# Mechanism of Cu Deposition on the $\alpha$-$Al_2O_3$ (0001) Surface

Javier Fdez. Sanz* and Norge Cruz Hernández

*Departamento de Química Física, Facultad de Química, E-41012, Sevilla, Spain*

(Received 30 July 2004; published 11 January 2005)

The growth mechanism of the Cu/$\alpha$-$Al_2O_3$ (0001) interface is studied by first-principles molecular-dynamics simulations as a function of the transition-metal coverage ($\theta$) and the temperature of the system. On the anhydrous surface growth of Cu(0) 3D clusters is predicted. On the partially hydroxylated surface, a Cu(I) monolayer, relatively stable upon the temperature rising, is first observed ($\theta < 1/3$ ML). Increasing Cu loading leads to Cu(I)/Cu(0) mixed phases that when heated aggregate into 3D particles increasing the number of Cu(0) atoms, in agreement with the Auger spectra of Kelber *et al.*. [Surf. Sci. **446**, 76 (2000).]

DOI: 10.1103/PhysRevLett.94.016104 PACS numbers: 68.43.Bc, 68.47.Jn, 81.15.Aa

Because of a wide range of technological properties, transition metals (TM), supported on relatively inert surfaces, constitute nowadays one of the most appealing subjects in both solid state and materials science [1]. In the past few years experimental studies concerning deposition of metals have been reported; however, the complexity of these systems makes it difficult to obtain direct, structural, or electronic information even in an ultrahigh vacuum and well-defined, controlled, experimental conditions, and interpretations are not exempt of contradictions. Theoretical approaches have proved useful tools for understanding the nature and mechanism of the deposition and nucleation of atoms and clusters [2,3].

An example of such contradictions is the case of the Cu/$\alpha$-$Al_2O_3$ (0001) interface, which constitutes the target of this work. Growth of deposited Cu particles has been experimentally studied using both native surfaces of $\alpha$-$Al_2O_3$ and thin films of $Al_2O_3$ grown on metallic substrates, and the results are amazing. When films ~20 Å thick epitaxially grown on metal substrates are used as support, x-ray photoelectron spectroscopy (XPS) and low energy ion scattering data show the formation of 3D clusters of metallic Cu even at the submonolayer regime [Volmer-Weber (VW) mechanism] as well as the absence of oxidized Cu [4]. In contrast, using a film of polycrystalline $Al_2O_3$ suggests a layer-by-layer growth mode and formation of Cu(I) at $\theta < 0.5$ ML Cu [5,6]. On the other hand, using bulk truncated $\alpha$-$Al_2O_3$ (0001) native surfaces, XPS studies indicated ordered layer-by-layer growth at least for the first one to three Cu atomic layers, [7] which would formally correspond to the Stranski-Krastanov growth mode (SK mode). In this case, the first Cu layer was found to be oxidized as Cu(I) ions, bound to the substrate through Cu-O ionic interactions. Yet, other studies of the Cu/$\alpha$-$Al_2O_3$ (0001) interface suggested a weak interaction of the TM with the basal surface, and that 3D Cu metallic particles are formed from the primary stages of Cu deposition [8,9]. Recently, Pang *et al.* reported 3D Cu clustering at $\theta > 0.3$ ML using noncontact atomic force microscopy [10]. However, it was not possible to image Cu at $\theta < 0.3$ ML, and, therefore, the possibility that small 2D islands of Cu are formed prior to the 3D clusters could not be ruled out.

