Atomic and electronic structures of Cu/$\alpha$-Al$_2$O$_3$ interfaces prepared by pulsed-laser deposition

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Abstract

Interfacial atomic structures of Cu/Al$_2$O$_3$(0001) and Cu/Al$_2$O$_3$(1120) systems prepared by a pulsed-laser deposition technique have been characterized by using high-resolution transmission electron microscopy (HRTEM). It was found that Cu metals were epitaxially oriented to the surface of Al$_2$O$_3$ substrates, and the following orientation relationships (ORs) were found to be formed: (111)$_{Cu}$//(0001)$_{Al_2O_3}$, [110]$_{Cu}$//[1100]$_{Al_2O_3}$ in the Cu/Al$_2$O$_3$(0001) interface and (001)$_{Cu}$//(1120)$_{Al_2O_3}$, [110]$_{Cu}$//[0001]$_{Al_2O_3}$ in the Cu/Al$_2$O$_3$(1120) interface. Geometrical coherency of the Cu/Al$_2$O$_3$ system has been evaluated by the coincidence of reciprocal lattice points method, and the result showed that the most coherent ORs were (111)$_{Cu}$//(0001)$_{Al_2O_3}$, [112]$_{Cu}$//[1100]$_{Al_2O_3}$ and (110)$_{Cu}$//(1120)$_{Al_2O_3}$, [111]$_{Cu}$//[0001]$_{Al_2O_3}$, which are equivalent to each other. These ORs were not consistent with the experimentally observed ORs, and it was possible that crucial factors to determine the ORs between Cu and Al$_2$O$_3$ were not only geometrical coherency, but also other factors such as chemical bonding states. Therefore, to understand the nature of the interface atomic structures, the electronic structures of the Cu/Al$_2$O$_3$ interfaces have been investigated by electron energy-loss spectroscopy. It was found that the pre-edge at the lower energy part of the main peak appeared in the O-K edge spectra at the interface region in both the Cu/Al$_2$O$_3$(0001) and Cu/Al$_2$O$_3$(1120) systems. This indicates the existence of Cu–O interactions at the interface. In fact, HRTEM simulation images based on O-terminated interface models agreed well with the experimental images, indicating that O-terminated interfaces were formed in both systems. Since the overlapped Cu atomic density in the experimental ORs were larger than that in the most coherent OR, it is considered that the on-top Cu–O bonds stabilize the O-terminated Cu/Al$_2$O$_3$ interfaces.

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1. Introduction

Metal–ceramic interfaces play an important role for a number of technological applications such as electronic packaging devices, composites, thermal barrier coatings, solid oxide fuel cells and catalysis. Functional and mechanical properties of these materials systems containing the metal–ceramic interfaces are strongly affected by the structures and properties of the interfaces. As a typical example, the Cu/Al$_2$O$_3$ system investigated in this study is commonly encountered in electronic packaging devices, in which Al$_2$O$_3$ is used as the insulating substrate to protect Cu wires from electrical leakage and thermal degradation. It is known that during the device operation electromigration occurs at the Cu/Al$_2$O$_3$ interfaces under the high-density electric currents [1–3], which determines the performance and lifetime of the electronic devices. Since such phenomena in the devices are closely related to the physical and chemical properties of the interfaces [4–6], it is, therefore,
important to understand the atomic and electronic structures of the Cu/Al2O3 interfaces in detail. So far, there have been a number of reports on the atomic structures of Cu/Al2O3 interfaces, mainly using high-resolution transmission electron microscopy (HRTEM). Ernst et al. [7] studied the atomic structures developed by internally oxidizing CuAl alloy. They found that the cubic Al2O3 precipitates had two orientation relationships (ORs): ‘parallel topotaxy’ and ‘twin topotaxy’. Furthermore, the interface is always parallel to the [111] planes of the Al2O3 precipitates, and the O-terminated interface was a better approximation for the real interface structure than the Al-terminated interface. Dehm et al. [8] studied the OR of Cu/α-Al2O3(0001) interface fabricated by a molecular-beam epitaxy (MBE) technique and found that the (111) plane of Cu is oriented to the surface of Al2O3 independent of growth temperatures. Schem et al. fabricated Cu/Al2O3(0001) [9] and Cu/Al2O3(1120) interfaces [10] by MBE, and studied their atomic and electronic structures by HRTEM and electron energy-loss spectroscopy (EELS). They found that the (111) plane of Cu was also oriented to the surface of Al2O3 in the both systems, and while the O-terminated interface was formed in the Cu/Al2O3(0001) system, the Al-terminated interface was formed in the Cu/Al2O3(1120) system. In contrast, they later reported that the presence of metallic Cu—Al bonds at the Cu/Al2O3 interfaces, independent of the substrate orientations [11]. They concluded that the electronic structures and the bonding mechanism are likely to be affected by the surface condition of the Al2O3 substrate before Cu deposition. But, the bonding mechanism and the factors to affect the bonding states have not been elucidated in detail yet. It is, therefore, important to clarify whether or not Cu/Al2O3 systems intrinsically have O-terminated or Al-terminated interfaces and what factors stabilize the Cu/Al2O3 interface using a different sample preparation method. The aim of this study is to characterize the orientation dependence of the atomic and electronic structures of the Cu/Al2O3 interfaces fabricated by a pulsed-laser deposition (PLD) technique using HRTEM and EELS and to understand the factors that stabilize the Cu/Al2O3 interfaces.

