XPS study of Interface Reaction between Titanium Thin Film and Sapphire Substrate.

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ABSTRACT

X-ray Photoelectron Spectroscopy(XPS) were used to study the microscopic properties of interface reaction between titanium thin film and sapphire substrate. XPS measurements of valance band, Ti2p and Al2p core level peaks indicate that titanium thin film does not react with oxygen into sapphire at room temperature, but at about 1073K titanium thin film begins to reduce the sapphire with the formation of TiO_2 and metallic Al at interface.

1. Introduction

The technology of metal/ceramic composite has been widely applied to aerospace, automobile and industrial machine etc.[1~2]. Furthermore the successful application of metal-ceramic bonding is very important in semiconductor device such as package[3]. The physical quality and mechanical integrity of the matrix fiber interface determines how effectively the loads are transferred from the matrix to the fibers[4]. And also the reactions at the interface between metal and sapphire are of importance to understand the mechanism of adhesion etc.. These interface reactions between metal thin film and sapphire(alpha-Al_2O_3) substrate have been studied[5~7]. Koyama et al.[8] indicated that there were no binding energy shift of Ti2p and Al2p core level peaks below 1073K. On the other hand, Selverian et al.[9] showed that titanium(Ti) reacted with sapphire at room temperature. It is still inconclusive whether the interface reaction between titanium and sapphire are occurred or not at room temperature. This problem is very important in that this chemical reaction at interface enhances the adhesion between metal and ceramic. On the other hand, in light of these conflicting observation , the interface reaction beween Ti and sapphire merits more study. In the previous paper[10], we have reported results for the interaction between submonolayer Ti and Zirconium(Zr) and sapphire which show that both samples do not react with sapphire substrate at room temperature, but Ti reacts more actively with sapphire than Zr does at high temperature. To clarify the interface reaction which occurred between Ti thin film and sapphire, we have carried out XPS experiment on thin Ti films on sapphire at room and high temperature.

2. Experimental procedure

Substrates were signal crystals of alpha-Al_2O_3 (sapphire) and were 8mm x 5mm and 1mm thick. To obtain carbon contamination free surface, the sapphire substrate was heat treated for 48 hours at 1273K in the furnace. XPS was performed on VG-ESCALAB 210 at Chungbuk National University. This is a routine analysis system comprising LEG1000 electron gun, dual(Al,Mg) and Monochromatic Al X-ray source and a hemispherical electrostatic analyzer placed at 45° to the electron beam and its base pressure was $5x10^{-9}$ Pa. XPS measurement was done with mono-Al X-ray source using constant pass energy mode with 25 eV. Electron flood gun was used to neutralize the charge build up on sapphire. Submonolayer and 5nm Ti film were prepared in situ by Ar^+ beam sputter deposition. From this, the contamination free thin films were obtained. For heating the specimen, IR-lamp was introduced in the pre-chamber[11]. After Ti sputter deposition in the main chamber, the specimen was transferred in the pre-chamber to heat it up. And then the specimen was transferred into main chamber for XPS analysis. Temperatures were changed from 300 to1073K. The Al2p, O1s, Ti2p core level peaks and the valence band peak were monitored as a function of the temperature and depth.

3. Results and Discussions

Figure 1 shows the full spectra from the clean sapphire substrate and submonolayer Ti deposited samples. As can be seen in fig.1(a), sapphire substrate was carbon contamination free surface. The deposited Ti peak of the fig.1(b) is corresponded to be a submonolayer. To see the interface reaction more in detail, the valence band, Al2p and Ti2p were monitored as a function of temperature and plotted in fig.2. Figure 2(a) shows the valence band spectra from submonolayer Ti on sapphire. The high and low binding energy peaks show the valence band of Al-O bonding and O2p of sapphire, respectively according to tight-binding method[12]. After submonolayer Ti deposition, the shape of the peaks does not change at room temperature. These results clearly show that there was no interface reaction at 300K. Figure 2(b) and (c) indicate Al2p and Ti2p. In these figures, core level peaks did not changed until 973K after submonolyer Ti deposition. To see the interface reaction at high temperature, temperature were changed from room

