Abstract of Dissertation

Structures of Metal/Ceramic hetero interfaces

(金属／セラミックス異相界面の微細構造解析)

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Metal/ceramic interface systems have become of great importance for a variety of scientific research and technological applications. In particular, Aluminum(Al)/ceramic substrate system is widely used in power electronics, which requires device reliability in severe application conditions. Thus, interface strength between Al metal and ceramics is of primal importance. In industries, Al-Silicon(Si) alloy is typically used to lower the bonding temperature. However, the fundamental mechanism of Al/ceramic hetero-interface formation; Si behavior during the bonding processes; interface structures and interfacial strength have not been clarified in detail.

A fundamental issue in characterizing interfacial structures is to identify the crystallographic orientation relationships between adjacent crystals. Orientation relationships (ORs) in metal/ceramic systems have been widely studied because they have direct influence on the hetero interface structures and their properties. Therefore, theoretical calculations are helpful to evaluate the stable ORs for geometrical coherency, which may indicate the minimization of the total interface energy resulting to a stable interface. One method in predicting the crystallographic orientation relationships in hetero systems based on geometrical coherency is coincidence of reciprocal lattice point (CRLP) model. CRLP determines the optimum ORs between two crystals through the calculation of the maximum overlap of the RLPs of two adjoining crystals. The sum of the overlapped volumes represents the degree of parallelism of the sets of planes of the two

lattices and their coincidence in interplanar spacings. It is considered that the maximum overlapped volume corresponds to the optimum three-dimensional geometrical coherency.

In this PhD thesis, high-resolution transmission electron microscopy (HRTEM) was used to investigate the stable orientation relationships and interface structures of model metal/ceramic systems formed by liquid-phase bonding and pulsed laser deposition (PLD). To theoretically predict the stable orientation relationships in metal/ceramic systems, coincidence of reciprocal lattice point (CRLP) calculation was performed.

Two common methods of fabricating metal/ceramic interfaces are by liquid phase joining process and thin film deposition. In this research work, a "sandwiched" structure of α-Al_2O_3(0001)/Al or Al-10weight%Si alloy/α-Al_2O_3(0001) was fabricated in vacuum using a hot-press process. The sandwiched structures were bonded at a temperature above the melting point of the metal. The same processing conditions were applied using commercially available epitaxial AlN(0001)/α-Al_2O_3(0001) substrates to study Al/AlN and Al(Si)/AlN hetero interfaces. PLD samples of Al/α-Al_2O_3 (0001), Al/AlN(0001), Si/α-Al_2O_3 (0001) and Si/AlN(0001) were prepared at a medium temperature range of 200-700^{o}C. Laser intensity was set at 40 mJ at a vacuum of 10^{-5}Pa in argon environment.

TEM samples were prepared by a standard procedure, using ion thinning method. The cross-sectional interface structure observations and diffraction analyses were performed using TEMs (JEOL JEM-4010, JEM-2010) operated at 400KV and 200KV, respectively. Compositional analyses of the interfaces were performed by a scanning transmission electron microscope (JEOL JEM-2100F) combined with energy dispersive x-ray (EDX) analysis and electron energy loss spectroscopy (EELS) analysis.

The TEM images clearly showed that the step structures of sapphire, ranging from a few nanometers to ~80nm, are formed at the interface during the bonding processes, although the initial substrate surface is expected to be flat. The detailed diffraction analysis showed that there

seems to be no strong preferred orientation relationship between Al and α-Al_2O_3. The Al/α-Al_2O_3 interface is atomically sharp in between the steps. The formation of step structures at the hetero interface is also reported elsewhere. Consistent with the earlier studies on aluminum oxidation at the interface, the present results suggest that molten Al and oxygen from the bonding environment and/or Al native oxide layer may react to each other to form epitaxial Al_2O_3 step structures during the bonding processes.

