PHYSICAL REVIEW B, VOLUME 64, 033410

In-plane relaxation of Cu(111) and Al(111)/α-Al_2O_3 (0001) interfaces

Iskander G. Batyrev and Leonard Kleinman
Department of Physics, The University of Texas at Austin, Austin, Texas 78712-1081

(Received 24 February 2001; published 26 June 2001)

The electronic structure and total energy of the Al and Cu alumina interfaces have been calculated with the plane wave pseudopotential method based on Lanczos diagonalization of the Kohn-Sham density matrix. For both interfaces we found in-plane relaxation, resulting in the rotation of the O triangle and expansion of the O-O bonds at the alumina surface. The calculated adhesive energies of the Cu(111)/alumina and Al(111)/alumina interfaces are several times smaller than that of the Nb(111)/alumina interface. The Cu(111)/Al-terminated alumina interface is found to have the smallest adhesive energy which is presumably related to the high degree of spatial delocalization of metal-oxygen bonds at the interface.

DOI: 10.1103/PhysRevB.64.033410 PACS number(s): 68.35.Gy, 71.15.Nc, 73.20.$-$r

The interaction between metals and ceramics is a question of vital interest. A basic problem in materials science is to relate the strength of interfaces to their atomic and electronic structure. In particular, metal/ceramic interfaces are a class of technologically important systems whose interactions need to be understood at a fundamental quantum-mechanical level. Our aim is to obtain theoretical values of the work of separation, as a step towards linking the mechanical behavior of interfaces with their structure on the atomic scale. The mechanical adhesion of metal/Al_2O_3 (0001) interfaces is a subject of ongoing experimental[1–3] and theoretical interest.[4–8]

What are the factors that favor the stable metal/alumina interface? Besides the thermodynamical arguments,[12] one of the basic parameters is the atomic misfit. In the Nb(111)/α-Al_2O_3(0001) interface the atomic misfit is less than 1.93% and the niobium surface of the interface is expanded compared with the free Nb(111) surface.[9–11] The small atomic misfit does not seem to be a necessary condition for the formation of a stable interface. In the stable and experimentally well characterized interfaces Cu(111)/α-alumina (0001) (Ref. 13) and Al(111)/α-alumina(0001) (Ref. 14) the misfit is -7.28% and -20.35% (for the $[1\bar{1}0]M//[2\bar{1}\bar{1}0]Al_2O_3$ orientation), respectively, and the metal surface of the interfaces is contracted. On the other hand there is no stable interface Mo(111)/α-Al_2O_3 (0001) to our knowledge, although the atomic misfit based on the experimental lattice constants is $+6.39\%$, much smaller than in the Al(111)/α-Al_2O_3 (0001) case. Interface misfit and the associated dislocation networks are critical features of the real metal/ceramic interfaces and the presence of dislocations does not necessarily result in an unstable interface. First principle simulation of the dislocations usually is restricted to Γ-point calculations because of the large computational effort.[15] In the work presented here, concentrating on adhesive energy calculations, we take into account the **k** dependence of the bands to be sure that effective convergence is achieved with respect to **k** point sampling, but we ignore dislocations to model the systems in question by coherent interfaces. Assuming the coherency we can use up to 200 atoms in the supercell with a short period in the plane of the interface, bearing in mind that our estimate of the work of adhesion is overestimated.

The concentration of oxygen is found to be important for a proper description of the oxide/metal interface[12] and alumina surface.[16,17] The surface of Al_2O_3 (0001) was found to be insulating or conducting, depending on the O concentration.[16] That is why attempts to discuss the electronic structure of metal/oxide overlayers without specifying the O concentration or degree of metal coverage of the oxide cannot be considered as adequate.[18]

The electronic structures and total energies were calculated by the plane wave (PW) pseudopotential (PP) method, based on Lanczos diagonalization of the finite temperature-density matrix.[19] We use density functional theory in the generalized gradient approximation.[20,21] The Troullier-Martins[22] form of nonlocal Kleinman-Bylander PP[23] was used. The Al pseudopotential successfully used in previous calculations of aluminum compounds[24,16,12] was generated according to Ref. 25. Oxygen and copper pseudopotentials were generated by using the kinetic energy filtering technique.[26] A PW cutoff of 40 Ry for Al/Al_2O_3 and of 50 Ry for Cu/Al_2O_3 was used in all calculations, with 2 **k** points in the irreducible wedge of the hexagonal Brillouin zone. The increase of the number of **k** points to nine results in the change of W_{sep} by 1%.

