JOURNAL OF MATERIALS SCIENCE **28** (1993) 830–834

Interfacial reactions between titanium film and single crystal α-Al_2O_3

M. KOYAMA, S. ARAI, S. SUENAGA, M. NAKAHASHI
Research and Development Center, Toshiba Corporation, 1 Komukai-Toshiba-Cho, Saiwai-Ku, Kawasaki 210, Japan

Titanium is commonly used to join metals and ceramics by active metal brazing methods. In this work, titanium was sputter deposited on to single-crystal α-Al_2O_3 substrates and the interfacial reactions between the titanium film and the Al_2O_3 substrate were studied. Al_2O_3 was reduced by titanium when samples were annealed at 973 and 1173 K for 300 s in an argon gas flow. Metallic aluminium was produced at the interface, and this diffused from the interface into the titanium film. At 1173 K, the intermetallic compound Ti_3Al and the intermediate titanium oxides, such as Ti_2O and TiO, were formed. The Al^0 diffusion is important in stimulating interfacial reactions.

1. Introduction

Applications of metal–ceramic interfaces are widely found in electronic devices and structural components. An important concern is to understand the interface between metals and ceramics.

In fibre-reinforced metal matrix composite systems at high temperature, interfacial reactions between bulk titanium and bulk Al_2O_3 have been studied and reaction products such as Ti–Al alloys [1], intermetallic compounds [2], and titanium oxides [3] have been detected. The reaction mechanisms resulting in these products have not been clarified.

In developing semiconductor devices, it is important to investigate the adhesion of metal films and ceramic substrates. Interfacial reactions between the titanium film and the Al_2O_3 substrate have been observed using *in situ* analysis methods such as XPS and UPS [4–6]. The surface electronic structure of Al_2O_3 and aluminium has been studied by calculation [7–9] and experiment [10–12]. Various types of titanium oxide have been studied in terms of the titanium core level binding energy [13]. It has been suggested that interfacial reactions are made possible by a charge transfer from titanium to oxygen [14]. In the case of annealed titanium films, oxygen affects the adhesion of films [15–17].

In joining metals and ceramics, active metal brazing techniques are generally used. A titanium-rich layer is found to be formed at the interface [18]. Titanium segregation and the interfacial reactions between a titanium-rich layer and the ceramic cannot be explained completely.

We have attempted to join metals and ceramics by supplying brazing metals through physical vapour deposition. The purposes of this present work were to obtain details of the interfacial reactions which occur between the deposited titanium film and the Al_2O_3 substrate and to clarify what behaviour contributes to interfacial reactions.

2. Experimental procedure

Substrates were single crystals of α-Al_2O_3. The purity of the Al_2O_3 was $> 99.9\%$ and the substrates were $10\,mm \times 10\,mm$ and 1 mm thick. The surface roughness of the substrates was less than 10 nm over a scanned range of 0.2 mm when measured with a stylus profilometer. After evacuation to 6.7×10^{-4} Pa, titanium was sputter-deposited on the single crystals of Al_2O_3 by the r.f. magnetron sputtering deposition method at room temperature. The sputtering gas was argon at a pressure of 6.7×10^{-1} Pa. The titanium film thickness was 150 nm. The deposition rate was 2.5 $nm\,min^{-1}$.

After pumping to 5.7×10^{-4} Pa, samples were annealed at 773, 973 and 1173 k for 300 s in high-purity ($> 99.9999\%$) argon gas flow to decrease the influence of oxygen. The heating rate was 0.83 $K\,s^{-1}$.

X-ray photoelectron spectroscopy (XPS) was used to probe the binding energies of the Al(2p), O(1s), and Ti(2p) core levels. Absolute binding energies could not be obtained due to sample charging. Depth profiles were analysed by argon ion etching from the titanium film surface down to the Al_2O_3 substrate. The actual interface between the titanium film and the Al_2O_3 substrate was defined as the point where the Ti/Al peak ratio was almost equal to 1. At this point, high-resolution XPS analysis was carried out to obtain the detailed electronic structure.

