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A computational study of Si–H bonds as precursors for neutral E' centres in amorphous silica and at the Si/SiO₂ interface

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ABSTRACT

Using computational modelling we investigate whether Si–H Bonds can serve as precursors for neutral E' centre formation in amorphous silica and at the Si/SiO₂ interface. Classical inter-atomic potentials are used to construct models of a-SiO₂ containing Si–H bonds. We then investigate the mechanism of dissociation of a Si–H bond to create a neutral E' defect, that is a 3-coordinated silicon with an unpaired electron localised on it. We show that the Si–H bond is extremely stable, but as a result of hole injection it is significantly weakened and may dissociate, creating a neutral E' centre and a proton attached to one of the nearby oxygen atoms. The proton can diffuse around the E' centre and has a profound effect on the defect levels. We show that at a Si/SiO₂ interface, the position of the proton can facilitate electron transfer from the Si substrate onto the defect, making it negatively charged.

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1. Introduction

Oxidised silicon still remains at the core of a wide variety of microelectronic devices ranging from charge-trapping memory cells to high power transistors. As a result, further understanding of charge trapping in thin SiO₂ layers at the atomic level represents the focal point of both experimental and theoretical research aimed at the development of physically sound models with considerable predictive capability. As we show below, the creation of E' centres (a O₃ ≡ Si moiety) by trapping of a hole on a Si–H bond in bulk amorphous silica (a-SiO₂) not only provides an explanation to a multitude of observations but also predicts metastable defect-proton configurations encountered in stress-induced degradation experiments.

Ever since the identification of the paramagnetic E' centre in SiO₂ as an unpaired electron localised in an sp³ hybrid orbital of an Si atom backbonded to three oxygen atoms, a number of attempts has been made at explaining the optical and electronic properties of SiO₂ in the presence of E' centres. The irradiation or hole injection induces trapping of positive charge in thin layers of a-SiO₂ grown on silicon surfaces by thermal oxidation. This effect has been correlated with paramagnetic E' centre signals and

led to the initial assignment of the neutral oxygen vacancy as the major hole trap in a-SiO₂ [1–3]. In this model, originally proposed for E' centres in α-quartz, upon trapping a hole, one Si atom from the two Si atoms constituting the vacancy remains neutral and hosts the localised unpaired electron while its counterpart becomes positively charged. Although this model has initially been accepted widely for its simplicity, it fails to account for a number of observations, such as the positive charge trapping without generation of E' centres [4], the formation of high density of E' centres without the corresponding density of positive charge [5], and the absence of correlation between the decrease of the E' centre density and the density of positive charge upon post-irradiation electron injection in SiO₂ [6].

More recent experiments using field-dependent recombination of holes trapped in SiO₂ with injected electrons [7] revealed that the paramagnetic state of the E' centre is not always correlated with the entity bearing the positive charge. It has been suggested that the positive charge is protonic in origin, a hypothesis later corroborated by a number of experimental results [7,8]. Consequently the O₃ ≡ Si–H entity in a-SiO₂ has been suggested as a possible E' precursor [7], where upon hole trapping hydrogen dissociates in the form of a proton leaving behind a neutral paramagnetic E' centre. The question remains as to whether the liberated proton is then trapped in SiO₂ or diffuses through and escapes the SiO₂ layer.

In this contribution we demonstrate that Si–H bonds in bulk a-SiO₂ and at the Si/SiO₂ interface can indeed be responsible for

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the creation of paramagnetic E' centres and how the presence of a proton nearby can affect the defect's levels.

2. Details of calculation

The ReaxFF force-field [9] was used to generate 20 models of amorphous silica, each containing 216 atoms, using molecular dynamics (MD) simulations within the LAMMPS code [10]. The force-field was parametrised to reproduce the properties of various SiO_2 polymorphs, Si polymorphs, SiO_x clusters and water molecules [11]. It allows the calculation of Si and O atoms in a range of oxidation states by exploiting the electronegativity equalisation principle [12]. To generate the amorphous structures, MD simulations were run starting from the $3 \times 3 \times 3$ cell of β -cristobalite under periodic boundary conditions.