The transverse dimensions of the supercell are those of the alumina unit cell. The perpendicular dimension was determined which, after relaxing the atomic positions,[27] resulted in the lowest energy. The alumina and metal slab with a vacuum region were relaxed in the same supercell to allow the same plane wave basis set to be used.

Mulliken population analysis is commonly applied in calculations performed using localized basis sets and sometimes results in a negative Mulliken charge. The projection technique of the PW states onto a localized basis set[28] is free of this drawback. The eigenstates obtained from the PW calculations $|\psi_\alpha(\mathbf{k})\rangle$ are projected onto the duals of Bloch basis functions $|\phi_\mu(\mathbf{k})\rangle$ constructed from atomic pseudo-orbitals generated from the pseudopotentials used in our calculation. The Mulliken charge related with atom A, $Q_M(A)$, is given by

$$Q_M(A)=Z_A-\sum_k \omega(\mathbf{k})\sum_\mu^A \sum_\nu^A P_{\mu\nu}(\mathbf{k})S_{\nu\mu}(\mathbf{k}), \qquad (1)$$

0163-1829/2001/64(3)/033410(4)/$20.00

TABLE I. Changes of in-plane oxygen atom separation Δ_{O1-O1} and inter-plane distance between interface O and next Al layer as a percentage of the bulk spacings and α, measured in degrees, shown in Fig. 1.

Parameter	Cu/Al(O)	Cu/Al(Al)	Al/Al(O)	A/Al(Al)
Δ_{O1-O1}	2.6	9.8	3.4	8.2
Δ_{O1-Al1}	14.8	49.6	8.9	45.2
α_{O1-O1}	3.2	5.5	3.2	7.9

where Z_A is the formal valence of the atom A, $P_{\nu\mu}(\mathbf{k}) = \Sigma_{\alpha}^{\mathrm{occ}} n_{\alpha} \langle \phi^{\nu}(\mathbf{k}) | \psi_{\alpha}(\mathbf{k}) \rangle \langle \psi^{\alpha}(\mathbf{k}) | \phi^{\mu}(\mathbf{k}) \rangle$ is the density matrix, n_{α} are the occupancies of the PW eigenstates, and $S_{\nu\mu}(\mathbf{k}) = \langle \phi_{\mu}(\mathbf{k}) | \phi_{\nu}(\mathbf{k}) \rangle$ is the overlap matrix of the Bloch basis set, orbitals μ and ν belong to the atom A and $\omega(\mathbf{k})$ is the weight associated with a calculated $\mathbf{k}$ point in the Brillouin zone.

The Mayer bond order related with the number of shared electrons in the bond (or overlap population between atoms A and B) is[29]

$$B_M(AB) = \sum_{k} \omega(\mathbf{k}) \sum_{\mu}^{A} \sum_{\nu}^{B} 2P_{\mu\nu}(\mathbf{k}) S_{\nu\mu}(\mathbf{k}) \qquad (2)$$

Our stoichiometric (0001) slab is comprised of six stoichiometric layers, each layer consisting of three oxygen atoms in a plane, with an Al atom above and below the plane. This slab terminated by Al atoms next to O atoms is denoted A(Al) and henceforth referred to as a neutral. The O terminated surface of alumina A(O) was constructed from the Al-terminated one by moving Al surface atoms from the top side of the slab to the bottom and adding an oxygen layer to the bottom side of the slab. The metal M part of the interface was chosen to have five M(111) layers. The Al_2O_3 (0001) surface could be terminated by an O-layer, Al-layer, or by two Al-layers corresponding to the high oxygen pressure, intermediate (corresponding to the neutral surface), or low pressure, respectively. In this way it is possible to estimate surface energy of Al_2O_3 (0001)[16,17] and interfacial energy[12,8] as a function of O_2 pressure. The thermodynamical approach developed in the aforementioned papers could be applied to Cu(111)/Al_2O_3 (0001) and Al(111)/Al_2O_3 (0001) interfaces, but we would like to concentrate here on in-plane surface relaxation and general qualitative trends in the work of separation.

