J Mater Sci (2010) 45:4265–4270
DOI 10.1007/s10853-010-4427-2

EUROMAT 2009

Ab initio simulations of the Ag(111)/Al_2O_3 interface at intermediate oxygen partial pressures

D. Passerone · C. A. Pignedoli · F. Valenza ·
M. L. Muolo · A. Passerone

Received: 20 November 2009 / Accepted: 17 March 2010 / Published online: 30 March 2010

Abstract The relative stability of different realizations of the Ag(111)/Alumina interfaces with varying oxygen partial pressures is investigated by means of ab initio density functional theory (DFT) simulations. Previous theoretical studies of similar systems always involve oversimplified geometries like stoichiometric Al-terminated, Al-rich, or O-terminated alumina interfaces. Such framework cannot explain the experimental behavior observed at intermediate oxygen partial pressure. Our approach, instead, suggests that the oxygen at the interface can play an important role at intermediate concentrations, leading to a more realistic interpretation of the experimental data.

Introduction

The microscopic characterization of interfaces with the help of ab initio simulations has reached a considerable level of accuracy and complexity.

With the increase of computational power and the development of new algorithms, realistic modeling of extended systems has become possible in physics, chemistry, and biology (see, e.g., [1]); in particular, in materials science, the microscopic characterization of interfaces by means of accurate electronic structure models based on density functional theory (DFT) can shed a new light on the interpretation of the results of advanced experimental investigations.

Metal/ceramics interfaces, for example, due to the broad technological applications in electronics, catalysis, medicine, and engineering, have been the object of extensive study (see, e.g., [2]).

Quantities directly accessible to experiments, like the work of adhesion and the work of separation (see, e.g., [3–6]; for a thorough review about the experimental determination of work of separation and its connection to wetting and adhesion, see [2]) could be computed for systems like metal/sapphire [7, 8], metal/ceramics in presence of titanium [9–14] and of Hf, S, and Pt [15]; several authors developed a theoretical framework to include entropic effects and partial pressure of other elements in the model [16–22], or of different orientation of the interface constituents [12–14].

Another very active field of research concerns the interfaces between semiconductors and oxides and their structural properties [23–28]; here, the additional problem is the presence of an amorphous phase like silica, requiring complex modeling techniques.

All these studies usually start from models of the interface in the slab geometry with the supercell approach: a suitable number of elementary crystal cells is explicitly included. The electronic degrees of freedom are part of the description, and structure of the interface is optimized with respect to the total energy of the system. The interface formation energies and work of separation can be extracted from a series of analogous calculations, but they usually refer to solid phases with plasticity suppressed. Ab initio thermodynamics or analogous approaches [19, 29–31] can connect finite temperature quantities (free energies and works of adhesion) to the results of zero temperature DFT calculations.

D. Passerone (✉) · C. A. Pignedoli
Empa, Swiss Federal Laboratories for Materials Testing
and Research, 8600 Dübendorf, Switzerland
e-mail: daniele.passerone@empa.ch
URL: http://www.empa.ch/abt127/

F. Valenza · M. L. Muolo · A. Passerone
Institute for Energetics and Interphases – IENI CNR,
Genoa, Italy

In this work, we will use the above cited methodologies to study, under a different viewpoint with respect to the existing literature, the Ag(111)/Alumina interface under oxygen contamination.

The interface between alumina and silver has been object of several studies, both theoretical and experimental.

From the experimental point of view, Chatain et al. [32] observed that the contact angle of Ag drops on Al_2O_3 kept decreasing after oxygen partial pressure was above a critical value. More recently, contact angle experiments were repeated by some of us at IENI CNR, Genoa [33] under careful control of the oxygen partial pressure and found a gradual decrease of the contact angle corresponding to an increase of the work of separation.

Such changes in the adhesion properties were already interpreted as a change in the interfacial stability upon increase of oxygen partial pressure.