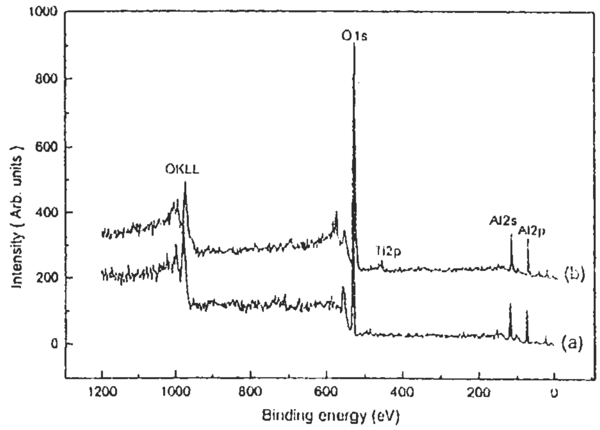

Fig.1 The full spectra (a) before and (b) after submonolayer Ti deposition on sapphire at room temperature.

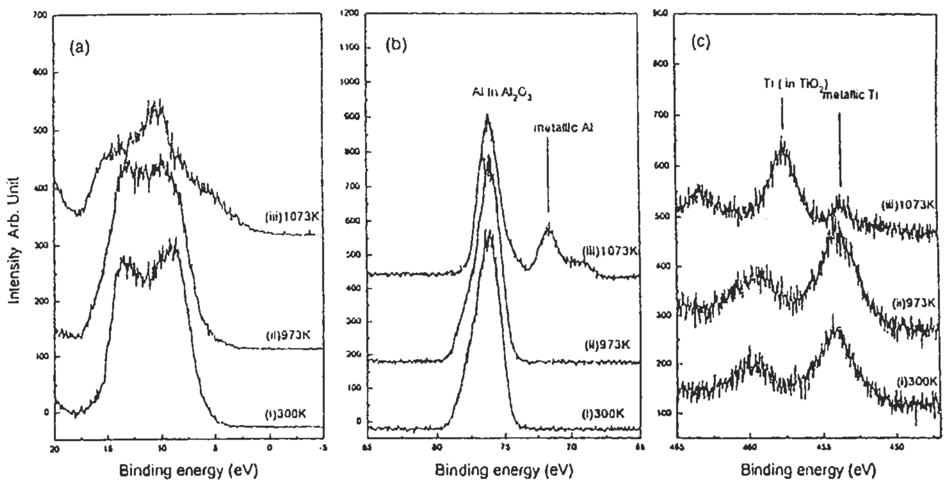

Fig.2(a) Valence band, (b) Al2p and (c)Ti2p photoemission peaks from submonolayer titanium on sapphire respectively at (i) 300K, (ii) 973K and (iii) 1073K heat treatment.

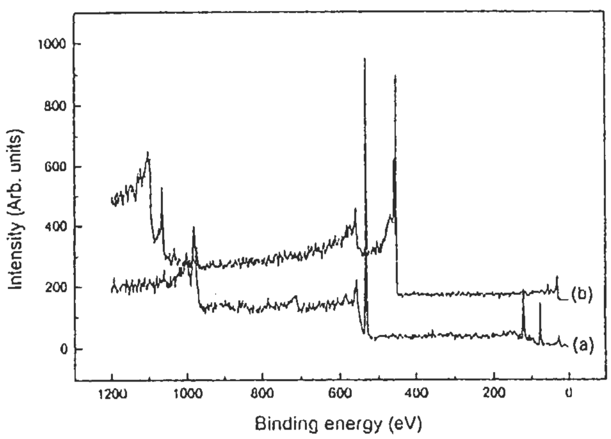

Fig.3 The full spectra (a) before and (b) after 5nm titanium deposition on sapphire at room temperature.