To relax the corundum structure (0001) one needs to take into account in-plane forces.[16,12] Neglecting the in-plane degrees of freedom of atoms results in the wrong in-plane and interplane relaxed structure.[6,24] It has been found that at the Al_2O_3 (0001) surface and Nb(111)/Al_2O_3 (0001) interface there is a general trend of in-plane relaxation: a rotation of the O triangles by about four degrees and expansion of the O-O bonds by 4%.[16,12] The same kind of trend is found in Cu(111)/Al_2O_3 (0001) and Al(111)/Al_2O_3 (0001) interfaces (Table I). The effect of rotation of the O triangle is of the same order of magnitude as that of the Nb(111)/Al_2O_3 (0001) interface and free alumina(0001) surface.[16] For Al-terminated Cu/Al_2O_3 and Al/Al_2O_3 (0001) interfaces the effect is bigger and correlates with the bigger distance between the oxygen and next Al plane of oxide (third row of Table I). The expanded triangle of O atoms pushes away the Al atom below it (Fig. 1). The bigger the expansion of the O-O interface-triangle bonds, the bigger the inward relaxation of the Al1. Experiments on grazing incidence X-ray scattering confirm this effect.[14] For the neutral Al_2O_3 (0001) surface the experiment resulted in 4.5% enhancement of O-O bond and the angle of rotation of the O triangles of 3.1°. The set of results for different interfaces and free alumina(0001) surfaces proves that the in-plane surface relaxation is a general property of the Al_2O_3 (0001) surface. It is enough to have a different medium above it; metal or vacuum, and the surface of Al_2O_3 tends to have the in-plane relaxation.

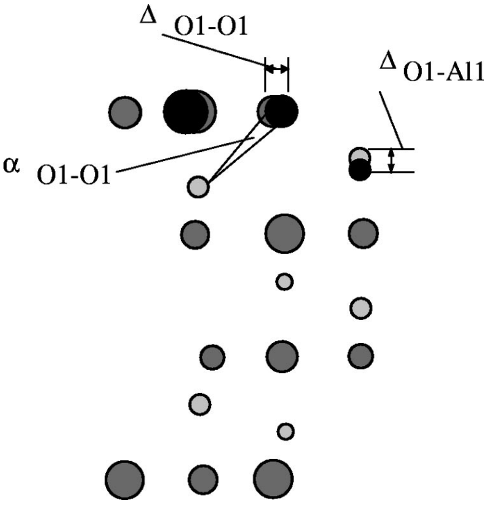

FIG. 1. Side perspective view fragment of the oxygen-terminated Al_2O_3 (0001) explaining the meaning of the atom notation in Table I (dark grey large circles-O atoms, light grey small circles-Al atoms, black large circles - in plane relaxed O1-atoms, small black circle relaxed Al1 atom). α_{O1-O1} is the angle of rotation of the O1 plane triangle relative vertical axis.

The work of separation, W_{sep} (or work of adhesion) defined as the difference between the total energy of the slab and the total energies of the two parts of the interface is calculated in the same supercell. The work of separation takes into account atomic in- and inter-plane relaxation under separation of the two parts of the interface, but does not allow any diffusion processes or relaxation of the transverse lattice constants of the metal M. We assume that dislocations would allow the metal to relax to its bulk lattice constant away from the interface so that the strain-energy errors in the two systems tend to cancel. What is not accounted for is the energy cost to create the dislocations. The surface energy of the oxide or metal decreases after atomic relaxation. The change of work of separation after relaxation could be positive, negative, or almost zero depending on the balance of the relaxation induced changes of the surface energies and that of the slab total energy. The Al-terminated (0001) surface of α-alumina exhibits an inward relaxation of about 70%, both from X-ray data[14] and calculation,[16,7] and therefore has a substantial change of its surface energy, much

TABLE II. W_{sep} (in J/m^2) of Al(111) and Cu(111)/ α-Al_2O_3 (0001) interfaces compared with those for the Nb(111)/Al_2O_3 interfaces.

