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Lodziana, Zbigniew; Nørskov, Jens Kehlet

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# Adsorption of Cu and Pd on $\alpha\text{-Al}_2\text{O}_3(0001)$ surfaces with different stoichiometries

Z. Łodziana

*Center for Atomic-Scale Material Physics (CAMP), Department of Physics, Technical University of Denmark, Building 307, DK-2800 Lyngby, Denmark and Institute of Nuclear Physics, ul. Radzikowskiego 152, Kraków, Poland*

J. K. Nørskov<sup>a)</sup>

*Center for Atomic-Scale Materials Physics (CAMP), Department of Physics, Technical University of Denmark, Building 307, DK-2800 Lyngby, Denmark*

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We report density functional theory calculations of the interaction of Cu and Pd with the (0001) surface of  $\alpha\text{-Al}_2\text{O}_3$ . The interaction of those metals with the oxide surface varies from covalent-like for the aluminum rich surface to ionic-like for the oxygen terminated surface. Stoichiometric hydroxylation of the surface does not increase the metal–oxide interaction significantly. We suggest that defects created upon hydroxylation are the main mechanism to explain the observed metal wetting of the oxide. © 2001 American Institute of Physics. [DOI: 10.1063/1.1421107]

## I. INTRODUCTION

Knowledge of the interaction of metals with oxides is of crucial importance if we want to understand a broad variety of phenomena related to, for example, composite materials, corrosion, and heterogeneous catalysts.<sup>1–3</sup> In all cases the metal–oxide interface determines many properties of the system. Yet relatively little is known about such interfaces, not least because they are hard to study experimentally.

Recently, a substantial amount of experimental and theoretical interest has focused on the  $\alpha\text{-Al}_2\text{O}_3$  (0001) surface and there is some hope that this may serve as a prototype oxide surface for which we can establish the first coherent picture of the interaction between an oxide and different metals.<sup>4,5</sup>

For the case of the stoichiometric  $\alpha$ -alumina (0001) surface polarization interactions together with some residual covalent or ionic effects have been suggested to be responsible for the adhesion of a monolayer (ML) of Pt,<sup>6</sup> and the adsorption energy has been calculated to be  $\sim 2 \text{ J/m}^2$  using density functional theory (DFT) and the local density approximation (LDA). Studies of the interaction of different metals on ultrathin alumina films<sup>7</sup> confirm this picture. Within DFT calculations the adhesion energies depend on the exchange correlation functional used. The more accurate generalized gradient approximation (GGA) usually lowers calculated values of the adhesion energies by  $\sim 0.4\text{--}0.6 \text{ J/m}^2$ .

Scanning tunneling microscopy (STM) experiments, on the other hand, suggest stronger metal–oxide interactions with adhesion energies  $\sim 2.8 \text{ J/m}^2$  for both Cu<sup>8,9</sup> and Pd.<sup>9,10</sup> The growth of Cu and Pd on  $\alpha$ -alumina is found to produce three dimensional (3D) islands, and can be characterized as being of the Volmer–Weber type.<sup>8,10</sup>

Hydroxylation of the alumina surface dramatically influences the interaction with metals. In the case of rhodium<sup>11</sup> a

large increase of the metal island density on alumina thin films was observed by Heemeier *et al.*<sup>12</sup> For copper on thin alumina films, XPS studies by Kelber *et al.*<sup>13,14</sup> suggest that hydroxylation of the surface significantly increases the ability of the oxide surface to be wetted by Cu.

In the present paper we use density functional theory (DFT) calculations to study in some detail the adhesion of copper and palladium on the  $\alpha$ -alumina (0001) surface. In particular, we focus on the dependence of the adhesion on the structure of the surface. We consider the stoichiometric aluminum terminated surface, the aluminum rich surface, and the oxygen terminated surface. In addition we study various hydroxylated surfaces, including the fully hydroxylated surface<sup>15</sup> and the gibbsite-like  $\text{Al(OH)}_3$  surface.<sup>16</sup> The main conclusion is that the adhesion depends strongly on the structure of the surface. In addition, we find that the most stable, hydroxylated surfaces interact very weakly with metal overlayers. This lends further support to the notion that defects are responsible for the nucleation of metals on the alumina surface and that the observed strong metal adhesion is correlated with these defects.

In the following we first briefly review the present knowledge about the structure of alumina surfaces. We then describe the calculational method used in the present work, and discuss how our calculations describe bulk alumina and alumina surfaces. This leads us to the presentation of our results for the adhesion of Cu and Pd on these surfaces, and finally, we discuss our findings in light of the available experimental evidence.