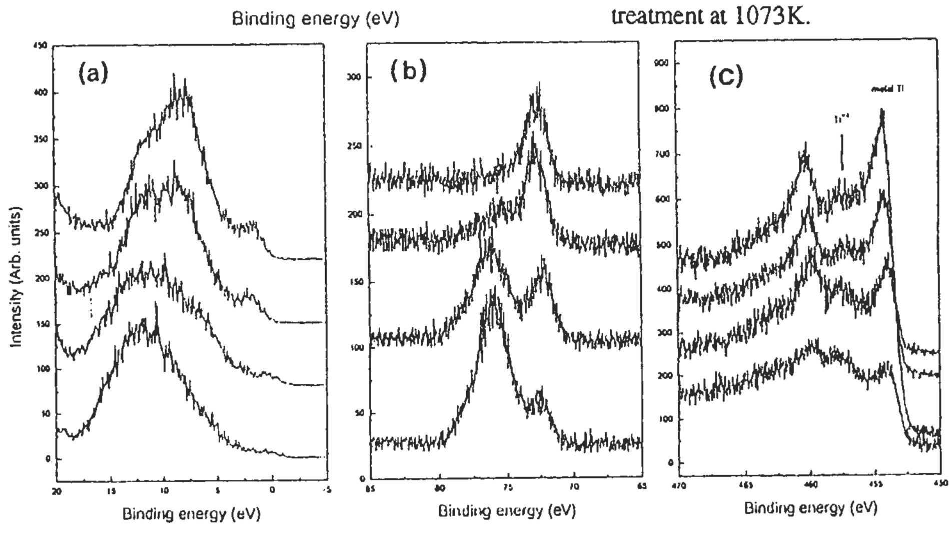

Fig.4(a) Valence band, (b) Al2p and (c) Ti2p photoemission peaks from titanium thin film during depth profile after heat treatment at 1073K.

temperature to 1073K as shown in fig.2. Until 973K, any binding energy shifts for either peaks were not observed. But, at 1073K, the binding energy of the aluminum core level relative to the oxide state shifts from oxide state of Al[fig.2b(ii)] to metallic Al[fig.2b(iii)]. It can be explained that Ti reacted with oxygen in the sapphire and Al was leaven alone. Therefore metallic Al was formed due to interface reaction(Ti-O). The binding energy shift of the Ti core level relative to the metallic state in fig.2c(iii) was found to be TiO_2, and interpreted in terms of charge transfer from Ti to oxygen[12]. Again the interface reaction can be seen clearly from the valence band region in fig.2a(iii) at high temperature. These figures show that Ti reacted with oxygen in sapphire at 1073K and that Ti became into oxidization and metallic Al were formed. Those oxidized Ti peaks were Ti^{+4} and metallic Al was Al^0. The same experiments were conducted in 5nm Ti film on sapphire to directly compare with Sarvarian's result.They claimed that the metallic Al peak slowly grew with increasing coverage Ti at 300K. Fig.3(a) and (b) show XPS full spectrum obtained from clean sapphire substrate and 5nm titanium deposited on substrate respectively. During deposition of Ti thin film, valence band, Al2p and Ti2p peaks were monitored to see the thickness dependency of interface reaction at room temperature. But we could not find out any chemical shifts from these peaks during deposition at 300K. Koyama et al.[8] reported that there was no any interface reaction in the metal/sapphire system at 300K from XPS measurement for thick film. Their results agreed with ours obtained from this experiment. After deposition, Ti film was heated at 1073K *in suit* and then valence band, Al2p and Ti2p were obtained during depth profile and plotted in figure 4. The valence band was absolutely different from sapphire or Ti metal valence band. According to tight binding theory, Al-O bonding was broken and the new peaks appeared near the 5eV in binding energy as shown in fig.4(a). These peaks indicate that oxide Ti and metallic Al were coexisted in this area. These phenomena were occurred because Ti atoms diffused into the sapphire due to heat treatment. And then the chemical reaction between Ti thin film and sapphire was occurred near the interface. As can be seen in fig.4(b), Al2p core level peak changed from metallic Al2p peak to Al2p peak in sapphire during the depth profiling. This result indicates that the reaction between Ti and sapphire was occurred at the interface of Ti thin film on sapphire. Ti2p peaks show the same result as shown in fig. 4(c). Metal Ti peak at 454 eV was dominant in the surface(top of figure) and oxide Ti peak at 458 eV was grown in interface. From this experiment, the interface reaction layer between titanium thin film and sapphire substrate can be assessed to be about 2nm after heat treatment at about 1073k. If these results are considered together, we are lead to a conclusion that the Ti reacts with sapphire at 1073K.

4. Conclusion

The microscopic properties of interface reaction between titanium and sapphire substrate have been studied using XPS. The XPS results provided a fairly completed picture of interface reaction between Ti thin film and sapphire in the temperature range of 300K to 1073K. Titanium reacted with the sapphire only above critical temperature of 1073K and oxide Ti and metallic Al were formed at interface. Ti is more exactly Ti^{+4} and metallic Al is Al^0. It was found that Ti is actively react with sapphire over 1073K.

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