Interface	Unrel	Rel
Al(111)/A(Al)	1.48	1.36 (1.08 [a])
Al(111)/A(O)	6.02	8.67 (10.1 [a])
Cu(111)/A(Al)	1.07	1.02
Cu(111)/A(O)	5.77	5.62
Nb(111)/A(O)	9.32 [b]	9.81 [b](10.6 [c])
Nb(111)/A(Al)	4.24 [b]	2.70 [b](2.6 [c])

[a] Reference 30.
[b] Reference 24.
[c] Reference 8.

bigger than that of the metal surface and the interface relaxation energy. This results in the decrease of W_{sep} after atomic relaxation shown in Table II. W_{sep} is biggest for O-terminated interfaces in all studied cases (Table II), which indicates the importance of the metal-oxygen covalent and partially ionic bonds for the strong adhesion of the interfaces. This trend for work of separation for Al(111)/Al_2O_3 and Nb(111)/Al_2O_3 found in our PP-PW calculations is in agreement with that made by the all-electron full potential linearized augmented plane wave method.[8,30]

Interestingly enough the boundary metal atoms Cu and Al get ionized at the interface by the influence of oxygen atoms as follows from Table III based on Mulliken population analysis. The absolute numbers of the analysis are based on the atomic basis set and have no strict physical meaning. However their relative values can yield useful information. The projection of the plane-wave density on localized basis sets to estimate Q_M from Eq. (1) and B_M from Eq. (2) turned out to be quite accurate (the spilling parameter[28] is less than 1.5% for occupied orbitals). Inside the metals the Mulliken numbers Q_M for the metals are equal to zero. Atoms of Al(111) strongly interact with O atoms even in the case of the Al-terminated interface where O atoms form the second layer. This can also be seen from the bond order numbers B_M in Table IV. The intersection of the Al(111) column and O1 row shows that the interaction of the boundary Al(111) atom and boundary interface is important for the O-terminated interface and for the Al-terminated interface as well. The boundary metal atom-subsurface O atom interaction is much weaker for the Cu(111)/ Al-terminated alumina interface.

TABLE III. Mulliken population Q_M of the metal/oxide interfaces. M means the first metal interface atom neighbors of the oxide.

Atom	Cu/A(O)	Cu/A(Al)	Al/A(O)	Al/A(Al)
M	0.32	0.17	0.39	0.40
O1	−0.85		−0.96	
Al1	1.55		1.62	
Al2	1.55	0.88	1.59	1.18
O2	−1.01	−1.00	−1.00	−0.98
Al bulk	1.57	1.57	1.57	1.57
O bulk	−1.00	−1.00	−1.00	−1.00

TABLE IV. Mayer bond-orders B_M for Cu(111)/Al_2O_3 (top half) and Al(111)/Al_2O_3 (bottom half) of the table. The Al (O) terminated interface B_M's are in (not in) parentheses.

Atom	Cu(111)	O1	Al1
Cu(111)	0.21(20)	0.31 (0.06)	0.01 (0.24)
O1	0.31 (0.06)	0.01 (0.01)	0.41 (0.26)
Al1	0.01 (0.24)	0.41 (0.26)	0.00 (0.00)
Atom	Al(111)	O1	Al1
Al(111)	0.22 (0.26)	0.46 (0.33)	0.01 (0.01)
O1	0.46 (0.33)	0.01 (0.01)	0.42 (0.41)
Al1	0.01 (0.01)	0.42 (0.41)	0.00 (0.00)

