FIRST-PRINCIPLES CALCULATIONS OF TENSILE STRENGTH OF COPPER-ALUMINA INTERFACES AND THE DEVELOPMENT OF INTERATOMIC POTENTIALS

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ABSTRACT

The adhesive and mechanical properties of a Cu(111)/Al_2O_3(0001) interface have been examined by using the *ab initio* pseudopotential method based on the density-functional theory. The Cu/Al_2O_3 interface is a typical metal/oxide interface frequently observed in coating technology and electronic devices. Both the Al-terminated (stoichiometric) and O-terminated (O-rich) interfaces have been dealt with, and the effects of the interface stoichiometry have been analyzed. The interfacial bond of the O-terminated interface is quite strong with both ionic and covalent Cu-O interactions, although that of the Al-terminated one is relatively weak with electrostatic and Cu-Al hybridization interactions. We have applied the *rigid-type ab initio* tensile tests to these interfaces, and obtained the interlayer potential curves at the interfaces. The Cu-O interface is twice as strong as the back Cu-Cu interlayer at the O-terminated interface, and the Cu-Al interface is twice as weak as the Cu-Cu interlayer at the Al-terminated interface. From these *ab initio* results, we have constructed effective interatomic potentials for large-scale molecular-dynamics simulations.

1 INTRODUCTION

Metal/oxide interfaces are used in various applications such as thermal-barrier coatings, composites, electronic and optical devices, micro or nano machines, various catalysts, and electrodes in fuel cells or batteries. Metal/oxide interfaces have unique electronic structure and bonding nature (Finnis [1]), because the interface is formed between two solids with completely different electronic structures. This point frequently causes peculiar structural, electronic, chemical and mechanical properties associated with nanostructures. It is essential to understand the structure and properties of metal/oxide interfaces at the atomic and electronic scales. *Ab initio* calculations based on the density-functional theory have been applied to metal/oxide interfaces ([1], Hong *et al.* [2], Benedek *et al.* [3], Batyrev *et al.* [4, 5], Zhang *et al.* [6, 7]). It has been shown that the behavior of electrons dominates the bonding between dissimilar materials. Recent studies have shown that the adhesion and properties strongly depend on the interface stoichiometry [3-7]. Namely, interfaces between metals and O-terminated (O-rich), cation-terminated (cation-rich) and stoichiometric oxide surfaces have quite different characters to each other, as found for C-terminated and Si-terminated interfaces of metal/SiC systems (Tanaka *et al.* [8]).

About the mechanical properties of metal/oxide interfaces, there have been only few theoretical studies at the atomic and electronic scales. Several classical molecular-dynamics simulations have been performed. However, for such simulations, it is essential to develop reliable interatomic potentials between metals and oxides (Benedek *et al.* [9], Albe *et al.* [10]), which is seriously difficult because of the complex nature of metal-oxide bonding. In this paper, we deal with a Cu/Al_2O_3 interface, which is a typical metal/oxide system frequently observed in coating technology and electronic devices. We examine the adhesive and mechanical properties of both the Al-terminated (stoichiometric) and O-terminated (O-rich) interfaces of the

$Cu(111)/Al_2O_3(0001)$ interface by using the *ab initio* pseudopotential method, and analyze the effects of the interface stoichiometry on the mechanical properties (Tanaka *et al.* [11], Yang *et al.* [12]). First, we obtain the stable configurations of the two interfaces and analyze the atomic and electronic structures, which are compared with recent electron microscopy observations (Sasaki *et al.* [13]). Second, we apply *ab initio* tensile tests to these interfaces, which can clarify the tensile strength and the behavior of atoms and electrons for tensile stretching (Kohyama [14]). We obtain the interlayer potential curves representing local mechanical properties. Finally, we construct the effective interatomic potentials to reproduce the *ab initio* interlayer potential curves as an essential technique of the multiscale simulations of metal/oxide interfaces.

2 METHOD OF CALCULATIONS

We use the plane-wave pseudopotential method based on the density-functional theory with the local density approximation (LDA) (Perdew *et al.* [15]). This scheme can reproduce the behavior of valence electrons and ions in solids quantitatively. We use the TM-type optimized norm-conserving pseudopotentials (Troullier *et al.* [16]) with the plane-wave cut-off energy of 80Ry. The RMM-DIIS (residual minimization/direct inversion in the iterative subspace) scheme (Kresse *et al.* [17]) is used for the electronic optimization. By this scheme, we can perform efficient parallel computations with respect to each band through our efficient code (Tamura *et al.* [18]).

