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Oxygen vacancy levels and electron transport in Al$_2$O$_3$

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The energy levels of the oxygen vacancy in $\alpha$- and $\theta$-Al$_2$O$_3$ were calculated using the screened exchange hybrid functional, and explain the electron hopping and trapping levels seen in deposited Al$_2$O$_3$ at $\sim$1.8 eV below its conduction band edge. The vacancy supports five accessible charge states, from 2+ to 2−. Electron hopping corresponds to the 0/− level, which lies 1.8 eV below the conduction band edge in $\theta$-Al$_2$O$_3$. This level lies much deeper than it does HfO$_2$. The +/0 level lies at 2.8 eV above oxide valence band in $\theta$-Al$_2$O$_3$ and thus below the Si valence band top. © 2010 American Institute of Physics. [doi:10.1063/1.3293440]

Al$_2$O$_3$ is an important dielectric, ceramic and catalyst. Amorphous Al$_2$O$_3$ is being considered as an alternative interpolydielectric in floating gate nonvolatile memories, due to its large band gap, low leakage current, and dielectric constant.\textsuperscript{[3]} It is used in metal gate complementary metal oxide devices as a dipole layer to shift the flatband voltage for p-type metal oxide semiconductor (PMOS) transistors.\textsuperscript{[4]} These applications require a knowledge of its electronic defect levels in order to explain its transport and charge trapping properties.\textsuperscript{[5–8]} Electron transport in Al$_2$O$_3$ is consistent with Poole–Frenkel hopping in a deep state lying at $\sim$1.8 eV below the conduction band (CB) edge. The main intrinsic defect in high dielectric constant oxides is the oxygen vacancy\textsuperscript{[9,10]} and Al$_2$O$_3$ is expected to be similar. Previous calculations of the O vacancy in Al$_2$O$_3$ have found energy levels at or below midgap.\textsuperscript{[11–15]} However, none find a deep level in the upper gap, which would account for the observed transport properties. In addition, most previous calculations used the local density approximation (LDA) which underestimates the band gap and makes predictions of defect levels unreliable. Here, we calculate the energy levels of the O vacancy in two different phases of Al$_2$O$_3$ using methods which require no band gap correction, and find that the 0/− state lies at 1.8 eV below $E_c$, which would account for its transport and trapping properties. We also find that the +/0 level lies proportionately much lower in the gap than in other high K oxides such as HfO$_2$, lying below the Si VB energy.

Our calculations use the CASTEP plane-wave pseudopotential total energy code.\textsuperscript{[16]} The LDA is often used to calculate the electron exchange correlation energy. To circumvent the band-gap problem of the LDA, we use here the screened exchange (sX) method, a hybrid functional, to correct this error.\textsuperscript{[17–19]} The sX functional replaces all the LDA exchange with a Thomas–Fermi screened Coulombic exchange potential. We use generalized gradient approximation (GGA) for initial studies of the defect and then use sX for the final geometry relaxations and the total energy values, spin-polarized where relevant. We use ultrasoft pseudopotentials for the GGA calculations with a plane-wave cut-off energy of 380 eV, and we use norm-conserving pseudopotentials for the sX calculation with a 800 eV cutoff. This converges total energy differences to better than 1 meV/atom. Brillouin zone integrations use a Monkhorst–Pack k-point mesh with a grid that converges energies to similar accuracy. Geometry optimizations used a self-consistent minimization scheme and Hellmann–Feynman forces, and are converged when forces are $<0.04$ eV/Å. The defect calculations correct for finite cell effects and band filling.

Al$_2$O$_3$ has a number of phases. The most stable phase is the hexagonal $\alpha$-Al$_2$O$_3$ phase (corundum and sapphire) with density 4.0 gm/cm$^3$ in which the Al site is sixfold coordinated and O is fourfold coordinated and has a band gap of 8.8 eV.\textsuperscript{[20]} An important phase for catalysis is the cubic $\gamma$-Al$_2$O$_3$.\textsuperscript{[21]} Vapor deposition of Al$_2$O$_3$ produces an amorphous phase with a much lower density (3.1–3.3 gm/cm$^3$) than sapphire. It also has a much lower band gap of about 6.2–6.5 eV.\textsuperscript{[22,23]} Diffraction experiments\textsuperscript{[24,25]} and molecular dynamic simulations\textsuperscript{[26,27]} show that this phase has lower atomic co-ordinations than corundum, with the Al coordination closer to 4 and O coordination closer to 2.67. We previously modeled this phase\textsuperscript{[28]} using monoclinic $\theta$-Al$_2$O$_3$ based on the $\beta$-Ga$_2$O$_3$ structure.\textsuperscript{[29]} It has both sixfold and fourfold Al sites and both three and twofold oxygen sites.