Indeed, Feng et al. [31], with ab initio calculations, have observed a crossover between the Al-terminated Ag/Al_2O_3 interface and the O-terminated one, after partial O_2 pressure exceeds 10^{-2} atmosphere. In their approach, the work of adhesion should remain constant on the interval 10^{-33}–10^{-3} atmosphere (when the Al-terminated Ag/Al_2O_3 interface is stable); this contrasts with the experiments of Chatain et al. [32] and the more recent one at IENI CNR in Genoa [33].

The authors attribute this discrepancy to a generic “possible reconstruction” of the stoichiometric interfaces.

In this article, we demonstrate the alternative explanation we already proposed in [33]: we claim that in an intermediate range of partial pressures the surface shows an oxygen density which is intermediate between the one of the O-terminated interface and the one of the Al-terminated one.

Methods

In this work, we used DFT as implemented in the code q-Espresso (http://www.q-espresso.org). We used ultrasoft pseudopotentials and the Perdew-Burke-Ernzerhof exchange-correlation functional (PBE), with a cutoff of 30 and 240 Ry for the plane-waves expansion of wavefunctions and charge density, respectively.

To model the interfaces we used fully periodic slabs with a maximum of 66 atoms. Ag(111) is modeled by a maximum of 12 layers, whereas α-Al_2O_3 is described by a hexagonal unit cell containing 12 Al and 18 O atoms. No vacuum region was included in the supercell, thus we mimic an infinite sandwich of Al_2O_3/Ag interfaces with two equivalent interfaces in each unit cell. In Fig. 1, two unit cells parallel to the interface are shown. This configuration naturally defines two stoichiometric interfaces to Ag (Al-terminated, Fig. 1, right panel). The removal of an Al atom creates an O-terminated interface (and we did it on both sides of the supercell).

Adding instead an additional O atom at the interface creates an Al-terminated/O-rich interface. Our claim is that such a situation at the interface can be stable in a given range of oxygen partial pressures.

To check this claim, we prepared our system in different initial configurations including an additional oxygen atom per unit cell. We included this atom either at the interface, in an interstitial position with respect to the buckled Ag first layer, or embedded under the Ag first layer, in tetrahedral or octahedral coordination, as it is found for the Ag(111) free surface [34]. In this article, we will focus on the former case, where the additional O atom lies among the Ag buckled atoms (see Fig. 1, right panel). Other intermediate situations are possible, where the oxygen at the interface is more diluted, as it will be discussed below.

Whereas in the O-terminated surface there is a deficiency of one Al atom per formula unit, corresponding to $2/3N_O - 3/2\ N_{Al} = 1$, in our Al-terminated/O-rich interface we have $2/3N_O - N_{Al} = 2/3$. We will show an example where this interface is more stable than the Al-terminated on a wide range of oxygen partial pressures.

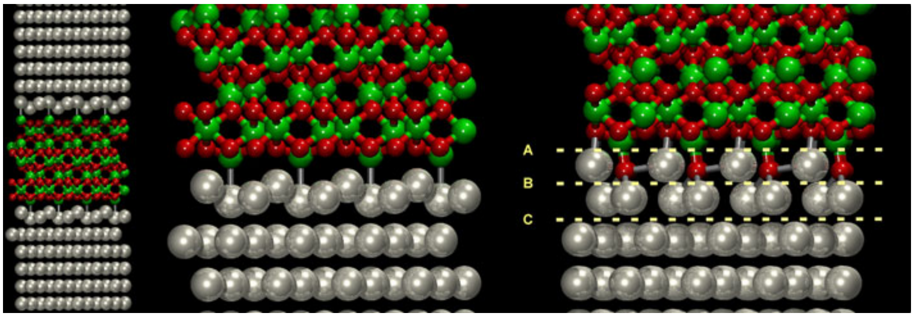

Fig. 1 *Left panel*: the simulated unit cell for the Al-terminated interface: periodic boundary conditions are assumed along all directions. Four unit cells in the direction parallel to the interface are shown. *Central panel*: detail of the Al-terminated interface. *Right panel*: detail of the Al-terminated/O-rich interface with the formation of a O/Ag complex that leads to a strong bond to alumina (as shown by the work of separation). A, B, C indicate the cleaving plane used for computing the work of separation (see text). *Metallic gray (brighter) atoms*: Ag; *red (smaller and with explicit bonds) atoms*: O; *green (larger with explicit bonds) atoms*: Al (Color figure online)

The atomic positions were fully optimized. The lattice parameter in the direction orthogonal to the interface was adapted in order to minimize the strain of the system along the same direction. In the direction parallel to the interface, the lattice parameter corresponds to minimal strain for the Al_2O_3 and thus results in compressive stress for the silver layers (“type I” interface in [31]).