Each system was given random velocities from a Gaussian distribution and equilibrated at 300 K and 1 atm. pressure using a Berendsen thermostat and barostat [13]. The temperature was then linearly ramped up to 5000 K and a hydrogen molecule was added to the silica melt. In order to ensure that Si–H bonds are present in the final structure, the distance in a pair of Si and H atoms was fixed 1.46 Å apart. The system was maintained at 5000 K for 40 ps and then brought down to 0 K at a rate of 8 K/ps. The resulting structures contained separate Si–H and Si–O–H bonds, as can be seen in Fig. 1. These structures were then characterised by calculating the distributions of bond lengths and angles, densities, and total structure factors [14].

The electronic structures of these models were then calculated using density functional theory (DFT) and non-local density functional HSE [15], implemented in the CP2K code [16]. The CP2K code uses a mixed Gaussian/plane-wave basis set. The double- ζ Gaussian basis set [17] was employed for all atoms in conjunction with the GTH pseudopotential [18]. The SiO_2 band-gap in these models is ≈ 8.9 eV. The calculations of hyperfine interactions employed all electron basis sets with contraction schemes 6-311G** for silicon and oxygen [19,20]. All geometry optimisations were performed to achieve forces on atoms less than 37 pN.

We also constructed several models of interfaces between crystalline Si (001) and a- SiO_2 , making the a- SiO_2 layer using a similar technique. The starting structure contained 25 layers of Si and 13

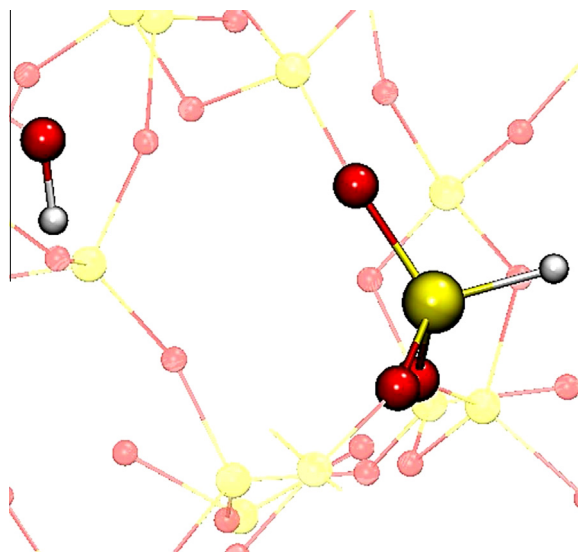


Fig. 1. A model of a- SiO_2 containing an Si–H bond and an Si–O–H bond. The Si atoms are yellow spheres connected to four atoms, O atoms are the darker red spheres connected to two atoms and H atoms are pale grey spheres. The distance between the Si–H bond and Si–O–H bond is ≈ 6 Å.

layers of β -cristobalite, strained to the lateral cell vectors of the Si substrate. Overall the Si substrate is ≈ 3 nm thick as is the SiO_2 layer. This system was modelled under 3D periodic boundary conditions and effectively contained two Si/ SiO_2 interfaces. Briefly, the interface structure generation included melting the SiO_2 layer at the temperature of 5000 K and equilibrating for 20 ps. The temperature of the SiO_2 layer was then brought down to 0 K at a rate of 100 K/ps. The Si layer and the Si/ SiO_2 interfaces were then heated up to 1000 K and then brought down to 0 K at a rate of 20 K/ps. The resulting structures contained defects at the interface, which were passivated with H atoms, and one 3-coordinated Si in the SiO_2 layer. The model has a distribution of Si–O bond lengths around 1.64 Å and Si–Si bond lengths around 2.3 Å. The O–Si–O angles are centred around 110° and the Si–O–Si angles are centred around 150° . The calculated band gaps and band offsets (shown in Table 1) are in good agreement with experiment.

