First-Principles Characterization of Atomic Structure of Al2O3(0001)/Cu Nano-Hetero Interface

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Atomic structures characterization of Al2O3(0001)/Cu nano-hetero interfaces has been performed by the first-principles pseudopotential method and in cooperation with HRTEM observations. The physical properties of the interfaces depend strongly on the interface stoichiometry. Bonding nature of the O-rich (O-terminated) interface is explained as strong covalent and ionic interactions, whereas that of the stoichiometric (Al-terminated) interface is weak covalent and electrostatic image interactions. The O-terminated interface has quite larger adhesive energy than that of the stoichiometric one. Recent HRTEM observations of the Al2O3(0001)/Cu interface have confirmed the O-terminated interface. However, the observed incoherent interface is not the same as an ideal coherent interface obtained by the first-principles. We explain the relationship between the present coherent interface and the practical incoherent one.

1. Introduction

Designing of structures and properties of interfaces between different materials such as ceramics-metal interfaces and semiconductor-metal interfaces is of great importance for development of nanoscience and nanotechnology. An alumina-copper interface is well known as a typical ceramics-metal system frequently used in mechanical and electronic applications, such as thermal and corrosion barriers and heat sinks. Recently, several theoretical1–5 and experimental6–9 studies have been performed for the alumina-copper interfaces and the results indicate that the interface stoichiometry strongly affects the interfacial properties. Zhang and co-workers1 have investigated the interface free energies depending on the stoichiometry as functions of the activity of Al and the oxygen partial pressure. The formed interface in O-rich atmosphere is predicted to be non-stoichiometric, O-rich, with large work of separation. In experiments, on the other hand, the stoichiometry of interface has still been discussed because of some differences for experimental conditions, though the surface of alumina is well defined as a stoichiometric one. Considering from the alumina surface structure, one would expect that the stoichiometric interface would be formed. However, atmosphere such as chemical potentials and temperature in the formation process could form various stoichiometric interfaces though dissociation or precipitation of alumina surface atoms to or from metals. The O-rich interface of the Al2O3(0001)/Cu system has been observed by high-resolution transmission electron microscopy (HRTEM) observations6 as well as the stoichiometric interface.7

Nevertheless, the atomic fine structures near the interface have not yet been determined. The major reason is that mutually complementary relationship between theoretical calculation and experiment is not enough constructed, although each method is developed independently. For example, theoretical calculations usually deal with coherent interface model, although experimentally observed interfaces often contain misfit dislocations or incoherent configurations. First of all, we have to clarify details of the interfacial structures by active collaborating between theoretical calculations and experiments.

In this paper, we have performed the first-principles calculations of Al2O3(0001)/Cu(111) interfaces and obtained the stable atomic configurations near the interfaces. The results are compared with those of HRTEM observations. In this interface, the interface stoichiometry should have serious effects on the electronic and mechanical properties. And then we explain the relationship between the ideal coherent interface dealt with by the first-principles calculation and the practical incoherent interface observed by HRTEM.

2. Theoretical Method

Present calculations use the first-principles pseudopotential method and the first-principles molecular dynamics. The soft-type norm-conserved pseudopotentials developed by Troullier-Martins10 are used. The residual minimization and direct inversion in the iterative subspace (RMM-DIIS)11,12 method and the conjugate-gradient method13 are used for the fast solution technique for the eigenstates in the ground states. Self-consistent charge densities are obtained from the efficient charge-mixing method.14,15 A plane-wave cutoff energy of 70 Ry is selected based on the tests of total energy convergence. In self-consistent calculations, four sampling k-points in the irreducible Brillouin zone of the supercell explained below are used.