Physical quantities in such kind of simulations depend on the translational state of the interface (see, e.g., [35–37]). As a showcase for our concept of O-dependence of interfacial structure, we limit our attention to the case where Ag atoms lie on top of Al atoms (Al-top) that was shown in [31] to produce the most stable interfaces for a similar exchange-correlation functional as used here.

When computing surface energies and metal chemical potentials we included the strain effect of the Ag in order to isolate the energetic cost of the interface—at least to some extent.

Results

When comparing the equilibrium structure of our model Al_2O_3/Ag interface with the corresponding stoichiometric interface, we observe dramatic changes in the Ag structure at the interface. The buckling which is typical for the Al-terminated, Al-top Ag(111)/Al_2O_3 interface is substituted by a bilayer with two Ag atoms at one level and one Ag and one O atom at the other level.

We note that this final configuration is more stable with respect to the one depicted in Fig. 5 of [33]. There, the Ag section of the slab was limited to four free layers per side, leading to a situation closer to a “Ag thin film adsorption” than to the interface between two extended systems.

In Table 1, we compare the relaxation of the Al and O atoms with respect to bulk alumina, in both interfaces. We note that the Alumina layers are not particularly affected by the strong modifications at the interface.

The modifications are all in the Ag part. We should add here as a comment, that at the temperatures considered experimentally when measuring the contact angles, Ag is obviously molten, and alumina is solid.

Table 1 Interlayer spacing (Å) for the two interfaces considered in this work

Atom (layers)	Al-terminated	Al-terminated/O-rich
O–Al (0–1)	–	1.78
Al–O (1–2)	0.47	0.51
O–Al (2–3)	0.89	0.91
Al–Al (3–4)	0.29	0.32
Al–O (4–5)	0.97	0.95

The layer number refer to the Alumina part of the sample, and layer 0 is the one of the additional oxygen atom

The important message (see Fig. 1, right panel) is that the presence of oxygen at the interface, although leaving the Al-terminated alumina side basically unchanged (Table 1), induces deep modifications in the Ag structure and electronic properties, leading in turn to a dramatic increase (as seen in the work of separation, see below) of the interface strength.

We now come to the strength of the interface: we compute the work of separation as the difference between the energy of the system with two symmetric interfaces and the sum of the energies of the two constituent subsystems ideally cleaved (Ag and Alumina) computed in the same simulation cell and after full relaxation. Thus, computing the work of separation within DFT implies three separate calculations, and the choice of the cleavage plane can affect the result.

Within our DFT model, the Al-terminated/Ag(111) interface shows a work of separation of bare 300 mJ/m^2, a slightly lower value with respect to the one published in [31] of 330 mJ/m^2.

Also the surface energy of the Al-terminated surface is 1.58 J/m^2, slightly lower with respect to previous DFT calculations.

Normally, experimental data refer to a finite temperature, well above $T = 0$ K; moreover, in the case of the Al-terminated alumina we are not aware of any experimental data where the termination of the surface is clearly defined. Therefore, there is no final answer about which surface energy must be considered more reliable.

For the Al-terminated/O-rich interface, we found different values for the work of separation according to the different possible cleavage planes. In Fig. 1 (right panel) we indicate with A, B, C three different cleavage planes and we obtain a work of separation of 1.42 (A), 1.79 (B), and 1.47 (C) J/m^2, respectively.

These values, substantially larger than the experimental ones, should be considered a limiting case for very high oxygen pressures (see below).

