



# *Ab initio* supercell calculations of the (0001) $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> surface with a partially or totally Al-substituted external layer

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## ARTICLE INFO

### Article history:

Received 15 May 2008

Received in revised form 28 January 2009

Accepted 13 April 2009

Available online 19 April 2009

### Keywords:

Computer simulation

Surface relaxation

Surface energy

Surface electronic phenomena

Aluminium oxide

Chromium oxide

## ABSTRACT

*Ab initio* supercell calculations employing the periodic Hartree–Fock formalism are presented of the (0001)  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> surface with a partially or totally Al-substituted external layer. In the simulations a fraction of the Cr atoms at the surface of the chromia slab are replaced by Al atoms, and the Al surface coverage is varied between zero (pure chromia) and 100% (Al-terminated chromia). The surface Al atoms are found to relax inwards considerably, with the magnitude of the relaxation decreasing with increasing Al surface coverage. The calculations also reveal that the surface energy of the slab decreases with increasing Al coverage. Finally, the electronic properties at the surface of the Al-substituted (0001)  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> slabs are investigated. Here the calculations show that the substitution of Cr by Al gives rise to an increase in the covalency of the Al–O bonds compared to slabs of pure alumina. In contrast, the influence of the surface Al atoms on the electrostatic potential in the (0001) plane of metal ions is relatively small. These findings support the utilisation of  $\alpha$ -chromia substrates for the templated growth of  $\alpha$ -alumina, which is consistent with recent experiments.

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## 1. Introduction

Alumina (Al<sub>2</sub>O<sub>3</sub>) is currently of considerable interest for applications as metal-catalyst support and high-temperature wear-resistant coating in the metal-cutting industry [1]. Recently, it has been reported that  $\alpha$ -alumina (corundum) can be grown on  $\alpha$ -chromia templates at relatively low substrate temperatures via magnetron sputtering deposition techniques [2,3]. For example, Schneider et al. [4] found evidence for the formation of chromia stabilized  $\alpha$ -alumina at substrate temperatures of ~220 °C by conventional reactive magnetron sputtering, while Andersson et al. [5] (using RF magnetron sputtering with substrate temperatures between 280 and 560 °C) found that  $\alpha$ -alumina continues to grow with the same orientation as the underlying chromia grains. Similarly, Pulugurtha et al. [6] deposited crystalline alumina thin films on tungsten carbide–cobalt substrates using a reactive inverted cylindrical ac magnetron sputtering technique with a chromium oxide prelayer, while very recently Wallin et al. [7] investigated the effects of residual water on the phase formation, composition and microstructure evolution of magnetron sputter deposited crystalline alumina thin films with and without chromia nucleation layers.

Theoretically, periodic Hartree–Fock (HF) calculations were applied to investigate the low-index surfaces of both  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> [8,9]. *Ab initio* calculations of silver and silver chloride adhesion on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (0001) were presented by Kotomin et al. [10], Zhukovskii et al. [11,12] and Chatterjee et al. [13]. Metal film growth on MgO (001) and BaTiO<sub>3</sub>

(001) surfaces was investigated in refs. [14–17]. Yong et al. [18] studied the adsorption of alkali metal cations on a hydroxylated corundum surface, while Bredow [19] investigated the adsorption of water at the Cr<sub>2</sub>O<sub>3</sub> (0001) surface. In our earlier work [9] we showed that the (0001) plane is the most stable facet of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> surface, while for  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> the low-index (10 $\bar{1}$ 2) plane has a slightly lower surface energy compared to the (1 $\bar{1}$ 26) and (0001) facets. Similarly, in ref. [20] we employed single-cell periodic HF calculations to study slabs of  $\alpha$ -chromia coated with  $\alpha$ -alumina, where we found a lowering of the surface energy for chromia coated with ultrathin films of alumina and an increase in strain energy with increasing alumina film thickness (due to the tensile stress in the alumina film arising from the 4% lattice mismatch between bulk  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub>). In the present work we use periodic HF *supercell* simulations to investigate Cr-terminated (0001)  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> slabs where a fraction of the Cr atoms at the surface is replaced by Al atoms. The main focus here lies in the determination of surface properties (such as surface relaxation, surface energy, Mulliken charges on the surface metal atoms and surface electrostatic potential contour maps) for a fractional Al surface coverage. The results of the simulations show that the surface energy of (0001)  $\alpha$ -chromia decreases for increasing aluminium surface coverage, which will help during the initial nucleation stage of  $\alpha$ -alumina thin-film growth on chromia templates.

