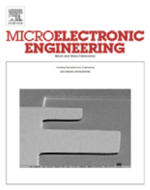
Microelectronic Engineering 86 (2009) 1668–1671

Contents lists available at ScienceDirect

Microelectronic Engineering

journal homepage: www.elsevier.com/locate/mee



Oxygen vacancy levels and interfaces of Al_2O_3

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ARTICLE INFO

Article history:
Received 25 February 2009
Received in revised form 2 March 2009
Accepted 2 March 2009
Available online 10 March 2009

Keywords:
Aluminium oxide
Defects
Electronic structure calculations
High dielectric constant

ABSTRACT

We have calculated the oxygen vacancy levels in Al_2O_3 using first principles methods. They are found to lie just below midgap in the oxide, equivalent to below the Si valence band edge when aligned to the silicon band structure. This low energy accounts for the behaviour of Al_2O_3 in oxide capping layers and as an insulator in future Flash memory.

1. Introduction

Al_2O_3 is a widely used ceramic and catalyst support material. Amorphous Al_2O_3 has been the main insulator in read–write heads for magnetic storage disks. Al_2O_3 is also an alternative dielectric for complementary metal oxide (CMOS) gate stacks, but its dielectric constant (K) of ~11 is smaller than for HfO_2. It is of interest in logic transistors because it remains amorphous to high temperatures like SiO_2. It is also used as a capping layer to give p-type flat band voltages [1,2]. It is being considered for use as an inter-poly dielectric in future Flash memories, where its wide band gap is of interest [3,4]. These applications require knowledge of its band offsets and defect energy levels, the subject of this paper.

2. Methods

Our calculations use the CASTEP pseudopotential total energy code [5], with the generalized gradient approximation (GGA) for the electron exchange correlation energy. GGA under-estimates the band gap so we also use the screened exchange (sX) or the weighted density approximation (WDA) to correct this error [6,7]. We have used ultra-soft pseudopotentials for the GGA and WDA calculations, with a plane-wave cut-off energy of 380 eV. For the screened exchange calculation, norm-conserving pseudopotentials are used and the cutoff of 800 eV.

3. Structure of amorphous Al_2O_3

Al_2O_3 has a number of phases. The most stable phase is the hexagonal α-Al_2O_3 phase (corundum, sapphire) in which Al site is sixfold co-ordinated and O is fourfold co-ordinated. It has a band gap of 8.8 eV. Another important phase is γ-Al_2O_3 which is cubic and used as a catalyst. Vapour deposition of Al_2O_3 results in an amorphous phase with a lower density (3.1–3.3 gm/cm^3) than sapphire (4.0 gm/cm^3). It also has a much lower band gap. X-ray and neutron diffraction experiments [8–11] and molecular dynamic simulations [12,13] show that the lower density phase has lower atomic co-ordinations than corundum, with the Al co-ordination closer to 4 and O coordination closer to 2.67.

To simplify calculations, we have created a periodic model of the low-density phase, which is based on the structure of monoclinic β-Ga_2O_3, as shown in Fig. 1. It has a 20 atom unit cell, or 10 atoms in the primitive cell. It has both sixfold and fourfold Al sites and both threefold and twofold oxygen sites.

4. Bulk electronic structure

Fig. 2a shows the band structure of bulk α-Al_2O_3 as calculated using the screened exchange method. The minimum gap is direct and is 8.7 eV, compared to the experimental value of 8.8 eV [14]. The upper valence band consists of O 2p lone pair states, and the conduction band minimum consists of Al s states.

Fig. 2b shows the bulk band structure of Al_2O_3 in the β-Ga_2O_3 form. Its GGA band gap is 5.35 eV, and 6.3 eV in sX approximation. Its band offsets to Si have been calculated by constructing an interface to Si and it gives a conduction band (CB) offset of 1.4 eV. This compares well with experimental band offset found by internal

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doi:10.1016/j.mee.2009.03.011

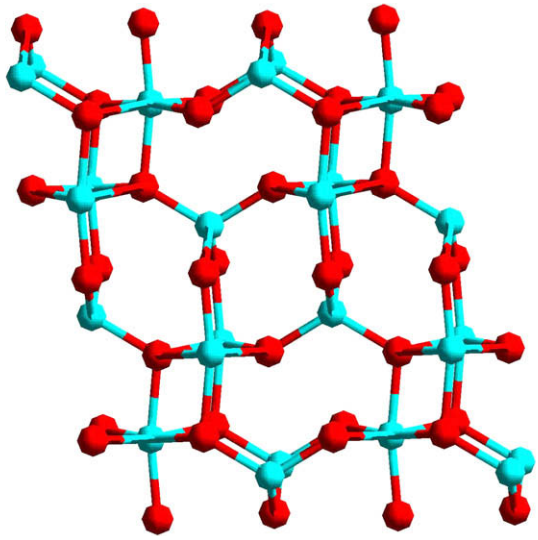

Fig. 1. Unit cell of Al_2O_3 in β-Ga_2O_3 structure.

photoemission by Afanasev [15,16] for amorphous Al_2O_3, It compares with the much larger CB offset of 3.1 eV for α-Al_2O_3 found both experimentally and theoretically [17,18]. Thus the reduction in density causes a lower band gap and a lower CB offset, and this accounts for the lower band gap and band offsets found for Al_2O_3 used in gate stacks.

