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The roles of charged and neutral oxidising species in silicon oxidation from ab initio calculations

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Abstract

We examine the roles of charged oxidising species based on extensive ab initio density functional theory calculations. Six species are considered: interstitial atomic O, O^-, O^{2-} and molecular species: O_2, O_2^-, O_2^{2-}. We calculate their incorporation energies into bulk silicon dioxide, vertical electron affinities and diffusion barriers. In our calculations, we assume that the electrons responsible for the change of charge state come from the silicon conduction band; however, the generalisation to any other source of electrons is possible, and hence, our results are also relevant to electron-beam assisted oxidation and plasma oxidation. The calculations yield information about the relative stability of oxidising species, and the possible transformations between them and their charging patterns. We discuss the ability to exchange O atoms between the mobile species and the host lattice during diffusion, since this determines whether or not isotope exchange is expected. Our results show very clear trends: (1) the *molecular species* are energetically preferable over *atomic* ones, (2) the *charged species* are energetically more favourable than *neutral* ones, (3) diffusion of *atomic species* (O, O^-, O^{2-}) will result in oxygen exchange, whereas the diffusion of *molecular species* (O_2, O_2^-, O_2^{2-}) is not likely to lead to a significant exchange with the lattice. On the basis of our calculation, we predict that charging of oxidising species may play a key role in silicon oxidation process. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

Since the introduction of silicon technology, there has been pressure to scale down the size of devices. This has led to the need for growing high quality silicon dioxide with a very low concentration of intrinsic defects, which implies a need for better control and understanding of molecular processes during silicon oxidation. This work addresses the question of character of the oxidising species and charging processes relevant to ultra-thin oxide layers.

Modern gate-dielectrics approach a thickness of a few nm, for which the deviations from classical linear–parabolic (Deal–Grove) theory [1] of oxidation are significant. Thermal oxidation at lower temperatures and lower pressures [2], electron-beam assisted oxidation [3], as well as plasma oxidation [4] cannot be described within a linear–parabolic regime. One idea has been that charged oxidising species lead to different kinetics due to the electrostatic field within the oxide layer and image forces arising from the difference in the electrostatic constant of silicon and silicon dioxide. The effects of image forces were examined by Stoneham and Tasker [5] and the electric field within oxide and ionic conductivity in this field was the basis for power-parabolic ionic oxidation model by Wolters and Zegers-van Duijnhoven [6].

The role of a charged species in silicon oxidation has been stressed previously several times. Early stopping field experiments [7] have shown that oxidation can be enhanced, retarded or even stopped by applying a bias voltage across the sample. More recent experiments [8,9] suggested that the growth may be ionic in nature. The kinetics of the oxidation process has been shown to be strongly affected by the presence of a low energy electron-beam, and an anomalous temperature dependence has been observed for oxides less than 2 nm thick [3]. The initial oxidation at low temperatures has been shown to be enhanced by electron impact with the

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possible dissociation of adsorbed O_2 molecules to form O and O^- species [10]. Plasma oxidation kinetics was observed to follow trends expected for ionic species [4]. Oxygen absorption on SiO_2 surface has been reported to result in O_2^- species [11]. Also, other phenomena such as telegraph noise [12] and fixed oxide charge point to charge transfer processes as possible causes.

2. Techniques

The calculations were performed using spin-polarised version of density functional theory (DFT) with Perdew–Wang functional and generalised gradient approximation (GGA) [13,14] implemented within VASP code [15,16]. The Kohn–Sham orbitals were expanded in a plane-wave basis set with a cut-off energy of 400 eV. Oxygen atoms were represented by 'ultra-soft' pseudopotentials whereas silicon atoms by norm-conserving ones. Our reference structure is 72-atom fully relaxed hexagonal periodic unit cell of alpha-quartz. For all other calculations, the lattice vectors were fixed and all atoms were allowed to relax. This means that the defects are separated by more than 10 Å and the Brillouin zone integration includes the Γ-point only. For charged unit cells, we employ a neutralising background and Makov–Payne monopole–monopole energy correction [17]. This calculation procedure and a big unit cell ensured that the influence of the periodic images of the defects is minimised and that our results correspond to isolated defects in a non-defective host lattice.

The geometry relaxation was performed with conjugate gradient (CG) energy minimisation. Two methods were used for transition state search. Firstly, the ascending and descending valley points method combined with CG energy minimisation provided two approximations to the position of transition state on both sides of the saddle point. Secondly, the direction between those two points was assumed to be a good approximation to the direction of the transition state and the system geometry was driven towards the saddle point by reversing the force along this direction and using a semi-Newtonian relaxation algorithm. The transition states found are the maximum energy geometries along the lowest energy path joining two energy minima on the many dimensional energy surface. All the relaxation procedures were terminated when forces on atoms were lower than 0.05 eV/Å.