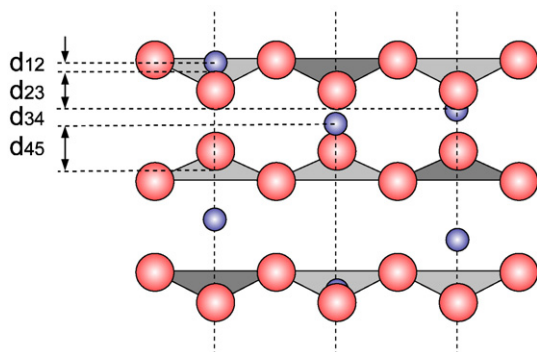
## 2. Computational details

All calculations are performed with the computer code CRYSTAL03 [21] (which is an *ab initio* Hartree–Fock linear combination of atomic

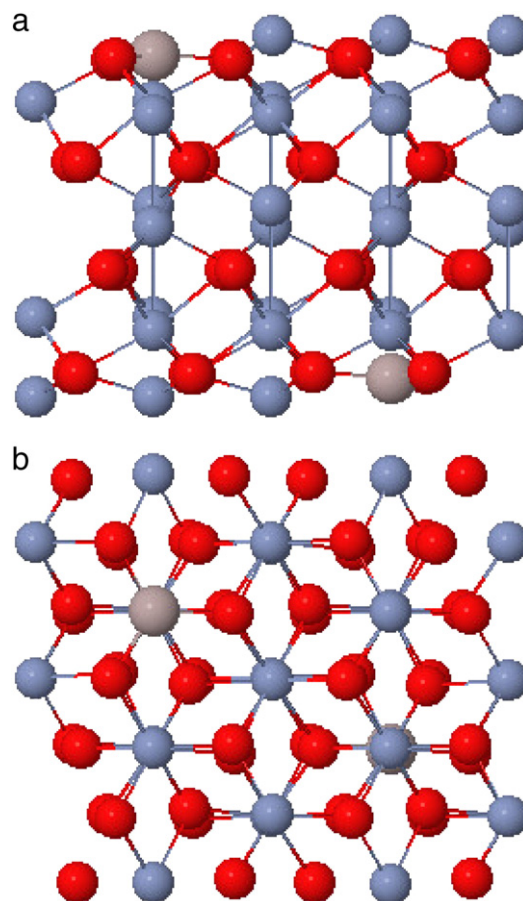
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orbitals program for solving the Schrödinger equation for periodic systems) using unrestricted Hartree–Fock wave functions. The surface is described by a slab model, i.e. the dimensions parallel to the surface have periodicity while the dimension perpendicular to the surface is free of constraints (a large enough boundary is set in this direction to ensure that the wave function decays to zero). The three-dimensional Ewald summation can therefore be employed to calculate long-range interactions in the slowly convergent Coulomb series for a two-dimensional geometry. Since there are unpaired 3d electrons in isolated  $\text{Cr}^{3+}$  ions, the use of the unrestricted open-shell Hamiltonian of the spin-dependent part of the wave function is necessary to obtain spin-polarized eigenfunctions of the Fock Hamiltonian [22]. The all-electron level basis sets were taken from previous studies of bulk  $\alpha\text{-Cr}_2\text{O}_3$  [22] and  $\alpha\text{-Al}_2\text{O}_3$  [23]. We have estimated the basis set superposition error using the counterpoise method and have found this error to be less than about 5% for the present calculations. The spin sequence on the Cr atoms along the three-fold axis can exhibit four different orders, corresponding to one ferromagnetic and three antiferromagnetic configurations. Although the first antiferromagnetic phase is the stable ground-state structure (its energy is 0.03 eV lower than the energy of the ferromagnetic phase), the geometries of the two bulk phases are virtually identical [8]. At the surface, however, the magnetic properties may lead to additional geometric effects. Consequently, we have carried out  $(2 \times 2)$  supercell calculations of ferromagnetic and antiferromagnetic chromia slabs and have found good agreement between the two sets of calculations. We therefore consider in the present work the computationally less demanding ferromagnetic structure with four spin-up symmetry-related chromium atoms in the primitive cell.

