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Formation of Al/CuO bilayer films: Basic mechanisms through density functional theory calculations

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ABSTRACT

We carry out Density Functional Theory calculations of the initial steps of CuO deposition onto Al(111) surface and Al deposition onto CuO(11−1) surface to investigate the basic mechanisms responsible for the growth of Al/CuO interface. Chemical pathways for adsorption and incorporation into the subsurfaces are examined, and associated activation energies are determined. We demonstrate that Al does penetrate the CuO surface with subsequent amorphization of the CuO upper layer. In turn, CuO undergoes a dissociative adsorption onto Al(111), leading to isolated Cu and O atoms of which further penetration in the Al surface is detailed. While Cu pathway for subsurface penetration is characterized by a low activation barrier (0.5 eV), O interaction with the Al surface is much more complex; aluminum oxidation is shown to occur at a nominal oxygen coverage through a drastic rearrangement of the Al surface atoms.

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1. Introduction

Nanothermites are widely studied nowadays [1] because of their capacity to release energy by applying a thermal, mechanical, electrical or optical stimulus. They are composed of a metal (typically Al) and a metallic oxide (as CuO) able to undergo a highly exothermic oxido-reduction reaction (>20 kJ/cm^3). The thermite materials offer also the advantages to be compatible with micro and nanotechnologies. They can therefore be integrated with electronic chips, to provide onboard micropower sources to produce specific gas or release locally heat and pressure. In that context, our laboratory has developed a PVD (Physical Vapor Deposition) process [2] to stack alternatively Al and CuO nanofoils (100 nm in thickness) directly on silicon or glass chips. The intimacy of both reactants (Al and CuO) reduces the diffusion widths and therefore accelerates the oxido-reduction reaction that can be expressed as: $Al + CuO \rightarrow Al_2O_3 + Cu + \Delta H$, with ΔH being the heat of reaction equal theoretically to 21 kJ/cm^3. At the Al–CuO nanofoils interface, intermixing invariably occurs to form a thin layer which rules the stability and sensitivity of the thermite. The intermixed-layer thickness has been observed by High Resolution Transmission Electron Microscopy and is of a few nanometers (see Fig. 1).

At the present time, the role played by this intermixed-layer on the initiation of the multilayered Al/CuO thermite is barely known, and its formation depending on the experimental conditions (process parameters or thermal cycling) remains one of the main issue of this research domain. This paper proposes to give a theoretical insight of the spontaneous formation of the intermixing zone at the interface of Al and CuO layers. To make an inventory of the possible interactions between those two species during the deposition process, an atomic-scale research is carried out using *ab initio* calculations. In view to address first the initial step of deposition, this preliminary study is aimed at establishing the intrinsic interaction of single atoms or molecules onto Al and CuO surfaces. This is viewed as the most simple and basic phenomenon taking place during a PVD process. Increasing the complexity of the gas phase species will be the subject of future work. Our aim is to understand how Al atoms can react on a CuO surface on one hand, and in turn how CuO molecules dissociate and react on an Al surface. The final application of our actual research is to build a model at a larger scale allowing the prediction of the characteristics of the intermixed layer depending on the experimental conditions. This will make it possible to analyze the influence of this barrier layer on the energy yielding of the device, which is a key problem to resolve in the future.

In this article, we first describe the methods and computational details, in Section 2. Then we present our results on Al/CuO(11−1) and CuO/Al(111) in Sections 3.1 and 3.2, respectively. Finally we discuss and summarize the present work in Section 4.

2. Methods and computational details

All the periodic Density Functional Theory (DFT) calculations are carried out using the Perdew–Burke–Ernzerhof [3] implementation of the generalized gradient approximation in VASP 5.2 (Vienna *Ab initio* Simulation Package). The Kohn–Sham Blöch functions are expanded on