The reaction products were also analysed by low incident angle X-ray diffraction (XRD) method [19], which allows for phase identification of crystalline phases in the thin film.

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3. Results and discussion

3.1. XPS investigation

The interfacial reaction between titanium and Al_2O_3 was analysed by X-ray photo emission spectroscopy (XPS). Al(2p), Ti(2p), and O(1s) photoemission spectra were taken at the titanium film surface, within the titanium film, at the interface between the titanium film and the Al_2O_3 substrate, and in the Al_2O_3 substrate.

Fig. 1a shows the Al(2p) photoemission spectra depth profile for a 773 K annealed specimen. The Al_2O_3 results in an Al^{3+} photoemission peak. At 773 K, only the Al^{3+} photoemission peak was detected. Fig. 1b shows the Al(2p) photoemission spectra depth profile for a 1173 K annealed specimen. Al^0 photoemission peaks were detected in the titanium film on the low binding energy side in addition to the Al^{3+} photoemission peaks. These Al^0 peaks indicate that the Al_2O_3 reduction had occurred.

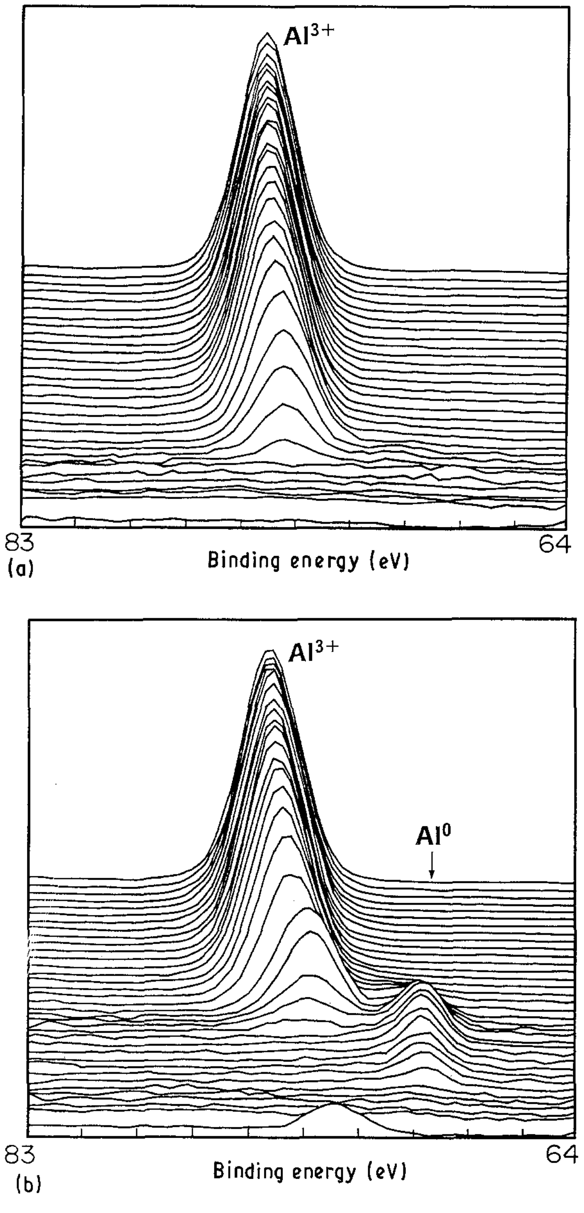

Figure 1 Al(2p) photoemission peak as a function of depth. The titanium film surface is at the front and the Al_2O_3 substrate at the back. The sample was annealed at (a) 773 K, and (b) 1173 K for 300 s. At 1173 K, metallic aluminium was observed on the lower binding energy side of the aluminium oxide peak.