For charged species in a periodic model, a neutralising background is needed to converge Ewald summations. This introduces some additional errors to the total energy expression which can be handled in first order by Makov–Payne monopole–monopole energy correction which improves the convergence of total energy with respect to the size of the unit cell. In our calculation, in the case of adding or removing an electron from the system, this electron comes from or goes to the zero energy level on the eigenvalue scale. This zero energy level is not related to the experimental vacuum level since the Ewald sum is defined up to a constant. In our calculations, the constant is determined by condition that average potential is equal to zero. This condition, in turn, assures that the zero energy level on the eigenvalue spectrum remains in the same position regardless of the charge state of the system. This means that any calculation of a charged defect with energy converged with respect to the size of the unit cell corresponds to an isolated point defect in an infinite non-defective crystal. The only meaningful comparisons are of energies between systems with the same number of electrons. The calculation of an electron affinity can be performed only if we know the energy level of electron source. In the case of DFT calculations, we can rely on the results concerning occupied states, i.e. valence band. We can then align the theoretical valence band with the experimental one, as shown in Fig. 1, and use the experimental band offset at the interface [18,19] to get the energy level of the electron source E_{el}. In all calculations, we assume that the electrons come from the bottom of the conduction band of silicon but shifting the electron source to other level is a matter of adjusting E_{el}.

The incorporation energies are calculated for the lowest energy configuration of the system with respect to the non-defected quartz structure and an isolated oxygen molecule:

$$E_{inc} = E_{system} - (E_{quartz} + fE_{O_2} + nE_{el}),$$

where $f = 1$ for incorporation of oxygen molecule, $f = 0.5$ for an atomic species and n is the number of excess electrons. The vertical electron affinities are calculated by adding an electron to the lowest energy configuration of the system and looking at the energy change without allowing for any relaxation:

$$E_{aff} = -E_{charged,\ unrelaxed} + (E_{system} + E_{el}).$$

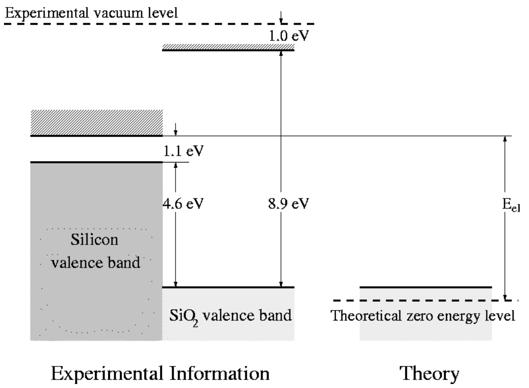
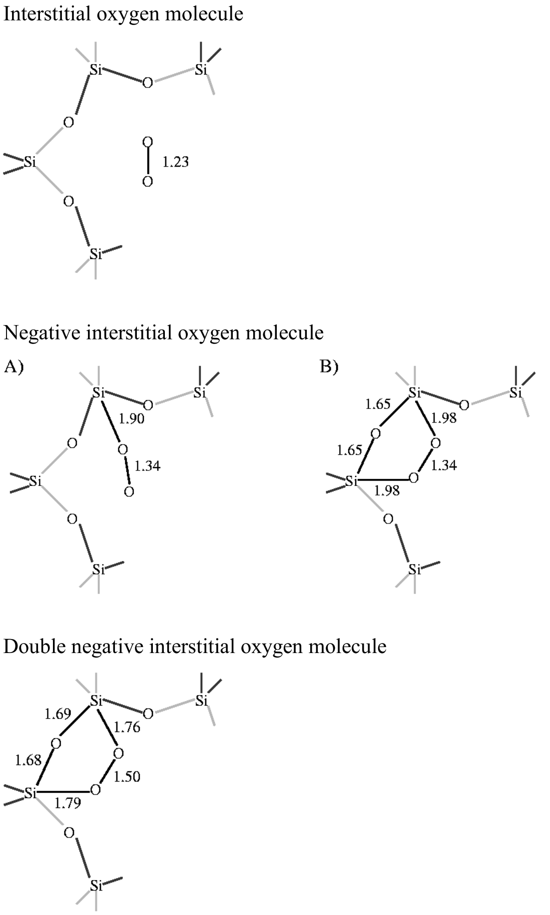


Fig. 1. Schematic representation of the method.

