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Study of diffusion barrier properties of ternary alloy ($Ti_xAl_yN_z$) in $Cu/Ti_xAl_yN_z/SiO_2/Si$ thin film structure

Y.K. Lee[a,*], Khin Maung Latt[a], Thomas Osipowicz[b], Cham Sher-Yi[b]

[a] *Division of Materials Engineering, School of Applied Science, Nanyang Technological University, Nanyang Avenue, Singapore 639798, Singapore*

[b] *Department of Physics, National University of Singapore, Lower Kent Ridge Road, Singapore 119260, Singapore*

Abstract

The effects of aluminum (Al) incorporation on the performance of a titanium nitride (TiN) diffusion barrier were investigated up to the temperature of 1000°C in the $Cu/Ti_xAl_yN_z/SiO_2/Si$ structure. The thermal stability of the structure was evaluated by using four-point probe, X-ray diffraction, and Rutherford Backscattering Spectroscopy. The $Cu/Ti_xAl_yN_z/SiO_2/Si$ system retained its structure up to 1000°C. The incorporation of Al into the Ti_xN_y film modified the microstructure of the Ti_xN_y film, especially the microstructure of grain boundaries in which oxide and nitride compounds of Al and Ti were formed during thermal annealing. As a result, the fast pathways for copper (Cu) diffusion were effectively blocked by these compounds and the stability of the barrier performance was enhanced up to 1000°C.

Keywords: Diffusion barrier; Titanium aluminium nitride; Unbalanced magnetron sputtering

1. Introduction

Copper (Cu) is expected to come into widespread use as an interconnecting metal line in micro-electronic devices and packaging applications. The demand for increasing a circuit performance, while downscaling the interconnect size to allow an increased circuit density, is placing huge demands for interconnect performance and reliability. Cu has been strongly considered as an interconnection material substitute for Al metallization because of its lower resistivity and higher electromigration resistance than Al and Al alloys [1]. However, Cu diffuses easily into the interlayer dielectrics and device regions in silicon (Si) substrates, then reacts with Si atoms to form Cu_3Si compounds at a very low temperature (~200°C) [2], and thus results in degradation of a circuit performance. Therefore, a barrier layer is essential to prevent Cu diffusion. In order to find a suitable diffusion barrier, a significant amount of research work has been performed, and various diffusion barriers, including refractory metal (Ta and W) [3,4] nitrides (TiN and TaN) [5,6] and compounds (TiW and Ta–Si–N) [7,8] have been proposed. Among the proposed diffusion barriers, TiN is presently one of the most widely used barrier material in Cu as well as Al metallizations. TiN is chemically very inert, stable, and has desirable properties such as its refractory nature at elevated temperatures, excellent mechanical, chemical and thermal inertness and good resistance to corrosion. These properties allow TiN to withstand the repeated thermal cycles used in multilevel metallization schemes.

In this article, in order to achieve a further enhancement on Cu diffusion barrier properties of TiN, Al atoms (~5 at%) were co-sputtered during TiN deposition. The role of Al in the TiN diffusion barrier for Cu was investigated. Al incorporated to TiN is expected to result in the strong binding of Ti–Al–O–N (co-existing oxide and nitride compounds of Al and Ti), followed by the suppression of the Cu diffusion into the barrier. The Ti–Al–O–N quaternary phase diagram [9] shows that

*Corresponding author. Tel.: +65-790-5174; fax: +65-792-6559.

E-mail address: asyklee@ntu.edu.sg (Y.K. Lee).

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the first interior tie line is part of interior tetrahedron that links the phases TiN, $TiAl_3$, AlN, Al_2O_3, and Ti oxides. It can be predicted that the reactions between Al and TiN during thermal annealing (~550°C) should form the phases that can effectively block the pathways of Cu diffusion.

2. Experimental details

$Ti_xAl_yN_z$ was deposited on thermal oxidized silicon substrate by reactively unbalanced magnetron sputtering using Ti and Al targets in a gas mixture of Ar and N_2 and subsequently Cu without breaking the vacuum. The samples were then annealed in a temperature range of 550–1000°C for 30 min in nitrogen (N_2) ambient. The four-point probe method was employed to measure the sample sheet resistance for surveying the overall reaction. To identify the new phases formed during the annealing, X-ray diffraction (XRD) analysis and Rutherford Backscattering Spectroscopy (RBS) were carried out to evaluate the interaction between Cu and $Ti_xAl_yN_z$. XRD measurements were performed with the grazing incident angle (5°) attachment in RIGAKU RINT-2000 diffractometer, using CuK_α X-ray at 50 kV and 20 mA from 20 to 80° with 0.05° step and 1°/min scanning rate.