Experimental measurements of the shape of facets[31] on Cu and Al particles on sapphire (0001) gave the work of adhesion, 0.49 J/m^2 (Ref. 32) and 0.95 $J/m,^2$ respectively. These values are in much better agreement with our neutral (as opposed to O-terminated) interface results in Table II, which indicates the likelihood that the experimental measurements have been made on mainly Al-terminated interfaces. This result also agrees with the conclusion made on the basis of Gibbs free energy theory of the oxide surface at finite temperature and pressure of oxygen gas[16] that the Al-terminated Al_2O_3 (0001) surface is in the thermodynamically stable equilibrium state, both at low and high oxygen pressure. Later on it was shown that some concentration of hydrogen adsorbed at the Al_2O_3 surface could make a stable termination of O layers bound to hydrogen atoms.[17] A deviation from the equilibrium state could be another reason for existence of O-terminated domains at the surface of real alumina.[33]

Other experimental measurements of the Cu(111)/Al_2O_3 (0001) interface gave the following results for the work of separation: 0.44 J/m^2 (Ref. 2) and 0.71 J/m^2,[33] and a theoretical value of 0.9 J/m^2 (Ref. 34) was calculated using a linear combination of atomic orbitals. Comparing the experimental and theoretical results one should bear in mind that the work of separation may well be affected by impurities and dislocations existing in all real interfaces. These effects are not included in the theoretical modeling. Thus we can speak only about qualitative comparison with experiment.

Our ‘‘ab-initio’’ simulations of the Cu(111)/Al_2O_3 (0001) and Al(111)/Al_2O_3 (0001) interfaces show that the highest works of adhesion have O-terminated interface which indicate the importance of the oxygen/metal interaction for the strength of bonding. From Table IV (bond order Al(111)-O1) one can see that this interaction is important both for O- and Al-terminated interfaces of Al(111)/Al_2O_3 (0001). In the case of Cu(111)/Al_2O_3 (0001) the interaction is substantial only for O termination of the interface. That may well be the reason that W_{sep} for the Al-terminated interface Cu(111)/Al_2O_3 (0001) is lower than that of the Al(111)/Al_2O_3 (0001) interface. Comparing the trends in W_{sep} for transition metals/Al_2O_3 (0001) one can see that the work of separation for Nb is larger than that for Cu, which is in agreement with the qualitative conclusion[4] that the filling of the anti-bonding band decreases the interface bonding strength. Bond order describing O_{2p}-$3d$ (or $3p$ in the case of Al) hybridization (Table IV) is much smaller than that in the Nb(111)/$\mathrm{Al_2O_3}$ (0001) interface, found to be equal to 0.6 for Nb1-O1 and 0.5 for Nb1-Al1.[24] It can be considered as an indication of less covalent character and less spatially localized O-metal bonds resulting in lower W_{sep}. Ignoring the details of electronic structure, this can be understood by noting that the negatively mismatched FCC metal (Al or Cu) (111) surfaces have four times as many atoms as that of the slightly positively mismatched BCC metal (Nb) (111) surface.

In summary we have found that in-plane relaxation is a general property of the $\mathrm{Al_2O_3}$ (0001) surface or interface. Our estimates of the work of adhesion of the metal/oxide interface and population analysis enable us to gain understanding of the bonding trends, relative crystalline and electronic structure of the interface metal.

ACKNOWLEDGMENTS

This work has been supported by the Welch Foundation (Houston, TX) and the NSF under Grant No. DMR0073546. One of the authors (I.B.) thanks Mike Finnis and Ali Alavi for discussions at the early stage of the research. The Advanced Computing Center of the University of Texas is gratefully acknowledged for computer resources.

