Charge state of the \( \text{O}_2 \) molecule during silicon oxidation through hybrid functional calculations

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We study the charge state of the diffusing \( \text{O}_2 \) molecule during silicon oxidation through hybrid functional calculations. We calculate charge transition levels of \( \text{O}_2 \) in bulk \( \text{SiO}_2 \) 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 \( \varepsilon_{0/1}^0 \) in bulk \( \text{SiO}_2 \) occurs at \( \sim \)1.1 eV above the silicon conduction band edge, implying that the \( \text{O}_2 \) 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,\(^4\) charge state of defects, etc.

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 \( \text{O}_2 \) molecule during the oxidation process has so far remained elusive. This is expected to determine the nature of the oxygen species occurring at the interfaces 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.\(^15\) It should further be noted that the interpretation of such measurements is not trivial because of the complexity of the underlying atomic processes.\(^16\) 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.\(^16\) 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 \( \text{O}_2 \) 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 \( \text{O}_2 \) 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 \( \text{SiO}_2 \) 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 \( \text{O}_2 \) 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 \( \alpha \) 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. Structural relaxations were carried out at the PBE level.

For the Si-SiO$_2$ interface, we used a superlattice structure, in which a crystalline Si layer (9 monolayers) and an amorphous SiO$_2$ layer (~17 Å) are periodically repeated. The interface structure was designed to incorporate a set of atomic-scale features inferred from experimental data. 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.

First, we addressed the band alignment at the interface, as detailed in Ref. 22. 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. For crystalline Si, we took the average electrostatic potential as reference, but used the semicore O 2s 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. This resulted in α = 0.11 for Si and α = 0.34 for SiO$_2$. The consistency of this scheme stems from the weak dependence of the interfacial dipoles on α. 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$_2$. The neutral O$_2$ is repelled by the oxide network and is found at the center of interstitial voids. To account for the structural disorder in SiO$_2$, we considered 10 different interstitial configurations corresponding to representative local minima of the diffusion path. The O$_2$ attaches to the oxide network by forming a bond to a Si atom. 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 $\epsilon$:

$$E_q^g(\mu) = E_q^{\text{tot}} - E_{\text{tot}}^{\text{SiO}_2} - E_{\text{tot}}^{\text{O}_2} + q(\epsilon_v + \mu + \Delta V),$$

where $E_q^{\text{tot}}, E_{\text{tot}}^{\text{SiO}_2},$ and $E_{\text{tot}}^{\text{O}_2}$ are the total energies of the defect cell, of the bulk oxide, and of the isolated oxygen molecule, respectively. The electron chemical potential $\mu$ is referred to the top of the SiO$_2$ valence band $\epsilon_v$, and $\Delta V$ 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. We set the charge transition level $\epsilon^{0/-}$ 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. Our PBE calculations yielded $\epsilon^{0/-}$ at 4.2 eV from the valence band edge, in accord with previous results obtained with gradient-corrected functionals. At the PBE0 level, $\epsilon^{0/-}$ 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 $\epsilon^{0/-}$ at 6.6 eV from the corresponding valence band maximum. The empirical adjustment of $\alpha$ is consistent with the mixed scheme for the band offsets. 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 lending support to this procedure.

Third, we consistently aligned the calculated charge

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**TABLE I: Band gaps of Si ($E_{g}^{\text{Si}}$) and SiO$_2$ ($E_{g}^{\text{SiO}_2}$), and valence ($\Delta E_v$) and conduction ($\Delta E_c$) 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. 23.**

|           | $E_{g}^{\text{Si}}$ | $E_{g}^{\text{SiO}_2}$ | $\Delta E_v$ | $\Delta E_c$ |
|-----------|-------------------|-----------------------|--------------|--------------|
| 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          |

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**FIG. 1:** (Color online) Charge transition level $\epsilon^{0/-}$ 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 $\epsilon^{0/-}$ 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.
three schemes give a similar picture, situating
schemes. The resulting alignment is shown in Fig. 1. The
oretical band offsets within each of the three considered
ertical oxide, respectively. The wavy lines pictorially rep
the potential energy along the diffusion path.

transition levels to the Si band edges through the theo-
etical band offsets within each of the three considered
mes. The three schemes give a similar picture, situating \( \varepsilon^{0/-} \) bet-
0.8 and 1.1 eV above the Si conduction band min-
ince the Fermi level at the Si-SiO\(_2\) interface falls
Si band gap, this result provides convincing evi-
dence that the diffusing O\(_2\) molecule is thermody-
nically most stable in its neutral charge state.

We emphasize that this conclusion is naturally drawn
provided the band offsets and the charge transition lev-
els 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. Such
an alignment scheme assumes that the position of the
charge transition level with respect to valence band max-
imum is already well described in the semilocal DFT cal-
culation. However, this is generally not the case. An
proved description of the band gap results in signif-
icant shifts of both the valence and the conduction bands
when referred to a reference potential external to the
electron system. At variance, charge transition levels
of localized impurities remain largely unaffected. This
property suggests yet another alignment scheme not re-
ylying 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 correc-
tions relying on recent \( GW \) (−1.8 eV) and quasiparticle
selfconsistent \( GW \) (−2.8 eV) calculations. The respec-
tive \( \varepsilon^{0/-} \) levels are found at 0.5 eV 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. The occurrence of a densified oxide af-
facts the incorporation energy of the neutral O\(_2\) molecule
which depends on the size of interstitial voids. Conse-
quently, the average formation energy of neutral O\(_2\) in
the densified oxide increases by 0.6 eV. This picture is
confirmed by both selected calculations on our interface
model and recent results in the literature. Figure 2
schematically illustrates this effect showing the evolu-
tion of the formation energy of the neutral O\(_2\) molecule
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 oxy-
gen 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 sta-
bilization because of the image-charge interaction arising
from the dielectric discontinuity at the interface. From
classical electrostatics, the stabilization energy reads

\[
\Delta E^-(z) = -\frac{1}{4\varepsilon} \left( \frac{\varepsilon_{Si} - \varepsilon_{SiO_2}}{\varepsilon_{Si} + \varepsilon_{SiO_2}} \right),
\]

where \( \varepsilon_{Si} \) and \( \varepsilon_{SiO_2} \) 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

![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.](image)

![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 \( \sim 10 \) Å, beyond which the oxide (SiO\(_2\)) recovers its normal density.](image)
approaches the interface:

\[ \varepsilon_{\mathrm{0}^-}(z) = \varepsilon_{\mathrm{0}^-}^{\mathrm{bulk}} - \Delta E^0(z) + \Delta E^-(z), \]

where \( \varepsilon_{\mathrm{0}^-}^{\mathrm{bulk}} \) corresponds to the charge transition level in bulk SiO\(_2\). We remark that both effects concur to lower \( \varepsilon_{\mathrm{0}^-}^{\mathrm{bulk}} \). To provide a quantitative estimate, we adopted for \( \varepsilon_{\mathrm{0}^-}^{\mathrm{bulk}} \) the position determined within the mixed scheme, viz. at 1.1 eV above the silicon conduction band minimum. The resulting evolution of \( \varepsilon_{\mathrm{0}^-}(z) \) 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\(^9\). At this small distance the oxidation reaction is already under way\(^2\) 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.\(^{24,40}\) 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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