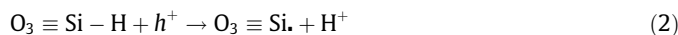
3. Si–H dissociation and the generation of a neutral E' centre

To investigate the possibility of thermal dissociation of the Si–H bond we calculated the formation energy of a neutral E' from the Si–H bond in the bulk of a- SiO_2 according to reaction:



This was accomplished by moving the H atom away from the $\text{O}_3 \equiv \text{Si}$ entity, re-optimising the system geometry and comparing the total energies of the two structures. We found that the H atom prefers to be located in the middle of a Si–O ring structure and does not bind to Si or O atoms. The average dissociation energy obtained from the 20 a- SiO_2 models is 4.2 eV, which indicates that the Si–H bond is very stable and would require high temperature for thermally activated dissociation to occur. The isotropic hyperfine constants calculated for the $\text{O}_3 \equiv \text{Si} \cdot$ models range from 40.0 mT to 47.8 mT, averaging at 44.4 mT.

We then investigated whether hole trapping would facilitate the Si–H dissociation in all 20 a- SiO_2 models, as in reaction:



In the neutral system the Si–H states are located close to the top of the SiO_2 valence band. In two of the 20 models the addition of a hole results in spontaneous dissociation of a Si–H bond releasing a proton and leaving behind a neutral E' centre. The proton binds to the nearest oxygen that is not bonded to the Si atom from which the proton dissociated, as can be seen in Fig. 2. The Si–H states of the two models in which the Si–H bond dissociated spontaneously are the highest in the a- SiO_2 band gap above the top of the SiO_2 valence band. These are also the ones that have the smallest H...O distance with the O atom which binds the proton. In the remaining 18 models there is a barrier to remove a proton, but the final dissociated state is always lower in energy than the Si–H state just after the hole trapping. The calculations using a nudged elastic band method [22] show that the barrier to proton removal increases as the H...O distance increases and in our 20 models does not exceed 0.5 eV when the proton has to cross the largest distance of 3.2 Å.

In all cases the proton binds to an oxygen atom, forming a hydronium-like configuration shown in Fig. 2 and leaving behind

Table 1

The calculated band gaps and band offsets, in eV, of the Si/ SiO_2 system compared to experiment. VBO is valence band offset, CBO is conduction band offset and B_g are the band gaps of Si and SiO_2 .

	VBO	CBO	$B_g(\text{SiO}_2)$	$B_g(\text{Si})$
Theory	4.2	3.7	9.0	1.23
Expt. [21]	4.4	3.4	8.9	1.2

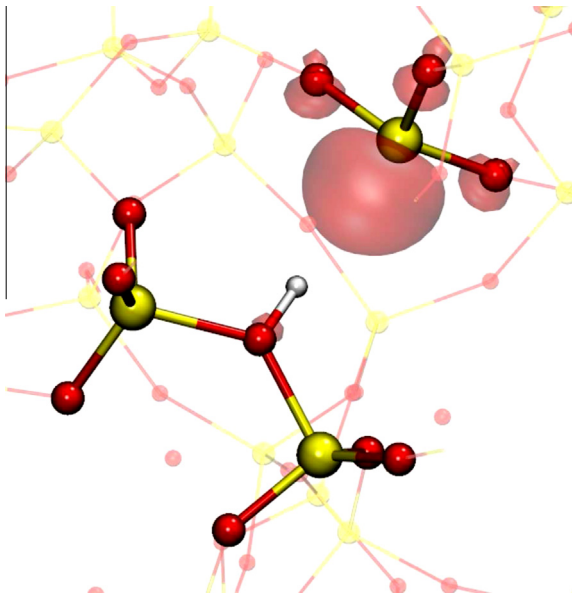


Fig. 2. The neutral E' centre showing an unpaired electron localised on a 3-coordinated Si atom and a proton bound to a bridging oxygen.

a 3-coordinated Si atom with an electron localised on this Si atom. Moving the proton to one of the O atoms belonging to the same tetrahedron as the 3-coordinated Si is also energetically favourable, but requires overcoming a higher barrier of 0.6 eV, as opposed to the 0.5 eV maximum required to cross a ring. The average relaxation energy, from our 20 systems, for a proton dissociating and binding to an oxygen atom across the ring is 0.66 eV. We note that an electron trapping by an E' centre with a proton less than ≈ 3 Å away leads to restoration of the Si–H bond.

Although the majority of the hyperfine splitting comes from the interaction of the unpaired electron with the nucleus of the Si atom on which it is localised (see Fig. 2), the hyperfine interaction with the proton is also possible if the Si...H distance is small enough. We find that if the Si...H distance is 2.3 Å or less this hyperfine splitting is about 1.6 mT.