3. Result and discussion

The variation of the sheet resistance as a function of annealing temperature for $Cu/Ti_xAl_yN_z/SiO_2/Si$ structure in N_2 ambient for 30 min is shown in Fig. 1. The measured sheet resistance is dominated by the Cu thin film since this film (200 nm and $\rho \sim 1.7\,\mu\Omega\,cm^{-1}$) is much thicker and has a much lower resistivity than TiAlN (100 nm and $\rho \sim 216.0\,\mu\Omega\,cm^{-1}$) and any other reaction product. It is noted that the measured sheet resistance mainly represents the condition and the quality of Cu overlayer since the top Cu layer carries nearly all the sensor current. The sheet resistance decreased by 14% after annealing at 550°C, which contributed to the grain growth of Cu layer and the reduction of crystal defects during the annealing, and remained almost constant up to 1000°C. Apparently, there is no noticeable change in sheet resistance. It can be concluded that there is no combined effect of the positive temperature coefficients of resistivity of each of the layers (Cu and $Ti_xAl_yN_z$), no interlayer diffusion, and no interfacial reactions resulting in the creation of new phases with higher resistivity. Fig. 1 clearly indicates that the incorporation of Al into the Ti_xN_y is very effective for the enhancement of barrier properties of the Ti_xN_y film in the $Cu/Ti_xAl_yN_z/SiO_2/Si$ system.

Fig. 2 shows the XRD spectra of a $Cu/Ti_xAl_yN_z/SiO_2/Si$ structure before and after annealing. The main observed compounds are Cu at 2θ angles of 43.30° (111), 50.70° (200) and 74.35° (220), TiN at 36.60° (111) and 61.90° (220), Ti_2AlN at 62.0° (110) and 72.0° (109), and Ti_3AlN at 21.67° (110) and 76.80° (311) for the as deposited sample. The Al peaks were not detected in XRD spectra because of the small amount of Al and/or it already combined with TiN due to co-sputtering. XRD analysis of as deposited sample showed that the texture was typical for sputtered deposited copper, mainly (111), (220) and other smaller components. After 550°C annealing, the Cu texture had changed as an increase in intensity of the peak at 43.30° (111) was observed and the Cu peak at 74.35° (220) had

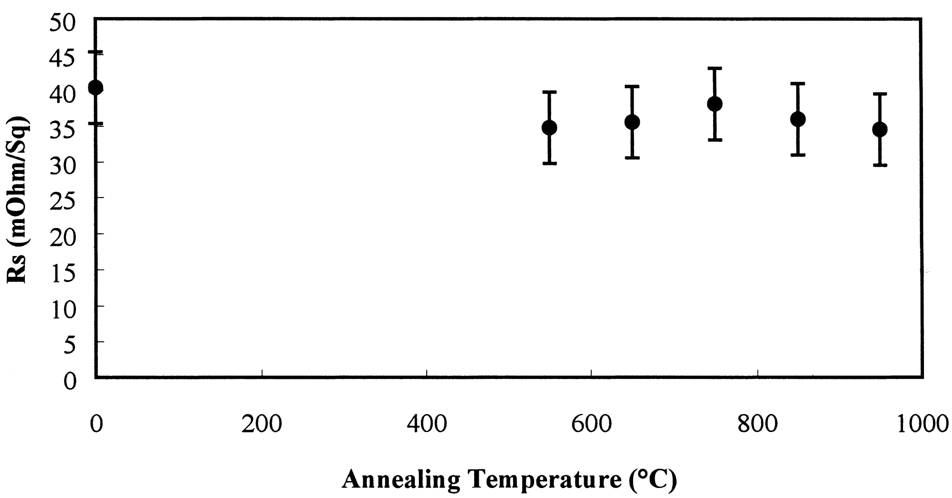

Fig. 1. Variation of sheet resistance in $Cu/Ti_xAl_yN_z/SiO_2/Si$ structure as a function of annealing temperature.