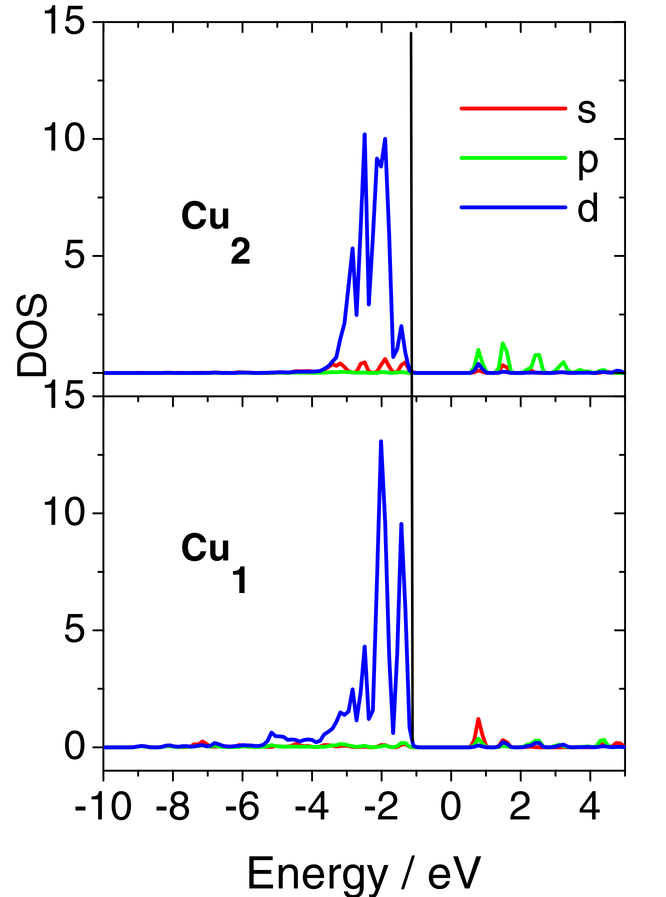
The temperature influence on the Cu deposition on partially hydroxylated $\alpha$-$Al_2O_3$ (0001) surfaces was examined by Kelber *et al.* [11]. The XPS data showed an initial layer-by-layer growth with formation of Cu(I) at $\theta < 0.35$ ML, while at a higher $\theta$, both Cu(I) and metallic Cu(0) were detected. The stability of these phases versus the temperature was checked by annealing samples at different $\theta$. The spectra showed that Cu(I) is stable at low $\theta$ ($< 1/3$ ML), even at 1000 K. However, after annealing 0.75 ML samples, a loss in the intensity of the Cu(I) band was observed. Also, experiments with partially dehydroxylated surfaces obtained from Ar-ion sputtering revealed that the presence of surface hydroxyls increases the interaction with Cu adatoms [12].

The interaction energy of Cu atoms with $\alpha$-$Al_2O_3$ (0001) has been theoretically analyzed from local-density approximation density functional theory (DFT) calculations using models of clean and hydroxylated surfaces [11,12]. At Cu coverage of 1 ML, Lodziana *et al.* reported generalized gradient approximation (GGA)-DFT interaction energies of 0.91 and 0.87–2.55 eV for clean and hydroxylated surfaces [13]. Recently we reported [14] a detailed theoretical study on the interaction of Cu atoms on a relaxed, clean, Al-terminated, $\alpha$-$Al_2O_3$ (0001) surface also based on GGA-DFT calculations. At $\theta = 1/3$ ML (the smallest one can reach using a $1 \times 1$ cell), our calculations suggested that Cu atoms appear to reduce the surface, more specifically outermost Al atoms, with formation of Cu(I) ions, while increasing the coverage led to a buckled adlayer with the Cu atoms forming zigzag chains, and coexistence of Cu(I) and Cu(0) species, in agreement with the interpretation of XPS data [11]. Although this analysis provided a first understanding of the metal-support interface, some key questions concerning the growth mechanism at the earlier stages of Cu deposition still remain open.

 © 2005 The American Physical Society

We report on first-principles simulations of the $Cu/\alpha\text{-}Al_2O_3$ (0001) interface based on periodic supercell DFT calculations at the low TM coverage regime. Both anhydrous and partially hydroxylated surfaces were considered. We show that Cu atoms dimerize on the anhydrous clean surface and, after further aggregation, give rise to 3D clusters even at low temperature ($T < 100$ K). In contrast, when the surface is partially covered by hydroxyl groups, a quasimonolayer of Cu(I) is first formed. Increasing the metal loading leads to Cu(I)/Cu(0) mixed phases that when heated aggregate into particles. The soundness of our results is ensured by the use of first-principles simulations and provides, for the first time, a rational on the intricate growth mode of Cu deposits on alumina depending on both coverage and temperature. The simulations are carried out using the VASP 4.6 code [15] and the GGA implementation proposed by Perdew *et al.* [16]. The $\alpha\text{-}Al_2O_3$ (0001) surface is represented through slabs spanned using a $2 \times 2$ supercell 12 layers thick (80 atoms) with a vacuum space between slabs of 10 Å. Calculations were performed at the $\Gamma$ point using ultrasoft pseudopotentials [17] and a plane-wave basis set (cutoff at 396 eV and energy converged to $\sim$1 meV/atom).