The comparison of the one-electron states of the E' centre with the proton less than 6 Å away and a neutral E' centre with no proton in the system demonstrates that the proton shifts the defect states down by up to ≈ 0.5 eV. The position of the proton depends on how easily the proton can diffuse through a-SiO₂. It has been suggested by Pasquarello et al. that proton diffusion occurs predominantly via a ring-crossing mechanism [23]. This involves the proton hopping from one oxygen to another across an Si–O ring. Barriers for this hopping range from almost zero to ≈ 1.5 eV, dependent on the distance between the initial and final O atoms. We also find that proton diffusion proceeds via ring-crossing with the E' centre making little difference to the energies previously calculated for proton diffusion [23].

4. Neutral E' centre at the Si/SiO₂ interface

To investigate the properties of the neutral E' centre at a Si/SiO₂ interface, we first created the neutral E' centre at the Si/SiO₂ interface without a proton present in the system, as described in Section 2. We calculated the positions of the defect levels of the centre as a function of its distance from the Si substrate. The defect was positioned at different distances from the Si substrate (shown in Fig. 3), ranging from 2.6 Å to 17.7 Å. The positions of the defect's occupied and unoccupied levels with respect to the Si valence band

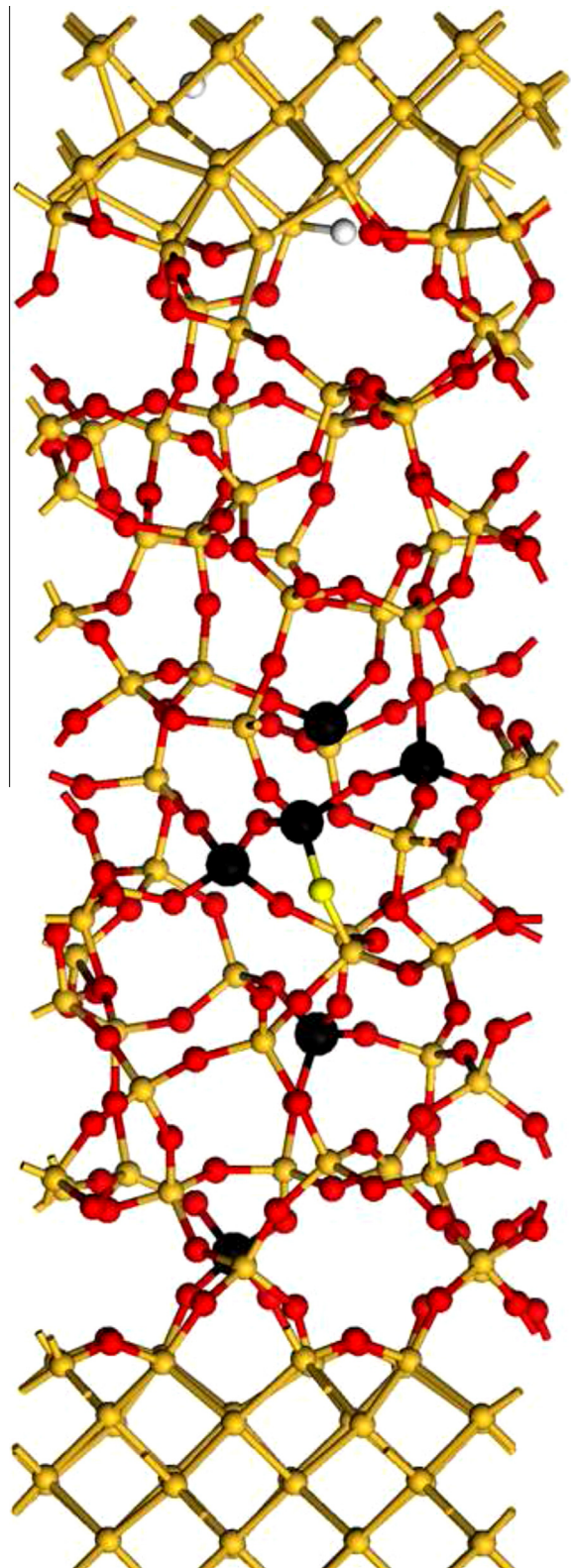


Fig. 3. Model of the Si/SiO₂ interface. The darker enlarged Si atoms are the positions we considered for the neutral E' whose defect levels are shown in Table 2. Note that only part of the Si substrate is shown in this figure.