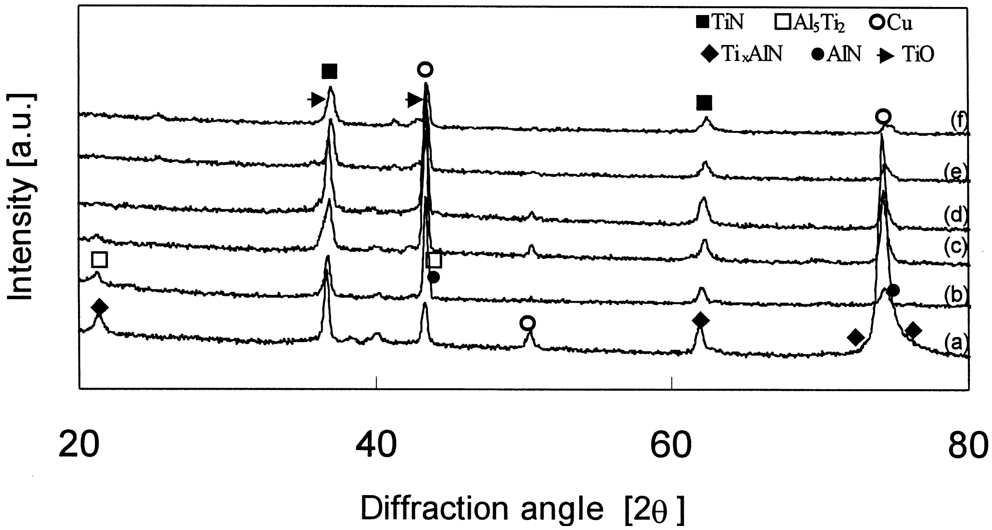

Fig. 2. XRD spectra of the $Cu/Ti_xAl_yN_z/SiO_2/Si$ structure before and after annealing at (a) 550°C, (b) 650°C, (c) 750°C, (d) 850°C, and (e) 950°C.

significantly decreased in intensity. The changes in both the Cu peak intensities may have resulted from a recrystallization process of the Cu layer in a (111) preferred orientation. But no specific TiN orientation change was observed during the Cu recrystallization to the (111) orientation. The formation of the Al_5Ti_2 phase at 21.28° (007) and 43.35° (0014), AlN phases at 43.9° (200) and 76.6° (311) were also observed after 550°C annealing. The Al_5Ti_2 phase actually transformed from Al_3Ti [10]. The titanium oxide (TiO) in XRD spectra began to be detected after annealing at 550°C, and became more prominent at temperatures higher than 550°C. As predicted by Al–Ti–O–N quaternary phase diagram, Figs. 1–4 in Ref. [9] indicate the formation of Ti oxides after annealing at 550°C. It was also reported that TiO compounds are more likely to form at the TiN grain boundaries [11,12]. Our XRD result showed that the TiO peak intensities increased with annealing temperatures. Oxygen for TiO was suspected to come from SiO_2 [12] underneath the layer because it had direct contact with non-oxidized $Ti_xAl_yN_z$. Hamamura et al. reported that oxygen can diffuse more deeply into the Ti layer from SiO_2 as annealing temperature increases [13], followed by the reaction of oxygen with the weakly bonded TiN. Moreover, other compounds such as Al_5Ti_2 and AlN were also formed after annealing at 550°C. TiN and its oxides (Ti_xO_y) that are likely to form at the TiN grain boundaries could react with the incorporated Al and result in the formation of $TiAl_3$, Al_2O_3, and AlN during annealing after 550°C. It is well known that the reaction between Al and Ti films results in the formation of $TiAl_3$ [14] (~450°C) and the transformation to Al_5Ti_2 (after 550°C). Although the AlN phase with small intensities was detected by XRD, it was strongly suggested [12,15] that AlN phase might form at annealing greater than 550°C. The reaction of Al with TiO_x should result in the formation of Al_2O_3, but it was not observed in our XRD spectra. This is due to the chemical reaction that occurred between Al and non-oxidized TiN, in which case only $TiAl_3$ and AlN could be formed [12]. Even after annealing at 1000°C, $Cu/Ti_xAl_yN_z/SiO_2/Si$ structure showed that any reaction product involving Cu, Ti, and Si such as Cu_xSi_y or Cu_xTi_y [16] was not observed in XRD spectra. This is consistent with RBS results at 950°C (see the following text). Therefore, the reactions between Al and TiN formed, as expected, the TiO, AlN, and Al_5Ti_2 phases during thermal annealing. Consequently, the fast pathways for Cu diffusion were effectively blocked by these compounds and the stability of the barrier performance was enhanced up to 1000°C.