We deal with the Al2O3(0001)/Cu(111) interface with the orientation relationship of [1-10]Cu||[1-100]Al2O3. In order to
examine the interface stoichiometry dependence, the two kinds of the interfaces, an Al-terminated (stoichiometric) interface, \((\text{Al}_2\text{O}_3/\text{Cu})_\text{Al}\), and an O-terminated (non-stoichiometric) interface, \((\text{Al}_2\text{O}_3/\text{Cu})_\text{O}\), are treated. The supercell of a stoichiometric interface consists of an \(\text{Al}_2\text{O}_3(0001)\) slab of four \(\text{Al}-\text{O}-\text{Al}\) layers and a \(\text{Cu}(111)\) slab of five \(\text{Cu}\) layers, where each \(\text{O}\) or \(\text{Cu}\) layer includes three atoms and each \(\text{Al}\) layer includes only one atom in each cell. O-terminated interfaces are constructed by removing top \(\text{Al}\) layers of both sides of an \(\text{Al}_2\text{O}_3\) slab. The stable atomic configurations were obtained from the atomic relaxation process. As well known, the lattice mismatch between alpha-\(\text{Al}_2\text{O}_3(0001)\) and fcc-\(\text{Cu}(111)\) planes is about \(7\%\).\(^{11}\) To eliminate the lattice mismatch, we made a coherent interface model, where the \(\text{Cu}\) region is expanded parallel to the interface. We deal with three high-symmetry models about the adhesive site of the interface \(\text{Cu}\) atom on the \(\text{Al}_2\text{O}_3(0001)\) surface. These sites are on top of the \(\text{Al}\) atoms (\(\text{Al}\)-site model), on top of the outermost \(\text{O}\) atoms (\(\text{O}\)-site model), and on top of the second-layer \(\text{O}\) atoms (\(\text{H}\)-site model). These three models have different rigid-body translations (RBT) parallel to the interface. The relaxation is performed under preserving the unit-cell symmetry, namely the three-fold rotation along the principal rotation axis and the inversion (\(C_3\)). Because of the symmetry condition, the interfacial \(\text{Cu}\) atoms at the \(\text{O}\)-site or \(\text{H}\)-site are planar, but they have degree of freedom for in-plane displacement away from the strict adhesive site, whereas the displacement of \(\text{Cu}\) atoms at the \(\text{Al}\)-site is fixed to be normal to the interface. The size of the supercell normal to the interface was determined by changing interface distances step by step and relaxing atoms to get the lowest energy for each supercell.

### 3. Results and Discussions

An adhesive energy, \(W_{\text{adh}}\), of the interface has been obtained from the energy difference between the interface and the two separated surface slabs with atomic relaxation, so that the larger \(W_{\text{adh}}\) means the more stable atomic configuration of the model. This is a discussion with respect to an internal energy. Exactly, it is necessary to discuss the stability using a free energy with an entropy term. However, the atomic configuration of the present interface is that at normal temperature, not at high temperature. In such a case, \(W_{\text{adh}}\) is a good approximation as an index of the stability. In this paper, we try to explain the observed atomic configuration only using the theoretical internal energy. \(W_{\text{adh}}\) is also very important for preliminary analysis of the interface toughness.

Present results are listed in Table 1. For the O-terminated interfaces, the \(W_{\text{adh}}\) of the \(\text{H}\)-site model is almost the same as, but slightly larger than, that of the \(\text{Al}\)-site one in a preliminary test. This is because the atomic configurations between two models are similar to each other. Hence we only list the results of the \(\text{H}\)-site and \(\text{O}\)-site models. For Al-terminated interfaces, on the other hand, the \(W_{\text{adh}}\) of the \(\text{O}\)-site model is largest, and the other models are smaller, so that we only list the result of the \(\text{O}\)-site model. One can see that the most stable \(\text{Cu}\) adhesive site of the O-terminated interface is the \(\text{H}\)-site and absolute value of \(W_{\text{adh}}\) is five times larger and more than that of the \(\text{Al}\)-terminated interface. This means that the former has extremely strong interface bonding than the latter. This tendency is in good agreement with previous theoretical calculations.\(^{1–5}\)

Table 1. Adhesive energies (\(W_{\text{adh}}\)) for the O-terminated and the Al-terminated interfaces with experimental data. \((\text{Al}_2\text{O}_3/\text{Cu})_{\text{H}}\) and \((\text{Al}_2\text{O}_3/\text{Cu})_{\text{O}}\) denote the \(\text{H}\)-site and \(\text{O}\)-site model of the O-terminated interface and O-site model of the Al-terminated interface, respectively. The unit is \(\text{Jm}^{-2}\).