and Si conduction band shown in Table 2 indicate that the location of the defect at the interface has a considerable effect on its electronic structure. This effect stems both from the difference in local environment at each defect location, and from the constraints

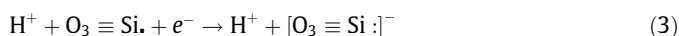
Table 2

Defect levels of neutral E' centres in Si/SiO₂ interface model as a function of distance from the Si substrate. The occupied levels are measured with respect to the Si valence band (i.e. below the top of the Si valence band) and unoccupied levels are with respect to the Si conduction band (i.e. above the Si conduction band).

Distance Å	Occupied level eV	Unoccupied level eV
2.6	0.80	None
8.5	1.29	1.57
12.7	1.41	1.17, 1.55
14.8	1.22	1.46
15.4	1.52	1.40
17.7	1.38	1.11, 1.43

imposed by the interface on the defect-induced distortion of the amorphous silica structure.

We then investigated the effect of a proton on the neutral E' defect. This was done in a system where the neutral E' species was 13 Å away from the interface. When the proton is located less than 6 Å away from the defect, it pushes the defect levels down. We modelled electron injection by adding an extra electron at the bottom of the Si conduction band. In the interface system this electron can exchange between the defect and the Si substrate. If the proton is less than 3 Å away from the neutral E' species, upon electron transfer from Si the Si–H bond is reformed, as in bulk a-SiO₂. However, if the proton is further than 3 Å away from the 3-coordinated Si, the electron transferred from Si is localised on the 3-coordinated silicon, making it negatively charged:



The structure of this negatively charged centre is similar to that of the neutral E' centre except that the Si–O bonds elongate to ≈ 1.74 Å and the O–Si–O angles decrease to $\approx 93^\circ$. The electron transfer to the neutral E' centre results in the Si atom moving away from its oxygen neighbours as the extra electron localises on the Si atom.

5. Discussion and conclusions

Our modelling confirms that Si–H bonds in a-SiO₂ act as precursors to formation of neutral E' centres and that E' centres can behave as electron traps in Si/SiO₂ systems. The Si–H dissociation is facilitated by hole injection and the barrier to Si–H dissociation is at most 0.5 eV in our models. Proton diffusion away from the neutral E' centre occurs via a ring crossing mechanism with barriers less than 1.5 eV. The electron injection can restore the Si–H bond if the proton is less than 3 Å away.

The hyperfine interaction of the neutral E' centre is in good agreement with the experimental values. An interesting aspect of this model is the 1.6 mT signal associated with the proton. Experimentally there is a weak satellite signal of 1.3 mT associated with the E' centre controversially attributed either to a ²⁹Si atom [24] or hydrogen atoms [25]. Our calculations suggest that this satellite signal may be related to hydrogen present in the system after Si–H dissociation. Experimentally the 1.3 mT signal has been seen to disappear at temperatures greater than 100 °C while the E' signal is increasing [26]. In this model the proton can diffuse away after overcoming some barrier, presumably leading to a disappearance of the 1.6 mT signal, even while neutral E' centres are being generated.

At the Si/SiO₂ interface, the energy levels of neutral E' centre are strongly affected by its location at the interface and by the position

of a proton near the defect. We find that the electron exchange between the Si conduction band and the neutral E' centre can be facilitated under certain conditions. Charge transfer between an oxide defect and the Si substrate has long been considered a cause for the bias temperature instability (BTI) [27]. In this model, an electron transfer from the Si substrate into the E' centre has been considered a potential candidate for BTI. Using DFT under zero bias and with a valence band offset of 4.2 eV we could not model directly the Si–H bond dissociation resulting from a hole injection. Future work will investigate how the application of the electric field facilitates the Si–H dissociation by hole trapping and rates of electron exchange between the neutral E' centre and Si substrate.

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