INTERFACIAL REACTIONS OF METAL FILMS WITH AlN SUBSTRATE①

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ABSTRACT Thin films of Ti and Ni deposited on AlN substrate by e-gun evaporation were annealed at the temperatures from 600 ℃ to 800 ℃ and from 600 ℃ to 850 ℃ for 1 h respectively. Solid-state reaction products between the metal films and AlN substrate under annealing were investigated by X-ray diffraction (XRD) and Ruthford backscattering spectrometry(RBS). $TiAl_3$ TiN, and Ti_4N_{3-x} including Ti_2N were found at the interface between Ti film and AlN substrate for the annealed samples. In Ni/AlN system, $NiAl_3$ and Ni_3N were formed at the interface between Ni thin film and AlN substrate for the samples annealed above 600 ℃. $NiAl_3$ formed at the interface was very dense and hindered the diffusion of Al and N atoms into Ni thin films. As a result, the interface reaction was limited in the vicinity of the interface region.

Key words thin films interfacial reactions AlN substrate

1 INTRODUCTION

Aluminum nitride (AlN) is a newer material of interest for electronic packaging. The main reasons are its extremely high thermal conductivity (about 260 W/mK) and chemical stability combined with a wide band gap (6.3 eV). It is being developed as a replacement for beryllia (BeO) in high-power packages and for packaging large chips[1]. Ti, as a reactive element, may raise high adhesion strength to ceramics by interfacial reactions. Ni may offer inherently oxidation resistance at elevated temperature. Both of them are important materials in thin film metallization of ceramics packaging. The characterization of the interface reactions between AlN and thin metal films is very important for process design and reliability in packaging applications. However, the interfacial reactions are complicated and can be affected by many factors such as temperature, impurities in AlN substrate etc. In addition, complex charging effects existing at the metal thin films/AlN interface preclude a detail evaluation of interfacial chemistry by X-ray photoelectron spectroscopy (XPS) or Auger electron spectroscopy (AES). Therefore, the detailed reaction mechanism and reaction products between pure AlN and the metal films under high temperature annealing are unclear at present[2, 3].

In this paper, pure AlN substrates are prepared by hot-pressing under nitrogen protecting. No aid-sintering substance is added into AlN powder intentionally to avoid the impurities influence on interfacial interaction. Solid-state reaction products at the interface of Ti/AlN and Ni/AlN systems under annealing are determined by XRD and RBS, and the reaction mechanism is also studied in this paper.

2 EXPERIMENT PROCEDURE

AlN substrates were prepared with pure AlN powder ball-milled for 24 h in anhydrous alcohol. The powder was green compacted at 300 MPa and then hot-pressed at 1 850 ℃ and 25 MPa for 1 h under nitrogen protecting. The relative density of AlN substrate was 99.6%. Polished AlN substrate was chemically cleaned with 10% HF for 1 min, then cleaned with acetone

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and alcohol before they were loaded into vacuum chamber. Prior to deposition, the substrates were also subjected to sputter cleaning in-situ for 3 min. Ti and Ni thin films were deposited on AlN substrate by e-gun evaporation respectively. The base vacuum for this work was 8×10^{-5} Pa. A quartz oscillator detector was connected with an IBM computer to measure the evaporation rate of the evaporated metal and the thickness of thin films. The deposition rate was controlled at 0.35~ 40 nm/s. Ti deposited on AlN by e-gun evaporation was annealed at the temperatures 600 ℃, 700 ℃ and 800 ℃ for 1 h respectively. The samples of Ni film deposited on bulk AlN by e-gun evaporation were annealed at 600 ℃, 700 ℃ and 850 ℃ for 1 h respectively. Specimen annealing was performed in a tube vacuum furnace with the vacuum better than 1.2×10^{-4} Pa during annealing.

X-ray diffraction (XRD) analysis was performed with powder diffractometer model D/max-RB (Rigaku) using Cu K_α radiation. The electron gun was operated at 40 kV with a beam current 120 mA. Step scan with sampling time of 2 s was employed to improve detection sensitivity. Ruthford backscattering spectrometry (RBS) analysis was carried out with 3SDH (NEC) accelerator, 2.1 MeV He^{2+} was impinged vertically to sample surface and backscattering ions were detected by Au/Si surface barrier detector at 165° position.

