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Two fold coordinated silicon atom: a hole trap in SiO_2

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Abstract

The capturing properties of a neutral diamagnetic two fold coordinated silicon atom with two paired electrons (silylene center $=$Si:) in SiO_2 are studied with *ab initio* density functional method. We prove that this defect is a hole trap in SiO_2. Hole capture results in creation of a paramagnetic two-fold coordinated silicon atom with unpaired electron $= Si\cdot(+)$. According to this prediction silylene centers can be with silicon-silicon bonds responsible for the positive charge accumulation in MOS devices at ionising radiation. © 2002 Published by Elsevier Science Ltd.

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Understanding the nature of charge traps in amorphous SiO_2 is crucial for the design of reliable and radiation tolerant metal oxide silicon (MOS) devices. Important experimental and theoretical efforts have been devoted to the study of the atomic structure of intrinsic defects in SiO_2 [1–5]. Four of the most important neutral intrinsic defects in SiO_2 are known at present. These are $\equiv$Si–Si$\equiv$ bond or oxygen vacancy [3–6], non-bridging oxide hole center (NBOHC $\equiv SiO\cdot$) [1,6–8], super oxide radical ($\equiv SiOO\cdot$) [8], and two-fold coordinated silicon atom with two paired electrons (silylene centers $=$Si:) [9–12]. Here (–) and ($\cdot$) denote normal chemical bond and unpaired electron.

It has been shown experimentally that a Si–Si bond can capture a hole via the reaction $\equiv Si{-}Si\equiv + h \rightarrow \equiv Si^{+}\cdot Si\equiv$ with creation of a positively charged paramagnetic E' center [2,5,13,14]. Using simulations it has been theoretically proven that Si–Si bond [2,5,13,14] and $\equiv SiO\cdot$ [1,15] in SiO_2 can capture an electron.

In the present paper we study the capturing properties of a fundamental intrinsic defect in SiO_2: a silylene center. In bulk SiO_2, a silylene center can be created with breaking of two SiO bonds on the same tetrahedron and creation of a peroxide bridge $\equiv$SiOOSi$\equiv$ according to the reactions [16]:

$$\equiv Si_2O_2SiO_2Si_2 \equiv \rightarrow \equiv Si_2O_2Si: + \equiv SiOOSi \equiv \qquad (1)$$

Also silylene centers can appear from Si–Si bonds with the reaction [12]:

$$O_3Si:SiO_3 \rightarrow O_4Si + :SiO_2 \qquad (2)$$

In SiO_2, an absorption band with energy 5.0 eV (B_2 band) has been observed [10]. Excitation of this band results in two luminescence bands with energies 2.7 eV (blue band) and 4.4 eV (ultraviolet band). According to [9–12,17] the B_2 absorption band in SiO_2 can be ascribed to silylene centers. Thus the 4.4 eV band is related with singlet-singlet transition in $=$Si: defect [11–12]. This band has decay time 4.0 ns. The 2.7 blue band is related with dipole forbidden triplet singlet transition and has decay time 10 ms [10]. However, some authors ascribed B_2 band to the Si–Si bond [10,18].

The 2.7 eV blue band have been observed in thermal SiO_2 on Si [19], in B, P, and Ar ion-implanted thermal SiO_2 [20,21], chemical vapor deposited SiO_2 [22] and in oxide, which was produced by oxygen implantation into Si [23]. Probably the origin of this band is the silylene center.

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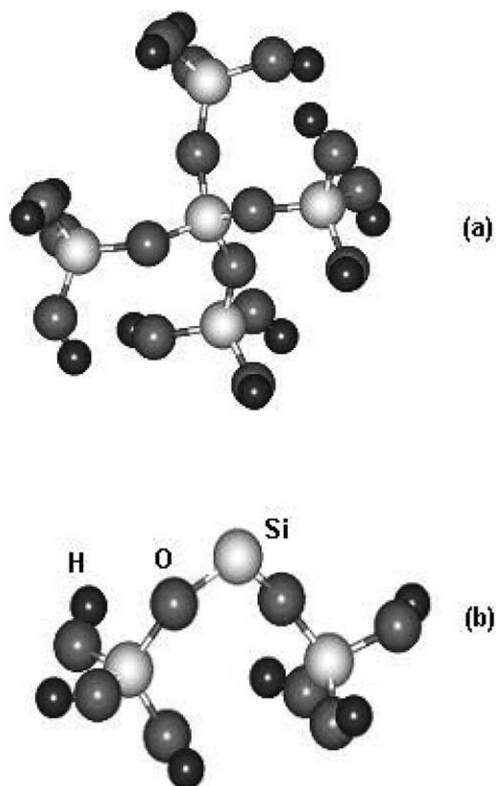

Fig. 1. Structure of $Si_5O_{16}H_{12}$ cluster for oxide bulk simulation (a) and $Si_3O_8H_6$ cluster for silylene defect simulation (b).