Figure 1(a) shows the band structure of bulk $\alpha$-Al$_2$O$_3$ as calculated using the sX method. The minimum gap is direct and is 8.7 eV, compared to the experimental value of 8.8 eV.\textsuperscript{[20]} The upper VB consists of high effective mass O 2p states, and the CB minimum consists of Al s states.

Figure 1(b) shows the bulk band structure of $\theta$-Al$_2$O$_3$. Its GGA band gap is 5.35 eV, and 6.58 eV in sX, compared to 6.2–6.5 eV experimentally.\textsuperscript{[22,23]} Its band offsets to Si were calculated by constructing an interface to Si and it gives a CB offset of 1.9 eV. This compares to a CB offset of 2.0 eV found by internal photoemission\textsuperscript{[25]} and 2.4 eV by photoemission\textsuperscript{[23]} for amorphous Al$_2$O$_3$. It compares with the much larger CB offset of 2.8 eV for $\alpha$-Al$_2$O$_3$.\textsuperscript{[30,31]}

The oxygen vacancy is expected to be the most important defect in Al$_2$O$_3$, as in other high K oxides. The defect calculations were carried out using a 120 atom supercell, whose size is fixed at that of the defect-free cell, and the defect created. The internal geometry is relaxed within sX with a single special k-point (1/4,1/4,1/3) for Brillouin zone integrations. This converges quantities faster than Γ.

The total energy ($E_{\text{tot}}$) is calculated for the defect cell of charge $q$, for the perfect cell ($E_{\text{p}}$) of charge $q$, and for a perfect cell of charge 0. This allows us to calculate the defect

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formation energy, $H_q$, as a function of the Fermi energy ($\Delta E_F$) from the VB edge $E_v$ and relative chemical potential ($\Delta \mu$) of element $\alpha$.

$$H_q(E_F, \mu) = [E_q - E_H] + q(E_v + \Delta E_F) + \sum_{\alpha} n_\alpha (\mu_\alpha + \Delta \mu_\alpha),$$

where $qE_v$ is the change in Fermi energy when charge $q$ is added and $n_\alpha$ is the number of atoms of species $\alpha$. The corrections for the background charge, finite cell size, band filling, etc., are included.\(^{32}\) The oxygen chemical potential ($\mu(O)$) is referred to that of the O$_2$ molecule, taken as zero, which is the O-rich limit. The O-poor limit, the Al–Al$_2$O$_3$ equilibrium, corresponds to $\mu(O) = -5.8$ eV [Fig. 2].

The neutral vacancy creates one gap state of $A_1$ symmetry, which is doubly occupied for $V^0$. In $\alpha$-Al$_2$O$_3$ its 0/+ level lies at 3.5 eV above the VB edge $E_v$ in sX, well below midgap. Using the VB offset of Si:$\alpha$-Al$_2$O$_3$ of 4.8 eV,\(^{31}\) this means that the vacancy level lies well below $E_v$ of Si. This is an important result; the vacancy level lies 0.9 eV below midgap in $\alpha$-Al$_2$O$_3$, unlike in HfO$_2$ where it is typically at the Si CB.\(^7\)

The calculated wave function of the $A_1$ state in Fig. 3(a) shows that it is symmetric and strongly localized in the vacancy. A second state of $V^0$ is seen, essentially at the CB edge. This is the $T_2$ vacancy state, and it is empty for $V^0$. In a defect molecule picture, the four Al ions adjacent to the vacancy supply four hybrid orbitals pointing into the vacancy, Fig. 3(c). The $A_1$ gap state is the symmetric combination of these hybrids, and the $T_2$ state is the triply-degenerate antisymmetric combination, as seen from its charge density in Fig. 3(b). This $T_2$ is also highly localized in the vacancy.

