Atomic and electronic structure of ultra-thin Al/AlO$_x$/Al interfaces

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Abstract

Interfaces between metals based on AlO$_x$ represent the most popular basis for Josephson junctions or, more recently, also for junctions exhibiting substantial tunneling magneto-resistance. We have performed a computational study of possible local geometric structures of such interfaces at the ab-initio DFT/GGA level of approximation to complement recent experimental data on ultra-thin AlO$_x$-based interfaces. We present two competing structures that we characterize with their electronic properties: fragmentation and interface energies.

Key words: metal-oxide interface, Aluminum oxide, density functional calculations

1 Introduction

Improvement in performance of Josephson junctions or magnetic tunnel junctions based on aluminum oxide tunneling barrier critically depends on the quality of the interface Al/AlO$_x$/Al. It is desirable to produce highly transparent, i.e. ultra-thin interfaces ($<1$nm) to achieve large critical currents while keeping the structures with sufficiently low density of interfacial defects. Several recent attempts to characterize such an ultra-thin barrier has been recently published. Rippard et al. [1] studied the dependence of the transmission spectrum of a ultra-thin interface (0.6 – 1.5nm) on the oxidation, finding a conduction band within the oxide only 1.2eV above the Fermi energy (effective barrier), which has been argued to origin from a disorder in the barrier. Regions of similar barriers, referred to as “hot spots”, were also observed by

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Gloos et al. [2]. An interesting study by Tan et al. [4] points to a novel stabilisation in the oxidation process and an inherent instability in AlO$_x$ films. They find that two structures - one corresponding to $x \approx 1.2$ and the other with $x \approx 1.0$ - can be switched using an electron gun, by exposure to oxygen or by overlaying the oxide with a metal having the work-function different from Al. Even though most of these barriers are known to be disordered, successful growth of an epitaxial AlO$_x$ barriers, which is an ultimate goal, has been also reported [3].

Theoretical studies, closest in nature to the Al/AlO$_x$/Al interface, are concerned with oxidisation of aluminum surface, an area studied primarily due to its importance in corrosion. Particularly relevant for our investigation are studies of the oxidised (111) surface of aluminum by Jennison et al. [5,6]. In their work the most energetically stable surface was found to be composed of an almost 2D layer of oxide with composition of Al$_2$O$_3$, separated from the bulk aluminum by a layer of chemisorbed oxygen. The resulting width of the oxide they found, $d \sim 0.5\text{nm}$, approximately coincides with the estimated widths of the thinnest Al/AlO$_x$/Al interfaces found by Gloos [2]. This similarity suggests to take the 1x1 structure of the (111) surface considered by Jennison as a starting candidate to represent the simplest ultra-thin interface.

2 Atomic structures

Two different geometries of the interface were considered, both based on the 1x1 surface supercell of an ideal (111) surface of Al. The first one was build starting from a geometry of the ultra-thin oxidised surface described by Jennison et al. [5,6]. By adding more atoms of aluminum and subsequent geometry optimisation combined with molecular dynamics we have identified the asymmetric structure A (see Fig. 1). We have checked that the structure was in a true energy minimum also for a 2x1 supercell. The interface consists of a chemisorbed oxygen (atoms O2 in Fig. (1)) bound to a full (111) layer of Al surface. Above the chemisorbed oxygen we find a 2/3-filled Al layer (Al2 atoms, hexagonal structure without the centers) forming with a full oxygen layer and 1/3-filled Al layer (Al1 atoms) an oxide AlO$_x$ with stoichiometry $x = 1.0$. The geometrical parameters are given in the table (1). The width of the interface, which we define as the vertical distance between the first non-bulk layer (Al1) and the last bulk-like layer (Al3) is $d_{\text{tot}}^A = 4.53\text{Å}$.