Another interface we considered for comparison is the O-terminated alumina/Ag(111) system. As already pointed out by previous authors [38] this interface should become stable for very high partial pressures of O_2 ($>10^{-2}$ atmosphere).

Here, we compare these three interfaces using an approach similar to that chosen by previous authors.

As in [35–37] we neglect the temperature effect on the chemical potentials, but we include it when connecting the chemical potential of aluminum and the partial pressure of oxygen through the aluminum activity; as a result, we use the following equation for the interfacial Gibbs energy G_I [31]:

$$G_{\mathrm{I}} = E_{\mathrm{slab}} - \frac{1}{3}N_{\mathrm{O}}\mu^{0}_{\mathrm{Al_2O_3}} - N_{\mathrm{Ag}}\mu_{\mathrm{Ag}} - \left[N_{\mathrm{Al}} - \frac{2}{3}N_{\mathrm{O}}\right]\Delta\mu_{\mathrm{Al}} - \left[N_{\mathrm{Al}} - \frac{2}{3}N_{\mathrm{O}}\right]\mu^{0}_{\mathrm{Al}}\ (0\ \mathrm{K}),$$

where E_{slab} is the energy of the interface slab, μ^{0}_{X} represent the chemical potentials in the bulk for the specie X and was calculated with separate bulk DFT calculations, and $\Delta\mu_{\mathrm{Al}}$ is the finite temperature correction for aluminum in equilibrium with oxygen when bulk alumina is formed by reaction of its constituents.

Given this equilibrium, we use the same dependence of $P_{\mathrm{O_2}}$ on $\Delta\mu_{\mathrm{Al}}$ as apparent in Fig. 6 of [31], namely,

$$\ln P_{\mathrm{O_2}} = f(T) - \frac{4}{3KT}\Delta\mu_{\mathrm{Al}},$$

where $f(T)$ includes the Gibbs reaction energy for alumina formation and the bulk increase in the chemical potential for Al, and $P_{\mathrm{O_2}}$ and $\Delta\mu_{\mathrm{Al}}$ are connected through the Al activity (see Eqs. 2 and 3 of [31]).

Taking the same values for the temperature dependent terms as in [31], we can plot directly the interfacial free energy as a function of $P_{\mathrm{O_2}}$ (Fig. 2).

Our results (showing a G_{I} of the order of 1.6 J/m^2 for the stoichiometric interface, 0.3 J/m^2 lower than the result published in [31]) draw two important conclusions: first, the Al-terminated stoichiometric interface ceases to be stable already at 10^{-11} atmosphere. Second, at this point, a Al-terminated interface with excess of oxygen taking active part to the bonding takes place, and the work of separation starts increasing, in agreement with contact angle experiments (see Figs. 3 and 4 of Muolo et al. [33]). We stress again that a treatment like the one in previous works (see, e.g., [38]), where a stoichiometric interface is considered as stable in a wide range of oxygen partial pressures, cannot reproduce a change in the work of adhesion in the same range, unless the oxygen segregation is taken into account in the reference surfaces after separation. Zhang and Smith [16] introduced this modification in the calculation of the work of adhesion and computed the effect of oxygen chemisorption on the free Ag surface (and not at the interface), finding an increased wetting upon partial pressure increase as in [32]. Concerning instead the explicit calculation of G_{I} for more general interfaces the same authors have explored this path [39] for the case of Ni/Alumina interfaces, but not within the scope mentioned here. In the reality different intermediate situations can take place and the role played by the additional O at the interface will be mediated by the disordered Ag liquid layer.

