Cu, Ag and Au atoms deposited on the $\alpha$-Al$_2$O$_3$(0001) surface: a comparative density functional study

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Received 6 October 2004; accepted for publication 12 November 2004
Available online 30 November 2004

Abstract

A comparative study of the interaction between single copper, silver and gold atoms and the regular Al-terminated $\alpha$-Al$_2$O$_3$(0001) surface is reported. The surface was simulated by means of periodic slabs and the calculations were undertaken using the spin-polarized density functional theory within the generalized gradient approach. For metal adsorption, five different sites were considered, two on top of Al and O atoms, and three on hollow positions in which the transition metal binds three surface O atoms. Metal–surface interaction is relatively weak with adsorption energies in the range 0.7–1.1 eV, following the order Cu > Au > Ag. The preferred site for Cu and Ag are the three fold hollow oxygen sites while Au atoms prefer to bind the surface on top of the oxygen atoms. Examination of the electron density plots shows that some charge transfer toward the surface takes place according to the sequence Cu > Ag > Au. An analysis of the bond mechanism based on model cluster calculations indicates that for Cu and Ag the largest contribution to the interaction energy arise from the charge transfer from the adsorbed atom to the surface while in the case of Au, the interaction is dominated by the polarization of the transition metal.

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Keywords: Copper; Silver; Gold; Adsorption; Aluminium oxide; Density functional calculations

1. Introduction

Properties of metal–ceramic interfaces constitute one of the most appealing challenges nowadays for material scientists, since they are the controlling keys to numerous technological applications [1,2]. The size of deposited transition metal particles, TM, often fall within the nanometer range, exhibiting exceptional physical or chemical properties, which may be of technical interest in such diverse industrial areas such as microelectronics, heterogeneous catalysis, photovoltaic cells and protective coatings for metals [3–5]. Understanding the bonding features of single atoms
and small clusters interacting with metal oxide surfaces are of great importance in unraveling the initial stage of interface formation. The adsorption of single TM atoms on the defect-free Al-terminated $\alpha$-Al$_2$O$_3$(0001) surface has been the subject of several recent theoretical works. Concerning late TM atoms, adsorption properties of Pd, Pt, Cu and Ag on the clean surface have been theoretically examined [6–12]. Analysis of the metal–surface bond shows different behavior depending on the electronic structure of the TM atom. For instance, calculations based on plane-waves and the periodic density functional theory, DFT, using a generalized gradient approach (GGA), show that at low Pd coverage ($\theta = 1/3$ ML, i.e. one adatom for every three surface oxygen atoms), Pd atoms bind the surface on top of the oxygen atoms (site O$_2$ in Fig. 1) [8]. Analysis of the interaction energy based on model cluster calculations showed that the main contribution comes from metal polarization and surface relaxation, with little charge transfer from the metal to the surface. At variance, when Cu atoms are deposited, our calculations showed that the surface is reduced with formation of Cu(I) species [12], in agreement with experimental data based on Auger spectroscopy [13]. Also, the preferred site is the hollow position in which Cu binds three oxygen surface atoms above an aluminium ion underlying a subsurface plane (site Al$_4$ in Fig. 1). Influence of the TM atom spin state has also been analyzed recently for the case of Co, Rh and Ir [14]. In general these atoms prefer to be adsorbed close to surface oxygen atoms. This was found to be independent of the spin state considered in the calculations. However, explicit consideration of the spin polarization is important because the interaction of the TM atom with the substrate may have important effects on its local electronic state. In fact, Co and Ir are found to maintain three unpaired electrons as in the isolated atoms; whereas, in the case of Rh a partial quenching of the total spin is observed.

Because of the high activity as oxidation catalyst of gold nanoparticles supported on metal oxides, a large number of works have been focused on these systems (see Refs. [15–17] for recent reviews). However, in spite of the high interest in these catalysts, only a small number of theoretical works have been devoted to analyze the gold–support interface; and those being mostly concern with rutile TiO$_2$(110) surfaces [18–22]. In a preliminary work we reported on a study of the Au/$\alpha$-Al$_2$O$_3$(0001) interaction based on DFT-GGA calculations [23]. Compared with Cu, the preferred site for gold is on top of surface oxygen atoms, the adsorption energy dropping from 1.09 for Cu to 0.81 eV for Au. The preferred site is actually similar to that of Pd atoms, although their interaction energy is significantly larger (1.4 eV) [8]. These results suggest that on going from Cu to Au a change in the metal–surface bond mechanism could take place although for a meaningful interpretation the features of the silver–surface interface need to be considered.