Fig. 3 shows the He^+ RBS spectra for $Cu/Ti_xAl_yN_z/SiO_2/Si$ structure as deposited, and after annealing at 950°C for 30 min in N_2 ambient. The surface energy of Cu has been indicated. No difference can be observed between the Cu peaks in the two spectra. The gradient of the tailing of the Cu peak is the same in both spectra, indicating that the $Cu/Ti_xAl_yN_z$ is unaffected by the annealing. However, some change to the tailing has occurred at the $Ti_xAl_yN_z/SiO_2$ interface. Nevertheless, it was reported [17,18] that there was no diffusion and/or reaction (between Ti and Si) at the interface of TiN/SiO_2 in the sputtered deposited $Cu/TiN/SiO_2/Si$ system. From the present results, it can be concluded that there are no solid phase reactions at the interfaces of $Cu/Ti_xAl_yN_z$ and $Ti_xAl_yN_z/SiO_2$.

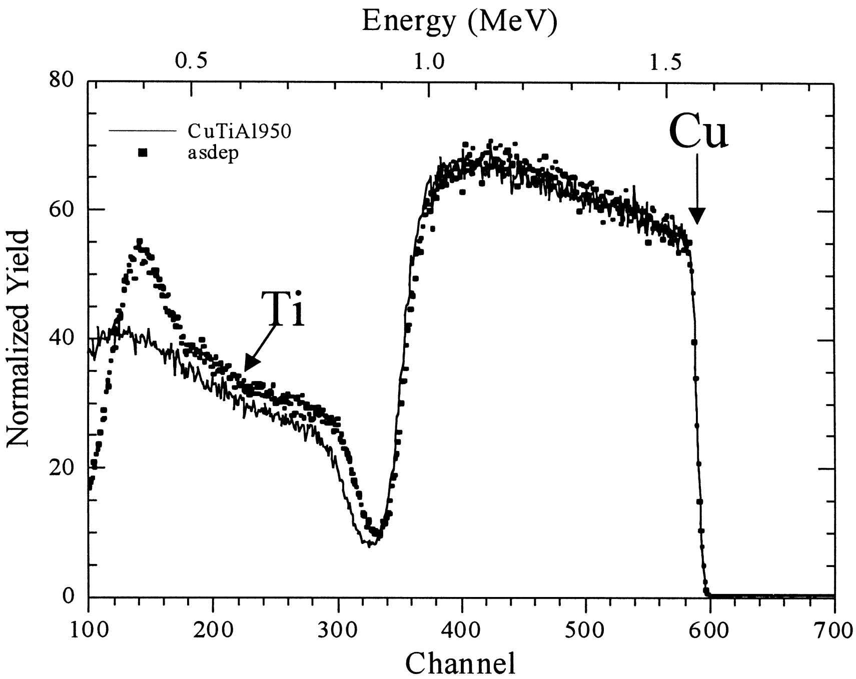

Fig. 3. 2 MeV He^{+} RBS spectra of the $Cu/Ti_xAl_yN_{yz}/SiO_2/Si$ structure before and after annealing at 950°C.

4. Conclusion

The barrier performance and thermal stability of the TiAlN diffusion barrier between Cu and SiO_2 were studied up to 1000°C by using various characterization methods. This structure demonstrates that the formation of TiO, AlN, and Al_5Ti_2 compounds makes up a more efficient and effective way in blocking the diffusion paths for Cu and stabilizes the $Ti_xAl_yN_z$ barrier as stuffing of the grain boundaries is more complete with the formation of these compounds. This, in turn, is believed to be an important factor for retarding Cu diffusion and hence, contributes to the stability of the $Ti_xAl_yN_z$ diffusion barrier up to 1000°C.

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