## II. THE STRUCTURE OF THE $\alpha\text{-Al}_2\text{O}_3$ (0001) SURFACE

There is agreement in the literature that the most stable (0001) surface of  $\alpha\text{-Al}_2\text{O}_3$  or corundum is a stoichiometric surface, terminated by a single Al layer.<sup>6,17,18</sup> This surface undergoes large relaxations, where the surface aluminum

<sup>a)</sup>Electronic mail: noriskov@fysik.dtu.dk

moves into the bulk, ending up almost coplanar with the oxygen.<sup>6</sup> This type of surface is the one most often observed under UHV conditions.<sup>17,18</sup>

The (0001) surface can reconstruct giving rise to a  $\sqrt{31} \times \sqrt{31}R\pm 9^\circ$  pattern,<sup>19</sup> which is aluminum rich, i.e., there is more than a single aluminum layer terminating the surface. This type of surface seems to be stable with respect to oxidation and hydroxylation, since it does not oxidize when exposed to air at room temperature.<sup>19</sup> The reconstruction disappears only when heating above 1000 °C. Ahn and Rablais<sup>17</sup> reported the (0001) surface of corundum under ultra high vacuum (UHV) conditions to be a mixture of the aluminum and oxygen terminated structures. The oxygen termination of the surface is unstable, but could be stabilized by the presence of hydrogen on the surface.<sup>17</sup> The hydrogen is difficult to detect and the surface could appear to be terminated by oxygen. Indeed Eng *et al.*<sup>20</sup> reported recently, that under ambient conditions, the surface of  $\alpha$ -alumina is  $\text{Al(OH)}_3$ -like rather than a stoichiometric, and moreover an overlayer of water is present on the surface.

The surface also gives rise to unusually large atomic vibrations, where the amplitude of the perpendicular vibrations of the surface aluminum atoms is twice as big as those in the bulk.<sup>21,22</sup> Another point is that even on the most well prepared (0001)  $\alpha$ - $\text{Al}_2\text{O}_3$  surfaces, so-called *c/6* steps of height 0.22 nm appear isotropically.<sup>23</sup> Such configurations expose additional oxygen to the surroundings.

For several of the industrially interesting phases of alumina the situation is even more complicated. The microscopic structure of the porous alumina is not known, and since the porous alumina usually exist in the  $\gamma$ ,  $\delta$ , or  $\theta$  phases, the resulting surfaces have different coordination numbers of the surface cations.<sup>24</sup> In the porous phases the surface is almost always covered by hydroxyl groups or even by molecular water.<sup>24</sup>

Thin alumina films on metallic supports gives yet another type of aluminum oxide surfaces.<sup>25</sup> It seems that there is no agreement in the literature what the structures of these thin films are. Generally there is a mixture of tetrahedrally and octahedrally coordinated aluminum. The structure of the thin film has been described as being of the  $\gamma$ -alumina type,<sup>26</sup> but Stierle *et al.*<sup>27</sup> have reported x-ray diffraction studies of an alumina thin film on a NiAl(100) substrate, and found that the structure of the film is closer to the  $\theta$ -phase. Besides complications in the particular film ordering, there is experimental evidence that the presence of octahedrally coordinated aluminum is strongly enhanced giving a closer similarity of the surface to the  $\alpha$ -phase.<sup>28</sup>

### III. CALCULATIONAL METHOD AND THE PROPERTIES OF BULK AND SURFACE ALUMINA

Our model of the (0001)  $\alpha$ - $\text{Al}_2\text{O}_3$  surface consists of a  $1 \times 1 \times 1$  unit cell, 4 oxygen layers and 12 Å of vacuum, c.f. Fig. 1. The bottom layer of oxygen and aluminum are frozen in their bulk configurations. To exclude electrostatic effects we applied a dipole layer in the vacuum part of the unit cell. Careful tests showed that the surface energy of a 4 layer slab, as used in our calculations, differs by less than 0.02 eV/Å

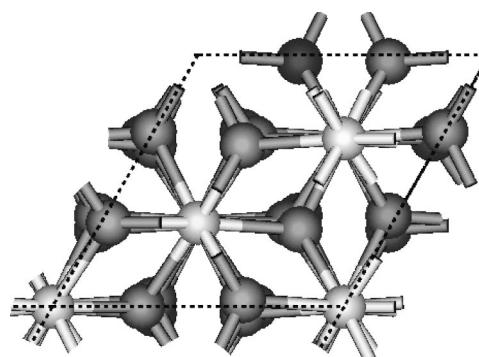


FIG. 1. Top view of the model unit cell. Dark spheres represent oxygen atoms; light-gray are aluminum. For the hydroxylated surface the OH group is attached to the surface Al, and hydrogen binds to one of the surface oxygens. In the gibbsite-like phase surface aluminum is replaced by three hydrogens.

from the one obtained in a calculation using a 9 layer thick slab. At the same time the relative interlayer spacing differs by less than 1%.

Our density functional calculations are based on the GGA-PW91 exchange-correlation functional.<sup>29</sup> The electronic density is determined by iterative diagonalization of the Kohn-Sham Hamiltonian. The ionic cores are represented by ultra soft pseudopotentials. The Cu  $3d4s4p$  and for Pd  $4d5s5p$  electrons are treated as valence electrons. A Monkhorst-Pack *k*-point mesh of the size  $2 \times 2 \times 1$  together with a plane wave energy cutoff of 340 eV is used. In some cases the density of the *k*-point sampling was increased as will be explained further below.