We deal with coherent (1X1) $Cu(111)/Al_2O_3(0001)$ interfaces, where the Cu layers are expanded along the interface. About the position of the interface Cu atom on the $Al_2O_3(0001)$ surface, we deal with three kinds of models, Al-site, O-site, and H-site models [7], where the Cu atom is located above the Al site, O site and hollow site of the hexagonal unit cell of the Al_2O_3 surface, respectively. These configurations correspond to the energy extremes. The Al-terminated (stoichiometric) interface is formed between the stoichiometric $Al_2O_3(0001)$ surface and the Cu(111) surface. The O-terminated (O-rich) interface is formed by removing the topmost surface Al atoms of the stoichiometric Al_2O_3 surface. The supercell consists of alternate stacking of $Al_2O_3(0001)$ and Cu(111) slabs. The $Al_2O_3(0001)$ slab consists of four O layers with Al layers above and below each O layer. The Cu(111) slab consists of five (111) layers. Each supercell has the C_{3i} symmetry, and two interfaces in the unit cell are symmetrically equivalent to each other. The size of the supercell normal to the interface has been optimized by iterating relaxation.

3 STABLE CONFIGURATIONS

Fig. 1 shows the most stable configurations for the O-terminated (O-rich) and Al-terminated (stoichiometric) Cu/Al_2O_3 interfaces. The H-site model is the most stable for the O-terminated interface, and the O-site model is the most stable for the Al-terminated one. These points are consistent with other *ab initio* results [7]. The adhesive energy defined from the relaxed surfaces is $6.96 Jm^{-2}$ for the O-terminated one, and is $1.27 Jm^{-2}$ for the Al-terminated one. For the O-terminated interface, the Cu-O distance is rather small (0.204nm) as compared with that in the Al-terminated interface (0.246nm). There exists substantial electron transfer from the interfacial Cu layer to the O layer, and there exists strong Cu 3d-O 2p orbital hybridization. This kind of covalent and ionic interactions should be the origin of the very large adhesive energy.

For the Al-terminated interface, there is slight electron transfer from Al_2O_3 to Cu. The charge redistribution by the interface formation from the surfaces shows electron increases at the interstitial sites of the 1st Cu layer near the surface Al atoms in addition to electron decreases at the Cu-atom sites near the surface O atoms. This kind of charge redistribution is similar to that observed in metal/MgO interfaces [2] and is consistent with the image-charge model (Tasker *et al.* [19]). In addition, we have found the interaction between the Al surface dangling orbitals and Cu orbitals. Thus the origin of adhesion for the Al-terminated interface seems to be the electrostatic effect and the Cu-Al orbital hybridization. It is interesting that there seem to exist no strong Cu-

O interactions in the Al-terminated interface. It can be said that the presence of the surface Al atom suppresses the reactivity of the surface O atom of Al_2O_3.

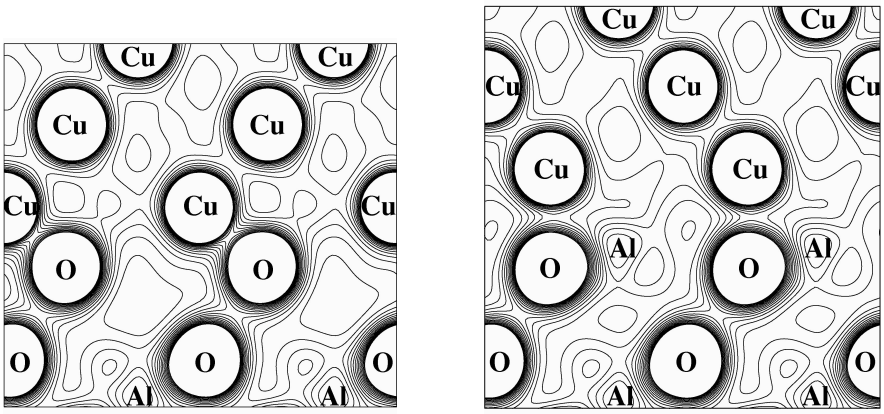

Figure 1: Stable configurations and electron charge distributions of the O-terminated (left) and Al-terminated (right) interfaces of the Cu(111)/Al_2O_3(0001) interface.