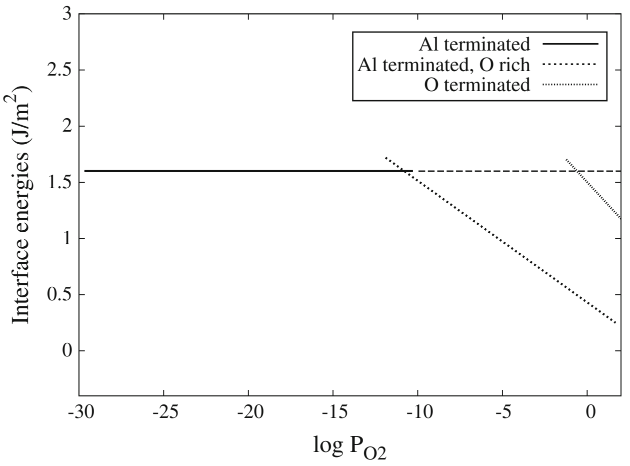

Fig. 2 Interfacial energies G_{I} as a function of the $\mathrm{O_2}$ partial pressure for the Al-terminated, Al-terminated, O-rich, and O-terminated Ag/Alumina interfaces. Already for 10^{-10} atmosphere the Al-terminated interface with an additional oxygen layer intermixed with Ag is favored

The concept remains valid, and shows also that, interestingly, this "Al-terminated" with additional O becomes competitive with the O-terminated interface (which is thought to be the more stable at high $\mathrm{O_2}$ pressures).

In our previous article, a thermodynamic analysis of the sessile drop experiments and of the oxygen adsorption at the solid liquid interface allowed to conclude that the maximum oxygen concentration at the interface is (at atmospheric pressure) 7×10^{14} atoms/cm^2, decreasing to about one fourth at 10^{-2} atmosphere. Since our Al-terminated, O-rich interface has a comparable oxygen concentration at the interface of 5×10^{14} atoms/cm^2, we can image a scenario where, for relatively high pressures ($>10^{-2}$), this interface is favorable, whereas for lower oxygen amount in the gas phase, similar interfaces could become more stable with a lower amount of oxygen (say, one atom each 2 unit cells). The verification of this point would require simulations with larger unit cells; if confirmed, we could attribute the gradually increasing work of separation upon $\mathrm{O_2}$ increase to the onset (starting from the stoichiometric Al-terminated one) of interfaces with an ever increasing concentration of atomic O *at the interface*, with the underlying alumina solid essentially unmodified concerning the atomic structure but binding to Ag in a substantially different way from the point of view of the electronic structure.

Finally, we face the issue of the electronic structure at the interface. We compute the projected density of states (PDOS) on atomic states, and we observe the modification of the electronic structure at the interface (Fig. 3).

In the case of the Al-terminated, O-rich interface, we note a dramatic difference between the Ag atom closer to the surface and the other two belonging to the first interfacial layer.

In the case of the Al-terminated stoichiometric interface, the results are similar to the ones already published, with a coincidence of peaks just below the Fermi energy