The above mentioned optimisations with several Al ad-atoms indicated that there is a tendency for the Al3 atoms to move up, towards the oxidised surface. To help the optimisation to explore the possibilities we have utilised a well known ductile character of gold as well as its almost identical bulk lattice constant - we have exchanged the overlayer of Al with Au. However, to form a
flat (111) surface we had to add two more Au atoms. The resulting structure was optimised into the final *symmetric structure* (S) shown in the Fig. (2). In contrast with structure A, the chemisorbed oxygen layer is missing and we find the AlO$_x$ oxide present in the upper half of the asymmetric interface instead, sharing the 1/3-filled Al layer with its mirror image. This can be directly checked by comparing the bond lengths and geometrical parameters given in the Table (1). Due to this sharing of the 1/3-filled layer the overall stoichiometry of S is $x = 6/5 = 1.2$ The width of the interface S is found to be $d^\text{tot}_S = 6.12 \text{Å}$. 

In both structures there are also other geometric alternatives due to the miscellaneous possibilities of stacking of bulk alumina atoms. There are three different layers - A, B, C - of bulk (111) aluminum and by swapping their order one can obtain new geometries. Examples we considered are CBA/BAC (see Fig. (2)) which is the S-structure, ABC/CAB and CAB/BAC.

Our calculations were performed using ABINIT [7] and CASTEP [8] programs for total energies per unit interface and fragmentation energies respectively. Within ABINIT we used Fritz-Haber-Institute pseudopotentials, which provide good convergence with plane wave cutoff of 60 Ry. The Brillouin zone integration was performed using 5 irreducible k-points within the Monkhorst-Pack (MP) mesh. Within CASTEP (calculation of fragmentation energies), Vanderbilt ultra-soft pseudopotential with plane-wave cutoff 25 Ry and 2x2x1 MP mesh. The exchange and correlation were described at the level of general gradient approximation (GGA). Geometries were optimised until the RMS forces were $< 0.05 \text{eV/Å}$. 

### 3 Interface Energy

The ground state structure can be characterised with a minimal interface energy $\Delta E$. The latter is defined as the difference between the total energy per supercell of a concerned and some reference system. If one of these two systems has $N$ more metallic atoms inside the interface, as it is the case here, we need to compensate for this difference by adding an appropriate bulk energy of these $N$ atoms. This is motivated by the fact that bulk represents a reservoir that supplies atoms into the interface while it is being transformed between alternative interface geometries/stoichiometries.

Since the S structure has two additional aluminum atoms$^1$, we calculate the

$^1$ In fact, there is one Al atom less inside the S interface compared to structure A. However, the structure S in our calculation has an extral full (111) bulk plane of Al which contains 3 atoms per surface cell, hence we have excess of two atoms in total.
interface energy as

$$\Delta E = E_S - (E_A + 2E_{Al}), \quad (1)$$

where $E_{Al}$ is the energy per atom in an ideal bulk aluminum, calculated with identical numerical precision as the interface supercell. The error introduced by a slight difference in the numerics has been checked to be $\leq 0.005eV$.

The resulting interface energy is $\Delta E = 0.072eV > 0$, i.e. the asymmetric structure is marginally lower in energy and hence it is more likely to be realised. Practically this means that in typically prepared disordered interfaces the local geometric and electronic structure of the “asymmetric” type will be more frequent than the one of the “symmetric type”. Furthermore, due to their energetic proximity, it is not surprising that one can switch between them, as it has been indeed experimentally done by Tan et al. [4] by means of electron bombardment or by overcoating with metals having different work function (Au in our case and Y, Nb, and Co by Tan et al. [4]). The calculated interface energy as well as the fact that using the Au electrode in place of the Al one drives the system towards the transition $A \rightarrow S$, represents further evidence that the experimentally observed behaviour by Tan et al. corresponds to the transition between local asymmetric and symmetric structures presented in our paper.

We have further examined the role of stacking of the fcc (111) planes in the metal on the interface energy. If the above treated structure S, with $CBA/BAC$ stacking, represents the reference value, we obtain $E_{ABC/CAB} - E_S = 0.10eV$ and $E_{CAB/BAC} - E_S = 0.28eV$. Therefore, the different order of (111) planes of one electrode with respect to the structure S leads to noticeable differences in the interface energy. However, all the candidates we checked were above the energy of the symmetric interface.