3. Results

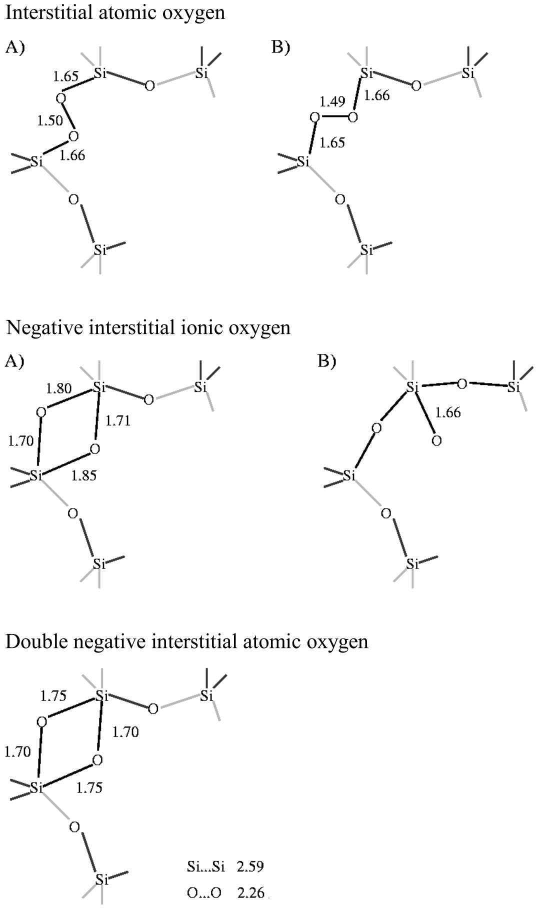
We have calculated properties of six oxidising species in alpha-quartz which we regarded in first approximation as acceptable mimic of amorphous silica. The typical relaxed geometries of the species are shown in Figs. 2 and 3. Our results are summarised in Table 1. A positive value of incorporation energy means that this energy has to be supplied to the system in order to incorporate the species into the lattice. Diffusion barrier gives the lowest possible energy barrier which a species encounters during diffusion from one energy minimum to another. We quote the diffusion barriers calculated along the *c* axis of alpha-quartz; diffusion barriers along other directions were calculated only for some species. A positive value of the vertical electron affinity means that the species can capture an electron from the bottom of Si conduction band. This value is calculated for the lowest energy configuration of the species. However, during diffusion there might be configurations for which the electron loss or capture will be more likely. The electron affinity of 1.1 eV means that the species can pick up an electron even from the top of the valence band of silicon.


Interstitial oxygen molecule

Negative interstitial oxygen molecule

Double negative interstitial oxygen molecule

Fig. 2. Molecular oxidising species.


Interstitial atomic oxygen

Negative interstitial ionic oxygen

Double negative interstitial atomic oxygen

Fig. 3. Atomic oxidising species.

There are important conclusions that can be drawn on the basis of our results:

- *Molecular species* are energetically more favourable than *atomic species* (for instance, incorporation energy of two interstitial atomic oxygens is 4.1 eV, whereas the incorporation energy of oxygen molecule is 2.1 eV, which also means that dissociation of interstitial oxygen molecule into two atomic species requires 2.0 eV of energy). This is a very general conclusion and does not depend on the position of the electron source since one can compare systems with the same number of oxygens and excess electrons.
- *Charged species*, with the assumption that electrons are available at the bottom of the conduction band or above, are energetically more favourable than the *neutral species* (compare the incorporation energies in Table 1). Charging can happen in circumstances which could be fairly common. There might be a dynamic limit if electron-tunnelling capture is slow.

Table 1
Properties of oxidising species in alpha-quartz

Species	Incorporation energy (eV)	Diffusion barrier along *c* (eV)	Diffusion barrier other axes (eV)	Electron affinity (eV)	Exchange with lattice
O_2	2.07	0.09		0.7	No
O_2^-	−0.5	0.57		−0.2	No
O_2^{2-}	−1.9	2.1		No affinity	No
O	2.03	1.30	1.42	−0.5	Yes
O^-	−0.7	0.19	0.60	−0.3	Yes
O^{2-}	−1.8	0.19		No affinity	Yes

- The mechanism of diffusion of atomic species will lead inevitably to oxygen exchange with the lattice, whereas diffusion of molecular species cannot easily lead to oxygen exchange with non-defective SiO_2 lattice.

4. Closing remarks

This work is a part of a broader programme on silicon oxide and its ultimate performance. In separate calculations, we are testing quartz as a mimic by modelling typical amorphous oxides. The preliminary results suggest that only properties of molecular species will be importantly different in amorphous structure (a lower incorporation energy, higher diffusion barrier). Other issues include the nature of the growing interface, the extent to which charged oxidising species explain some of the novel features of thin oxide and the ways in which charge end energy localisation can contribute to electrical breakdown.

Acknowledgements

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