2. Experimental procedure

In this study, Cu metal with 99.99% purity (Kojundo Chemical Laboratory Co., Ltd) was used for deposition on the (0001) and (1120) surfaces of Al2O3 (Shinkosha Co., Ltd) by PLD. The Al2O3 substrates were heated at 1073 K during deposition, and pressure in the chamber was set to 10−6 Pa just before deposition. A KrF excimer laser beam (wavelength = 248 nm, pulse duration = 20 ns, repetition frequency = 20 Hz) was focused onto a rotating copper target to produce a photon power density of about 2 J/cm²/pulse. Then Cu metal was deposited until the thickness reached up to about 60 nm by a deposition rate of 1 nm/min. Subsequently, the interface structures in the specimens were investigated by HRTEM using a JEOL JEM-4010 operated at 400 kV. Thin foils for HRTEM observations were prepared by a standard procedure involving mechanical grinding to a thickness of 50 µm and dimpling to a thickness of about 20 µm at the center of the disks and additional Ar+ ion beam thinning at accelerating voltage of about 4 kV. Geometrical coherency between Cu and Al2O3 crystals was calculated by the coincidence of reciprocal lattice points (CRLP) method [12] in order to examine preferential ORs between the two crystals. The experimental images were analyzed in comparison with simulated images based on possible model structures using the Temas program [13]. To reveal chemical bonding states of the interfaces, EELS measurements were carried out with the probe size less than 2 nm using a Gatan 666 PEELS spectrometer with energy resolution of 1.2 eV attached to a Topcon EM-002BF field emission TEM at accelerating voltage of 200 kV.

3. Results and discussion

3.1. HRTEM observations

Conventional-TEM observation prior to HRTEM analysis has shown that deposited Cu had an island-like shape [14]. Fig. 1(a) shows the HRTEM image of the Cu/Al2O3(0001) interface, where an incident beam direction was selected in the [1100] direction of Al2O3. It should be noted that HRTEM images were systematically taken at defocus values from 0 to −60 nm at steps of about 10 nm. The interface was atomically sharp and no amorphous phase was observed. In addition, it was found that the (111) plane of Cu metal was epitaxially oriented to the (0001) surface of Al2O3 in the following relationship,

\[
(111)_{\text{Cu}}//\langle0001\rangle_{\text{Al2O3}}, \hspace{1cm} [2\bar{2}0]_{\text{Cu}}//\langle1\bar{1}\bar{1}0\rangle_{\text{Al2O3}}.
\]  