<table>
<thead>
<tr>
<th>Interface Model</th>
<th>((\text{Al}_2\text{O}<em>3/\text{Cu})</em>{\text{H}})</th>
<th>((\text{Al}_2\text{O}<em>3/\text{Cu})</em>{\text{O}})</th>
<th>((\text{Al}_2\text{O}<em>3/\text{Cu})</em>{\text{Al}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present work</td>
<td>6.96</td>
<td>5.85</td>
<td>1.27</td>
</tr>
<tr>
<td>Previous calculations</td>
<td>5.94,(^{11}) 5.62,(^{31}) 7.03(^{32})</td>
<td>0.58,(^{11}) 0.90,(^{32}) 0.94(^{33})</td>
<td>0.50,(^{31}) 0.82(^{33})</td>
</tr>
<tr>
<td>Experiments</td>
<td></td>
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of the stoichiometric (0001) surface is removed, and hence some charge transfer will occur easily from the interfacial Cu atoms to the O atoms in order to compensate lost electrons distributed by removed Al. On the other hand, the Al-terminated interface is a stoichiometric interface, where the Al$_2$O$_3$ surface is chemically stable. Thus, the interfacial Cu atoms cannot strongly interact with Al$_2$O$_3$, even though the O layer comes sufficiently near to the interfacial Cu atoms. Even in this case, there exist substantial interactions between the surface Al atoms and the interface Cu atoms, which result in the slight movement of the surface Al atoms toward the Cu atoms as compared with strong in-ward relaxation of the surface Al in the free surface.

The interlayer distance ($D_{\text{layer}}$) between interface layers and the interatom distance ($D_{\text{bond}}$) between Cu and O atoms in the O-terminated interface or between Cu and Al atoms in the Al-terminated one are important quantities for analyzing the interface structure. $D_{\text{layer}}$ and $D_{\text{bond}}$ for each interface are listed in Table 2. As mentioned in above section, the interface Cu layer of the H-site and O-site models is planer. Thus, each $D_{\text{layer}}$ of the interface Cu atom is equivalent. On the other hand, the $D_{\text{bond}}$ of the O-terminated interface is different each other because the interface Cu and O atoms have degree of freedom for in-plane displacement, whereas that of the Al-terminated interface is unity. Thus, the listed $D_{\text{bond}}$ of the O-terminated interface is estimated by taking the average of three different interatom distances between Cu and O atoms. For the O-terminated interface, $D_{\text{layer}}$ of the H-site model is smaller than that of the O-site model, while $D_{\text{bond}}$ is larger. This is because in the H-site model the interfacial Cu atoms are able to sink deeply in hollow space of the Al$_2$O$_3$. For the O-site model, the $D_{\text{layer}}$ is slightly different from the $D_{\text{bond}}$ because of small displacement of Cu atoms from the on-top site. This is consistent with the symmetry condition including

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**Fig. 1** Calculated stable atomic configurations and electron-density distributions of (a) the H-site model and (b) the O-site model of the O-terminated interfaces and (c) the O-site model of the Al-terminated interface. Contours of the valence-electron density are plotted from 0.01 a.u. to 0.15 a.u. with a spacing of 0.01 a.u. $D_{\text{layer}}$ and $D_{\text{bond}}$ denote an interlayer distance and interatom distance, respectively.

(d) the electron-density redistribution of the O-site model of the Al-terminated interface. The solid and dashed lines are accumulated and depletion regions, respectively. Contours of the valence-electron density are plotted from $-0.018$ a.u. to 0.018 a.u. with a spacing of 0.0036 a.u.
the degree of freedom of the in-plane displacement.

One can obtain the important notice that the H-site model with smaller $D_{\text{layer}}$ and larger $D_{\text{bond}}$, is more energetically favorable than the O-site model with larger $D_{\text{layer}}$ and smaller $D_{\text{bond}}$. This indicates that in the present coherent interface the coordination number is an important factor. The interfacial Cu atom seems to gain the energy benefit, in making contact with larger number of O atoms.

About the comparison with experiments, the most serious problem is that the actual interface is incoherent.$^{6-9}$ The lattice mismatch in the present interface is not small as mentioned above. It seems that the incoherent interface formation has energetically advantage rather than the dislocation formation with conserving the coherent interfaces locally. In the present study, coherent interfaces are treated because of limitation of computational resources and because of our purpose of obtaining essential features of interfacial bonding. Thus, we have to clarify the relationship between the present coherent interface model and the actual incoherent interface.