Occupyin g a $T_2$ state with one electron gives $V^-$. There is an asymmetric distortion which splits the triply degeneracy [Fig. 3(c)] and this pulls down one $T_2$ state into the gap. The 0/- level is calculated to lie at 6.35 eV above $E_v$, or 2.4 eV below $E_c$. The $-1/2$-state is calculated to lie at +7.35 eV above $E_c$. This is well below $E_c$. The important point is that a state that lies close to $E_c$ for $V^0$ now becomes a deep state for $V^-$ in the sX method.

Similar vacancy calculations are carried out for the low-density $\theta$-Al$_2$O$_3$ phase. There are two types of oxygen vacancy, at threefold and twofold sites. We calculate that the 0/+ level lies at around 2.8 eV above oxide VB edge in sX. Including the band offset, this is below the $E_v$ of Si. The 0/- level is calculated to lie at 4.8 eV above $E_v$, that is 1.7 eV below the CB edge. The $-1/2$-transition level is also found in the gap.

![Fig. 1](image1.png)  
**FIG. 1.** Band structure of (a) $\alpha$-Al$_2$O$_3$ and (b) $\theta$-Al$_2$O$_3$ in sX.

![Fig. 2](image2.png)  
**FIG. 2.** (Color online) Formation energies of O vacancies in (a) $\alpha$-Al$_2$O$_3$ and (b) $\theta$-Al$_2$O$_3$ for $\mu(O)=0$. The Al–Al$_2$O$_3$ equilibrium is at $\mu(O)=-5.8$ eV.

![Fig. 3](image3.png)  
**FIG. 3.** (Color online) Charge density plots of the $A_1$ and $T_2$ states of $V^0$ of $\alpha$-Al$_2$O$_3$. (c) vacancy level splittings for each charge state.
For both phases, the Al ions adjacent to the vacancy relax away from the vacancy for V$^+$ and V$^{2+}$, and toward the vacancy for V$^-$. This relaxation shifts the transition levels from their energy in the unrelaxed vacancy. However, the shift is not large enough to convert the center into a negative U; all its five charge states are stable in turn as the Fermi vacancy for V$^-$. This relaxation shifts the transition levels posited Al$_2$O$_3$. The calculated 0/ level of the oxygen vacancy of θ-Al$_2$O$_3$ was found experimentally. Despite the fact that oxygen is electronegative, and trapping level of at 1.6–2.0 eV below the CB edge found originally noted that there was “Fermi level pinning” of Si. This trapping level much lies deeper in Al$_2$O$_3$ at 1.8 eV compared to 0.4 eV in HfO$_2$, as summarized in Fig. 4. The transport path is therefore deeper in Al$_2$O$_3$ than it is in HfO$_2$. This is found experimentally. This is advantageous for its use in Flash memories.

The second point is the energy of the +/0 level. It was originally noted that there was “Fermi level pinning” of polycrystalline silicon or high work function metal gates on HfO$_2$ toward the upper band gap. In contrast, on Al$_2$O$_3$ there was pinning toward the VB. There have been various ideas about its cause. Shiraishi et al. proposed that in HfO$_2$ it arises from the spontaneous creation of O vacancies adjacent to the p-type poly-Si gate. Because the O vacancy 0/+ level in HfO$_2$ lies well above the Si VB energy, the vacancy ionizes to V$^{2+}$ due to charge transfer to the Si acceptors, and this causes an upwards band-bending. The vacancy level of most other high K oxides also lies above the Si VB only in Al$_2$O$_3$ does this level lie below the Si VB edge, so it does not ionize, so there is much less driving force to create such vacancies. On the other hand, an O interstitial has accessible states below $E_C$, so electrons can fall from the poly-Si VB into the interstitial states, making them negative I$^{2-}$, and causing a downwards band-bending. This mechanism was supported by a calculation of an interface between Si and an Al$_2$O$_3$ network.

In summary, we calculated the vacancy formation energies and energy levels using the sX hybrid functional. We identify the −/0 level as the cause of trapping and hopping, and this level lies much deeper than it does in HfO$_2$.