As a starting point we consider the properties of bulk alumina. The lattice parameters of the hexagonal corundum unit cell are calculated to be  $a = 4.724$  Å and  $c = 12.894$  Å. This should be compared to the experimental values of 4.759 Å and 12.99 Å.<sup>30</sup> The electronic band gap is found to be  $\Delta E = 7.77$  eV. This is smaller than the experimental one (8.75 eV<sup>30</sup>) as can be expected.

The surface properties we find are the following. The surface energy is  $\sigma = 1.56$  J/m<sup>2</sup> and 3.74 J/m<sup>2</sup> for the relaxed and unrelaxed (0001) surface, respectively. These values can be compared to 1.76 J/m<sup>2</sup> and 3.77 J/m<sup>2</sup> reported by Manassisidis *et al.*<sup>31</sup> An experiment-based estimate of the surface energy of  $\alpha$ -alumina is  $\sim 1.69$  J/m<sup>2</sup>.<sup>32</sup>

The calculated surface relaxation for different surface stoichiometries is presented in Table I. A large inward relax-

TABLE I. A comparison of the surface relaxation in % for different surface terminations. The surface terminations are denoted as ... Al—stoichiometric, ... Al-Al—Al-rich; ... O<sub>3</sub>—oxygen terminated; ... H<sub>2</sub>O—hydroxylated; (OH)<sub>3</sub>—gibbsite-like.

Ref. layer	... Al—	... Al-Al—	... H <sub>2</sub> O	... (OH) <sub>3</sub>	... O <sub>3</sub> —
Al <sub>1</sub> -O <sub>2</sub>	-87.5	-19.4	-14.2	-	-
O <sub>2</sub> -Al <sub>3</sub>	3.2	15.2	0.2	6.0	-14.4
Al <sub>3</sub> -Al <sub>4</sub>	-46.4	8.6	-33.1	-36.4	-10.3
Al <sub>4</sub> -O <sub>5</sub>	20.4	-19.9	8.4	10.4	15.3
O <sub>5</sub> -Al <sub>6</sub>	5.2	15.5	1.5	-0.4	-5.9

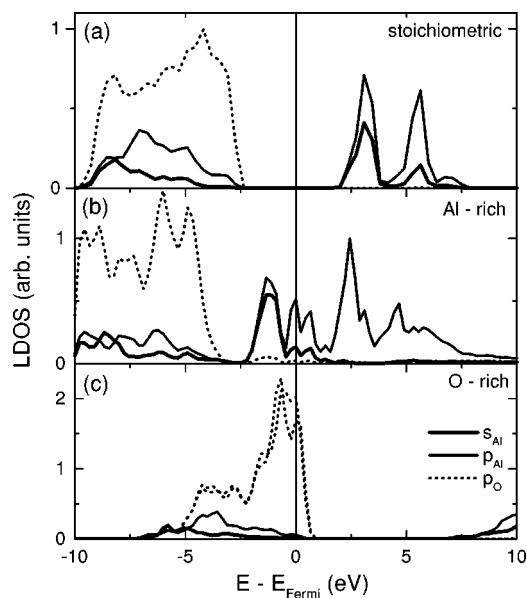


FIG. 2. Atom projected densities of states (LDOS) for the surface aluminum and oxygen on stoichiometric surface (a), aluminum rich surface (b), and oxygen terminated surface (c), of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. Solid lines represent  $s$  (thick) and  $p$  (thin) bands of Al, dotted lines are  $p$ -states of oxygen.

ation of surface Al is observed for the stoichiometric surface only. Going to another surface termination significantly influences the relaxation pattern.

The surface stoichiometry affects the electronic properties of the surface as well. In Fig 2 we show calculated local densities of states (LDOS) for the surface oxygen and aluminum atoms for different surface structures. The stoichiometric surface is known to be insulating with a band gap somewhat smaller than the bulk.<sup>30</sup> The oxygen  $2p$  states lie at the top of the valence band and are localized below the Fermi level. For the aluminum rich surface, on the other hand, additional electrons are available to occupy  $3s$  and  $3p$  Al states, resulting in a localized surface conduction band [cf. Fig 2(b)]. The metallic-like character of the Al-rich surface of corundum has been reported previously.<sup>33,34</sup> For the reconstructed  $\sqrt{31} \times \sqrt{31}$  surface we would expect the metallization to strongly influence the surface reactivity. For the oxygen terminated surface, on the other hand, the  $2p$  shell could be unfilled. The top of the valence band is then shifted above the Fermi level and the surface has a localized band—this time a band of holes [Fig 2(c)]. In the cases of Al-rich and O-rich surfaces, when any signs of metallization can be expected, we recalculated all results with the denser  $k$ -point grid of  $4 \times 4 \times 1$ . A denser integration mesh does not influence qualitatively our results and the adsorption energies are smaller by  $\sim 0.1$  eV ( $\sim 1\text{--}2\%$ ).