In the TEM observation of Al-Si alloy/α-Al_2O_3 interface, the step height is significantly reduced compared with the pure Al case. Presence of Si at the interface was detected by TEM-EDS. Precipitates were also observed at the interface by TEM. These precipitates were confirmed to be Si by electron diffraction and STEM-EELS analyses. HRTEM images of the interfaces between silicon precipitates and sapphire substrate showed two different orientation relationships with sapphire for the bonding temperatures of 645°C and 610°C. At the higher temperature bonding condition (645°C), a stable OR between epitaxial Si and α-Al_2O_3 substrate was determined to be $[1\bar{1}0]Si//[1\bar{1}00]\alpha$-$Al_2O_3$, $(111)Si//(0001)\alpha$-Al_2O_3. While at the lower bond temperature (610°C), a different OR between the Si precipitate and the α-Al_2O_3 substrate was observed. In both temperatures, silicon precipitates formed atomically sharp interfaces with sapphire (0001) surfaces. Experimentally found strong preference of silicon at the interface suggests that aluminum oxidation at the interface may be strongly influenced by the Si segregation. First principles calculations also support the tendency for Si to segregate at the interface. The formation of silicon precipitates with stable interface structures may also be one of the reasons to inhibit step growth reaction at the interface.

Pure Al and Al-10weight%Si alloy were also bonded to AlN(0001) ceramic substrate. AlN is considered to be a very good thermal conductor for power electronics applications. The detailed diffraction analysis showed that there seems to be no epitaxial relationship between Al and AlN in the liquid state bonded interfaces. Unlike in the Al/α-Al_2O_3 interfaces, Al/AlN interface is

relatively flat without any step structures. In the Al-Si alloy/AlN case, Si segregation at the interface was also confirmed by TEM-EDS. Upon extending the bonding time to a few hours, formation of a textured layer of Al-Si was observed by TEM. In specific areas at the interface, Al (with some dissolved Si) formed an orientation relationship with AlN substrate with about 4^o tilt of Al(111) on AlN(0001) interface plane. A stable unique OR was discovered for the observed tilt on Al(111) and was identified as $[1\bar{1}0]Al//[11\bar{2}0]AlN$, $(001)Al//(2\bar{2}03)AlN$ by CRLP calculations. The preferred parallelism of Al(001) and $AlN(2\bar{2}03)$ suggests a strong interaction between the two planes.

To determine the stable interface structures for Al and Si on ceramic substrates using a different bonding process, a simple pulsed laser deposition technique was used. Al and Si islands were formed on the α-Al_2O_3 and AlN substrates using PLD method. The OR of epitaxial Al/α-Al_2O_3 was determined to be $[1\bar{1}0]Al//[1\bar{1}00]\alpha$-$Al_2O_3$, $(111)Al//(0001)\alpha$-Al_2O_3. In contrast, the detailed diffraction analysis showed that there seems to be no epitaxial orientation relationship between Al and AlN. Only a textured growth of Al(111) plane parallel to the basal plane of AlN was observed. CRLP calculation showed that preferred Al/AlN OR has a lower geometrical coherency and with the associated higher misfit parameter compared with the most stable OR of Al/α-Al_2O_3. CRLP calculation then supports the textured Al(111) plane on AlN(0001) which can orient itself in multiple directions without experiencing a large change in misfit at the interface. Similarly, Si shows a texture of (111) plane to be parallel to α-Al_2O_3 (0001) and AlN(0001). Locally oriented Si/α-Al_2O_3 was observed in specific areas at the interface. The orientation relationship was determined as $(111)[1\bar{1}0]Si//(0001)[1\bar{1}00]\alpha$-$Al_2O_3$, which is the same as the most stable orientation relationship of Si precipitates in liquid-phase bonded Al-Si/α-Al_2O_3 interface. PLD Si/AlN also shows a textured layer with local epitaxial relationship of $(111)[1\bar{1}0]Si//(0001)[11\bar{2}0]AlN$.

CRLP can predict the most stable *primary* OR as well as other preferentially stable orientations, which hereafter will be referred as *secondary* ORs. Lattice misfits of the perpendicular planes to the interface werer also calculated for each respective OR. Lattice misfit with respect to the substrate was estimated as: $\delta = (d_{sapphire} - d_{metal})/d_{sapphire}$ x 100%. The minimum misfit of the perpendicular planes at the interface was considered in this thesis.