On the other hand, Fig. 1(b) shows the HRTEM image of the Cu/Al2O3(1120) interface taken along the [0001] direction of Al2O3. In this interface, again no amorphous phase was observed at the atomically sharp interface, and it was found that the (001) plane of Cu metal was epitaxially oriented to the (1120) surface of Al2O3 in the following relationship,

\[
(001)_{\text{Cu}}//\langle1\bar{1}20\rangle_{\text{Al2O3}}, \hspace{1cm} [1\bar{1}0]_{\text{Cu}}//\langle0001\rangle_{\text{Al2O3}}.
\]

It is noted, however, a following minor OR(3) was also formed, while the OR(2) was dominant, where the ratio of the dominant OR to the minor OR was about 9:1, which was confirmed from the island morphology observed by atomic force microscopy,

\[
(111)_{\text{Cu}}//\langle1\bar{1}20\rangle_{\text{Al2O3}}, \hspace{1cm} [1\bar{1}0]_{\text{Cu}}//\langle0001\rangle_{\text{Al2O3}}.
\]  

These ORs probably depend on the deposition conditions such as deposition rate and growth temperature, and so on.
In this paper, however, we will focus on characterizing the dominant OR(2) because the interface with this OR is considered to be stable in the present experimental condition.

The misfit parameter $d$ between Cu and Al$_2$O$_3$ crystals parallel to the interface plane is defined as

$$d_{\text{Cu}(111)/\text{Al}_2\text{O}_3(0001)} = \frac{|d_{\text{Cu}(111)} - d_{\text{Al}_2\text{O}_3(0001)}|}{d_{\text{Al}_2\text{O}_3(0001)}} = 38\%$$

$$d_{\text{Cu}(001)/\text{Al}_2\text{O}_3(1120)} = \frac{|d_{\text{Cu}(001)} - d_{\text{Al}_2\text{O}_3(1120)}|}{d_{\text{Al}_2\text{O}_3(1120)}} = 38\%.$$  

where $d$ is interplanar spacings for respective planes. As expected from the large misfit, these interfaces can be classified into an incoherent interface. In fact, no strain field caused by misfit dislocations along the interfaces can be seen, indicating that the Cu metals and Al$_2$O$_3$ substrates formed incoherent interfaces.

### 3.2. Evaluation of geometrical coherency

Since it cannot be understood from only experimental observations whether or not the experimental ORs are geometrically preferred ones, the ORs with geometrically high coherency were evaluated by the CRLP calculation. In the previous study by Ikuhara et al. [15], the CRLP calculation was applied to V/Al$_2$O$_3$ interfaces, and the calculated OR with high coherency was formed to be consistent with the experimental one. Therefore, this calculation can predict the most coherent OR between two different crystals. In this method, the overlap of reciprocal lattice points of two adjoining crystals was utilized to obtain a geometrically optimum OR between two crystals. Assuming reciprocal lattice points as reciprocal lattice spheres with finite volumes, the geometrical coherency was evaluated by summing the overlapped volumes of the reciprocal lattice spheres of two crystals, when one crystal was rotated three-dimensionally with respect to another. The sum of all overlapped volumes represents the degree to which sets of planes in the two lattices are parallel and their interplanar spacings are equal. Physically, it may be argued that the maximum overlapped volume corresponds to a state of optimal coherency between the two lattices, in which they can best accommodate each other by the least amount of elastic strain and thus minimize the elastic strain energy of the composite.

In the present case, radii of reciprocal lattice spheres were taken to be 0.15 times as long as the length of primitive reciprocal vectors of each crystal. At the beginning of calculations, the (111), (110) and (112) plane of Cu was initially set parallel to the (0001), (1100) and (1120) plane of Al$_2$O$_3$, respectively, as shown in Fig. 2 (a). Secondary, total overlapped volumes of reciprocal lattice spheres of Cu and Al$_2$O$_3$ were calculated by three-dimensionally rotating around [110], [112] and [111] axes for Cu, where rotation angles around [110], [112] and [111] axes were defined as $\omega$, $\phi$, $\theta$.

