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Charge state of the O_2 molecule during silicon oxidation through hybrid functional calculations

Audrius Alkauskas,[1,2] Peter Broqvist,[1,2] and Alfredo Pasquarello[1,2]
[1]*Ecole Polytechnique Fédérale de Lausanne (EPFL), Institute of Theoretical Physics, CH-1015 Lausanne, Switzerland*
[2]*Institut Romand de Recherche Numérique en Physique des Matériaux (IRRMA), CH-1015 Lausanne, Switzerland*

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We study the charge state of the diffusing O_2 molecule during silicon oxidation through hybrid functional calculations. We calculate charge-transition levels of O_2 in bulk SiO_2 and use theoretical band offsets to align these levels with respect to the Si band edges. To overcome the band-gap problem of semilocal density functionals, we employ hybrid functionals with both predefined and empirically adjusted mixing coefficients. We find that the charge-transition level $\varepsilon^{0/-}$ in bulk SiO_2 occurs at ~ 1.1 eV above the silicon conduction-band edge, implying that the O_2 molecule diffuses through the oxide in the neutral charge state. While interfacial effects concur to lower the charge-transition level, our estimates suggest that the neutral charge state persists until silicon oxidation.

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Determining the nature and origin of point defects at semiconductor-oxide interfaces is a major step in the development of electronic devices.[1] Since direct experimental characterization of interfaces is often difficult, simulation methods based on density-functional theory (DFT) are increasingly being used as an alternative tool for the investigation of atomic-scale properties. However, the study of defect levels within standard DFT schemes is still largely hindered by the well-known band-gap problem. Indeed, calculated band gaps and band offsets are generally severely underestimated and the alignment of defect levels with respect to the relevant band edges is consequently affected. A correct alignment is a prerequisite for understanding issues such as oxide charging,[2] defect passivation, Fermi-level pinning,[3] stress-induced leakage current,[4] and charge state of defects.

Silicon oxidation is a fundamental process in which charging issues are expected to play a key role.[5] Our understanding of this process relies to a large extent on the model proposed by Deal and Grove, in which oxide growth proceeds through the diffusion of the oxygen molecule across the oxide followed by its incorporation at the silicon substrate.[6] While supporting this general picture, DFT calculations have been instrumental to achieve an atomic scale description of various aspects of silicon oxidation, such as the diffusion mechanism,[7,8] the oxidation reaction,[9,10] the role of spin,[11] the layer-by-layer oxidation,[12,13] and the release of interstitial silicon.[14] However, the charge state of the O_2 molecule during the oxidation process has so far remained elusive. This is expected to determine the nature of the oxygen species occurring at the interface[15] and consequently the oxidation reaction and the atomic structure at the Si-SiO_2 interface.[5,9,16]

Experimental attempts to determine the charge state of the oxidizing molecule rest on the study of the oxide growth kinetics in applied electric fields, but result in conflicting conclusions.[17] It should further be noted that the interpretation of such measurements is not trivial because of the complexity of the underlying atomic processes.[7] Theoretical work based on gradient corrected DFT calculations concluded that the oxygen molecule diffuses through the oxide in a metastable neutral charge state, assuming the stable negatively charged state only in the vicinity of the substrate where electron tunneling can occur.[15] This leads to a description of silicon oxidation in which neutral and negatively charged oxygen species play competing roles.[15] This inference directly stems from the position of the charging level of the O_2 molecule relative to the silicon band edges. However, the theoretical determination of such an alignment is subject to the band-gap problem.

In this work, we determine the charge state of the O_2 molecule during silicon oxidation by locating its charge-transition level with respect to the relevant band edges at the Si-SiO_2 interface. To overcome the band-gap problem, we use hybrid density functionals which give enhanced band gaps compared to semilocal functionals.[18] Our results indicate that the neutral state of the oxygen molecule is thermodynamically most stable in bulk SiO_2 for electron chemical potentials lying in the Si band gap. In the vicinity of the substrate, the image-charge interactions and the higher oxide density concur to lower the charge-transition level. Nevertheless, our estimates of their effects suggest that the O_2 molecules preserve their neutral state until the onset of oxidation.