The Ag/$\alpha$-Al$_2$O$_3$(0001) interface was examined by Verdozzi et al. [9] using a local density ap-

![Fig. 1. Portion of the Al terminated $\alpha$-Al$_2$O$_3$(0001) surface showing the adsorption sites. Left: side view showing the layer labeling. Right: top view with explicit referring to oxygen sites. Red and gray spheres correspond to oxygen and aluminum atoms, respectively. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)](image-url)
The adsorption energy at 1/3 ML was estimated to be 1.1 eV. On the other hand, Zukhovski et al. [10] reported on theoretical calculations on this interface carried out at the Hartree–Fock level with a posteriori electron correlation corrections. In contrast, the adsorption energy reported by these authors for the Al-terminated surface at the same coverage was only 0.54 eV. The dispersion of these results precluded a reliable comparison with our DFT-GGA calculations for Cu and Au, and suggested the possibility of performing an analysis of the metal–surface bond properties of these systems. With this aim, we report in this paper on a comparative study of the interaction between Cu, Ag and Au with the Al-terminated \( \alpha \)-Al\(_2\)O\(_3\) (0001) surface based on DFT-GGA calculations carried out on the same grounds for the three metals. Two types of computational models were used. First, the calculations were performed under periodic conditions in order to get optimized geometries and adsorption energies. Secondly, using model cluster calculations, a partition energy scheme was employed in order to obtain the different contributions for the metal–surface bond.

This paper is organized as follows: In Section 2, models and computational methods are described. The results and discussion are presented in Section 3. Finally, the main conclusions are outlined in Section 4.

2. Models and computational methods

For the calculations performed under periodic conditions the supercell approach was used. The unreconstructed \((1 \times 1) \ \alpha\)-Al\(_2\)O\(_3\) (0001) surface was represented by a 12-layer thick unit cell consisting of a rhombic prism belonging to the hexagonal system to which periodic 3D conditions were imposed, allowing a vacuum width of 10 Å between the slabs. This vacuum width was wide enough to prevent layer-to-layer interactions. The supercell was obtained by truncating the bulk \( \alpha \)-Al\(_2\)O\(_3\) structure, leaving one Al layer exposed with an oxygen layer right beneath it; this surface termination is generally known as Al-terminated \( \alpha \)-Al\(_2\)O\(_3\) (0001) surface. Other surface terminations are also possible but the present study will be concerned exclusively with adsorption on the Al-terminated surface because, since the LEED experiments it seems to be established that under UHV conditions this is the favored termination [24]. The thickness of the slab is determined by examining the convergence of the surface relaxation against the number of layers. As previously shown, the relaxation of the outermost surface ions computed using the 12-layer thick slab (20 atoms/unit cell) is almost identical to that obtained with thicker slabs [6].

DFT calculations under periodic conditions were carried out using the VASP code [25–27] and the generalized gradient approach, GGA, implementation proposed by Perdew et al. [28]. Since the electron configuration of the TM atoms is open shell, d\(^{10}\)s\(^{1}\), spin-polarized calculations were undertaken. Ultrasoft pseudopotentials [29] were employed to remove the core electrons from the calculations, and a plane-wave basis set was used to span the valence electronic states. The cut-off energy for the plane-waves was 337 eV and the Monkhorst–Pack set of \( 8 \times 8 \times 1 \) \( k \) points was used. Structural minimizations were performed using a conjugated-gradient technique, the residual forces on the atoms being less than 0.1 eV/Å. Adsorption energies were calculated as the difference between the metal–surface system energy and the sum of free surface and isolated metal energies.

In the model cluster calculations the surface is represented by a finite cluster of aluminium oxide embedded in an array of formal point charges intended to render the electrostatic effects. The procedure used to build the cluster and the environment has already been reported in Ref. [8]. Briefly, the cluster is embedded in a set of formal charges set to \( q_O = -2e \) and \( q_{Al} = +3e \) according to the high ionic character of corundum. In order to avoid a spurious polarization of the cluster atoms by the surrounding point charges, the border ions are represented through compact model potentials [30] with a residual charge that, beyond the classical interaction between these residual charges and the cluster, introduce Coulomb and exchange HF lattice–cluster interactions.
3. Results and discussion