We start by adding one, two, and four Cu atoms on the clean alumina surface, i.e., $\theta = 1/12$, 1/6, and 1/3 ML. For $\theta = 1/12$ ML the optimization leads to a structure similar to that obtained using the $1 \times 1$ cell, with Cu atoms bound to the surface through triads of oxygen atoms. Also, the density of states [(DOS), spin-polarized] shows that the $4s$ band is empty indicating that Cu atoms are oxidized to Cu(I). The addition of a second Cu atom can occur at one of the three equivalent sites or near the first adatom. The calculations show the latter to be preferred with the formation of a $Cu_2$ dimer. The DOS curves projected on the transition metals show that the Cu closer to the surface is oxidized to Cu(I) while the other Cu exhibits a peak at the Fermi level corresponding to the $4s$ band (Fig. 1). This picture corresponds therefore to the Cu(0)-Cu(I) mixed valence $Cu_2^+$ dimer. Adding two more Cu atoms corresponds to $\theta = 1/3$. If the Cu atoms lie separated from each other there is formation of a monolayer of formally Cu(I) ions as revealed by the DOS curves. However, such a monolayer is about 2 eV less stable than the two separated $Cu_2^+$ dimers. These results indicate that at this coverage, both Cu(I) and Cu(0) peaks should be observed in the Auger spectra in disagreement with the experiment. Yet, one can wonder if the transition-metal Cu(I) monolayers are just metastable configurations that could be reachable at a low coverage regime $\theta \leq 1/3$. To check out this possibility we performed *ab initio* molecular dynamics (MD) simulations of the system corresponding to a Cu monolayer, $\theta = 1/3$, at several temperatures. The simulations show that even at $T = 100$ K, the Cu atoms quickly aggregate, giving rise to small clusters on the surface. A snapshot of the simulations showing a quasitetrahedral Cu



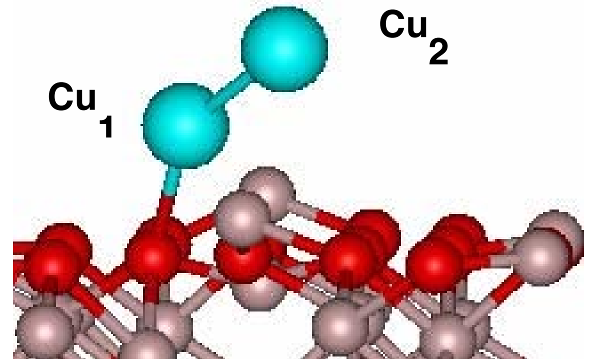




FIG. 1 (color online). Structure of the $Cu_2$ dimer supported on $\alpha\text{-}Al_2O_3$ (0001) and projected DOS. Cu: large gray spheres (blue); O: dark spheres (red); Al: small gray spheres.

cluster is reported in Fig. 2. The DOS of the isolated $Cu_4$ cluster shows the $3d^{10}\,4s$ nature of the atoms as expected. When the cluster is supported the DOS curves look quite similar, the main difference being a slightly smaller intensity of the $4s$ band together with a larger participation of the top Cu atom $4p_z$ orbital. The description corresponds therefore to a metal cluster likely partially oxidized, in which all atoms approximately have the same oxidation