#### IV. ADSORPTION OF METALS

The adsorption of metals on the corundum surface was studied by placing one monolayer (ML) of metal pseudomorphically on the surface and performing a complete optimization of the interface structure. 1 ML is defined with respect to the oxygen layer (3 atoms per surface unit cell). In Table II we present the calculated adhesion energies for one mono-

TABLE II. Adhesion energies for the 1 ML coverage in J/m<sup>2</sup>. The surface terminations are denoted as ... Al—stoichiometric; ... Al-Al—Al-rich; ... O<sub>3</sub>—oxygen terminated; ... H<sub>2</sub>O—hydroxylated; (OH)<sub>3</sub>—gibbsite-like; ... OH—with radical •OH.

Surface	Cu	Pd
... Al—	0.91	0.99
... Al-Al—	3.26	5.14
... O <sub>3</sub> —	6.18	4.21
... H <sub>2</sub> O—	1.14	0.62
... (OH) <sub>3</sub> —	0.87	0.36
... •OH—	2.55	1.16

layer of Cu and Pd on different alumina surface stoichiometries. The adhesion energies were calculated as  $E_{ad} = -E_{slab} + E_{Al_2O_3} + E_{metal}$ , with  $E_{slab}$  representing the energy of the alumina slab with the metal adsorbed,  $E_{Al_2O_3}$  being the energy of the alumina slab, and  $E_{metal}$  the energy of a free monolayer of adsorbed metal. The latter energy is calculated for the lattice parameters of metals pseudomorphic with those of alumina.

The adsorption energies vary substantially from one alumina surface to the next in the manner similar to those observed for Ag,Nb/alumina.<sup>35</sup> For the stoichiometric alumina surface the adhesion of Cu and Pd are about the same, but any deviation from perfect stoichiometry gives rise to large differences. For the aluminum-rich surface Pd binds much stronger to the surface, while for the oxygen terminated surface the situation is the opposite. The gibbsite-like surface is the least reactive, while the hydroxylated surface is slightly more reactive. We also show the data for metals adsorbed on the corundum surface with nonstoichiometric amount of water in the last row of Table II. Those surfaces can be seen as remaining after a hydrogen transport out of the surface OH-groups has occurred. The GGA adhesion energy value of Cu on such a slab compares well to LDA result  $\sim 3$  J/m<sup>2</sup> reported in Ref. 14, where such a system was studied with more details.

Copper and palladium are fcc metals with lattice constants 3.6147 Å and 3.8907 Å, respectively. The lattice constant misfit with respect to the (0001)  $\alpha$ -alumina is then 8% and 16%. The valence electronic configuration of Cu is characterized by a filled  $d$  shell and a singly occupied  $s$  orbital. This prevents Cu from easily changing its electronic configuration during bond formation with the surface. For the palladium we have an unfilled  $d$  shell, and this gives a far more complicated interaction picture. Below we consider in more detail the nature of the metal/alumina bonding.

#### A. Stoichiometric, aluminum-rich, and oxygen terminated surfaces

The separation of the copper above the stoichiometric surface is found to be 1.24 Å and for palladium it is 1.43 Å. In both cases the metal atoms prefer to occupy the hcp sites over the oxygen. The adsorption of metals results in relatively large surface relaxations, where the topmost surface aluminum moves towards the surface. The relaxation is more

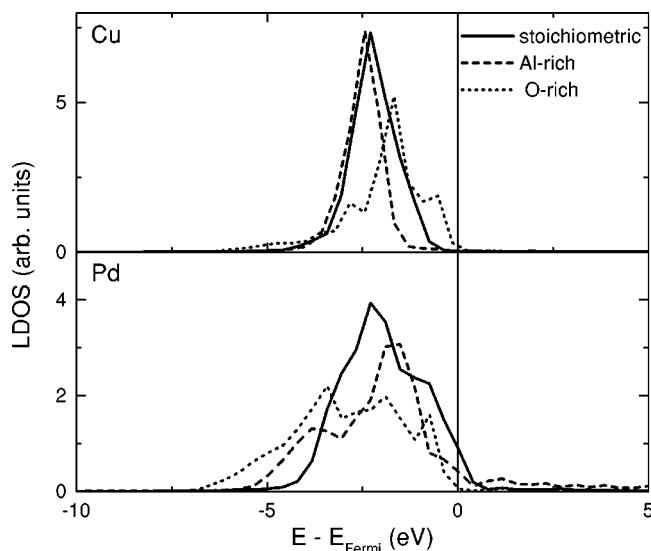


FIG. 3. Local densities of states (LDOS) for the  $d$ -band of metals adsorbed on various surface stoichiometries. Copper (top) and palladium (bottom). Solid lines are for stoichiometric, dashed for Al-rich and dotted for O-rich surfaces. The positions of the center of  $d$ -bands are aligned with respect to the positions of oxygen  $s$ -states for oxygens from third layers from top of the surface.

pronounced for Pd (O-Al separation is 0.56 Å) than for Cu (0.41 Å). For the aluminum-rich surface, the surface relaxation with an adsorbed metal overlayer is even more pronounced and now the oxygen–aluminum separation equals 0.77 Å for Cu, and 0.82 Å for Pd. The separation between the surface aluminum and Cu is 1.84 Å and for Pd it is 1.85

Å. For the oxygen terminated surface the situation differs, since the surface Al is replaced by the adsorbed metal atoms, and the copper atoms are smaller and move closer to the surface.

