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Characterization of interfacial reactions between ionized metal plasma deposited Al–0.5 wt.% Cu and Ti on SiO_2

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Abstract

It was reported that the reaction between Al and Ti takes place and Al_3Ti compound is formed during the annealing at 500°C. Annealing at higher temperatures, such as 550 and 600°C, the Al_3Ti compound transforms to Al_5Ti_2. It is believed that the Al_5Ti_2 is thermodynamically stable comparing with Al_3Ti. In the present research, the interfacial reactions in Al–0.5 wt.% Cu/Ti/SiO_2/Si structure have been investigated in the samples prepared by ionized metal plasma (IMP) and then annealed at various temperatures from 200 to 600°C for 30 min in Argon ambient. The results obtained by Rutherford backscattering spectroscopy and transmission electron microscopy show that there is a Ti layer (52 nm in thickness) between Al_5Ti_2 and SiO_2 and there is no formation of the ternary compound — $Al_xTi_ySi_z$, which is detrimental in the contact metallization layer. It indicates that the Ti layer deposited by IMP technique acts as a barrier to retard the reaction between Al_5Ti_2 and SiO_2 and consequentially protect the contact metallization layer.

Keywords: Diffusion barrier; Ionized metal plasma (IMP); Aluminum; Titanium; Interfacial reaction

1. Introduction

Aluminum–Copper (Al–0.5 wt.% Cu) alloy is widely used in Si integrated circuit (IC) interconnect metallization because of its reliability to restrict the electromigration and stress-induced migration [1]. This alloy is preferred material in the microelectronic applications because of its simple processing, low resistivity, and process compatibility. It is believed that the Cu addition in the Al can modify the grain size distribution [2] and suppress the vacancy electromigration at grain boundaries of Al phase [3,4]. A popular explanation of this effect is that Cu coats the Al grain boundaries and inhibits the diffusion and hence the electromigation induced transport of Al atoms along the grain boundaries [5,6].

On the other hand, Ti is currently used as a diffusion barrier/underlayer of Al–0.5 wt.% Cu alloy in applications requiring high temperature processes, such as high temperature sputtering and reflow developed for via-filling [7,8]. The Ti barrier enhances the wettability of Al alloy with underlayer materials, and this enables complete Al filling in via holes with high aspect ratio [9]. In our present work, Ti barrier was deposited by ionized metal plasma (IMP) sputtering as a deposition technique. It will overcome the generic PVD processing limitations such as poor step coverage without losing the excellent metallurgical diffusion barrier properties. In addition to enhancing the step coverage of the metal films, the IMP process also affects film properties such as crystal orientation, roughness and atomic composition of the sputtered Ti film.

In Al–0.5 wt.% Cu/Ti/SiO_2/Si structure, Ti is underneath of the Al alloy layer. Therefore, the reaction between the Al alloy and Ti occurs during Al sputtering or reflow at high temperature. Obviously, the Al alloy/Ti interfacial reaction is important for improving the electrical properties of Al–0.5 wt.% Cu/Ti/SiO_2/Si structure. It was reported that the reaction products between Al and Ti, such as Al_3Ti and Al_5Ti_2, increase the electromigration (EM) resistance as a current bypass [10] when voids are formed in the Al alloy interconnection. In high temperature Al sputtering or reflow, tem-

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perature above 500°C may actually be employed, therefore interfacial reaction studies at above 500°C are essential. In this work, the interfacial reactions in Al–0.5 wt.% $Cu/Ti/SiO_2/Si$ structure annealed at various temperatures have been investigated with Rutherford backscattering spectroscopy (RBS) and transmission electron microscopy (TEM) in detail.