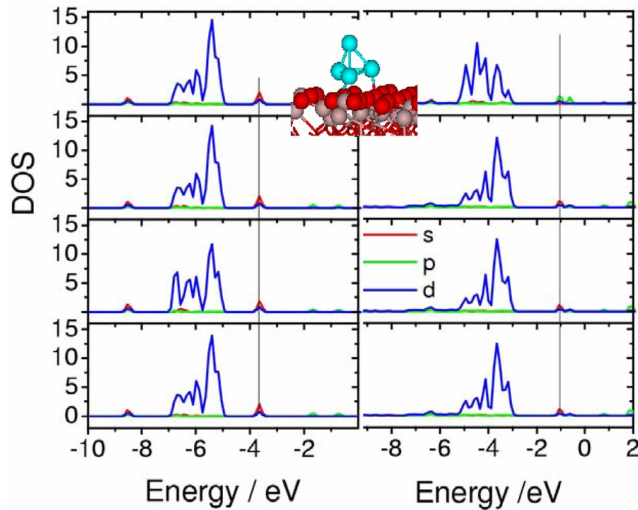



FIG. 2 (color online). DOS for the $Cu_4$ cluster isolated (left) and supported on $\alpha$-$Al_2O_3$ (0001) (right).

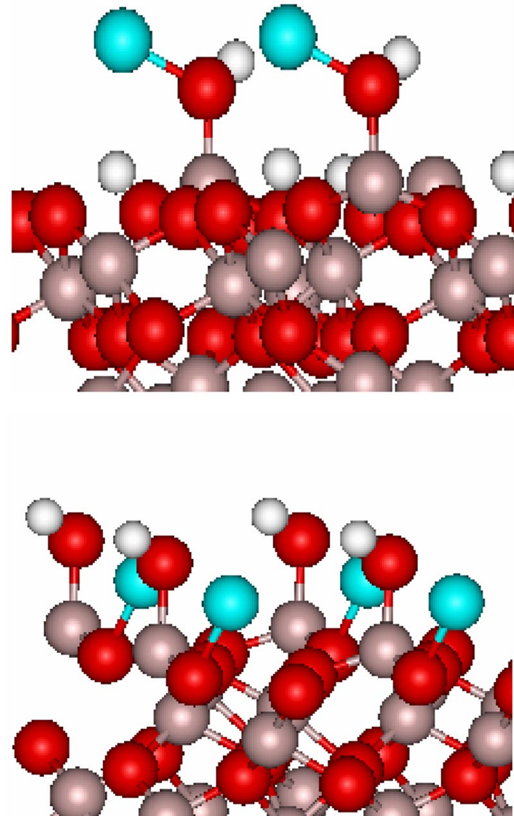


FIG. 3 (color online). Cu atoms interacting with a hydroxylated $\alpha$-$Al_2O_3$ (0001) surface (top) and after the surface reaction (bottom).

state. This description clearly disagrees with the Auger spectra [11], although agreeing with the formation of 3D clusters of Cu(0) observed when, for instance, a film is used [4].

Beyond structural details, the major difference between the aluminum oxide surfaces used in the last two experiments relies on the presence of hydroxyls. Actually, $\alpha$-$Al_2O_3$ (0001) surfaces are always hydroxylated [18], and those used in Ref. [11] had an estimated OH coverage of 0.47 ML. To consider the presence of $H_2O$ we start by adding one molecule per cell and compute the adsorption energy for both molecular and dissociative processes. The latter is favored by 0.4 eV in agreement with previous work [19]. The next step is to add Cu atoms to this partially hydroxylated surface. In the first stage, Cu atoms will interact with the outermost OH so we start by considering the interaction between the TM and the hydroxyls. The geometrical minimization leads to a structure (Fig. 3, top) in which the outermost oxygen atoms are bound to H (0.99 Å), Al (1.78 Å), and Cu (1.95 Å). The adsorption energy is 1.25 eV at $\theta = 1/12$ and the DOS analysis shows that the Cu atom is partially oxidized to Cu(I).