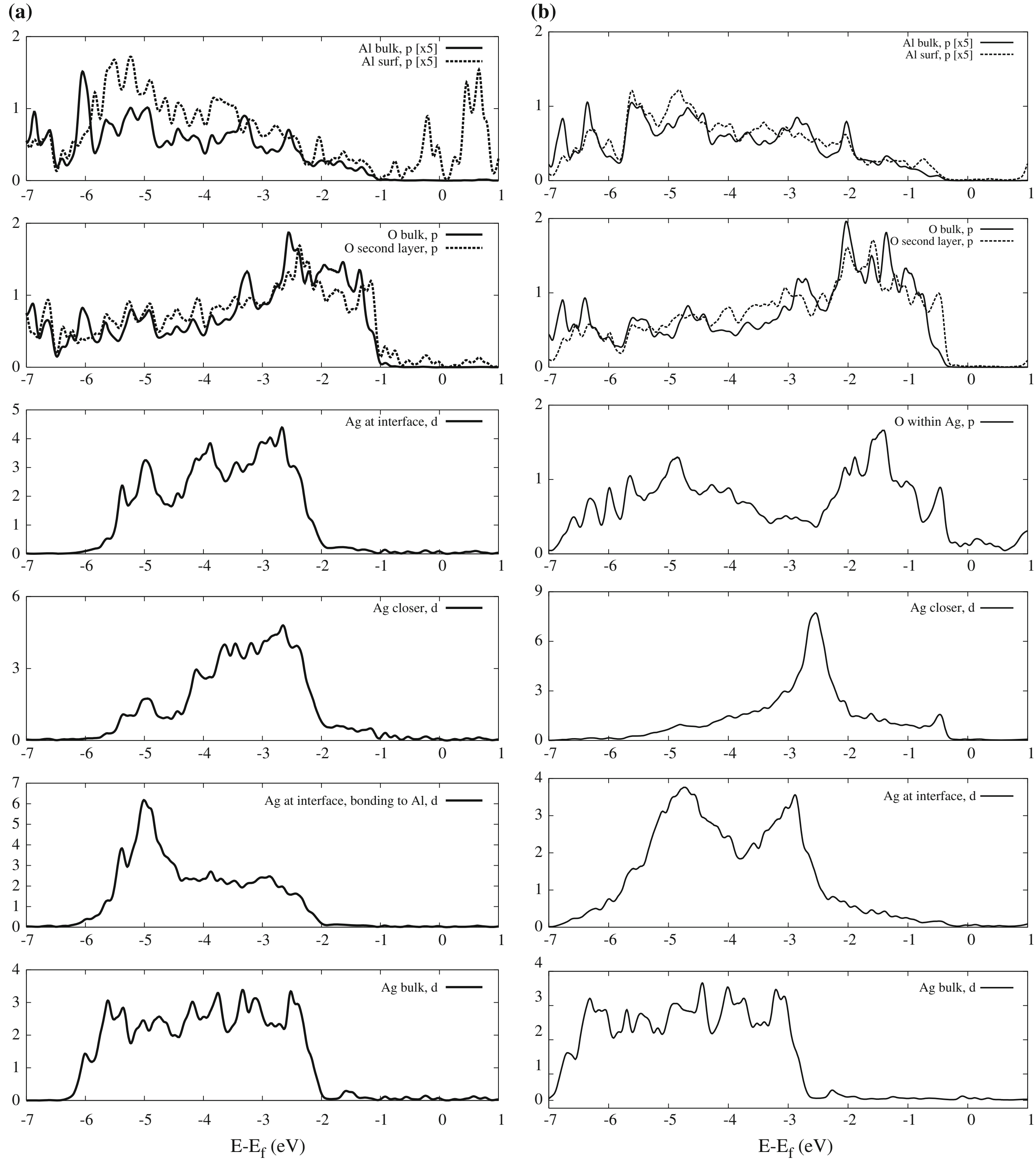

Fig. 3 Density of states projected on different atoms: the signal coming from the Ag interfacial atoms is dramatically different in the case of Al-terminated (*left panel*) and Al-terminated/O-rich (*right panel*)

corresponding to the directional bond between Al and O. The Ag PDOS is modified for the Ag atom binding directly to Al (see Fig. 1, left), corresponding to a direct bonding between the two species.

In the case of the O-rich interface, instead, we observe some very interesting features like a peak coincidence at $E = 0.6$ eV involving Al, O, and Ag. Moreover, for the Ag atom closer to the interface, a sharp peak at $E = -2.6$ eV could signal an electron localization or a hybridization with oxygen p states in the second layer.

In any case, the profile for the Ag d states is so different between the two cases that it could be possible to design a spectroscopy experiment more sensitive to the interface atoms with respect to the bulk; this can help proving the stability of the O-rich interface for intermediate partial pressures of oxygen, as supposed in [31, 33] and indicated by our calculations.

Conclusions

We studied with the help of DFT calculations a Ag(111)/Alumina interface with a surface oxygen concentration which is intermediate between the Al-terminated stoichiometric interface and the O-terminated interface. We show that in a large range of partial pressures of oxygen in the gas phase, our Al-terminated/O-rich-Ag(111) interface is more stable with respect to the former two interfaces.