In a wide survey of metal/α-Al_2O_3 systems, four common ORs were experimentally identified which belong to either (111)Metal//(0001)α-Al_2O_3 or (110)Metal//(0001)α-Al_2O_3. OR **A** was identified as: (111)[$0\bar{1}1$]Metal//(0001)[$0\bar{1}10$]α-Al_2O_3. OR **B** can be obtained by a 30^o rotation of the metal around the [111] axis with respect to OR A, and described as: (111)[$1\bar{1}$ 0]Metal//(0001)[$2\bar{1}\bar{1}0$]α-Al_2O_3. On the other hand, in precipitation and some textured film processes, stable ORs sometimes become very different from the above ORs. These ORs are Pitsch-Schrader (**PS**) described as (110)[001]Metal//(0001)[10 $\bar{1}$ 0]α-Al_2O_3, and **Burgers** described as (110)[$\bar{1}$11]Metal//(0001)[$1\bar{1}00$]α-Al_2O_3.

CRLP predicted ORs are in good agreement with the experimentally observed ORs in the whole range of metal lattice parameters. While (111)Metal//(0001)α-Al_2O_3 is widely observed in epitaxial thin film deposition processes for both bcc and fcc metals, (110)Metal//(0001)α-Al_2O_3 iss commonly found in precipitation methods where parallelism of close-packed planes is a key factor for the growth mechanism of the precipitates. CRLP predicted these orientations as *secondary* preferentially stable ORs. These results suggest that CRLP is most powerful in the predication of stable ORs of metals on α-Al_2O_3, which are grown by film deposition methods.

In order to demonstrate the applicability of CRLP to predict not only for *primary* ORs but also for *secondary* ORs, Al and Si/α-Al_2O_3 systems were considered as representative systems from the list of surveyed metal/α-Al_2O_3 systems. OR **A** matched the experimentally observed most stable OR for the epitaxial Al/α-Al_2O (PLD) and for the high temperature Si precipitate in the liquid-phase bonded Al-Si/α-Al_2O_3 interface. In addition, the three-dimensional profiles

suggest the tendency of Al and Si to form its *secondary* ORs around two orthogonal axes (Ω, K). The second and third peaks were found for Al (OR **B** and OR **C**) around the [111] rotational axis (Ω). OR **C** was identified as: $(111)[5\bar{1}\bar{4}]\text{Metal}//(0001)[1\bar{1}00]\alpha\text{-}Al_2O_3$ at $\Omega=11^o$, which was experimentally observed similarly for Pt and Cu. However, Si showed a significant secondary peak at $K=35^o$ around the $[10\bar{1}]$ rotational axis, which matched with the **PS** relationship as also observed experimentally in this present study on liquid-phase bonded Al-Si interface. In these model systems, CRLP clearly showed the most stable OR as well as the tendency for forming *secondary* ORs, which well matched with the previous experimental reports.

In summary, this PhD thesis has shown the stable interface structures in metal/ceramic systems using two common bonding methods, which are liquid phase joining and pulsed laser deposition. The liquid state hot-press process conditions, did not show any epitaxial relationship of aluminum on sapphire. Silicon was observed to significantly decrease the sapphire step structures at the interface. It was found that the bonding temperature of 645^oC is enough for silicon precipitate to form an epitaxial relationship with sapphire. The same low energy OR can be found in most FCC metals epitaxial with the basal plane of sapphire. The present results indicate that Si is likely to segregate to the $\alpha\text{-}Al_2O_3$ surface and affect the interfacial reaction between Al and sapphire. On the other hand, Al on AlN showed a 4^otilt of Al(111) with respect to AlN(0001), which corresponds to a unique OR. In pulsed laser deposition method, epitaxial thin film of Al on $\alpha\text{-}Al_2O_3(0001)$ was successfully fabricated. In contrast only a textured Al(111) on AlN(0001) was observed. While Si on $\alpha\text{-}Al_2O_3(0001)$ and AlN(0001) showed texturing with localized epitaxy. CRLP method was used to predict the stable ORs, which were found in this present study as well as in a wide range of other metal/$\alpha\text{-}Al_2O_3$ hetero interface systems. CRLP calculations could successfully estimate these preferential ORs and their relative stabilities. CRLP is thus considered to be a powerful tool to predict the most stable OR and other preferentially stable *secondary* ORs for most metal/$\alpha\text{-}Al_2O_3$ systems.