Besides this pure addition process a true surface reaction may occur. Indeed, in a recent experiment, Chambers *et al.* [20] showed that Co deposition on fully hydroxylated sapphire surfaces is accompanied by oxidation to $Co^{2+}$ and removal of OH. The reaction energy for the process, $2OH^- + Co_{(ad)} \rightarrow H_2 + 2O^{2-} + Co^{2+}{}_{(ad)}$, was estimated to be exothermic by 1.5 eV from GGA calculations. If we consider a similar reaction for our system, there are two different possibilities depending on which hydrogen atom is reduced. Our calculations show that the most stable structure is that in which the Cu atom removes inner hydrogen and binds the surface through an oxygen triad (Fig. 3, bottom). The associated process, $OH^- + Cu_{(ad)} \rightarrow \frac{1}{2}H_2 + O^{2-} + Cu^+{}_{(ad)}$, is exothermic by 1.35 eV. Therefore, the overall reaction, surf-OH + Cu (gas) $\rightarrow \frac{1}{2}H_2$ + surf-O-Cu, is exothermic by 2.6 eV. (It is worth noting that the process leading to $Cu^{2+}$ ions is endothermic by 0.12 eV.) Lodziana *et al.* have not observed such hydrogen elimination likely because of the different metal coverage explored [13].

From an energetic point of view, the surface hydrogen reaction is preferred, but we are indeed going to see that only this process is compatible with the Auger data. Let us consider the addition of a second Cu atom to the cell, $\theta = 1/6$. If the mechanism is a pure addition, the new Cu atom can interact with either a free surface hydroxyl or a Cu adsorbed atom forming a ${Cu_2}^+$ dimer. Calculations show the ${Cu_2}^+$ dimer to be more stable by 1.3 eV and corresponds as usual to a Cu(I)-Cu(0) pair, in disagreement with the Auger data. Analogously, if the mechanism is based on surface reaction, the second Cu atom can either remove a further H atom or bind a $Cu^+$ surface ion to give a ${Cu_2}^+$ dimer. Calculations show that formation of the ${Cu_2}^+$ dimer is now disfavored by 1.5 eV. Hence, at this coverage only the Cu-H exchange is compatible with the Auger data. Adding two more Cu atoms leads to the limit $\theta = 1/3$. Again, we may consider the two possibilities. Following the pure addition mechanism, two ${Cu_2}^+$ dimers are 3.2 eV

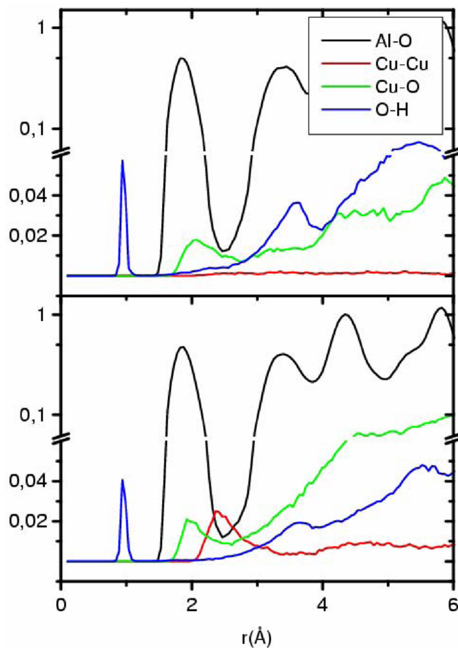



FIG. 4 (color online). Radial distribution function computed for the Cu/$\alpha$-$Al_2O_3$ (0001) system at $\theta = 1/4$ (top) and $2/3$ (bottom). Logarithmic scale after the break.

more stable than four separated Cu atoms. In contrast, substitution of two hydrogen atoms for the two new Cu atoms is 0.9 eV more stable than the formation of two $Cu_2^+$ dimers on the surface. There are some other intermediate alternatives, but these limit arrangements are enough to make clear that the exclusive presence of Cu (I) experimentally observed at $\theta \leq 1/3$ is possible only if the Cu adsorption is accompanied by a surface reaction involving hydrogen reduction. Actually, it is the H-H bond energy that compensates for the Cu(I)-Cu(0) energy of the $Cu_2^+$ dimer. If more Cu atoms are added to the surface it is obvious that no more Cu(I) can be formed as the presence of two relatively closed positive ions would be energetically disfavored. Instead, there is formation of $Cu_2^+$ dimers that aggregate in a way similar to that found for the nonhydroxylated surface.