4 Fragmentation energies

A useful criterion for comparison of the stability of different oxide structures represent fragmentation energies. In our particular case both examined structures have the same area of the surface cell which simplifies the evaluation. We define fragmentation energy of a slab as

$$E_{\text{frag}} = E_{\text{lower}} + E_{\text{upper}} - E_{\text{whole}},$$

where $E_{\text{whole}}$ is the energy of the whole, fully optimized structure (slab) in the supercell and $E_{\text{lower}}$ and $E_{\text{upper}}$ are similarly obtained energies of the two parts of the whole structure (fully optimized to the nearest local minimum and in
the same supercell). The fragmentation energy depends on the location of the cut. In this way we can obtain many different fragmentation paths, each one with its own energy. We are interested in the lowest-energy pathway which limits the stability of a given structure.

Assume we have several different structures, $s_1, s_2, ..., s_N$, each one having its weakest path with energy $E_{s}^{\text{min}}$. Based on the fragmentation energies we define the most stable structure as the one with the highest $E_{s}^{\text{min}}$.

We have examined a limited set of fragmentation paths for the two structures A and S, indicated in the Fig. (3). Corresponding fragmentation energies are listed in the table inside the figure. Thus, according to the given criterion and the limited set of examined fragmentation cuts, we conclude that the structure A is more stable.

5 Conclusions

In conclusions, we have presented optimised geometries for the Al/AlO$_x$/Al interface. Two geometries - one asymmetric with chemisorbed oxygen (A) and one with symmetrical arrangement (S) - were found to differ only by $E_S - E_A \approx 0.07\text{eV}$ (per interface cell), yet they are principally different in stoichiometry ($x = 1.0$ and $x = 1.2$ respectively) and interface width ($d = 4.53\text{Å}$ and $d = 6.12\text{Å}$ respectively). The asymmetric structure is not only energetically more favorable, but it is also more stable against fragmentation when compared to the symmetric structure. These findings are in agreement with recent experiments [4], identifying reproducible switching between two different oxide films, but indicate that in contrast to their interpretation, the morphological change takes place deeper in the interface between the oxide and substrate. Second, in agreement with this experiment, we have confirmed that the two geometries can be switched by depositing metal with work function different from the one of the substrate Al.

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Fig. 1. The asymmetric structure. O₂ are the chemisorbed oxygen atoms bound to a full (111) layer of bulk aluminum Al₃. 1/3 filling of Al₁, fully filled layer of O₁ and 2/3 filling of Al₂ layer represent the actual oxide.

Fig. 2. Symmetric structure S. The structure is symmetrically ordered with respect to the 1/3 filled plane of aluminum atoms Al₂. The letters A, B, and C indicate the stacking of the (111) planes in the electrode.

| path | A  | S  |
|------|----|----|
| 1    | 2.48 | 1.27 |
| 2    | 1.92 | 7.52 |
| 3    | 2.85 | 2.31 |
| 4    | 3.70 | 2.44 |
| 5    | 2.24 | 10.4 |
| 6    | 3.76 | —   |

Fig. 3. Left panel: Images of A and S structures with fragmentation cuts shown schematically. Right panel: Calculated fragmentation energies in eV.
|     | d₁  | d₂  | d₃  | d₄  | d₅  | d(O₂-Al₃) | d(O₁-Al₂) | d(O₁-Al₁) |
|-----|-----|-----|-----|-----|-----|-----------|-----------|-----------|
| A   | 2.6 | 1.0 | 0.59| 1.8 | 1.14| 1.9       | 1.75      | 1.88      |
| S   | 1.75| 1.16| 0.59| 2.58| N/A | N/A       | 1.77      | 1.95      |

Table 1
Geometrical parameters and bond lengths of the considered interfaces A and S, all units are in Å.