Fig. 2(b) and (c) show the variation of geometrical coherency against the rotation angle $\omega$ and $\phi$ at $\theta = 0$ and $30^\circ$, respectively. It is noted here that the CRLP calculations were performed for $\theta$ values varying 0–180° in this study. However, most coherent peaks were confirmed to appear at $\theta = 0$ and 30°. For simplicity, therefore, only the results at $\theta = 0$ and 30° are displayed in Fig. 2(b) and (c). It can be seen in Fig. 2(b) (at $\theta = 0^\circ$) that the most prominent peaks are present at $(\omega \phi \theta) = (55^\circ, 55^\circ, 0^\circ)$ and $(125^\circ, 55^\circ, 0^\circ)$. These two sets of rotation angles, which are equivalent to
each other, represent the following ORs with respect to (0001) and (112\bar{0}) of Al₂O₃,

(11\bar{1})\text{Cu}/[(0001)]\text{Al₂O₃}, \quad (11\bar{2})\text{Cu}/[(0\bar{0}1)]\text{Al₂O₃}, \quad (1\bar{1}0)\text{Cu}/[(1\bar{1}2\bar{0})\text{Al₂O₃}], \quad (1\bar{1}1)\text{Cu}/[(0\bar{0}01)]\text{Al₂O₃}.

These ORs predicted by the CRLP method are not consistent with the experimentally observed OR(1) and (2). The experimental OR(1) at \((\omega\phi\theta) = (0°, 0°, 0°)\) and OR(2) at \((\omega\phi\theta) = (0°, 145°, 0°)\) showed much less coherency, which correspond to the small peaks indicated by arrows in Fig. 2(b). In Fig. 2(c) at \(\theta = 30°\), the highest peaks can be observed at \((\omega\phi\theta) = (0°, 0°, 30°), (110°, 0°, 30°), (180°, 0°, 30°), (0°, 0°, 30°), (70°, 180°, 30°)\) and \((180°, 180°, 30°)\), and these ORs are also equivalent to OR(6) and (7). Furthermore, the peak at \((\omega\phi\theta) = (0°, 90°, 30°)\) represents the experimental OR(3), it is obvious that its coherency is again much smaller than those due to the OR(6).

From the above results, it can be said that the experimental ORs in the present Cu/Al₂O₃ interfaces cannot be understood from the geometrical coherency between the two crystals. This indicates that detailed atomic structures and chemical bonds play an important role for determining the preferred ORs for the Cu/Al₂O₃ system, which will be discussed in the following sections in detail.

### 3.3. Atomic structures

In order to investigate the atomic structures at the Cu/Al₂O₃ interfaces, HRTEM simulations were performed and compared with the experimental images. For HRTEM simulations, possible structural models for the Cu/Al₂O₃(0001) and Cu/Al₂O₃(112\bar{0}) systems have to be constructed. It should be noted, however, that the Al₂O₃ lattice is composed of the Al and O sublattices, and thus the terminated planes on the Al₂O₃ substrate at the interfaces have to be taken into account. In the present case, O-terminated and Al-terminated interfaces can be considered for both the Cu/Al₂O₃(0001) and Cu/Al₂O₃(112\bar{0}) systems. Therefore, the two types of interface structures with different termination planes were constructed for the respective Cu/Al₂O₃ systems. For image simulation, the defocus values and the specimen thicknesses were varied systematically so that the simulated images could agree well with the HRTEM images.

Fig. 3 shows structural models of (a) O-terminated and (b) Al-terminated interfaces in the Cu/Al₂O₃(0001) system, and their simulated images at a defocus value of \(-5\) nm and a specimen thickness of 4.5 nm are displayed in (c) and (d), respectively, because they matched well with the HRTEM image. It should be noted that the interlayer distances of 0.185 nm for the O-terminated model and 0.255 nm for the Al-terminated model across the interface were used to the respect energetically stable bond lengths of Cu–O and Cu–Al, which were reported by Kasowski et al. [16] using ab initio calculation. As can be seen from Fig. 3(c) and (d), bright spots in the Cu region correspond to Cu columns, while those in the Al₂O₃ region correspond to O columns in these imaging conditions. Comparing with the contrast at the interfaces between these two models, the spaces between Cu and O columns show bright contrast in the Al-terminated interface, while those from the O-terminated interface do not show such contrast. In addition, the periodicity of the bright spots is also different between the two models. From the comparison with the experimental image in Fig. 1(a), the simulated image based on
the O-terminated model agreed well with the experimental image, which can be confirmed from the magnified experimental image, together with the simulated result in Fig. 4. It can be concluded, therefore, that the Cu/Al2O3(0001) interface has an oxygen termination at the interface.