The stability of the Cu(I) phase versus $\theta$ and $T$ was tested through *ab initio* MD simulations in the B-O surface in which samples corresponding to $\theta = 1/4$ and $2/3$ ML were regularly heated from 300 to 1000 K during 5.6 ps, and then a further 8 ps run was performed using the Nosé thermostat. The time step was 2 fs and the H mass set to 3. The simulations show that the Cu(I) phase is stable in the $\theta = 1/4$ sample, Cu atoms remaining separated with large amplitude oscillations on the surface, giving rise to an unstructured Cu-Cu partial radial distribution function, $g(r)$ (Fig. 4). The initial configuration for the $\theta = 2/3$ sample consists of four $Cu_2^+$ dimers ideally distributed on the surface and behaves in a completely different way. Some Cu atoms directly anchored to oxygen triads leave the surface and aggregate, forming an irregular Cu particle, in which true Cu-Cu bonds are observed. The Cu-Cu $g(r)$ shows a clear peak at 2.54 Å consistent with a Cu-Cu metal bond, while the DOS indicates that with respect to the initial configuration, there is a loss of identity of the Cu(I) and Cu(0) atoms that now appear hard to distinguish as most of them show the 4*s* band fractionally occupied.

In summary, the results emerging from the present calculations indicate that the growth mechanism of Cu deposits on alumina strongly depends on whether it is hydroxylated or not. For a clean anhydrous surface, there is a 3D VW growth whatever the coverage is. Some charge transfer from the metal particles to the surface may occur, but the overall behavior is that of unoxidized Cu. In contrast, in the presence of hydroxyls an exothermic surface reaction takes place with formation of Cu(I). Up to $\theta = 1/3$ such a reaction is energetically preferred against dimerization and therefore 3D clustering. Beyond this coverage Cu(0) begins to growth, likely as a partial second layer and as further 3D growth (SK mode). The evolution of these phases with the temperature simply indicates that 3D metal particles are more stable at high coverage.

Financial support from the Spanish Ministerio de Ciencia y Tecnología, Project No. MAT2002-0576, and from the Ramón y Cajal program (N. C. H.) are acknowledged.

*Corresponding author.
Electronic address: sanz@us.es

[1] C. R. Henry, Surf. Sci. Rep. **31**, 231 (1998).
[2] A. Bogicevic and D. R. Jennison, Phys. Rev. Lett. **82**, 4050 (1999).
[3] L. Giordano *et al.*, Phys. Rev. Lett. **92**, 96105 (2004).
[4] Y. Wu, E. Garfunkel, and T. E. Madey, J. Vac. Sci. Technol. A **14**, 1662 (1996).
[5] J. G. Chen *et al.*, Surf. Sci. **279**, 223 (1992).
[6] F. S. Ohuchi, R. H. French, and R. V. Kasowski, J. Appl. Phys. **62**, 2286 (1987).
[7] S. Varma, G. S. Chottiner, and M. Arbab, J. Vac. Sci. Technol. A **10**, 2857 (1992).
[8] S. Gota *et al.*, Surf. Sci. **323**, 163 (1995).
[9] M. Gautier, J. P. Duraud, and L. P. Van, Surf. Sci. **249**, L327 (1991).
[10] C. L. Pang *et al.*, Surf. Sci. **460**, L510 (2000).
[11] J. A. Kelber *et al.*, Surf. Sci. **446**, 76 (2000).
[12] C. Niu *et al.*, Surf. Sci. **465**, 163 (2000).
[13] Z. Lodziana and J. K. Norskov, J. Chem. Phys. **115**, 11 261 (2001).
[14] N. C. Hernández and J. F. Sanz, J. Phys. Chem. B **106**, 11 495 (2002).
[15] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993).
[16] J. Perdew *et al.*, Phys. Rev. B **46**, 6671 (1992).
[17] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
[18] M. A. Henderson, Surf. Sci. Rep. **46**, 1 (2002).
[19] K. C. Hass *et al.*, J. Phys. Chem. B **104**, 5527 (2000).
[20] S. A. Chambers *et al.*, Science **297**, 827 (2002).