Both  $\alpha\text{-Al}_2\text{O}_3$  and  $\alpha\text{-Cr}_2\text{O}_3$  have the corundum-type structure (space group  $R\bar{3}c$ ) with hexagonal close-packed (0001) layers of O atoms and two thirds of the octahedral holes in between filled by metal atoms (Fig. 1). The structural parameters for the chromia template are taken from the literature ( $a_0 = 5.048 \text{ \AA}$  and  $c_0 = 13.735 \text{ \AA}$  [22]). In the present calculations, we choose a 12-layer Cr-terminated slab of  $\alpha$ -chromia (four unit layers of  $\text{Cr}_2\text{O}_3$  with the stable single Cr-layer termination) arranged in a  $2 \times 2$  supercell (i.e. a total of 80 atoms in the simulation cell). The Cr atoms in the two planes at the centre of the slab are fixed to their bulk positions during the geometry optimisation in order to reduce the total CPU time. Initially, the pure chromia slab is relaxed until the total energy converges. The relaxed geometry of the supercell is in excellent agreement with single-cell calculations of thicker slabs [20]. We then introduce Al atoms at the surface of the slab in the following way: first, on either side of the slab one of the four surface Cr atoms in the supercell is replaced by an Al atom (i.e. corresponding to 25% Al surface coverage, see Fig. 2); this slab is then relaxed until the total energy has converged. Using this



**Fig. 1.** Schematic side view of (0001)  $\alpha\text{-Cr}_2\text{O}_3$  where the chromium atoms (light blue) are located on the  $C_{3v}$  rotation axes of triangles formed from oxygen atoms (red). Darker shading represents smaller oxygen triangles. The interplanar distances are defined by  $d_{12}$ ,  $d_{23}$ ,  $d_{34}$  and  $d_{45}$  (Table 1). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 2.** Energy-minimised configuration of the (0001)  $\alpha\text{-Cr}_2\text{O}_3$  ( $2 \times 2$ ) supercell slab with 25% Al surface coverage. The side view (a) shows the 12-layer slab (80 atom supercell) and the top view (b) shows the location of the surface Al atom. Key: chromium (light blue), aluminium (light brown), oxygen (red). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

relaxed slab, we replace a second, neighbouring Cr atom by an Al atom (i.e. 50% surface coverage) and relax the slab again. This procedure is repeated until all four Cr atoms at the surface are substituted by Al atoms (i.e. 100% coverage). The remaining  $\alpha\text{-Cr}_2\text{O}_3$  layers at the centre of the slab form the  $\alpha$ -chromia template. The energy-minimised configuration of the (0001)  $\alpha\text{-Cr}_2\text{O}_3$  ( $2 \times 2$ ) supercell slab with 25% Al surface coverage is shown in Fig. 2.

In CRYSTAL, the level of numerical approximation in evaluating the Coulomb and exchange contributions to the Hartree–Fock matrix appearing in the self-consistent field equations is controlled by five tolerances. The values used in the present calculations are (7 7 7 7 and 14). The shrinking factors, which determine the number of sampling points in the irreducible Brillouin zone (IBZ), are chosen as (6 6). Consequently, there are 20  $k$ -points in the slab IBZ. The remaining parameters for controlling the geometry optimisation process are the same as in the literature [24].

### 3. Results and discussion

The calculated interplanar spacings of the four outermost atomic planes after full relaxation of a (0001)  $\alpha\text{-Cr}_2\text{O}_3\text{:Al}$  ( $2 \times 2$ ) supercell slab as a function of Al surface coverage are shown in Table 1. As can be seen from this table, replacing just one of the Cr atoms at the surface by Al (25% coverage) gives rise to an increase in the interplanar spacing of the outermost Cr atoms  $d_{12}(\text{Cr})$ , while the single Al atom is almost coplanar with the O atoms underneath, i.e.  $d_{12}(\text{Al}) \approx 0$ . Interestingly, an increase in the Al surface coverage increases both

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