We analyzed the electronic structure of the two most important configurations, and propose as plausible mechanism for the gradual increase in adhesion observed experimentally the onset of modifications of the Ag structural and electronic properties, due to an increasing amount of oxygen at the interface. Such oxygen does not represent a particular termination of the Alumina surface, instead probably diffuses through the molten Ag drop. We are currently performing calculations with more dilute quantities of oxygen to eventually describe a complete set of stable interfaces, all with different structures on the metal side and with different bonding to the ceramic. We believe that this will represent a more realistic theoretical frame for explaining the long-lasting open experimental question concerning this important composite material.

Acknowledgements We thank the Swiss National Supercomputing Centre (CSCS) for computational resources. A.P., M.L.M. and F.V. acknowledge the support of the FIRB contract RBIP064N2X-MITGEA of the Italian Ministry of University and Research.

References

1. Allen F, Almasi G et al (2001) IBM J Res Dev 40:310
2. Finnis MW (1996) J Phys Condens Matter 8:5811
3. Eustathopoulos N, Chatain D et al (1991) Mater Sci Eng A 135:83
4. Eustathopoulos N (1998) Acta Mater 46:2319
5. Passerone A, Muolo ML et al (2006) J Mater Sci 41(16):5088. doi:10.1007/s10853-006-0442-8
6. Sadan H, Kaplan WD (2006) J Mater Sci 41:5099. doi:10.1007/s10853-006-0437-5
7. Kruse C, Finnis MW et al (1996) Philos Mag Lett 73:377
8. Finnis MW, Kruse C et al (1995) Nanostruct Mater 6:145
9. Lee YM, Yu J (1995) Ceram Int 21:395
10. Yamazaki T, Suzumura A (1996) Mater Trans JIM 37:1103
11. Kostlmeier S, Elsasser C (2000) J Phys Condens Mater 12:1209
12. Dudiy SV, Lundqvist BI (2001) Phys Rev B 64:045403
13. Christensen M, Dudiy S et al (2002) Phys Rev B 65:045408
14. Dudiy SV, Lundqvist BI (2004) Phys Rev B 69:125421
15. Jiang Y, Smith JR (2009) J Mater Sci 44:1734. doi:10.1007/s10853-008-3084-1
16. Zhang W, Smith JR (2000) Phys Rev Lett 85:3225
17. Xiao-Gang W, Smith JR et al (2002) Phys Rev B 66:073411
18. Wang XG, Smith JR et al (2003) J Am Ceram Soc 86:696
19. Wei-Xue L, Stampfl C et al (2003) Phys Rev B 68:165412
20. Chatterjee A (2006) Mol Simul 32:155
21. Feng JW, Zhang WQ et al (2007) J Inorg Mater 22:119
22. Meyer R, Ge QF et al (2007) Surf Sci 601:134
23. Bongiorno A, Pasquarello A (2000) Phys Rev B 62:16326
24. Bongiorno A, Pasquarello A (2002) Mater Sci Eng B 96:102
25. Bongiorno A, Pasquarello A et al (2003) Phys Rev Lett 90:186101
26. Giustino F, Bongiorno A et al (2005) J Phys Condens Matter 17:S2065
27. Fischer D, Curioni A et al (2006) Appl Phys Lett 88:012101
28. Devynck F, Giustino F et al (2007) Phys Rev B 76:075351
29. Finnis MW (1998) Phys Status Solidif A 166:397
30. Batyrev IG, Alavi A et al (2000) Phys Rev B 62:4698
31. Feng J, Zhang W, Jiang W (2005) Phys Rev B 72:115423
32. Chatain D, Chabert F, Ghetta V, Fouletier J (1994) J Am Ceram Soc 77:197
33. Muolo ML, Valenza F, Passerone A, Passerone D (2008) Mater Sci Eng A 495:153–158
34. Li WX, Stampfl C, Scheffler M (2003) Phys Rev B 67:45408
35. Batyrev I, Alavi A, Finnis MW (1999) PRL 82:1510
36. Zhang W et al (2002) Acta Mater 50
37. Hashibon A, Elsasser C, Ruehle M (2005) Acta Mater 53:5323
38. Smith JR, Zhang W (2000) Acta Mater 48:4395
39. Zhang W, Smith JR (2006) Phys Rev B 74:081403R