The atom-projected densities of states for Cu and Pd adsorbed on the different surfaces are presented in Fig. 3.

For clarity we show only the  $d$ -projections of the adsorbed metal. In the case of copper the shape of the  $d$ -band is unaffected when the metal is put on the stoichiometric surface. We have a similar situation for copper on the aluminum-rich surface, but for the oxygen terminated surface the  $d$ -DOS broadens, suggesting significant rearrangement of electrons within the  $d$ -shell. Splitting of bands in the Al-rich regime suggests an interaction between the Pd overlayer and the surface Al. On the oxygen terminated surface the shape of the  $d$ -DOS indicates significant rearrangements within the shell.

More insight into electronic rearrangements in the vicinity of the surface can be obtained by examining the charge density within the interface region. In Fig. 4 we show charge density difference plots for metals on the different alumina surfaces considered. They were calculated by subtracting the charge densities of the separated slab and metal overlayer in their relaxed configurations. Thus some care must be taken in the interpretation, because the relaxed configurations of the interface differ from those when the oxide or metal are relaxed separately.

For the stoichiometric surface we observe a small charge redistribution both for Cu and Pd. The situation is far more interesting in the case of the aluminum-rich surface. As

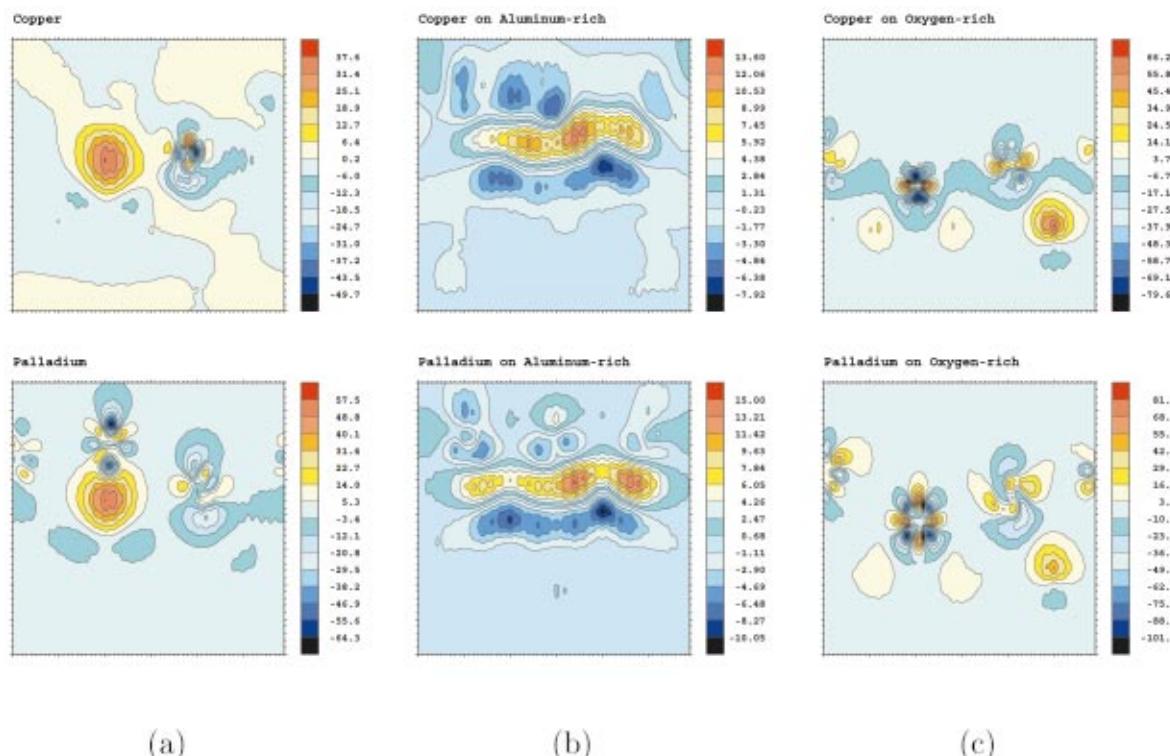


FIG. 4. (Color) The charge density difference plots for Cu (top) and Pd (bottom). Metals are (a) on stoichiometric surfaces, (b) on an Al-rich surface, (c) on the oxygen terminated  $\alpha$ - $\text{Al}_2\text{O}_3$ .