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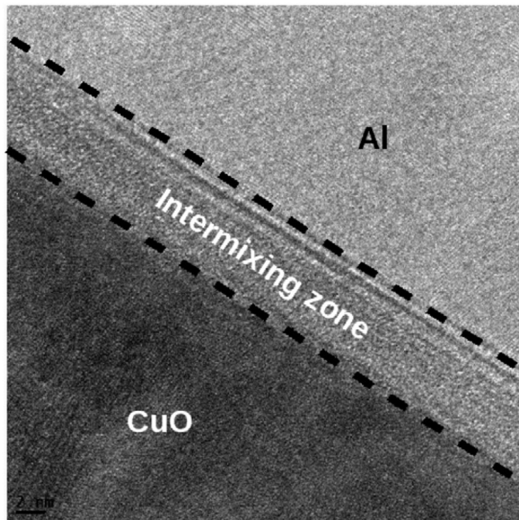

Fig. 1. High resolution TEM photography of the Al/CuO interface.

a planewave basis set up to an energy cutoff of 400 eV, a Monkhorst–Pack mesh of $2\times2\times1$ k-points is used for the Brillouin-zone integration, and projected-augmented waves are used to represent the inner electrons.

Aluminum (111) surface is modeled by a six-layer slab containing 96 atoms with 14 Å of vacuum to mimic a real surface, in an orthorhombic $11\times10\times25$ Å simulation box. The bottom layer is fixed during geometry optimization to reproduce the bulk behavior, and the Cu and O adatoms are deposited only on one side of the slab.

The supercell for CuO(11−1) is monoclinic (dimension: $13\times12\times41$ Å), it can be seen in Fig. 2: it contains 192 atoms, with planes of 16 Cu atoms alternated with two semi-planes of 8 O atoms. Again, during optimization the bottom layer is fixed and Al atoms are added on one side of the slab.

Calculations are performed using the LSDA + U method [4] in order to correctly represent the electronic structure of the material: indeed, CuO is a semi-conductor which presents an antiferromagnetic character at low temperature [4]. This electronic constraint on the great number of atoms justifies the long time necessary for each geometry optimization.

We systematically calculate the heat of reaction, or binding energy, as the difference between the energies of the initial and the final states:

$$E_b = E_{adsorbate+surface} - (E_{adsorbate} + E_{surface}).$$

Where $E_{adsorbate+surface}$ is the energy of the complex, and $E_{adsorbate}$ and $E_{surface}$ are the respective energies of the separated adsorbate and slab. In the following, we consider four types of reactions: surface adsorption, dissociation, incorporation into the subsurface and substitution in a substrate lattice site.

The Nudged Elastic-Band (NEB) method developed by Henkelman et al. [5] in Austin has been employed to determine the activation barriers ($E^{\ddagger}$) of certain reactions, such as oxygen vertical diffusion in Al. They give us additional information on the kinetic rate of reactions.

3. Results

3.1. Al on CuO(11−1)

Fig. 3a shows the energy diagram of the adsorption and further penetration of an Al atom on CuO surface. It is constructed as follows: the energy for each configuration is calculated by placing an Al atom near a known site and running an optimization. Then, either the atom stays in this site and we obtain the total energy of this final state, or it moves away and the site is said unstable. In this latter case, it simply does not appear on the graph. The binding energies are reported on this diagram, which is readable from the left to the right to follow the penetration path.

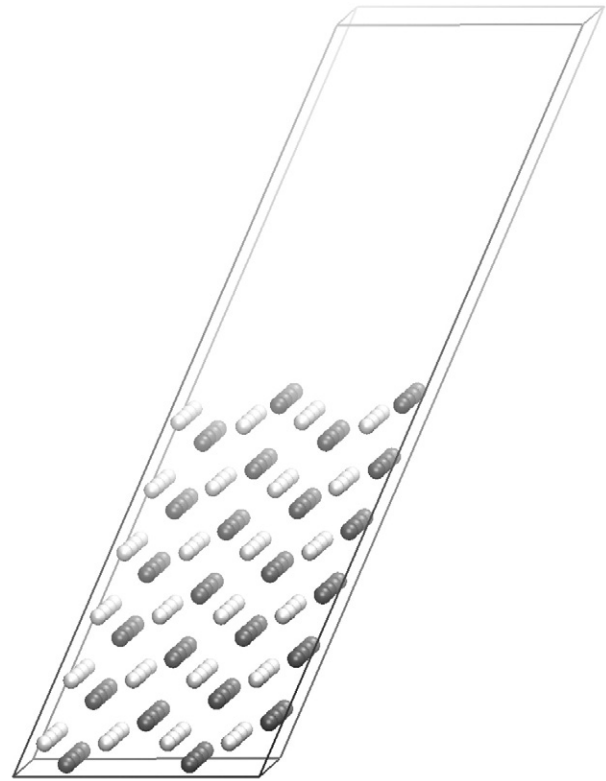

Fig. 2. View of the CuO(11−1) simulation box. Copper atoms are in white and oxygen in gray.