High-resolution XPS analysis was carried out to measure the concentrations of Al^0 and Al^{3+} at the interface. Fig. 2 shows these results. A Gaussian decomposition routine was used to resolve the overlapping peaks in the Al(2p) photoemission spectrum into Al^{3+} and Al^0 components. At 773 K, the Al(2p) photoemission spectrum included a small contribution from the Al^0 peak (about 4%) and a large contribution from the Al^{3+} peak (about 96%). On the other hand, at 1173 K the Al(2p) photoemission spectrum consisted of a 37% Al^0 peak and a 63% Al^{3+} peak at the interface. There is a tendency for Al(2p) photoemission spectra to have a higher peak percentage of Al^0 as the temperature increases.

On the other hand, Ti(2p) photoemission spectra did not exhibit a clear temperature dependence. Fig. 3 shows the Ti(2p) photoemission spectra at 773, 973 and 1173 K. These spectra have similar peak shapes. At the interface, the electronic structure of titanium was metallic; Ti^0 and/or an intermediate oxidation state of titanium; TiO_x ($x < 2$). No Ti^{4+} peak, which indicates TiO_2, can be seen in Fig. 3.

Reduction of Al_2O_3 is expected through charge transfer from titanium to oxygen at the interface. Johnson and Pepper [20] suggested that a chemical bond is established between the metal d-orbital electrons and the non-bonding 2p-orbital electrons in the oxygen anions on the Al_2O_3 surface. Selverian *et al.* [21] concluded that titanium near the interface forms bonds predominantly with oxygen, and then with aluminium in the top layer of Al_2O_3. These reactions

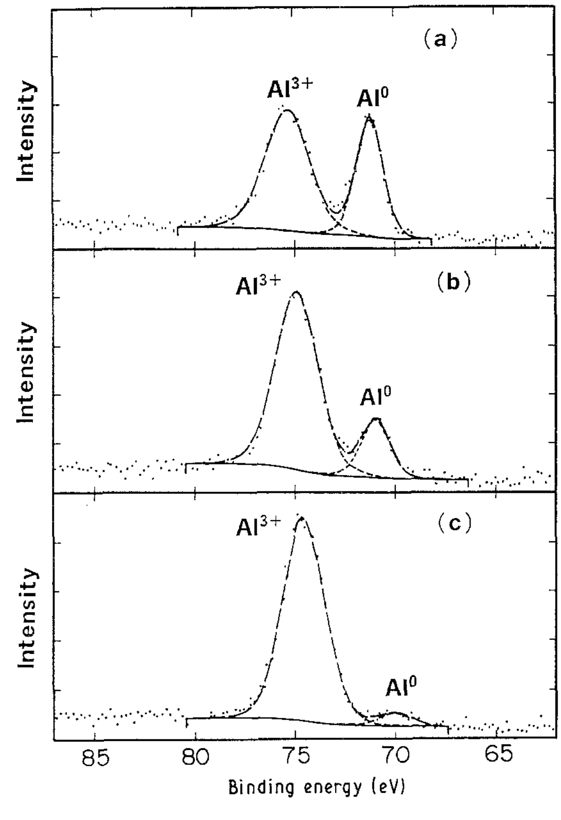

Figure 2 Al(2p) peaks on the surface after 300 s annealing at (a) 1173 K, (b) 973 K, and (c) 773 K. (b) and (c) show the existence of metallic aluminium on the lower binding energy side of the aluminium oxide peak. At 1173 K, the metallic aluminium peak is larger than at 973 K.