---

[1] D. Korn, G. Elßner, H.F. Fischmeister, and M. Rühle, Acta Metall. Mater. **40**, 355 (1992).
[2] D. Chatain, L. Coudurier, and N. Eustathopoulos, Rev. Phys. Appl. **23**, 1055 (1988).
[3] F.S. Ohuchi and M. Kohyama, J. Am. Ceram. Soc. **74**, 1163 (1991).
[4] P. Alemany, R.S. Boorse, J.M. Burlitch, and R. Hoffmann, J. Phys. Chem. **97**, 8464 (1993).
[5] M.W. Finnis, J. Phys.: Condens. Matter **8**, 5811 (1996).
[6] C. Kruse, M.W. Finnis, V.Y. Milman, M.C. Payne, A. De Vita, and M.J. Gillan, J. Am. Ceram. Soc. **77**, 431 (1994).
[7] C. Kruse, M.W. Finnis, J.S. Lin, M.C. Payne, V.Y. Milman, A. De Vita, and M.J. Gillan, Philos. Mag. Lett. **73**, 377 (1996).
[8] W. Zhang and J.R. Smith, Phys. Rev. B **61**, 16 883 (2000).
[9] G. Gutekunst, J. Mayer, and M. Rühle, Scr. Metall. Mater. **31**, 1097 (1994).
[10] G. Gutekunst, J. Mayer, and M. Rühle, Philos. Mag. A **75**, 1329 (1997).
[11] G. Gutekunst, J. Mayer, V. Vitek, and M. Rühle, Philos. Mag. A **75**, 1357 (1997).
[12] I. Batyrev, A. Alavi, and M. Finnis, Phys. Rev. B **62**, 4698 (2000).
[13] G. Dehm, M. Ruehle, G. Ding, and R. Raj, Philos. Mag. B **71**, 512 (1995).
[14] P. Guenard, G. Renaud, A. Barbier, and M. Gautier-Soyer, Surf. Rev. Lett. **5**, 321 (1998).
[15] R. Benedek, A. Alavi, D.N. Seidman, L.H. Yang, D.A. Muller, and C. Woodward, Phys. Rev. Lett. **84**, 3362 (2000).
[16] I. Batirev, A. Alavi, and M. Finnis, Faraday Discuss. **114**, 33 (1999).
[17] X.-G. Wang, A. Chaka, and M. Scheffler, Phys. Rev. Lett. **84**, 3650 (2000).
[18] L. Thien-Nga and A.T. Paxton, Phys. Rev. B **58**, 13 233 (1998).
[19] A. Alavi, J. Kohanoff, M. Parrinello, and D. Frenkel, Phys. Rev. Lett. **73**, 2599 (1994).
[20] A.D. Becke, Phys. Rev. A **38**, 3098 (1988).
[21] C.T. Lee, W.T. Yang, and R.G. Parr, Phys. Rev. B **37**, 785 (1988).
[22] N. Troullier and J.L. Martins, Phys. Rev. B **43**, 1993 (1991).
[23] L. Kleinman and D.M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).
[24] I. Batyrev, A. Alavi, and M. Finnis, Phys. Rev. Lett. **82**, 1510 (1999).
[25] X. Gonze, R. Stumpf, and M. Scheffler, Phys. Rev. B **44**, 8503 (1991).
[26] M.-H. Lee, Ph.D. thesis, The University of Cambridge, 1991.
[27] We used the Broyden-Fletcher-Goldfarb-Shano (BFGS) method with a Hessian to find the relaxed atomic positions. See R. Fletcher, *Practical Methods of Optimization* (John Wiley, Chichester, England, 1980).
[28] D. Sanchez-Portal, E. Artacho, and J.M. Soler, Solid State Commun. **95**, 685 (1995).
[29] I. Mayer, Chem. Phys. Lett. **97**, 270 (1983).
[30] W. Zhang and J.R. Smith, Phys. Rev. Lett. **85**, 3225 (2000).
[31] J.J. Brennan and J.A. Pask, J. Am. Ceram. Soc. **51**, 569 (1968).
[32] D. Chatain, I. Rivollet, and I. Eustathopoulos, J. Chim. Phys. **84**, 201 (1987).
[33] R.M. Pilliar and J. Nutting, Philos. Mag. **16**, 181 (1967).
[34] G.L. Zhao, J.R. Smith, J. Reynolds, and D.J. Scrolovitz, Interface Sci. **3**, 289 (1996).