We considered the class of hybrid density functionals based on the generalized gradient approximation of Perdew, Burke, and Ernzerhof (PBE),[19] which are obtained by replacing a fraction α of PBE exchange with Hartree-Fock exchange. The functional defined by $\alpha=0.25$ is referred to as PBE0 and has received some support from theoretical considerations.[20] In our calculations, core-valence interactions were described through norm conserving pseudopotentials, and valence wave functions were expanded in a plane-wave basis set. The basis set is defined by an energy cutoff of 70 Ry. The pseudopotentials were generated at the PBE level and used in all calculations. The electronic-structure calculations corresponding to large supercells were performed with a Brillouin-zone sampling restricted to the Γ point. For bulk silicon, we determined the band edges using a converged k-point sampling. The integrable divergence of the Hartree-Fock exchange term was explicitly treated.[21] Structural relaxations were carried out at the PBE level. We used the QUANTUM ESPRESSO (Ref. 22) and CPMD (Ref. 23) codes.

For the Si-SiO_2 interface, we used a superlattice structure, in which a crystalline Si layer (nine monolayers) and an

TABLE I. Band gaps of Si (E_g^{Si}) and SiO$_2$ ($E_g^{\mathrm{SiO_2}}$), and valence (ΔE_v) and conduction (ΔE_c) band offsets at the Si-SiO$_2$ interface, calculated at the PBE level, at the PBE0 level, and through the use of the mixed scheme (Ref. 27). The experimental values are taken from Ref. 28.

	E_g^{Si}	$E_g^{\mathrm{SiO_2}}$	ΔE_v	ΔE_c
PBE	0.6	5.4	2.5	2.3
PBE0	1.8	7.9	3.3	2.8
Mixed	1.1	8.9	4.4	3.4
Expt.	1.1	8.9	4.4	3.4

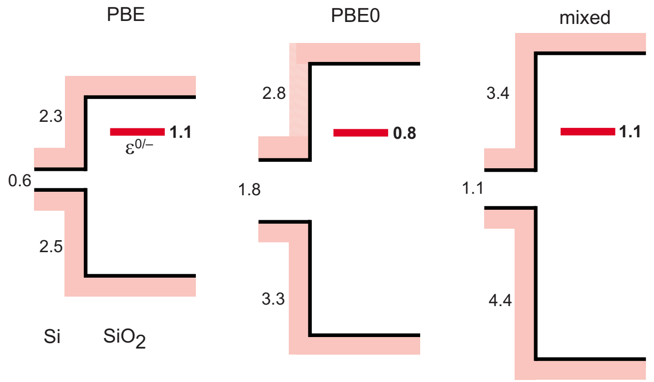

FIG. 1. (Color online) Charge-transition level $\varepsilon^{0/-}$ of the interstitial O$_2$ molecule in bulk SiO$_2$ aligned with respect to the Si band edges, as calculated through the PBE, the PBE0, and the mixed scheme. Values in bold give the position of $\varepsilon^{0/-}$ relative to the Si conduction-band edge. Other values correspond to the Si band gap, the valence-band offset, and the conduction-band offset. Energies are given in eV.

amorphous SiO$_2$ layer (~17 Å) are periodically repeated.[24] The interface structure was designed to incorporate a set of atomic-scale features inferred from experimental data.[25] The simulation cell in the transverse directions corresponds to a $\sqrt{8}\times\sqrt{8}$ Si(100) interface unit. The model contains 131 Si atoms and 86 O atoms. For bulk amorphous SiO$_2$, we used a disordered 72-atom model structure obtained previously.[26]

First, we addressed the band alignment at the interface, as detailed in Ref. 27. Band gaps calculated at the PBE0 level are generally larger than the PBE values, but the agreement with experiment is not systematically improved (Table I). We determined band offsets by aligning bulk band extrema through a local reference level determined in the interface calculation.[27] For crystalline Si, we took the average electrostatic potential as reference, but used the semicore O 2*s* levels for amorphous SiO$_2$ to overcome the difficulties associated with the structural disorder. As seen in Table I, the valence and conduction-band offsets calculated at the PBE level underestimate the experimental results by about 2 and 1 eV, respectively. The use of PBE0 reduces these discrepancies by a factor of 2. To achieve a better description of the band alignment, we also considered a mixed scheme in which, for each interface component, we tuned the Hartree-Fock exchange fraction α to reproduce the experimental band gap.[27] This resulted in $\alpha=0.11$ for Si and $\alpha=0.34$ for SiO$_2$. The consistency of this scheme stems from the weak dependence of the interfacial dipoles on α.[27] The band offsets obtained in the mixed scheme show excellent agreement with experiment (Table I).