5. Oxygen vacancy

The oxygen vacancy is expected to be the most important defect, as in other high *K* oxides. The oxygen vacancy has been studied many times previously as a 'colour centre'. We first calculated the O vacancy in α-Al_2O_3 using a 120 atom supercell, with a one *k*-point mesh, $k = (1/4, 1/4, 1/3)$. An O atom was removed and the atomic positions were relaxed in GGA. The neutral vacancy creates one gap state of A_1 symmetry, which is doubly occupied for V^0. This level lies at 2.4 eV above the valence band edge E_v in GGA, slightly below midgap. This is re-calculated using the sX function but with the GGA geometry, and the level lies at 3.9 eV above the oxide valence band (VB) edge or 4.8 eV below the CB. This is seen in the calculated local density of states Fig. 3a. Using the conduction band offset of Si:Al_2O_3 of 3.1 eV, this means that the vacancy level lies below the E_v of Si. This is an important result, the vacancy level lies slightly below midgap in α-Al_2O_3, unlike in HfO_2 where it is typically at the CB of Si [4]. It is noted that previous GGA calculations [19,20] also found that the eigenvalue lay below midgap.

The calculated wavefunction of the A_1 state in Fig. 4a shows that it is strongly localized. A second strongly localized vacancy state is also found in the density of states at 9.0 eV in Fig. 3a, essentially at the CB edge. This is the T_2 state of the vacancy, and is empty. In a defect molecule picture, which is perhaps not really valid for such an ionic solid, the four Al ions adjacent to the vacancy supply 4 hybrid orbitals pointing into the vacancy region. The A_1 gap state is the symmetric combination of them and the T_2 state is the triply degenerate anti-symmetric combination of them, Fig. 4(b).

The O vacancy can exist in all five charged states in Al_2O_3, from −2 to +2. In the +2 state, the A_1 level is empty. For this condition, the gap state rises to 4.5 eV in Fig. 3b, due to the outward relaxation of the adjacent Al^{3+} ions. For the +1 state, the A_1 level is half-filled and the relaxation is less than for the +2 state. The states are summarized in Fig. 5a.

Despite O being electronegative, the O vacancy also supports a V^{2-} configuration. This results in two gap states. In this V^{2-} configuration, the vacancy distorts to split the T_2 level degeneracy and the electrons occupy one of these levels. This results in two gap states, as seen in Fig. 5. The Al^{3+} ions relax towards the vacancy for the negative vacancy. Fig. 5a summarizes the different charge states.

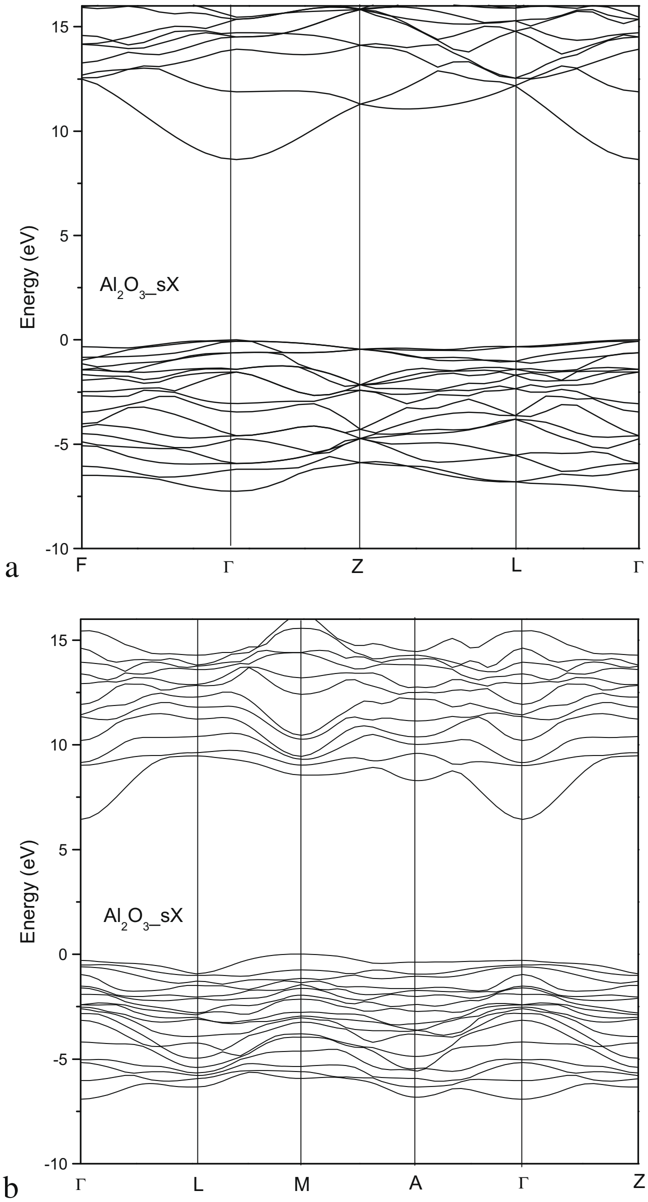

Fig. 2. Band structure of (a) α-Al_2O_3 and (b) the low density phase, in screened exchange.

We now consider the vacancy states in the β-Al_2O_3 structure. There are two types of vacancy, at threefold and twofold sites. For these we calculate that the states of the neutral vacancy lie at around 2.3 eV above oxide VB edge in GGA. In sX we find that they lie at about 3.0 eV above VB. This means with the 1.4 eV CB offset to Si and 6.3 eV band gap, that the vacancy states also lie below E_v of Si. Fig. 5b summarizes the different charge states of the vacancy levels.

These results account for the behaviour of Al_2O_3 when causing flat band voltage shifts and in Flash memories. Al_2O_3 is known to give p-type shifts. In the first experiments of Hobbs et al. [1], the gate electrode was poly-Si. We recently accounted for this result in a large model of the Al_2O_3–Si interface [21], which was found