In the similar way, HRTEM simulations were carried out for the Cu/Al2O3(1120) system, and the results are shown in Fig. 5. In this case, the simulated images at a defocus value of −55 nm and a specimen thickness of 5.5 nm were applied. Fig. 5(c) and (d) show simulated images based on Fig. 5(a) and (b). According to the theoretical value reported by Kasowski et al., the interlayer distances were again set to be 0.185 and 0.255 nm for the O-terminated and the Al-terminated models, respectively. It is noted, here, that bright spots in the Cu region correspond to Cu columns, whereas those in the Al2O3 region correspond to Al columns in the present imaging conditions. Subsequently, these simulation images were compared with the experimental image in Fig. 1(b). However, the distances between Cu and Al columns across the interface in these simulation images were found to be much longer than that in the experimental image. For that reason, an additional structural modification was considered. The interlayer distances were gradually changed so as to fit the experimental image and finally the experimental image matched with the simulated image with the interlayer distances of 0.166 and 0.238 nm for the O-terminated and the Al-terminated models, respectively. It can be seen that these two simulated images, as shown in Fig. 5(e) and (f), exhibit quite similar arrangements of bright spots at the interfaces. Indeed, both simulated images agreed well with the experimental image, as shown in Fig. 6. It was, therefore, hard to determine which model is comparable with the actual Cu/Al2O3(1120) interface only by HRTEM image simulations. For this reason, it is necessary to reveal chemical bonding states at the interface.

3.4. Electronic structures

EELS is a powerful technique for investigating the chemical bonding states in the narrow region such as grain boundaries and hetero-interfaces. This is because the near edge structures of core-loss peaks in an EELS spectrum (electron energy-loss near-edge structure, or ELNES) reflect local structural and chemical environment of constituent atoms. To reveal the chemical bonding states of the Cu/Al2O3 interfaces, EELS spectra were recorded in the vicinity of and at the interface by focusing electron beam...
onto specimen with the probe size less than 2 nm. All spectra were acquired by 10 s or less and accumulated just one time to decrease a readout noise. Fig. 7 shows O–K edge spectra taken from (a) the interface and (b) the Al₂O₃ substrate in the Cu/Al₂O₃(0001) system. Note that the pre-peak appeared in the spectra from the interface, as indicated by the arrow, under the main peak in the O–K ELNES of the interface region.

Fig. 5. Structural models of the Cu/Al₂O₃(1120) interface viewed along [110]Cu//[0001]Al₂O₃, showing (a) the O-terminated and (b) the Al-terminated interfaces. Black, gray and white circles represent Cu, Al and O atoms, respectively. Simulated HRTEM images based on the models (a) and (b) at the defocus value of −55 nm and the specimen thickness of 5.5 nm are shown in (c) and (d), respectively. Simulated HRTEM images based on the models (a) and (b) are also shown by (e) and (f), but the interlayer distance L is set to be 0.166 and 0.238 nm, respectively.

Fig. 6. HRTEM image of the Cu/Al₂O₃(1120) interface, in which the simulated images of Fig. 5(e) and (f) are inserted in the right and left hand side of the HRTEM image of Fig. 1(b), respectively. Since simulated images of the Al-terminated and O-terminated agreed well with the experimental image, it is hard to determine the termination layer at the (1120) surface of Al₂O₃ only by HRTEM image simulation method.