Second, we determined the relevant charge-transition level between the neutral and the negatively charged state of the interstitial O$_2$ in bulk SiO$_2$.[15,29] The neutral O$_2$ is repelled by the oxide network and is found at the center of interstitial voids.[7] To account for the structural disorder in SiO$_2$, we considered ten different interstitial configurations corresponding to representative local minima of the diffusion path.[7] The O$_2^-$ attaches to the oxide network by forming a bond to a Si atom.[15,29] Our study comprises 12 of such atomic configurations. Formations energies of the oxygen molecule in its charge state q were determined as a function of electron chemical potential[30]

$$E_f^q(\mu)=E_{\mathrm{tot}}^q-E_{\mathrm{tot}}^{\mathrm{SiO_2}}-E_{\mathrm{tot}}^{\mathrm{O_2}}+q(\varepsilon_v+\mu+\Delta V), \qquad (1)$$

where E_{tot}^q, $E_{\mathrm{tot}}^{\mathrm{SiO_2}}$, and $E_{\mathrm{tot}}^{\mathrm{O_2}}$ are the total energies of the defect cell, of the bulk oxide, and of the isolated oxygen molecule, respectively. The electron chemical potential μ is referred to the top of the SiO$_2$ valence band ε_v, and ΔV is the correction needed to align the electrostatic potential far from the defect to that in the unperturbed bulk (0.15 eV in our case). The total energies of the negatively charged species were corrected for the spurious interaction due to the periodic boundary conditions.[31] We set the charge-transition level $\varepsilon^{0/-}$ in correspondence of the value of the electron chemical potential for which the average formation energies of the neutral and the negatively charged oxygen species are equal.[32] Our PBE calculations yielded $\varepsilon^{0/-}$ at 4.2 eV from the valence-band edge, in accord with previous results obtained with gradient-corrected functionals.[7,15] At the PBE0 level, $\varepsilon^{0/-}$ lies at 6.1 eV from the respective valence-band maximum. In addition, we used a hybrid functional with $\alpha=0.34$ in order to reproduce the SiO$_2$ band gap and obtained $\varepsilon^{0/-}$ at 6.6 eV from the corresponding valence-band maximum. The empirical adjustment of α is consistent with the mixed scheme for the band offsets.[27] Furthermore, charge-transition levels of the Si dangling bond obtained through such an adjustment of the band gap were found to agree with experiment within 0.06 eV,[33] lending support to this procedure.

Third, we consistently aligned the calculated charge-transition levels to the Si band edges through the theoretical band offsets within each of the three considered schemes. The resulting alignment is shown in Fig. 1. The three schemes give a similar picture, situating $\varepsilon^{0/-}$ between 0.8 and 1.1 eV above the Si conduction-band minimum. Since the Fermi level at the Si-SiO$_2$ interface falls within the Si band gap, this result provides convincing evidence that the diffusing O$_2$ molecule is thermodynamically most stable in its neutral charge state.

We emphasize that this conclusion is naturally drawn provided the band offsets and the charge-transition levels are calculated within the *same* theoretical scheme. For instance, the use of $\varepsilon^{0/-}$ calculated at the PBE level in combination with experimental offsets gives a charge-transition level falling below the valence-band maximum, leading to a qualitatively different description.[15] Such an alignment scheme as-

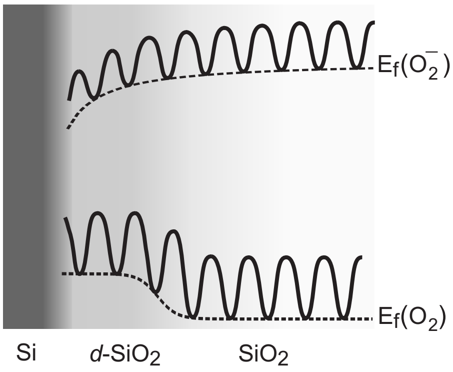

FIG. 2. Schematic representation of formation energies of the neutral (bottom) and negatively charged (top) O_2 molecule near the Si-SiO_2 interface as function of distance to the Si substrate. *d*-SiO_2 and SiO_2 represent the densified and the normal oxide, respectively. The wavy lines pictorially represent the potential energy along the diffusion path.

sumes that the position of the charge-transition level with respect to valence-band maximum is already well described in the semilocal DFT calculation. However, this is generally not the case. An improved description of the band gap results in significant shifts of both the valence and the conduction bands when referred to a reference potential external to the electron system.[34,35] At variance, charge-transition levels of localized impurities remain largely unaffected.[34] This property suggests yet another alignment scheme not relying on the use of hybrid functionals. Assuming that the charge-transition level calculated at the PBE level does not shift, we first determined valence-band corrections relying on recent *GW* (−1.8 eV) and quasiparticle self-consistent *GW* (−2.8 eV) calculations.[35] The respective $\varepsilon^{0/-}$ levels are found at 0.5 and 1.5 eV above the silicon conduction-band edge when aligned through experimental band offsets. This provides further support for the results in Fig. 1.