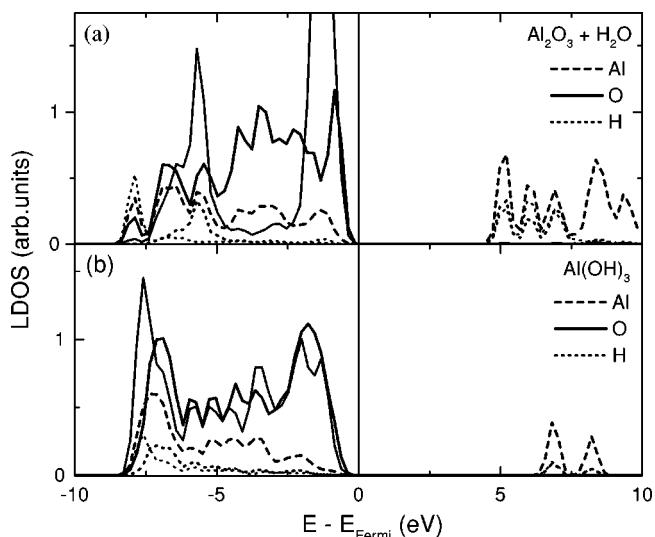


FIG. 5. Atom projected densities of states (LDOS) for the surface atoms of the hydroxylated  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (a) and gibbsite-like (b) surfaces. Dashed lines are for Al, solid lines are for O, and dotted lines are for H.

shown in Fig. 4(b), a charge accumulation is present between the oxide surface and the metal overlayer. Charge is more localized for the Pd which corresponds to a stronger bond (cf. Table II). When the surface is terminated by oxygen, a charge redistribution within the *d*-bands already suggested by the LDOS plots can be seen in Fig 4(c). Both copper and Pd have rearrangements in the *d*-shell.

## B. Hydroxylated surfaces

Under most ambient and industrially interesting conditions, the surface of alumina is hydroxylated. The dissociative adsorption of water leaves hydroxyl groups on the surface cations and hydroxylates the surface oxygen. An increase of the water vapor pressure results in a transformation into a gibbsite-like [Al(OH)<sub>3</sub>] structure. We considered hydroxylated (with a maximum water coverage of 10 OH/nm<sup>2</sup>) and gibbsite-like (15 OH/nm<sup>2</sup>) surfaces to check how the hydroxylation could influence the interaction of the oxide surface with metals.

First we examine the local electronic properties of the hydroxylated surfaces. The local densities of states for this type of surfaces are presented in Fig 5. In fact the overall LDOS for the hydroxylated surfaces do not differ significantly from those of the stoichiometric one. The oxygen *p* states are now more pronounced below the Fermi level Fig. 5(a), the features of the added oxygen show its bonding to the surface Al. In the gibbsite-like surface the band gap increases by about 2 eV; c.f. Fig. 5(b), with respect to the corundum analog. From the LDOS plots it would be expected that the hydroxylated surfaces should be less reactive than the nonhydroxylated surfaces since the band gap is the same or larger.

Placing 1 ML of metal over the hydroxylated surface always results in freezing hydroxyl groups between the metal overlayer and the oxide surface. Consequently, the metal overlayer is farther from the surface than in the case of the

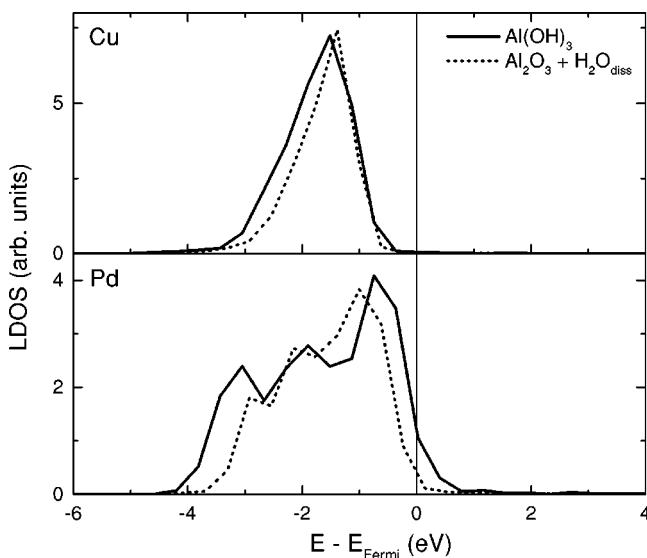


FIG. 6. Atom projected densities of states (LDOS) for the *d*-band of Cu (top) and Pd (bottom) on hydroxylated surfaces of corundum. The solid lines are for the gibbsite-like surface and dashed are for the hydroxylated  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. The positions of the center of *d*-bands are aligned with respect to the positions of oxygen *s* states for oxygens from third layers from the top of the surface.

nonhydroxylated surfaces. The separation of the metal overlayer and the surface aluminum is 2 Å for both Cu and Pd.