3 RESULTS AND DISCUSSION

3.1 Ti/AlN *System*

Fig. 1 shows the XRD patterns of Ti film deposited on AlN substrate. Only diffraction peaks of Ti and AlN were observed for the as-deposited sample, which meant that if compounds like aluminide, nitride or others were formed at the interface, the formed layer should be amorphous or thinner than the detection limit. For the sample annealed at 600 ℃ for 1 h, the $TiAl_3$, TiN, and Ti_4N_{3-x} (JCPDS 39-1015) phases were detected. Diffraction peaks of Ti, Ti_2N and Ti_4N_{3-x} overlapped partly with one of AlN diffraction peaks, which resulted in obvious broadening of the AlN diffraction peak. With annealing temperture increasing, Ti, TiN (200), Ti_2N and Ti_4N_{3-x} diffraction peaks intensity decreased and the intensity of $TiAl_3$ and TiN(111) diffraction peaks increased by mutual reaction. After the sample annealed at 800 ℃ for 1 h, TiN(200) peak disappeared. To confirm the results from XRD patterns and to determine the distribution of reaction products, the interfacial reactions were further investigated by RBS.

Fig. 1 X-ray diffraction (CuK_α radiation) patterns of Ti films/AlN samples before and after annealing at 600 ℃, 700 ℃ **and** 800 ℃ **for 1 h**

Fig. 2 shows the RBS spectrum of the sample annealed at 700 ℃ for 1 h. The spectra of the samples annealed at 600 ℃ and 800 ℃ are not shown, however, they are similar to the spectrum annealed at 700 ℃. Steps B and C appeared at the back edge of Ti signals. Step D and E appeared at the front edge of Al and N signals respectively. The general shape of the spectrum indicated that Ti-Al and Ti-N compounds were

Fig. 2 Backscattering spectrum of Ti/AlN sample after annealing at 700 ℃ for 1 h

formed at the interface. Judging by the channels of Al, N and Ti element, step D and C were at the same depth. The atomic ratio of Al/Ti at this depth were calculated from the height ratio of step D/step C according to the formula (46) in reference [5]. The result showed that the Al/Ti atomic ratio was 2.91 and approximately equall to 3, which meant that the layer was $TiAl_3$ phase. This further verified XRD analysis results. The front edge of Al signals only arrived at the depth corresponding to step C, so the layer corresponding to step B should be Ti-N compounds formed by interfacial reactions, which was also verified by calculating atomic density of Ti in the layer. Thus, Ti reacted with AlN to give a laminate structure, $TiAl_3$ was formed near AlN. TiN and Ti_4N_{3-x} were formed above $TiAl_3$ layer. This reaction phase distribution sketch is shown in the right upper corner of Fig. 2.

Cater *et al*[3] found that TiN_x was formed at Ti/AlN interface at 573 K by XPS. Yasumoto *et al*[6] found $TiAl_3$ at the interface after annealing at 700 ℃ for 5 min. However, the present results showed that $TiAl_3$, TiN, Ti_2N and Ti_4N_{3-x} were formed after annealing from 600 ℃ to 800 ℃ for 1 h. In addition, $TiAl_3$ phase was formed near AlN substrate and TiN, Ti_2N and Ti_4N_{3-x} were formed above the $TiAl_3$ layer. According to the results mentioned above, the interface reaction between Ti and AlN consisted of the following steps: at first AlN is reduced by Ti, then N and Al atoms diffuse into Ti film and Al atoms aggregate at the interface because the diffusion rate of N atoms is higher than that of Al, at last $TiAl_3$ is formed at the interface. Nitrogen atoms diffuse into Ti films to form TiN and Ti_4N_{3-x} including Ti_2N. Ti_4N_{3-x} phase is unstable. When the concentration of nitrogen in Ti film reaches 30% ~ 50% at reference [7], Ti_4N_{3-x} phase(including Ti_2N) transforms into TiN phase. Obviously, the diffusion rate of nitrogen atoms has a great influence on interface reaction. High temperature annealing expedites the diffusion of nitrogen atoms into Ti films. The final interface reaction between Ti film and AlN obeys Eqn. (1)