When the diffusing oxygen molecule approaches the Si substrate, two different interfacial effects acting on the neutral and the negatively charged O_2 molecule need to be considered. X-ray reflectivity measurements indicate the occurrence of a densified interfacial oxide, showing a density of 2.4 g/cm^3 and extending over a distance of about 10 Å.[36] The occurrence of a densified oxide affects the incorporation energy of the neutral O_2 molecule which depends on the size of interstitial voids.[7] Consequently, the average formation energy of neutral O_2 in the densified oxide increases by 0.6 eV.[7,37] This picture is confirmed by both selected calculations on our interface model and recent results in the literature.[13,38] Figure 2 schematically illustrates this effect showing the evolution of the formation energy of the neutral O_2 as it approaches the interface. In the following, we express the correction with respect to the bulk formation energy as $\Delta E^0(z)$, where z is the distance to the substrate.

The formation energy of the negatively charged oxygen molecule mainly results from the formation of a bond with a Si atom of the oxide network and is therefore not very sensitive to the modified structural properties of the near-interface oxide. However, as the negatively charged species approaches the silicon substrate, it undergoes stabilization because of the image-charge interaction arising from the dielectric discontinuity at the interface. From classical electrostatics, the stabilization energy reads

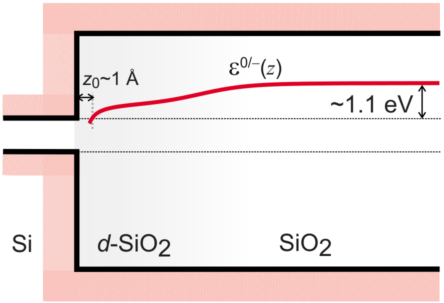

FIG. 3. (Color online) Evolution of the charge-transition level $\varepsilon^{0/-}$ for the interstitial O_2 molecule as a function of distance z to Si substrate. The charge-transition level drops below the Si conduction-band minimum at a distance $z_0 \approx 1$ Å. We used $\varepsilon_{Si} = 12$ and $\varepsilon_{SiO_2} = 4$. The densified oxide (*d*-SiO_2, shaded) extends over ~10 Å, beyond which the oxide (SiO_2) recovers its normal density.

$$\Delta E^-(z) = -\frac{1}{4z\varepsilon_{SiO_2}}\left(\frac{\varepsilon_{Si} - \varepsilon_{SiO_2}}{\varepsilon_{Si} + \varepsilon_{SiO_2}}\right), \tag{2}$$

where ε_{Si} and ε_{SiO_2} are the static dielectric constants of Si and SiO_2, respectively. This effect is also illustrated in Fig. 2.

As a consequence of the two effects discussed above, the charge transition-level also evolves as the O_2 molecule approaches the interface

$$\varepsilon^{0/-}(z) = \varepsilon^{0/-}_{bulk} - \Delta E^0(z) + \Delta E^-(z), \tag{3}$$

where $\varepsilon^{0/-}_{bulk}$ corresponds to the charge-transition level in bulk SiO_2. We remark that both effects concur to lower $\varepsilon^{0/-}$. To provide a quantitative estimate, we adopted for $\varepsilon^{0/-}_{bulk}$ the position determined within the mixed scheme, viz. at 1.1 eV above the silicon conduction-band minimum. The resulting evolution of $\varepsilon^{0/-}(z)$ is shown in Fig. 3. We found that the charge-transition level lies above the Si conduction-band edge as long as the distance of the O_2 to the Si substrate exceeds ~1 Å.[39] At this small distance the oxidation reaction is already under way,[9] suggesting that the negatively charged oxygen molecule plays only a minor role during silicon oxidation. The presence of charged oxygen species had previously been invoked to explain the growth kinetics in the thin-oxide regime.[15] However, alternative mechanisms based on a spatially varying diffusion rate do not require the charging of the diffusing O_2 molecule.[9,40] In the present picture, the neutral O_2 interstitial is the dominating oxidizing agent. Other oxygen species can only occur upon the reaction of O_2 with Si-Si bonds.[9]

In conclusion, we addressed the charge state of the O_2 molecule during silicon oxidation overcoming the band-gap problem through a scheme based on hybrid density functionals. The oxygen molecule is found to diffuse in its neutral charge state until the onset of oxidation. More generally, the defect level alignment scheme proposed in this work is expected to be very useful for addressing charging issues associated to defects at interfaces.

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