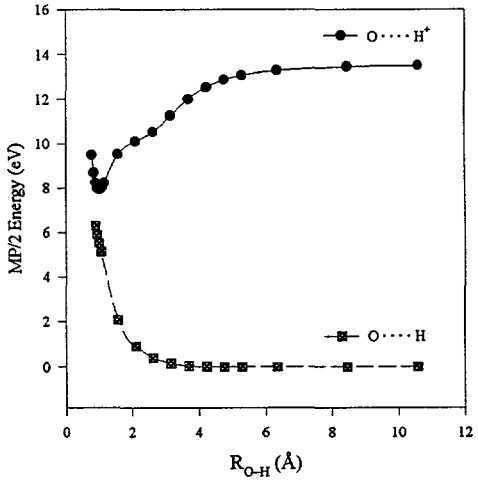


Figure 4. Potential energy curve for $((HO)_3Si)_2O\text{-}H^+/H^0$ interaction

We now discuss these calculations in light of some experimental data. First, our calculations show that positively charged over-coordinated oxygen centers are quite stable. Thus, earlier suggestions[2,5] that over-coordinated O centers may be a source of positive charge in $SiO_2$ thin films may be true. Second, the calculated binding energy of the $O\text{-}H^+$ bond is quite high (6.8 eV). Experimentally, it has been suggested that $H^+$ motion in the $SiO_2$ network occurs by hopping between neighboring O atoms, possibly by forming temporary bonds to the lone pair orbitals of the O atoms[14], thus explaining why the activation energy ($E_a$) of ionic $H^+$ (0.8 eV)[15] is much larger as compared to the activation energy of atomic $H^0$ motion (0.18 eV)[16] in $SiO_2$. Clearly, the calculated binding energy of the $O\text{-}H^+$ bond is higher than the activation energy for motion of $H^+$ in

$SiO_2$. This is reasonable given that the dissociation energy is the energy required to move the proton from its equilibrium position in the $O\text{-}H^+$ bond to vacuum; whereas, the activation energy for $H^+$ motion is the energy required for hopping between two adjacent potential wells. The latter energy will be much smaller than the calculated dissociation energy due to potential well overlap in the $SiO_2$ network.

Last, we note that these quantum mechanical calculations were performed on a finite size cluster with a fixed geometry; no relaxation of the cluster was allowed as a function of O-X bond length. Furthermore, other effects such as Coulombic and phonon-electron interactions may considerably alter the energetics of any local structure. Nonetheless, the calculations provide some additional insight into the nature and relative stability of over-coordinated oxygen centers in silicon dioxide.

## SUMMARY

We have presented the results of *ab initio* calculations on the stability of trivalent bridging O centers in $a\text{-}SiO_2$ bonded to either $H^+$, $H^0$, and $Si^+$. Both the HF and MP/2 calculations suggest a strongly bonded $O\text{-}H^+$ complex, with the $R_e(O\text{-}H^+)\sim1.0$ Å and $D_e(O\text{-}H^+) > 5.5$ eV. In the case of smaller cluster, the corresponding value of the dissociation energy is somewhat larger and that of the equilibrium distance is smaller. The electron -correlated calculations yield somewhat larger values for the $R_e(O\text{-}H^+)$ and $D_e(O\text{-}H^+)$. The $Si^+$ ion forms only a weak but stable bond with a bridging O. The calculated equilibrium $R(O\text{-}Si^+) = 3.4$ Å is twice the corresponding value for normal R(O-Si) in $a\text{-}SiO_2$. The potential energy curve for the interaction of the neutral $H^o$ atom with a bridging O atom is calculated to be strongly repulsive.

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