NEB method is employed to calculate the barrier energy associated to the penetration of one Al in the first Cu layer, in a lattice site. We consider it as the only interesting activation energy to know, all the other reactions being endothermic, so unlikely to happen.

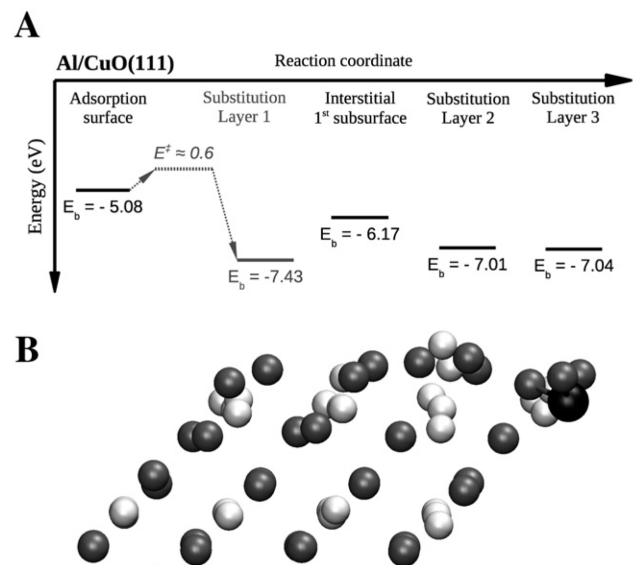

Fig. 3. a) Energy diagram of the vertical diffusion reaction path of Al through CuO(11−1); b) illustration of the upper layer amorphization with one inserted Al atom (in black).

As shown in Fig. 3a, adsorption of one Al atom is highly exothermic ($E_b = -5.08$ eV) and we expect that the released heat is sufficient to overcome the 0.6 eV activation barrier for further penetration of the Al into the first Cu layer. Fig. 3a also shows that this substitutional position is the most stable, with 2.35 eV gain in energy due to an increase of the coordination number, and that it leads to an amorphization of the surface (see Fig. 3b).

As said before, calculations on these structures take a really long time and the amorphization makes the NEB method very difficult to employ. Those are the reasons why we approximated only one barrier energy and why we considered only one Al atom on CuO(11−1) so far.

3.2. CuO on Al(111)

This reaction shows a completely different behavior. We observe the spontaneous barrierless dissociation of the CuO molecule on the Al(111) surface. The reaction is again highly exothermic with 6.12–6.66 eV gain in energy, depending on the final distance between Cu and O atoms on the substrate, the farther being the most favorable situation. From this point, the investigations are carried out separately for Cu and O.

3.2.1. Cu on Al(111)

Fig. 4a shows the energy diagram of the adsorption and further penetration of a Cu atom on Al surface, based on the same protocol as Fig. 3a. The final structure of the incorporated atom is shown in Fig. 4b. Both the adsorption and insertion in the first layer, leading to a so-called "dumbbell-like structure", are exothermic and seem to be almost equiprobable: $E_b = 2.8$ and 2.9 eV, respectively. These numbers are not useful for our deposition process, since Cu is only deposited in its molecular form. But it shows that the adsorption site may be fcc or hcp with equal probabilities (see Fig. 4a), and that starting from either above sites, the Cu penetration is only slightly exothermic. The activation barrier for the formation of this dumbbell-like structure is calculated with NEB method and is equal to 0.5 eV. We can say that this low barrier will be passed at RT, allowing the system to stabilize in the dumbbell configuration, for one isolated copper atom. Indeed, further penetration of Cu atom is again unfavorable, even in the second subsurface layer.