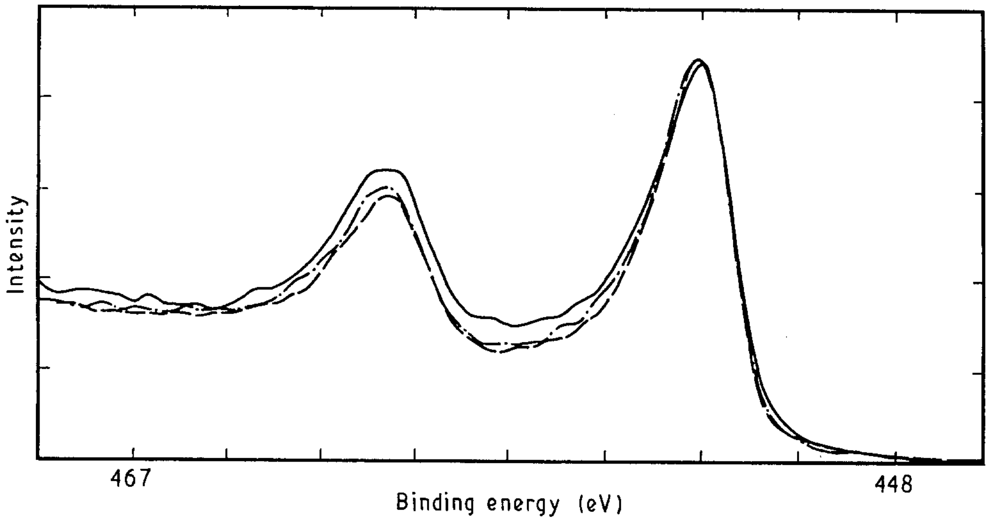

Figure 3 Ti(2p) photoemission peak as a function of temperature at the interface of the titanium film and the Al_2O_3 substrate. This shows that the Ti(2p) peak consists of metallic titanium and intermediate oxide titanium and does not exhibit a clear temperature dependence. (——) 1173 K, (– – –) 973 K, (—•—) 773 K.

result in mixed bonding involving aluminium, oxygen and titanium. Interfacial reactions and the formation of bonding between metals and ceramics explains these models. If titanium is adjacent to the Al_2O_3 lattice and the titanium has a charge transfer ability, interfacial reactions can occur continuously. TiO_2, which is the completely oxidized state, does not have this ability.

Subsequently, the diffusion behaviour was studied. Fig. 4a and b show depth profiles of Al^0, Al^{3+}, Ti, and O for samples annealed at 773 and 1173 K. At 773 K, the profiles of Al^{3+} and O, which mark the Al_2O_3 substrate, dropped off at the interface and Al^0 was not clearly detected. The interfacial reaction does not occur at 773 K. At 1173 K, the profile of Al^{3+} and O dropped slowly at the interface and Al^0 was clearly detected. The Al^0 concentration was greatest at the interface and it decreased gradually from the interface to the titanium film surface. If Al^0 diffused mainly through the grain boundaries, this path would be easier than that of lattice diffusion, so it could be expected that Al^0 will segregate at the titanium film surface. In fact, Al^0 segregation at the titanium surface is not observed by XPS analysis. Thus it is assumed that Al^0 diffuses mainly through the lattice. Burger *et al.* [22] studied Nb/Al_2O_3 diffusion bonding and found that Al_2O_3 particles were present in the niobium grains. This result is explained by considering that reduced Al^0 diffuses through the niobium lattice as in our description. It is thought that the Al^0 is reoxidized in the niobium grains by the oxygen.

At 1173 K, the Al^0 diffusion indicates that the interfacial reaction, which is Al_2O_3 reduction by titanium, occurs continuously. But Chaug *et al.* [14] reported that, in ultrahigh vacuum interfacial reactions such as Ti–O bonding are limited to within a monolayer, while Selverian *et al.* [21] also suggest that in ultrahigh vacuum titanium does not substitute for aluminium in the Al_2O_3 lattice. A difference between Selverian *et al.'s* work and this work is the Al^0 diffusion behaviour. In order to continue with the interfacial reaction, the titanium which has charge transfer ability must be adjacent to Al_2O_3 at all times. If the Al^0 lies in the interface, it is expected that the charge transfer from titanium to oxygen might be suppressed. If no Al^0 diffuses at all or diffuses within the limits of several layers, the interfacial reaction might be suppressed. The continuous interfacial reaction yields Al^0 continuously. Diffusion of that Al^0 into the titanium film is thought to cause the increase in apparent titanium film thickness. Zhao *et al.* [23] studied thermal Hf/Al_2O_3 reactions by Rutherford backscattering spectroscopy (RBS) and reported that the width of the hafnium signal increased and its height decreased. Zhao *et al.'s* results agreed with this work.