Sasaki and co-workers$^{6}$ have observed the alpha-Al$_2$O$_3$(0001)/Cu interface using HRTEM. As shown in Fig. 3 in Ref. 6), the HRTEM observation has found that the interface is atomically sharp without amorphous-like phases and any strain field derived from the misfit dislocation. The obtained HRTEM image indicates the formation of the incoherent interface. Furthermore, the following orientation relationship (OR) exists; (111)$_{\text{Cu}}$||(0001)$_{\text{Al}_2\text{O}_3}$ and [1-10]$_{\text{Cu}}$|[1-100]$_{\text{Al}_2\text{O}_3}$, which is the same with our models. On the other hand, the preferred OR with geometrically high coherency across the interface$^{25}$ is (111)$_{\text{Cu}}$||(0001)$_{\text{Al}_2\text{O}_3}$ and [11-2]$_{\text{Cu}}$|[1-100]$_{\text{Al}_2\text{O}_3}$. This inconsistent result indicates that interfacial practical bonding plays an important role to construct the actual OR. In order to clarify the interfacial bonding nature, they have performed the HRTEM image simulations and compared with the observed images, as shown in Fig. 7 and Fig. 8 in Ref. 6). Consequently, the authors concluded the most reasonable one for explaining the observed images is the O-terminated interface.

A very important point of notice is that the $D_{\text{layer}}$ evaluated by the HRTEM image simulations is 0.185 nm, which is extremely in good agreement with the present $D_{\text{layer}}$ of the O-site model of the O-terminated interface. This model is energetically metastable one as listed in Table 1. Here we consider the relationship between the ideal “coherent” interface models obtained by the first-principles calculation and the actual “incoherent” interface. Figure 2 shows the concept of coherent-incoherent relationship. First, for the coherent models where the Cu atoms are located on-top of the outermost atoms of an Al$_2$O$_3$ slab such as (Al$_2$O$_3$/Cu)$_0$ and (Al$_2$O$_3$/Cu)$_k$, $D_{\text{layer}}$ is larger than the other models where the Cu atoms can sink deeply in hollow space of an Al$_2$O$_3$ surface. Second, the image simulation of the HRTEM observation has shown that the incoherent interface can be regarded as a mixture of the three kinds of coherent interface models with different RBT parallel to the interface, as shown in Fig. 9 in Ref. 6). In Fig. 9 of Ref. 6), it is clear that the interface with the lattice misfit reveals a moiré-like pattern consisting of locally coherent interface regions with different RBTs. Third, in this sense the largest $D_{\text{layer}}$ of the coherent models should be dominant one for the incoherent interface as a mixture of the coherent ones. In the O-terminated interface, the O-site model has the largest $D_{\text{layer}}$ as explained above. Thus, it is reasonable that $D_{\text{layer}}$ of the O-site model is similar to the observed one of the incoherent interface. For the Al-terminated interface, on the other hand, $D_{\text{layer}}$ of the O-site model is quite good agreement with the observed value of the incoherent interface. However this is not the largest $D_{\text{layer}}$ within the Al-terminated interfaces, which is that of the Al-site model. Therefore $D_{\text{layer}}$ of the incoherent interface estimated from the coherent Al-terminated interfaces seems to be too large if we supposed that the observed interface is Al-terminated one. In this way, the observed incoherent interface can be explained quite reasonably by the ideal coherent interface models of the O-terminated interfaces based on the first-principles calculations.

### 4. Conclusion

First-principles calculations of Al$_2$O$_3$(0001)/Cu interfaces have been performed and revealed that the interface stoichiometry is of great importance for the interfacial properties. $W_{\text{adh}}$ of the O-terminated interface is quite larger than that of the Al-terminated one, and the H-site model is the most energetically stable within the O-terminated interfaces. All the results are consistent with previous calculations. $D_{\text{layer}}$ of the O-site model of the O-terminated interface is in good agreement with that of the HRTEM observation. We have succeeded in explaining the observed incoherent interface using the ideal coherent interface models by the first-principles calculations.

### Acknowledgements

We thank Dr. W. Zhang and Prof. J. R. Smith for fruitful discussions on calculations. This work was performed as a part of “Nanostructure Coating Project” carried out by New Energy and Industrial Technology Development Organization in Japan. The present calculation was supported by “Promoted Research Project for High Performance Com-
puting” in Tsukuba Advanced Computing Center (TACC) of the National Institute of Advanced Industrial Science and Technology (AIST) in Japan.

REFERENCES

9) E. Saiz, A. P. Tombsia and R. M. Cannon: Ceramic Microstructure,

Fig. 2 Conceptual figures of coherent-incoherent relationship. Left and center figures indicate present coherent interface models and right figure indicates a practical incoherent interface model. Top and bottom sides are Cu and Al₂O₃ region, respectively. Bulges indicate the interface atoms, which are Cu atoms in Cu slab, and O and Al atoms in O-terminated and Al-terminated Al₂O₃ slabs, respectively.