$$4Ti + 3AlN = TiAl_3 + 3TiN \quad (1)$$

The free energy change of this reaction as a factor of temperature was calculated according to the thermodynamics data from reference [8]. The result is shown in Fig. 3. This reaction has $\Delta G = -202$ kJ/mol at $T = 298.15$ K, which indicates that the reaction is thermodynamically favoured at the room temperature. However, no reaction products were observed for as-deposited sample, which indicated that the reaction was controlled by dynamics factors (e.g. the diffusion Al and N atoms etc.) or that the formed products were too thin to detect. Ti film metallization of AlN raises high adhesion strength to AlN substrate after high temperature annealing.

However, the mechanism of the obtained high adhesion strength is unclear at present. According to the results mentioned above, $TiAl_3$ is one of the metallic compounds having a high tensile strength close to 2.0×10^2 MPa. Thus, high adhesion strength is considered to be resulted from the formation of aluminide by reaction between Ti thin film and AlN substrate.

3.2 Ni/AlN *System*

Fig. 4 shows the XRD patterns of Ni film deposited on AlN substrate. Only the diffraction peaks of Ni and AlN were detected for the as-deposited samples. After the samples annealed at 600 ℃, 700 ℃ and 850 ℃ for 1 h respectively, $NiAl_3$ and Ni_3N diffraction peaks appeared. This indicated that the following reaction occurred and that $NiAl_3$ and Ni_3N were formed at the interface.

Fig. 4 X-ray diffraction (Cu K_α radiation) patterns of Ni films/AlN samples before and after annealing at 600 ℃, 700 ℃ and 850 ℃ for 1 h

Fig. 3 Relationship between free energy change ΔG (kJ/mol) and temperature(K)

$$10Ni + 3AlN = NiAl_3 + 3Ni_3N \quad (2)$$

With annealing temperature increasing, the number of the diffraction peaks for $NiAl_3$ and Ni_3N increased obviously. However, the increasing intensity of these diffraction peaks was not obvious, which might imply that $NiAl_3$ formed at the interface was very dense and hindered the diffusion of Al and N atoms into Ni thin films. As a result, the interface reaction was limited in the vicinity of the interface region. Fig. 5 shows RBS spectrum of the sample annealed at 850 ℃ for 1 h. Step A appeared at the back edge of the Ni singnals and step B appeared at the front edge of Al signals. The atomic ratio of Al and Ni in the reacted layer was calculated from the height ratio of step B and step A. The result showed that the atomic ratio of Al/Ni was 2.94 and approximately equall to 3. On the other hand, N signals moved forward and indistinct step appeared at the front edge of the N signals, which meant that Ni-N compound was formed at the interface. These results verified XRD results mentioned above. Low adhesion strength of Ni film to AlN was found by

Fig. 5 Backscattering spectrum of Ni/AlN sample after annealing at 850 ℃ for 1 h

Yusumoto *et al*[7] and no interface reaction phase was detected for Ni thin films/AlN system after high temperature annealing in their studies. Thus, they thought that the reason for low adhesion strength was because no reaction layer were formed at the interface. However, according to the present results, low adhesion of Ni film to AlN might result from that the forming of $NiAl_3$ phase at the interface after high temperature annealing.

4 CONCLUSIONS

In this paper, pure AlN substrates were prepared by hot-pressing. Thermally induced interfacial reactions of Ti or Ni thin films with AlN substrate were investigated. AlN is reduced by Ti. Al and N atoms diffusing into Ti film and Al atoms aggregating at the interface are due to the higher diffusion rate of N atoms. $TiAl_3$ phase was formed at Ti/AlN interface and TiN, Ti_4N_{3-x} including Ti_2N were formed above $TiAl_3$ layer under annealing at 600 ~ 800 ℃ for 1 h. The formation of aluminide may contribute to high adhesion strength between Ti thin film and AlN substrate. $NiAl_3$ and Ni_3N were formed when annealing above 600 ℃ for 1 h at Ni film/AlN interface. The mutual reaction was limited in the vicinity of the interface region. These results contributed to clarification of enhancement mechanism of adhesion by interfacial reactions and provided experimental evidence for the thin films metallization of AlN in packaging applications.

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