Fig. 7. O–K ELNES observed at (a) the interface and (b) the Al₂O₃ substrate in the Cu/Al₂O₃(0001) system. Note that the pre-peak appeared in the spectra from the interface, as indicated by the arrow, under the main peak in the O–K ELNES of the interface region.
substrate in the Cu/Al₂O₃(0001) system. A main peak appeared at around 539 eV in both the interface and the Al₂O₃ substrate. In the spectrum from the interface region, the pre-edge at about 533 eV, indicated by the arrow in Fig. 7(a), and the main broad peak around 539 eV can be observed, which did not appear in the spectrum from the Al₂O₃ substrate.

The pre-edge in the O–K ELNES of the interface region is attributed to an interaction between Cu and O across the interface. This can also be imagined from the result in Fig. 4, where this interface has the O-terminated interface plane. In order to understand the Cu–O interaction at the interface, the band structures of the Cu/Al₂O₃ system are schematically shown in Fig. 8. It is well known that Al₂O₃ is an insulator with a wide band gap of 8.7 eV [17]. When Al₂O₃ is joined with metallic Cu, it is likely that the 3d- and 4sp-bands of Cu appear in the band gap, and then interact with O-2p bands. Due to the interactions between the Cu and O bands, the detailed density of states (DOS) in the lower part of the conduction band should be different from that in bulk Al₂O₃. The observed O–K ELNES corresponds to the partial DOS of O-2p in the conduction band. Therefore, it can be said that the pre-edge peak in the interface spectrum of Fig. 7(a) is considered to be due to the Cu–O interactions across the interface.

In the case of Cu/Al₂O₃(1120) system, the similar differences in the O–K ELNES between the interface and the Al₂O₃ substrate were observed, as shown in Fig. 9(a) and (b). A similar, but larger pre-edge appeared in the O–K ELNES of the interface region, which did not appear in that of the Al₂O₃ substrate region. As shown above, it can be said that this change comes from the Cu–O interactions across the interface. Although the previous HRTEM simulation could not determine the termination layer at the surface of Cu/Al₂O₃(1120), the results of EELS measurements suggest that the O-terminated interface is also formed at the Cu/Al₂O₃(1120) interface.

Even though terminated atom species of Al₂O₃ surface was identical with O atoms in both the Cu/Al₂O₃(0001) and the Cu/Al₂O₃(1120) systems, there was difference in the interlayer distance. As shown above, the interlayer distance of the O-terminated model in the Cu/Al₂O₃(1120) system (0.166 nm) was shorter than that in the Cu/Al₂O₃(0001) system (0.185 nm). It is possible that the electronic structure can be different between the Cu/Al₂O₃(0001) and Cu/Al₂O₃(1120) systems. Indeed, the intensity of the pre-edge of the O–K ELNES in the Cu/Al₂O₃(1120) system was much larger than that of the Cu/Al₂O₃(0001) system, as shown in Figs. 7(a) and 9(a), respectively. This difference probably reflects the degree of the Cu–O interaction and thus positively supports the formation of the shortened interlayer distance at the Cu/Al₂O₃(1120) interface.

Scheu et al. [9] reported that the Cu/Al₂O₃(0001) system fabricated by MBE had the same OR as the present OR(1). They also have found the similar pre-edge in the O–K ELNES obtained from the interface region, and suggested the formation of the O-terminated interface. In contrast, they later reported that the OR of the Cu/Al₂O₃(1120) system and the Cu/Al₂O₃(1120) systems fabricated by MBE with Ar⁺-ion sputter-cleaned Al₂O₃ substrate, had the same OR(1) in the Cu/Al₂O₃(0001) system, but had the different OR in the Cu/Al₂O₃(1120) system as the following [11]: (111)Cu//(1120)Al₂O₃ and of [112]Cu//(0001)Al₂O₃, which was also different from the present results of OR(2) and (3). They concluded that the Al-terminated interface was formed because the Cu-L₂,₃ ELNES from the interface region was similar to that of bulk CuAl₂. The termination layers are thus different between the specimens fabricated by different procedures. This is considered to be due to the Ar⁺-ion sputtering treatment of Al₂O₃ substrate before Cu
deposition. A recent study suggested that a heating process is not sufficient to remove hydroxyl groups on the Al\textsubscript{2}O\textsubscript{3} substrate surface \[18\] and that absorbed hydroxyl groups will stabilize Cu–O bonds at the Cu/Al\textsubscript{2}O\textsubscript{3} interface \[19\]. It is, therefore, plausible that the Ar\textsuperscript{+}-ion sputtering treatment removes the hydroxyl groups and forms the Al-terminated interface.