To check the possibility of the transport of hydrogen out of the interface region, we made two types of calculations. First we performed molecular dynamics simulations of the (Cu,Pd)/hydroxylated surface system at temperature 300 K. We did not observe any signs of hydrogen transport out of the interface region on a time scale of 0.5 ps, which indicates that any strong general driving force responsible hydrogen removal at high water coverage do not exist. This result, however, does not exclude the possibility of hydrogen evaporation, which could be hampered by the small size of our simulation unit cell and the limited simulation time scale. The other check consisted in investigating the energy of some possible static configurations when hydrogen is transported over the metal overlayer. We considered two cases when hydrogen from the surface OH or from ad-OH is transported above the metal, only from one OH group at a time. All configurations were allowed to relax. In the cases when hydrogen is transported it tends to occupy a hollow site on the metal plane. In all cases the energy cost of moving the hydrogen was  $\sim 0.5\text{--}1$  eV, which makes this process very difficult to occur. This result does not exclude, however, the possibility of hydrogen transport, at lower water coverages, as realized by some experiments, or in the presence of defects a proton transfer within the surface could be much easier.

The *d*-bands of neither Cu nor Pd show any significant changes for metals adsorbed on the surfaces, see Fig. 6. The relative difference in the positions of the *d*-band center with respect to the Fermi level reveals a fragile balance of the electrons in the surface region.

## V. DISCUSSION

The interaction of Cu and Pd overlayers with a stoichiometric alumina surface is weak, see Table II, and the interactions are mainly due to polarization effects; see Fig. 4. For nonstoichiometric surfaces of the corundum the interaction can be stronger and in these cases the mechanism of interaction depends strongly on the stoichiometry of the surface. For the Al-rich surface localized metallic electrons are available, which introduces the possibility of covalent bond formation. In fact we observe a splitting of the  $d$ -band for Pd. The charge density difference plots show significant charge accumulation in the vicinity of the interface. These observations indicate that the bond between the oxide surface and the metal has a covalent character. When we look at the energies of formation of Cu-Al and Pd-Al alloys, we notice that the formation energy of Pd-Al is equal to 0.66 eV/atom, while for Cu-Al it is only 0.08 eV/atom.<sup>36</sup> The large difference in those energies is refound in the difference between the adhesion energies of Cu and Pd on the Al-rich surface.

On the oxygen terminated surface, on the other hand, the mechanism of interaction seems to be ionic. The electronic structure of both Cu and Pd is strongly distorted, and some charge transfer occurs. Since copper is smaller it gets closer to the surface which makes electrostatic interactions stronger and accordingly the adsorption bond of Cu is stronger than for Pd.

The potential reasons for the discrepancies between experimentally measured<sup>10</sup> and calculated<sup>7</sup> adhesion energies of Cu/Pd/ $\text{Al}_2\text{O}_3$  was already discussed.<sup>37</sup> Our results suggest that the particular stoichiometry of the surface plays, beside elastic relaxations,<sup>37</sup> a very important role in the interface properties. As can be seen from Table II any deviation from perfect surface stoichiometry results already in the enhancement of metal/oxide interaction. We may presume that the differences in the values of the experimental and theoretical adhesion energies resemble different alumina surfaces encountered in both cases.

We find that the interaction between the two metals and the hydroxylated surfaces is very weak. This is in conflict with some experiments. XPS studies have been interpreted to show that with an increasing degree of hydroxylation, copper starts to wet an alumina surface.<sup>13,14</sup> The experiment cannot, however, distinguish between actual wetting where a monolayer (or more) spreads over the surface, and a significant increase of the metal island density. Atomic scanning tunneling microscopy (STM) suggests the latter situation. For rhodium deposited on clean and hydroxylated thin alumina films STM shows that with increasing hydroxylation the surface domain boundaries lose significance as the nucleation sites and the density of metallic islands increases on the surface.<sup>12</sup> The islands are distributed more homogeneously and the average island size reaches 10 atoms/island.<sup>12</sup> The electronic structure of rhodium is very similar to that of Pd, so we expect the mechanism of the metal/oxide interaction to be similar. The homogenous distribution of a metal islands may suggest that the hydroxylation introduces some surface defects. Defects can be seen as a locally nonstoichiometric regions of the surface and could be responsible for the enhancement of interaction.