Silylene centers have also been observed in luminescence spectra of oxynitride SiO_xN_y at different composition [24].

We performed ab-initio density functional theory (DFT) calculation in Amsterdam Density Functional (ADF) program [25]. All calculations were made in cluster model. Fragments of crystalline α-quartz were used for calculations. Broken Si–O bonds on the cluster boundaries were saturated with H atoms. For simulating SiO_2 bulk we used a $Si_5O_{16}H_{12}$ cluster consisting of 33 atoms and including 3 correct coordinated spheres (Fig. 1a). For $=$Si: defect simulation we used a $Si_3O_8H_6$ cluster, consisting of 17 atoms (Fig. 1b). Bulk $Si_5O_{16}H_{12}$ cluster is consistent with defect $Si_3O_8H_6$ cluster in the way that defect cluster was built from bulk by truncating two Si–O bonds. This is important for our method of finding energy gain, as we need these clusters to have similar boundary condition.

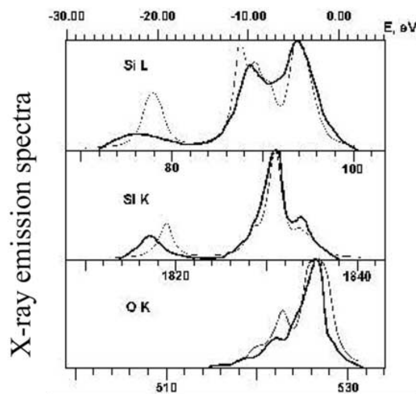

Fig. 2. Experimental (heavy line) and simulated (thin line) X-ray emission spectra of SiO_2.

The Kohn–Sham molecular orbitals were constructed using Slater-type exponential basis functions. The basis set include double-zeta basis with polarization 3d functions for all Si atoms, which corresponds to basis set III in ADF terminology [25]. The position of all Si and O atoms has been fully optimized at the non-local DFT level using Becke [26] form of exchange and Lee-Yang-Parr [27] form for correlation functional. Positions of terminal H atoms have been fixed to represent embedding in solid.

For evaluating whether the given cluster has ability to capture electrons or holes we calculate it's bonding energy in different charged states and find the energy gain using the next relations:

$$\Delta E^e = (E^0_{bulk} + E^-_{def}) - (E^-_{bulk} + E^0_{def}) \quad (3)$$

$$\Delta E^h = (E^0_{bulk} + E^+_{def}) - (E^+_{bulk} + E^0_{def}) \quad (4)$$

where E^0_{bulk}, E^-_{bulk}, E^+_{bulk} and E^0_{def}, E^-_{def}, E^+_{def} denote bonding energy of neutral, positively and negatively charged clusters simulated bulk SiO_2 and defect silylene center respectively. In the case of negative value ΔE^h (ΔE^e) we say that $=$Si: is hole (electron) trap.

To check if our cluster model is reliable enough for simulation of the electronic structure of bulk oxide, we made simulation of bulk SiO_2 X-ray emission spectra to compare with experiment. Calculations were performed in frozen orbital approximation. Dipole matrix elements were calculated between core (Si 1 s,2p and O 1 s) orbital and valence orbitals. Such a matrix elements include, in principle, all inter-atomic matrix elements between Slater-type functions centered on different atoms. Calculated spectra were broadened by a convolution with a Lorentzian curve with width parameter 0.5 eV.

We found that including in basis set Si 3d polarization functions is necessary to obtain correct X-ray emission spectra. Our calculation also shows that while for Si K and O K emission spectra contribution of non-local transitions is negligible, in the case of Si $L_{2,3}$ spectra it is necessary to take such transitions into account. Fig. 2 shows our calculations, in comparison with experimental Si K, Si L and O K spectra of thermally grown wet SiO_2 on silicon taken from ref [28]. A good agreement is generally observed here between calculated and experimental data. After this comparison we apply our model for defect cluster simulation.