Let us start this section with the calculations performed under periodic conditions. Adsorption of TM atom on the \(\alpha\text{-Al}_2\text{O}_3(0001)\) surface may occur at five different sites of high symmetry. These sites are shown in Fig. 1 and labeled with a letter and a number indicating the type of atom and the atomic layer in the surface, respectively. Sites Al\(_1\) and O\(_2\) represent on top sites while Al\(_3\), Al\(_4\) and O\(_5\) actually are hollow sites in which the adatom coordinates three surface oxygen atoms and in the subsurface there are aluminum atoms (medium, Al\(_3\) and lower, Al\(_4\)) or oxygen atoms (O\(_5\)). For the hollow sites, it is necessary to point out that this is just a labeling scheme and we do not mean that we expect a direct interaction between the TM atom and these deeply lying layers. As we have already reported, the interaction of a Cu atom with the surface is accompanied by a relatively large surface relaxation\([12]\), which is also expected for the rest of the TM atoms considered here. To analyze separately the contribution of such a relaxation to the interaction energy two series of calculations were performed. In the first one (unrelaxed) the surface atoms were kept fixed at the positions obtained from the surface optimization, and only the TM atom distance to the surface was optimized. In the second series of calculations (relaxed) the positions of both the TM atom and the six outermost surface layers of atoms were optimized. The results for the three TM atoms obtained from both approaches are reported in Table 1 (unrelaxed surface values in parentheses). Starting with the adsorption energies obtained with the unrelaxed surface, one can see that the largest interaction corresponds to Cu atom (0.70 eV), followed by Au (0.52 eV), and Ag (0.41 eV). As expected, when the surface is allowed to relax, the interaction energies increase for the three TM atoms. The increment is large for Cu (\(~0.4\) eV) and smaller for Ag and Au (0.2 and \(~0.3\) eV, respectively). In other words, the contribution of the relaxation is dramatic as these increments represent roughly 50–60% of the total interaction energy. It is also worth noting that the sequence of the adsorption energies Cu > Au > Ag is preserved and slightly amplified. The preferred sites of adsorption are different depending on the TM metal and if surface relaxation is introduced. Considering only the relaxed results, both Cu and Ag prefer to bind the surface interacting through oxygen triads above aluminum atoms of the forth layer (Al\(_4\) sites). In contrast, gold atoms prefer to adsorb on top of surface atoms, with small difference between oxygen (O\(_2\) site 0.81 eV) and aluminum (Al\(_1\) site 0.78 eV).

Surface relaxation involves a shortening of the metal–surface distance. Considering only the most stable sites, this lowering is dramatic for Cu (\(~0.87\) Å) and smaller for Ag (\(~0.44\) Å) and Au (\(~0.27\) Å). Since the TM–surface distance is defined as the distance between the TM atom and the first aluminum layer, this shortening actually reveals the surface relaxation of the outermost Al layer, i.e. the Al\(_1\) atoms, as indicated by the change in the \(z\) coordinate of these atoms, \(\Delta z\). As reported in Table 1, after surface optimization the \(z\) coordinate increases by 0.393, 0.244 and 0.271 Å for Cu, Ag and Au, respectively. Compared with the changes of the TM–surface distances, it appears that for Au most of the shortening corresponds to the surface Al\(_1\) relaxation, while for Cu both Al\(_1\) relaxation and further surface atoms rearrangement allows for a closer TM–surface interaction. For Ag an intermediate situation is found. The trend found in the variation of TM–surface distances can be understood taking into account both the ionic radii and the preferred site for adsorption. Smaller Cu atoms can be better accommodated on the surface, mainly when interacting at the hollow sites, than relatively large Au atoms sitting on top of surface ions.

To explain the large outward relaxation of the outermost aluminum atoms induced by the TM deposition two main reasons may be invoked. First, such displacements could originate by a weakening of the attraction of the outermost aluminum atoms by the surface oxide ions. Since aluminum oxide is assumed to be essentially an ionic solid, this weakening should be indicative of a reduction of aluminum atoms by the TM atom. Second, the TM deposition involves some recovering of the lost coordination of the surface with respect to the bulk, which tends to restore the interlayer distance. With the aim of tracing the
charge transfer from the TM atom to the surface, the projected density of states, DOS, curves and the differential electron density properties will be analyzed. In Fig. 2, the DOS curves for the three M/\(\alpha\)-Al\(_2\)O\(_3\) interfaces obtained from the GGA calculations at the Al\(_4\) site are reported. The DOS projected on Cu (top left) shows that upon adsorption the Cu 4s band disappears while some peaks in the s and p bands of Al and O surface atoms become apparent. The loss of the 4s band indicates that the adsorption is accompanied by oxidation of the TM atom as already reported\(^{[12]}\). However, the corresponding DOS curve projected on Au (top right of Fig. 2) clearly shows the 6s band just below the Fermi level, together with some peaks in the p band of O surface atoms, indicating that in this case, the electron transfer from the TM to the surface is small if it exists at all. The case of Ag falls between Cu and Au: the 5s band is smaller than the Au 6s one, but it is still perceptible precisely at the Fermi level.