2. Experimental details

The Si substrates were cleaned in a dilute solution of HF in order to remove the native oxide. To fabricate the Al–0.5 wt.% $Cu/Ti/SiO_2/Si$ structure, a 300 nm thick SiO_2 layer was deposited on a Si wafer and then the SiO_2 deposited Si substrate was loaded into the IMP sputtering chamber for the deposition of Ti (100 nm) and subsequently Al alloy (200 nm) without breaking vacuum. The IMP deposition process has been described in detail elsewhere [11]. The samples in this research were annealed from 200 to 600°C for 30 min in Argon 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 analysis (XRD) and RBS were carried out to evaluate the interaction between Al and Ti. XRD measurements were performed with the grazing incident angle (1°) attachment in RIGAKU RINT-2000 diffractometer, using Cu K_α X-ray at 50 kV and 20 mA from 20 to 80° with 0.05° step and 4° min^{-1} scanning rate.

In order to investigate the mechanism of the intermixing formation, X-ray diffraction measurement with different grazing incident angles from $\gamma = 0.5$ to 1.5° was carried on the intermixed sample annealed at 500°C. The penetration depth (t) of X-ray, from the film surface down to the substrate, can be determined by the absorption coefficient μ of the film and grazing incident angle γ [12]. The penetration depth, t can be expressed in

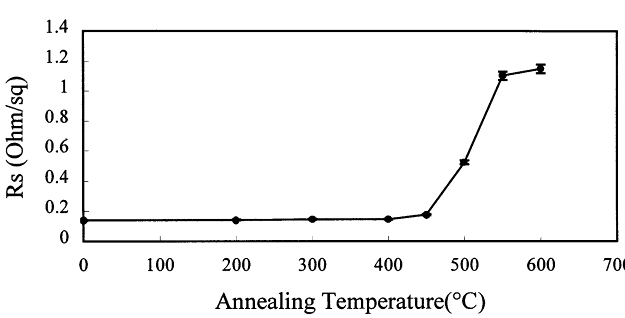

Fig. 1. Variation of the sheet resistance in Al–0.5 wt.% $Cu/Ti/SiO_2/Si$ structure as a function of annealing temperature.

$$t = \frac{\sin \gamma}{\mu}$$

Therefore, the XRD can determine the area in 200 nm thickness of Al alloy layer with 0.5° grazing incident angle, and the determination thickness of XRD can be increased to reach the deeper area, which locates in the Ti layer, with 1 and 1.5° grazing incident angles.

The surface morphology was observed by JEOL 5410 scanning electron microscopy (SEM) and the Al/Ti and Ti/SiO_2 hetero-interfaces were characterized by JEOL 200LX TEM.

3. Result and discussion

Fig. 1 shows that the variation of the sheet resistance as a function of annealing temperature for Al–0.5 wt.% $Cu/Ti/SiO_2/Si$ structure in argon ambient for 30 min. The measured sheet resistance is dominated by Al thin film because Al film (200 nm) is much thicker than the Ti layer (100 nm) while the resistivity of Al (2.65 μΩ cm) is much lower than that of Ti (42.0 μΩ cm) and the other reaction products. It is noted that the measured sheet resistance mainly represents the condition and the quality of Al alloy overlayer since the top Al alloy layer of 200 nm carries nearly all the sensor current. The sheet resistance remained almost constant up to 400°C.

However, the sheet resistance increases slightly after annealing at 450°C and increases abruptly after annealing at 500°C where the interfacial reaction may occurs. Increase in the sheet resistance is due to the combined effects of the positive temperature coefficients of the resistivity in each layer, the interlayer diffusion, and the interfacial reactions that produce the high resistivity new phases.

Fig. 2 shows SEM surface morphologies of the Al–0.5 wt.% $Cu/Ti/SiO_2/Si$ structure before and after annealing. In the sample annealed at 500°C, pinholes were formed (as shown in Fig. 2(b)), while the surface morphologies of the samples, annealed at temperatures below 450°C, are like the morphology of the sample as deposited (Fig. 2(a)). It also implies that the reaction occurs during the annealing at the temperature above 450°C. Annealing the sample at 550°C, the reaction fully takes place and the reaction products distribute in the sample surface uniformly, as shown in Fig. 2(c).