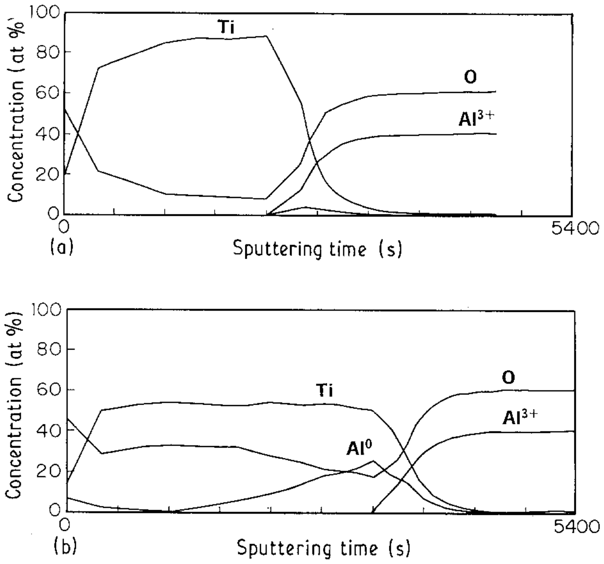

Figure 4 The depth profiles of Al^0, Al^{3+}, Ti and O after annealing at (a) 773 K, and (b) 1173 K for 300 s. The titanium film surface is to the left and the Al_2O_3 substrate to the right. At 773 K, no Al^0 was detected but at 1173 K, Al^0 was obvious. The Al^0 concentration was greatest at the interface and it decreased gradually from the interface to the titanium film surface.

Both the oxygen resulting from Al_2O_3 decomposition and that from the atmosphere might influence the

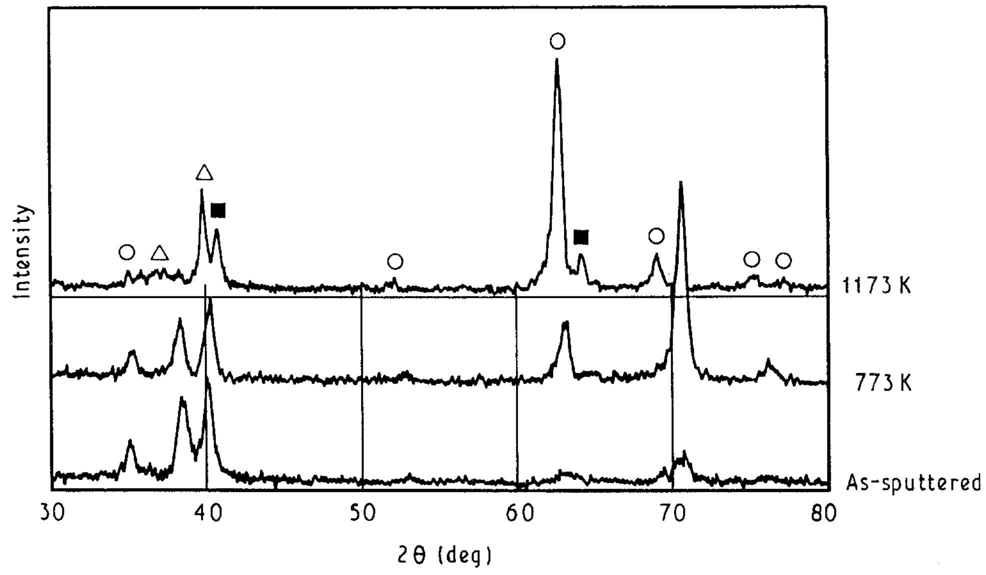

Figure 5 GIXD analysis of the reaction products after annealing at 1173 K and 773 K for 300 s and as-sputtered sample. The incident X-ray angle was 1.0°. The as-sputtered and the 773 K annealed samples showed only titanium peaks, but the 1173 K annealed sample indicated (○) Ti_2O, (△) TiO and (■) Ti_3Al in addition to titanium peaks.