Table 1
Adsorption energies (eV) and metal–surface distances (Å) from GGA periodic calculations

<table>
<thead>
<tr>
<th>Adsorption site</th>
<th>Cu(^{a})</th>
<th>Ag</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_{\text{ads}})</td>
<td>(\Delta z)</td>
<td>(E_{\text{ads}})</td>
<td>(d (\text{surf.}))</td>
</tr>
<tr>
<td>(0.40)</td>
<td>(0.33)</td>
<td>(0.78)</td>
<td>2.511</td>
</tr>
<tr>
<td>(0.94)</td>
<td>(0.51)</td>
<td>(0.81)</td>
<td>1.965</td>
</tr>
<tr>
<td>(0.75)</td>
<td>(0.46)</td>
<td>(0.39)</td>
<td>1.245</td>
</tr>
<tr>
<td>(1.09)</td>
<td>(0.61)</td>
<td>(0.49)</td>
<td>1.054</td>
</tr>
<tr>
<td>(0.95)</td>
<td>(0.55)</td>
<td>(0.71)</td>
<td>1.423</td>
</tr>
</tbody>
</table>

Values in parentheses correspond to the unrelaxed surface. \(\Delta z\) (Å) refers to the shift of the outermost Al atoms when the surface is allowed to relax. Underlined \(E_{\text{ads}}\) indicates the most stable sites.

\(^{a}\) Ref. [12].

Fig. 2. GGA density of states at \(\theta = 1/3\) ML obtained for M/\(\alpha\)-Al\(_2\)O\(_3\) interfaces projected on the transition metal atom (top), surface aluminum atom (middle) and surface oxygen atom (bottom). Left M = Cu; center M = Ag, and right M = Au.
Plots of the differences in the electron density, $\Delta \rho$, for the three interfaces are reported in Fig. 3. These differences are computed according to:

$$\Delta \rho = \rho(\text{M}/\alpha-\text{Al}_2\text{O}_3) - \rho(\alpha-\text{Al}_2\text{O}_3) - \rho(\text{M}),$$

and are plotted as surfaces of isovales of $\Delta \rho = +0.04 \text{ e/Å}^3$ (blue) and $\Delta \rho = 0.04 \text{ e/Å}^3$ (red). Starting with the Cu case, one can see that upon adsorption the electron density decreases around the TM atom and increases on the surface, in particular on top of the Al$_1$ site. This plot agrees with the two-dimensional maps of $\Delta \rho$ reported previously [12], and confirms the charge transfer from Cu towards the surface. Comparing the plot of the three TM atoms one can see that going down the group the charge transfer from TM atoms to the surface gradually diminishes in agreement with, for instance, the trend observed when Cu, Ag and Au are deposited on the TiO$_2$(110) rutile surface [20]. This behavior of course agrees with the variation of the oxidation capability or noble metal character down the group. The drop in the degree of TM oxidation involves a gradual diminution of the electrostatic contribution to the TM–surface interaction and, therefore, a diminution of the adsorption energy would be expected. Indeed, this is the case for the Cu and Ag pair, but not for Au, for which, compared to Ag, the interaction energy increases even if both the DOS and differential electron density features clearly indicate that the electron donation to the surface is smaller, if any.