Fig. 3(a) and (b) are the cross-section morphologies of the sample as deposited and the sample annealed at 600°C for 30 min, respectively. From Fig. 3(a), it can be seen that the 300 nm SiO_2 layer, 100 nm Ti layer and 200 nm Al–0.5 wt.% Cu the alloy layer were deposited on Si wafer. The interfaces of Al–0.05 wt.% Cu alloy/Ti and Ti/SiO_2 are “clean” and discrete. It implies that there is no reaction occurring during the IMP deposition processes. After annealing the samples at temperatures over 500°C, the reaction between Al–0.05 wt.%

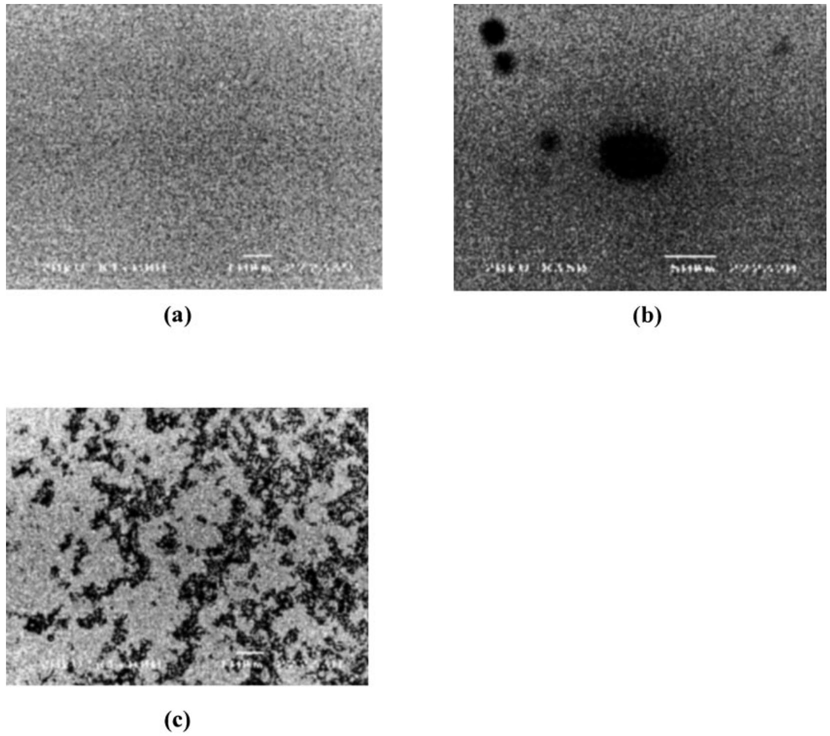

Fig. 2. SEM surface morphologies of the Al–0.5 wt.% Cu/Ti/SiO_2/Si structure (a) as deposited (b) annealed at 500, (c) annealed at 550°C.

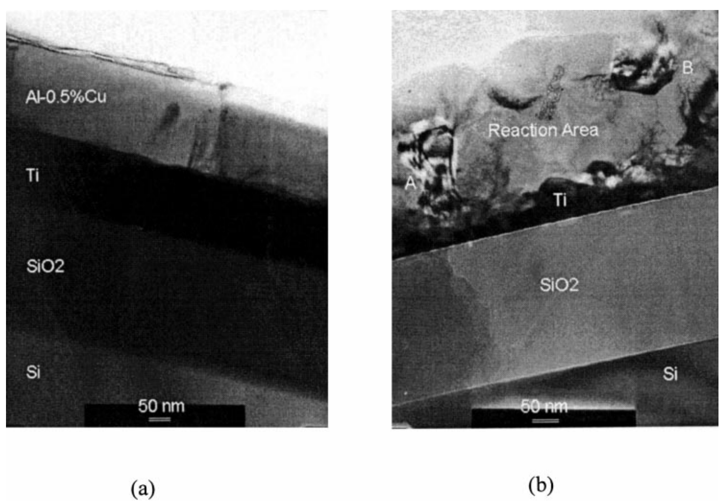

Fig. 3. Cross-section morphologies (TEM) of the Al–0.5 wt.% Cu/Ti/SiO_2/Si structure (a) as deposited, (b) annealed at 600°C.