To understand if silylene center in SiO_2 can capture

electrons or/and holes we calculated bonding energies of negatively and positively charged clusters using Eqs. (3,4). Our results show that the electron capture by a = Si: defect is energetically unfavorable. The energy gain for hole capture by silylene center is –3.2 eV. Our calculation predicts that silylene center is a hole trap in SiO_2 via the reaction

$$=\mathrm{Si}: -\mathrm{e} \rightarrow \ =\mathrm{Si}\cdot(+) \qquad (5)$$

According to our predictions, hole capture by a neutral diamagnetic silylene center results in creation of a positively charged paramagnetic two-fold coordinated silicon atom with unpaired electron $= \mathrm{Si} \cdot (+)$.

Because our model doesn't take into account the exact environment of a defect = Si: atom in the "up half-space" we can view this cluster as a model for surface defect [12]. Also our model doesn't take into account the long-range coulomb polarization, induced on the lattice by a positively charged defect. Hence we can believe that our calculations predict the capturing and magnetic properties of defects, but the value of the energy gain is only roughly estimated.

In [29,30] an isodensity polarized continuum model (IPCM) was used for the evaluation of long-range coulomb polarization effects in cluster calculations for defects in SiO_2 and Si_3N_4. IPCM model was compared with classical Born estimation [31] and a good agreement was found.

In a classical approximation, assuming the charge spread in a sphere of radius R, the energy change due to electronic polarization of the lattice can be estimated as:

$$\mathrm{E} = -[\mathrm{q}^2/(8\pi\mathrm{R})][\epsilon_0^{-1} - \epsilon_\infty^{-1}] \qquad (6)$$

where ϵ_0 and ϵ_∞ are free space and high frequency permitivities. From Eq. 4, the corresponding correction to ΔE^h is:

$$\Delta\mathrm{E_P} = -(\mathrm{q}^2/8\pi)[\mathrm{R}_{\mathrm{def}}^{-1} - \mathrm{R}_{\mathrm{bulk}}^{-1}][\epsilon_0^{-1} - \epsilon_\infty^{-1}] \qquad (7)$$

where $2R_{def}$~5.5 A and $2R_{bulk}$~8 A correspond to the size of the defect and bulk clusters used in the calculation. Taking $\epsilon_\infty \sim 2.25\epsilon_0$ for SiO_2, we obtain for ΔE_p value −0.45 eV. This estimation shows that long-range effects are relatively small with respect to local effects due to atomic and electronic relaxation.

We have also calculated, using the same cluster model, the capturing properties of Si–Si bond defects. We used a $Si_5O_{16}H_{12}$ cluster for simulating bulk SiO_2 and a $Si_5O_{15}H_{12}$ cluster for simulating a Si–Si bond defect. We applied for the simulation the same basis set and density functional as for = Si: calculations. We found that a Si–Si bond is a hole trap with energy ~1 eV.

It is generally believed that the positive charge accumulation in MOS devices is related with hole capture by neutral Si–Si bond and creation of positively charged E' center [2,5,13,14]. However thermally stimulated current experiments have shown a continuous hole traps distribution in the energy range 1.1–2.2 eV [32], with two well defined peaks at E_1~1.2 eV and E_2~1.9 eV (Fig. 1) [32]. This double-peak structure might arise from the presence of two kinds of trapping centers. Taking into account the uncertainty on our theoretical calculation, we argue that our theoretical values ~1 eV and ~3.2 eV obtained respectively for the trapping energy of Si–Si bonds defects and silylene centers might correspond qualitatively to these two experimental peaks. Further experimental investigations are needed to test this hypothesis.

In conclusion the capturing properties of the two-fold coordinated silicon atom with two paired electrons were studied with ab initio DFT method in cluster models. For this defect, we have found that the capture of a hole is energetically favorable. Hole capture leads to the creation of a paramagnetic two fold coordinated silicon atom with unpaired electron. We argue that silylene centers in SiO_2 can be, with Si–Si bonds, responsible for positive charge accumulation in MOS devices at ionizing radiation and hot hole injection.

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