The calculated alteration of the adsorption energies, as well as the fact that for Au there is a qualitative change in the preferred site, suggests that beyond the electrostatic contribution other effects are significant. To quantify the different contributions to the TM–surface interaction energy we have performed a Constrained Space Orbital Variation, CSOV, analysis [31–34] using the model cluster approach. Basically, the CSOV technique allows one to separate the polarization and charge transfer contributions to the interaction energy between two fragments. In Table 2 the estimated contributions calculated for the preferred sites are reported. The initial Pauli repulsion between the frozen densities of the TM atoms and the cluster model is offset by the sum of the various bonding contributions. First, inter-unit charge transfer from the surface to the TM atom and from the TM atom to the surface provides the covalent contributions to the chemical bond. It is important to note that these contributions are obtained when allowing the orbitals of a given unit to vary in the virtual space of the other unit and, hence, include the BSSE contribution. In general, BSSE is small enough and can be neglected but in metal–support interactions removing the BSSE is essential [35] and, therefore, additional analysis is required. In fact, charge transfer from the surface to the TM atom range between 0.22 and 0.28 eV, but this comes almost exclusively from BSSE, i.e.
the same energy lowering is found when adding the TM basis to the substrate. This is illustrated in Table 2 for the case of Au, for which the charge transfer from the surface amounts by $0.22 \text{ eV}$, close to the contribution of this step to the BSSE correction ($0.17 \text{ eV}$). This is at variance with the charge transfer from the TM atom to the surface energy contribution that is significantly larger than the corresponding BSSE step ($0.08 \text{ eV}$), showing thus that this bonding mechanism is physically meaningful. As can be seen, this contribution is large for Cu ($0.51 \text{ eV}$) and diminishes by 50% for Ag and Au ($0.23, 0.24 \text{ eV}$). For these two TM atoms, the difference is meaningless and difficult to interpret mainly by taking into account that the adsorption site is not the same. Let us now consider the polarization contributions. The intra-unit polarization contribution from the substrate is relatively small, as expected for an ionic system. However, the TM polarization makes a relatively large contribution, mainly for Au, for which it becomes the main contribution: $0.37 \text{ eV}$. Summing up the physical contributions and correcting for the BSSE results in a total interaction energy of $0.90, 0.43$ and $0.61 \text{ eV}$, for Cu, Ag, and Au respectively, in reasonable agreement with the values found from using the periodic approach. Comparing now the different contributions of each atom the result is that the metal–support bond for Cu is dominated by the charge transfer to the surface and to a lesser extent by metal polarization. For Ag the two contributions are almost equivalent while in the case of Au, the dominant bonding mechanism is the metal polarization. These results are coherent with the observed change in the site of adsorption: Cu atoms are electronically depleted and bind the surface through oxygen triads. Instead, to improve the bonding, the more deformable and noble Au atoms prefer to bind on top of Al and O atoms, increasing the metal polarization contribution to the bond in a mechanism close to that observed in the Pd/α-Al$_2$O$_3$ interaction [8].

### Table 2

Contributions (eV) to the metal–support interaction energy ($E_{\text{ads}}$) estimated by means of a Constrained Space Orbital Variation analysis performed from model cluster calculations.

<table>
<thead>
<tr>
<th></th>
<th>Pauli</th>
<th>Surf Pol</th>
<th>Surf → M</th>
<th>M Pol</th>
<th>M → Surf</th>
<th>Rest</th>
<th>$E_{\text{ads}}$/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>+0.31</td>
<td>−0.22</td>
<td>−0.28</td>
<td>−0.24</td>
<td>−0.51</td>
<td>−0.10</td>
<td>−0.90$^a$</td>
</tr>
<tr>
<td>Ag</td>
<td>+0.22</td>
<td>−0.10</td>
<td>−0.23</td>
<td>−0.24</td>
<td>−0.23</td>
<td>−0.09</td>
<td>−0.43$^a$</td>
</tr>
<tr>
<td>Au</td>
<td>+0.17</td>
<td>−0.05</td>
<td>−0.22</td>
<td>−0.37</td>
<td>−0.24</td>
<td>−0.08</td>
<td>−0.61$^a$</td>
</tr>
</tbody>
</table>

Table entries: Pauli repulsion; surface polarization (Surf Pol), surface to adsorbed metal charge transfer (Surf → M), metal polarization (M Pol), metal to surface charge transfer (M → Surf) and residual contributions (Rest).

$^a$ BSSE corrected.

$^b$ BSSE contribution of charge transfer from counterpoise method.

4. Conclusions

In this paper, we report a comparative study of the interaction between single copper, silver and gold atoms with the Al-terminated γ-Al$_2$O$_3$-(0001) surface based on theoretical calculations. The surface was simulated by means of periodic slabs and the calculations were undertaken using the spin-polarized density functional theory within the generalized gradient approach. Cu and Ag atoms preferred to interact with the surface at the hollow oxygen sites, while for gold the most stable sites were on top of surface atoms. The TM–surface bonding was relatively weak, with interaction energies ranging between −0.6 and −1.1 eV, following the order Cu > Au > Ag. Analysis of the density of states curves and the properties of the electron density surfaces shows that some charge transfer toward the surface takes place according to the sequence Cu > Ag > Au. Analysis of the different contributions to the bonding energy based on model cluster calculations indicates that going down the group there was a change in the bond mechanism. For Cu the largest contribution to the interaction energy arises from the charge
transfer to the surface and in lesser extent some transition metal polarization. For Ag and Au, the contributions to the energy coming from the charge transfer to the surface were similar, although smaller than for Cu. For Ag and Au, the TM polarization becomes significant, and in the case of Au, (the most polarizable), the bonding energy was dominated by this contribution. This change in the bond mechanism is coherent with the change observed in the adsorption site.

Acknowledgments

Financial support from the Spanish Ministerio de Ciencia y Tecnología, (MAT2002–0756), the Ramón y Cajal program (awarded to N.C.H.), and the Junta de Andalucía (FQM-132), is fully acknowledged.

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