The relative stability between the Al-terminated and O-terminated interfaces can be theoretically analyzed by calculating the free energy $F=E-TS-\Sigma n_i\mu_i$ as a function of the atomic chemical potentials μ_i. Recently, such a thermodynamic analysis has been performed for the same system [7], which indicates the relative stability of the O-terminated interface in usual atmosphere in air. About the comparison with the recent electron microscopy observations [13], the observed interface has an incoherent configuration because of the lattice misfit. It is considered that the incoherent interface consists of a mixture of the three kinds of configurations with different rigid-body translations, namely the Al-site, O-site and H-site models. In such a case, the largest interface distance in the three models should determine the observed interface distance. Our *ab initio* value of the largest interface distance for the O-terminated interface is 0.183nm in the O-site model, which is in good agreement with the observed distance (0.185nm [13]). This indicates the real existence of the O-terminated interface. Our results of the interface electronic structure of the O-terminated interface also can explain the observed electron energy-loss spectroscopy [13].

4 IDEAL TENSILE STRENGTH

In order to examine the mechanical properties of the two kinds of interfaces clearly, we have performed the *ab initio* tensile test. We adopt the *rigid-type* tensile test. This is an ideal cleavage simulation, where total-energy calculations are iterated for the increase of a selected interlayer distance or interface distance in a small increment. Of course, usual *relaxed-type* tensile tests with full atomic relaxation [14] can reproduce more realistic mechanical behavior. However, for the present rather simple configurations, the *relaxed-type* test can only reveal the weakest point originating failure. The *rigid-type* test can clarify the local strength of each selected interlayer or interface, and can provide rich information for the development of interatomic potentials as discussed later.

We have applied the tensile test to the Cu-O interface, the Cu-Al interface and the interlayers between the 1st and 2nd Cu layers of the O-terminated and Al-terminated interfaces. Fig. 2 shows the total-energy change curve for stretching and compression of each selected interlayer. The curve for the Cu-Cu interlayer of the Al-terminated interface is similar to that of the O-terminated interface, which means that the interfaces have no strong effects on the Cu-Cu back bonds. The depth of each curve corresponds to the ideal fracture energy, which is needed to separate the interface into two surfaces without relaxation. The maximum gradient of each curve corresponds to the ideal tensile strength of each interlayer, which is the upper limit of the tensile strength. It is clear that the Cu-O interface (about 50GPa) is twice as strong as the Cu-Cu interlayer (about 25GPa) at the O-terminated interface, and that the Cu-Al interface (about 12GPa) is twice as weak as the Cu-Cu interlayer (about 25GPa) at the Al-terminated interface, intrinsically. The failure should occur at the Cu-Al interface for the Al-terminated interface, and should occur in the Cu side for the O-terminated one. It is interesting that the Cu-Al and Cu-Cu curves can be well fitted by the universal binding energy relation (UBER) curve (Rose *et al.* [20], Banerjea *et al.* [21]), although the fitting of the Cu-O curve is not so good. It can be said that the UBER curve is suitable to bonds with metallic or covalent characters and is not suitable to bonds with strong ionic characters or significant charge transfers.

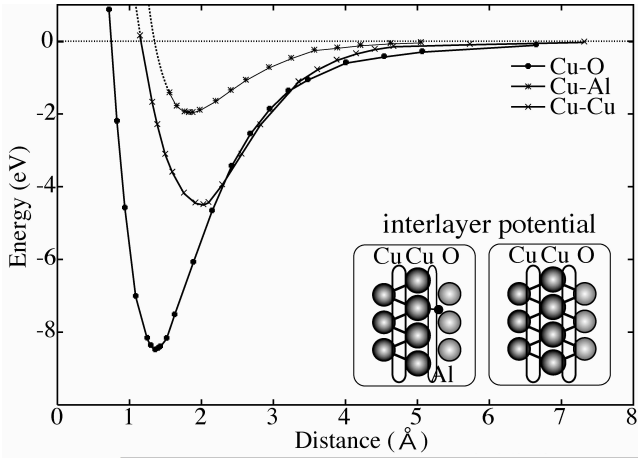

Figure 2: Energy changes in the *rigid-type* tensile tests for the Cu-O and Cu-Cu interlayers of the O-terminated Cu(111)/Al_2O_3(0001) interface and for the Cu-Al interlayer of the Al-terminated one.

5 EFFECTIVE INTERATOMIC POTENTIALS

The real mechanical behavior of metal/oxide systems should be greatly dominated by the behavior of cracks, defects or dislocations. Such behavior cannot be fully dealt with by *ab initio* calculations at present, although *ab initio* calculations can clarify the intrinsic nature and strength of interfaces accurately. It is desirable to perform large-scale molecular-dynamics simulations or multiscale simulations in order to deal with such effects, where the development of reliable interatomic potentials is essential. However, it is not so easy to develop reliable potentials for metal/oxide interfaces as compared with potentials for bulk solids, because the electronic structure or bonding nature at metal/oxide interfaces cannot be simply modeled. There have been only few

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