In this study, we found that both the Cu/Al\textsubscript{2}O\textsubscript{3}(0001) and the Cu/Al\textsubscript{2}O\textsubscript{3}(112\bar{0}) systems fabricated by PLD had the O-terminated interfaces, which was confirmed by the appearance of the pre-edge in the O–K ELNES from the interface region. It can be said, therefore, that the present Cu/Al\textsubscript{2}O\textsubscript{3} systems probably have hydroxyl groups at the interface.

3.5. Effect of oxygen on-top copper atoms

As shown above, there was a discrepancy between the experimental ORs and the most coherent ORs. For CRLP calculation, we used only geometrical information such as lattice parameters. In order to take the chemical interaction into account, atomic configurations just at interface were considered. Fig. 10 shows the atomic configurations of the O-terminated Cu/Al\textsubscript{2}O\textsubscript{3}(0001) interface based on (a) the experimental OR(1) and (b) the most coherent OR(6), in which the Cu layer and the O layer closest to the interface are only shown. Small black and large gray circles represent Cu and O atoms, respectively. Note that Cu atoms are located in on-top, bridge and hollow sites of O atoms due to the difference of lattice parameters between Cu and Al\textsubscript{2}O\textsubscript{3} crystals.

Fig. 10. Atomic configurations of the Cu/Al\textsubscript{2}O\textsubscript{3}(0001) interface based on (a) the experimental OR(1) and (b) the most coherent OR(6), in which the Cu layer and the O layer closest to the interface are only shown. Small black and large gray circles represent Cu and O atoms, respectively. Note that Cu atoms are located in on-top, bridge and hollow sites of O atoms due to the difference of lattice parameters between Cu and Al\textsubscript{2}O\textsubscript{3} crystals.

Table 1

| OR       | Overlapped atomic density (nm\textsuperscript{-2}) |
|----------|-----------------------------------------------|
| OR(1) Exp | 0.75                                          |
| OR(6) CRLP | 0.61                                       |
| OR(2) Exp | 0.32                                          |
| OR(7) CRLP | 0.21                                       |

Note. The overlapped atomic densities of the experimental ORs tended to be larger than those of the most coherent ORs in both systems.
of all, a circular cell was used for calculation. Since the cell size should be large enough so that the overlapped atomic density is independent of the cell size, it was set to 10 nm in radius. Secondly, the overlapped atomic density was calculated by changing \( a \), and the result showed that the overlapped atomic density was proportional to the arbitrary constant \( a \). Therefore, the arbitrary constant was set to \( a = 0.1 \) for the present calculation.

Table 1 shows the calculated overlapped atomic densities based on the models of Fig. 10 for the Cu/Al\(_2\)O\(_3\)(0001) system and of Fig. 11 for the Cu/Al\(_2\)O\(_3\)(11\(\bar{2}\)0) system. It was found that the experimental ORs tended to have a larger overlapped atomic density than the most coherent ORs in both the Cu/Al\(_2\)O\(_3\)(0001) and the Cu/Al\(_2\)O\(_3\)(11\(\bar{2}\)0) systems. This indicates that the on-top Cu atoms (overlapped Cu atoms) on the O atoms influence the stability of the Cu/Al\(_2\)O\(_3\) interface. Hernández et al. [20] reported using ab initio calculations that the interlayer distance of the on-top Cu atoms was larger than that of the hollow Cu atoms in the Cu/Al\(_2\)O\(_3\)(0001) interface. However, calculating the Cu–O bond lengths based on their report, the Cu–O bond lengths of the on-top and hollow O sites resulted in 0.208 and 0.252 nm, respectively, which indicate that the Cu–O bonds of the on-top O sites were likely to be shorter than those of the hollow O sites. In fact, there is a similar tendency in the Cu/MgO(111) system [21].