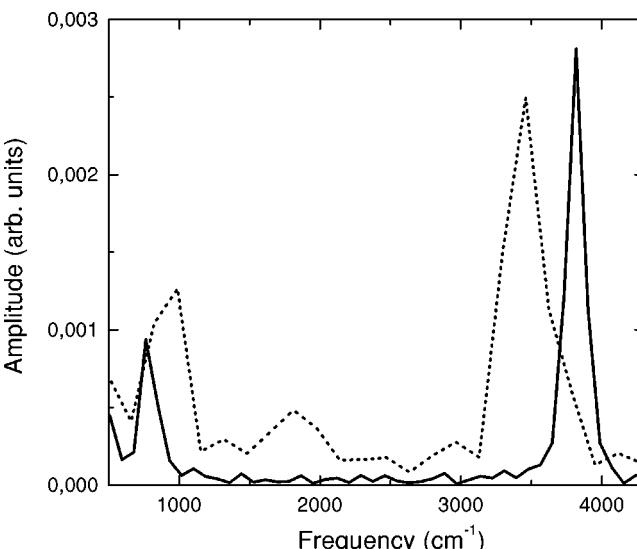


FIG. 7. Amplitude of the Fourier transform of the time dependent O–H separation on an  $\alpha$ - $\text{Al}_2\text{O}_3$  surface. The black line is for a pure hydroxylated surface and the dotted line is for a hydroxylated surface with an overlayer of copper.

The increased interaction of the Rh with the hydroxylated surfaces of alumina has been explained as a process of the consumption of surface hydroxyl groups.<sup>12</sup> Hydrogen diffuses out of the interface region leaving the oxygen terminated surface. This surface in turn strongly interacts with the metallic overlayer; see Table II. Our calculations show that it costs a substantial amount of energy to move the hydrogen from below the metal to above it when OH coverage is as high as 10 OH/nm<sup>2</sup>. However, at lower water or metal coverages the situation could be different. This interesting problem is waiting for explanation.

One of the main pieces of evidence that hydrogen is removed from the interface is the observation of a loss of OH stretch frequencies due to metal adsorption.<sup>12</sup> This can be explained in a different way. Our molecular dynamics simulations of the 0.5 ps time evolution of the Cu-hydroxylated alumina slab, did not reveal any signs of hydrogen transport out of the interface region, but the stretching frequencies of OH lowered considerably. The amplitude of the Fourier transform of the time dependent O–H separation is shown in Fig. 7. For the hydroxylated surface the stretch frequencies are in the region around  $\nu(\text{OH}) \sim 3850 \text{ cm}^{-1}$ , and they lower to 3500–3600 cm<sup>-1</sup> when the overlayer of Cu is present. As they fall into the “H-bond” region for IR spectroscopy these bands may become “lost” in the background. Moreover, decreasing of the vibrational frequencies is always related to softening a particular force constant; in our case the O–H bond. So one can interpret the observed softening as an initial stage of hydrogen desorption. Detailed studies of this point require a much bigger supercell and a time scale of at least of couple ps. They will be possible within a few years with the present increase of computer power.

Some comment is also needed to the suggestion of Kelber *et al.*<sup>13,14</sup> that hydroxylation of the (0001) surface of corundum increases the adhesion of Cu on that surface. Their calculations apply a model with only one OH group per sur-

face unit area. This makes the system different from those which result from the dissociation of water molecules, and thus from systems that are realized experimentally. The adsorption of a single OH molecule leads not to an adsorbed hydroxyl group OH<sup>-</sup> but rather to a •OH-hydroxyl radical. The interaction of radical with metals is strong. This we have also found; c.f. Table II.

To summarize, our DFT study of the interaction of Cu and Pd with surface of  $\alpha$ -alumina showed that the interaction very strongly depends on the surface stoichiometry. The adsorption energy varies from 0.91 (0.99) J/m<sup>2</sup> for the stoichiometric surface to 6.18 (4.21) J/m<sup>2</sup> for the oxygen terminated surface for copper (palladium). The adhesion energy of Cu on a Al<sub>2</sub>O<sub>3</sub> film has been deduced from STM experiments to be 2.8 J/m<sup>2</sup>.<sup>8</sup> This is incompatible with our results for the stoichiometric surface, and suggests that either the whole surface is nonstoichiometric or, more likely, that the metal clusters nucleate at defects or clusters of defects. Defects are essentially localized regions of a different stoichiometry. Depending on the defect concentration, the adhesion energy should be somewhere in between that for the stoichiometric and the defected surfaces, which is definitely what is observed. A more detailed comparison will have to await a better characterization of the state of the surface where the metal is adsorbed. High coverage hydroxylation does not give rise to a stronger metal–aluminum oxide interaction, and therefore cannot explain the observed wetting of aluminum oxide by Cu following hydroxylation.<sup>13</sup> Instead we again suggest that defects created upon surface hydroxylation may be responsible interaction changes, since our results clearly show that both oxygen deficient and oxygen-rich surfaces interact stronger with metals than the stoichiometric one. They also may influence a kinetic processes of hydrogen transport. Defects can occur in particular during the formation of the fully hydroxylated Al(OH)<sub>3</sub>-like surface, since that process involves substantial mass transport of Al.

*Note added in proof:* During the reading of the proof manuscript we were alerted to the experimental evidence of the inhomogeneous hydroxylation of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. Hydroxide clusters were observed on the reconstructed surface composing a quasi regular pattern of defects.<sup>38</sup>

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