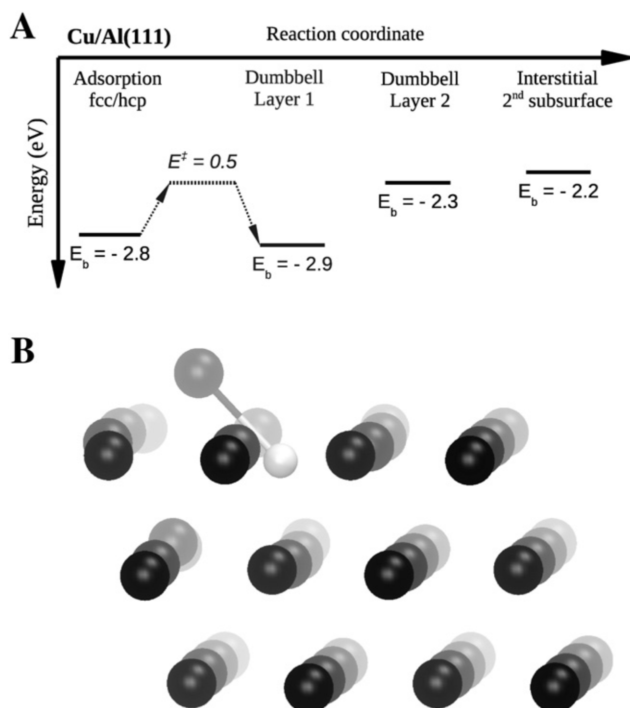

Fig. 4. a) Energy diagram of the vertical diffusion path for Cu through a Al(111) surface; b) illustration of the Al–Cu dumbbell-like structure.

We next consider the same reactions for a second Cu atom arriving on the Al(111) surface, the first one being already adsorbed on a fcc or hcp site. Qualitatively, we observe similar results: the Cu atom is inserted in the first subsurface layer, in dumbell-like configuration, with an activation barrier of 0.45 eV. Quantitatively the barrier is slightly lower and the energy difference between the adsorbed and dumbbell states is larger (0.3 eV rather than 0.1 before). We confirmed that this barrier is actually overcome at the low experimental deposition temperature of 300 K, by performing Molecular Dynamic simulations (data not shown, the system spontaneously goes to the dumbbell configuration). These simulations were not performed in the case of Al/CuO, because of a considerably higher energy gain during the adsorption process. These results allow us to say that the behavior of Cu on Al is a function of the surface coverage. In other words, the penetration of Cu in the Al surface should be a more important process when a higher quantity of copper will be considered.

Interestingly, experiments on growth of Cu films on Al(111) surfaces show the interdiffusion to be a fast mechanism [6] leading to CuAl alloying even at low temperatures. Furthermore, Buchanan et al. [7] indicate that the film growth is of a multilayer type, the second layer being partially formed before the first is completed. This should be verified through further investigations. With this knowledge and our actual results, we can therefore conclude that the first Cu atoms are inserted in the Al(111) subsurface until some critical coverage where penetration will be replaced by deposition onto the substrate. But globally, during the PVD process, there will be an intermixing existing between the two species leading to an irregular interface, like we did observed in Fig. 1.

3.2.2. O on Al(111)

The reference work concerning the oxygen adsorption on an Al(111) surface is that of Kiejna and Lundqvist's [8,9] for the theoretical part, and Brune's for the experimental results and Scanning Tunneling Microscopy (STM) images [10,11]. In these papers, the effect of different oxygen coverages was studied and the corresponding binding energies and work functions were compared. We reproduced some of their calculations and found similar results. For example, the calculated binding energies are comparable: for adsorption of 1 O atom in a fcc site, we obtained −7.65 eV and Kiejna and Lundqvist, −7.16 eV [8]. For an oxygen monolayer on Al(111), the adsorption energy per atom is −8.12 eV in our work and −7.63 in this reference, which means our results are consistent (the constant 0.47 eV shift is explained by the difference in computational methods employed).