It can be said, by taking account of the image force potential model [22], that the shorter Cu–O bond length is caused by the stronger interaction between Cu and O atoms, while the longer Cu–O bond length is caused by the weaker interaction. It is, therefore, possible that the on-top Cu–O bonds enhance the Cu–O bond strength across the interface. The result that the most coherent ORs are not formed but the observed ORs are formed is due to the fact that the observed ORs have larger overlapped atomic densities (on-top Cu–O bonds) than the most coherent ORs. From the present analysis, we can conclude that the interfaces are likely to be formed so as to make the larger numbers of the on-top Cu–O bonds across the interfaces. Therefore, the number of the on-top Cu–O bonds is one of the factors that can determine the stability of the Cu/Al\(_2\)O\(_3\) interfaces.

3.6. Conclusions

In order to understand the atomic and electronic structures in the Cu/Al\(_2\)O\(_3\) system, HRTEM observations, EELS measurements and geometrical analyses were performed for the Cu/Al\(_2\)O\(_3\) interfaces fabricated by PLD technique. The results of these investigations are summarized as follows.

1. The (111) plane of Cu metal was epitaxially oriented to the (0001) surface of Al\(_2\)O\(_3\) and the following OR was obtained: \((111)_{\text{Cu}}//[0001]_{\text{Al}_2\text{O}_3}\); \([110]_{\text{Cu}}//[1100]_{\text{Al}_2\text{O}_3}\). On the other hand, the (001) and (111) planes of Cu metal were epitaxially oriented to the (11\(\bar{2}\)0) surface of Al\(_2\)O\(_3\), and the following ORs were obtained: \((001)_{\text{Cu}}//(11\bar{2}0)_{\text{Al}_2\text{O}_3}\), \([110]_{\text{Cu}}//[0001]_{\text{Al}_2\text{O}_3}\) (dominant OR), \((111)_{\text{Cu}}//(11\bar{2}0)_{\text{Al}_2\text{O}_3}\), \([110]_{\text{Cu}}//[0001]_{\text{Al}_2\text{O}_3}\) (minor OR).

2. The most coherent ORs predicted by CRLP calculation were the following ORs: \((111)_{\text{Cu}}//(0001)_{\text{Al}_2\text{O}_3}\); \([112]_{\text{Cu}}//[1100]_{\text{Al}_2\text{O}_3}\) with respect to Al\(_2\)O\(_3\)(0001), and \((110)_{\text{Cu}}//(11\bar{2}0)_{\text{Al}_2\text{O}_3}\), \([111]_{\text{Cu}}//[0001]_{\text{Al}_2\text{O}_3}\) with respect to
Al₂O₃(1120). However, these most coherent ORs were not consistent with the experimental ORs observed for the Cu/Al₂O₃ systems.

3. There was the appearance of the pre-edge at the lower energy part of the main peak in the O–K ELNES in both the Cu/Al₂O₃(0001) and the Cu/Al₂O₃(1120) systems. It was concluded that the O-terminated interfaces were formed in both the Cu/Al₂O₃(0001) and the Cu/Al₂O₃(1120) systems, which were confirmed by EELS analyses and HRTEM image simulations.

4. Considering the atomic configuration of O-terminated interfaces, it was found that the experimental ORs in both the Cu/Al₂O₃(0001) and the Cu/Al₂O₃(1120) systems had larger overlapped Cu atomic densities at the interface than the most coherent ORs, respectively. We can conclude that the interfaces are likely to be formed so as to make the larger numbers of the on-top Cu–O bonds across the interfaces. Therefore, the number of the on-top Cu–O bonds is one of the factors that can determine the stability of the Cu/Al₂O₃ interfaces.

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