Al^0 diffusion behaviour and the interfacial reaction. In ultrahigh vacuum Al^0 does not diffuse and the interfacial reaction is limited to several layers. The valence–electron density at titanium can be diminished by bonding to oxygen [16]. In the case of the Nb/Al_2O_3 system, interfacial reactions depend on the oxygen concentration in the niobium grains and on the partial pressure of oxygen in the vacuum system [22]. The oxygen might allow enhanced Al^0 diffusion, thus activating the interfacial reaction. But an excess of oxygen promotes oxidation of titanium and the formation of TiO_2. When Ti^{4+} was observed, no Al^0 was detected in our experiment. It is supposed from this result that the Ti^{4+} cannot transfer charge to oxygen, so the interfacial reaction is suppressed.

3.2. Low incident angle XRD investigation

XPS analysis revealed Al^0 formation at 1173 K. The low incident angle XRD method was used to study whether Al^0 existed in the dissolved form in the titanium matrix and/or as a Ti–Al intermetallic compound. Fig. 5 shows the XRD patterns of an as-deposited sample, a 773 K annealed sample, and a 1173 K annealed sample.

As-deposited and 773 K annealed samples exhibited only Ti peaks. 973 K-annealed samples showed similar peaks, but titanium peaks shifted slightly towards lower values of 2θ, in comparison with those of the as-deposited sample. This shifting of titanium peaks is considered due to interfacial reaction products such as metallic aluminium and oxygen diffusing into the titanium matrix and forming a solid solution with titanium.

At 1173 K, in addition to slightly shifted titanium peaks, peaks of Ti_2O, TiO, and Ti_3Al were also detected. The results of XRD analysis agreed with those of XPS analysis and showed that metallic aluminium exists in the titanium matrix as a solute and/or as Ti_3Al.

The formation of Ti_3Al depends on temperature and composition. To form Ti_3Al in a thermal equilibrium state, the concentration of Al^0 needs to be about 18 at % at 1173 K and about 14 at % at 973 K [24]. The formation of Ti_3Al may be possible when the temperature is high enough to cause the interfacial reaction and an adequate amount of Al^0 exists at the interface. At 1173 K, there is a high concentration of Al^0 present at the interface, as shown in XPS analysis, so Ti_3Al formation can be achieved.

To attempt actual brazing of metal and ceramics, it is necessary to understand which microstructures in the interface region effectively improve the joining strength. Kim *et al.* [25] attributed an enhancement of titanium film adhesion to the increased dimensions of intermediate titanium oxide layer which formed at the interface due to diffusion of oxygen. Titanium oxides exist in various stoichiometric and non-stoichiometric states [26]. The titanium oxidation state and microstructure were changed by altering various parameters such as temperature and the environment. Unfortunately, it is not clear which titanium oxides are best as regards joining strength. Tressler *et al.* [2] investigated the phase composition and morphology, and reported that interfacial reactions formed complex layers consisting of TiO and Ti_3Al phases. Various structures such as compound phase [21], oxide phase [27] and Ti–Al–O particles [2] have been reported. It was found through the present study that the Al^0 diffusion is important for the interfacial reaction. It is necessary to understand what phases and microstructures are favourable for Al^0 diffusion and to find methods of producing such microstructures.

4. Conclusion

Titanium films with a thickness of 150 nm were sputter-deposited on to single-crystal α-Al_2O_3 substrates and annealed for 300 s at 773, 973 and 1173 K in high-purity argon gas. Samples were analysed by XPS and the low incident angle XRD method.

At 973 and 1173 K, it was found that Al_2O_3 was reduced by titanium, producing metallic aluminium (Al^0). At 1173 K, the metallic aluminium formed Ti_3Al. To stimulate the interfacial reaction, it is necessary for the Al^0 to move away from the interface and diffuse into the titanium film. It is important to clarify what phases and microstructures are favourable for the Al^0 diffusion.

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*Received 27 April
and accepted 30 June 1992*