Moreover, we observed cooperative effects among oxygen atoms, *i.e.* different behaviors in the presence or absence of other oxygen atoms already adsorbed on the surface, in a more obvious way than for the copper case. This group effect of oxygen on Al was also observed and pointed out by Brune with STM images [10]. In his next article [11], he approximated that, when adsorbed oxygen atoms are thermalized at 300 K, the surface diffusion barrier is around 1.0 eV, which is consistent with the values we found (*cf* Fig. 5).

Fig. 5 represents the energy diagram of the adsorption, surface migration (left) and further penetration (right) of isolated oxygen atoms on Al(111) surface. We observe two different adsorption sites: fcc and hcp, showing respectively 7.65 and 7.25 eV adsorption energy. The activation barrier for the fcc to hcp transition is 0.68 eV, but is only 0.27 eV for the hcp to fcc transition. This leads to high migration rates towards fcc configuration. Contrary to the two previous cases examined in Sections 3.1 and 3.2.1, the oxygen penetration into the subsurface, even in the first layer, is energetically unfavorable with 0.75 eV energy loss. Moreover, the high activation energy of 1.73 eV for this penetration makes it kinetically impossible to occur at low deposition temperatures. These preliminary results are contradictory to the common view pointing towards an easy oxidation process. Again,

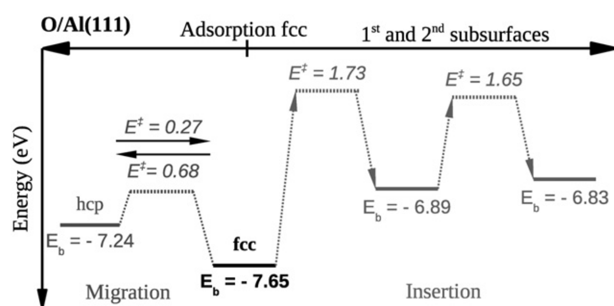

Fig. 5. Compared energy diagrams of surface migration and incorporation of an oxygen atom on Al(111).

these results are valid at low coverages. On-going research effort is performed to shed light into possible cooperative effects between incident oxygen atoms that could facilitate the subsurface incorporation at higher oxygen coverages. We also did preliminary calculations concerning the role played by defects on the surface. We constructed a monoatomic step along the [1–10] axis. Our calculations showed that the adsorption energy of one O atom is slightly smaller than the clean surface adsorption value (−7.54 and −7.65 eV, respectively). So the oxygen atoms deposited on the Al surface should not have any preference for adsorption on the steps, which is confirmed by Brune's observations [11, Sec. III.C]. However, although the presence of linear defects doesn't influence the oxygen adsorption sites, it seems to facilitate the process of oxide nucleation, likely because of the mobile Al atoms along the monoatomic step [11, Sec. III.D] favoring the formation of oxide islands.

In summary, while an exact picture of the initial step of Al oxidation is still lacking to date, our results and assumptions are in agreement with previous conclusions already reported in the literature [9,11].

4. Discussion and conclusion

The preliminary results presented in this article show that, at low coverages, interdiffusion between CuO and Al is present but quite weak. Our first results showed that copper and aluminum atoms can penetrate respective substrates and intermix on a small thickness, not deeper than the first subsurface layer, while oxygen atoms will stay on the substrate surface at low coverage.

As a perspective, investigation of interdiffusion at high surface coverages, where cooperative effects might change binding energies and final configurations, is mandatory to fully understand the formation of intermixed layers. Join effects of copper and oxygen atoms both adsorbed on the surface, or presence of atmospheric water molecules can also be considered to complete our work.

The last studied case of oxygen on Al(111) is very similar to the aluminum oxidation, extensively studied at both experimental and theoretical levels. According to the results reported in the literature [9,11], oxygen atoms will only penetrate the Al surface after a critical coverage is reached, estimated to one complete or to half layer depending on the authors. But this issue is not definitely established and needs further work.

Finally, valuable information can be extracted from these preliminary results about the events occurring at the atomic-scale during the first stages of the PVD process, when a small number of atoms that is deposited on the substrate. They will be completed in order to build an adequate mesoscopic model of the growth and initiation of nanostructured energetic materials, taking atomistic mechanisms into account.

Acknowledgments

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