Cu alloy and Ti took place and formed Al_xTi_y compounds. Fig. 3(b) shows that the interface of Al–0.05 wt.% Cu/Ti disappears but the interface of Ti/SiO_2 remains discrete and “clean” in the sample annealed at 600°C for 30 min. The precipitates can also be observed in the reaction area, as shown in Fig. 5. The unreacted Ti layer between reaction area and SiO_2 acts as the diffusion barrier.

To identify the new phases formed during annealing, XRD and RBS were employed. Fig. 4 shows the XRD spectra of the samples: Fig. 4(a) as deposited, and from Fig. 4(b)–(g) annealed at 300, 400, 450, 500, 550 and 600°C, respectively. In the sample as deposited, the Ti (110) and (103) peaks locate at 62.95 and 70.75°, and the Al (111), (200) and (220) peaks are at 38.50, 44.73 and 65.13° respectively. The small peak intensities at more than two crystallographic orientations were mainly due to rougher surfaces of Al and Ti films [10] deposited by IMP sputtering. However, the intensity of Al peaks decreases with increasing the annealing temperature. Subsequently, the Al peaks disappear completely and the intensity of Ti (110) peak at 62.95° also decreases significantly when the annealing temperature reaches 500°C. Annealing at 500°C, Al_3Ti is formed and the Al_3Ti (112), (103), (200) and (204) peaks are shown at 39.1, 41.95, 47.2 and 65° in the XRD spectra. With annealing above 550°C, the Al_3Ti transforms to

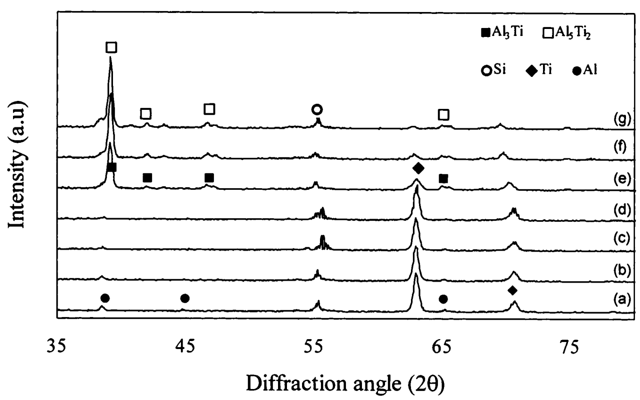

Fig. 4. The XRD spectra of samples (a) as deposited, (b) annealed at 300°C, (c) annealed at 400°C, (d) annealed at 450°C, (e) annealed at 500°C, (f) annealed at 550°C, (g) annealed at 600°C.

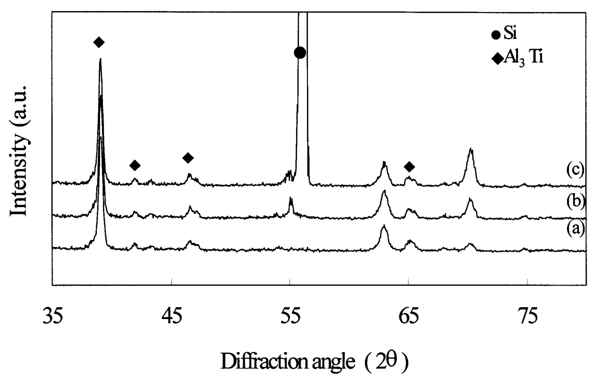

Fig. 5. The XRD spectra of Al–0.5 wt.% $Cu/Ti/SiO_2/Si$ structure annealed at 500°C for 30 min in Ar ambient with different grazing incident angles (a) 0.5°, (b) 1.0° and (c) 1.5°.

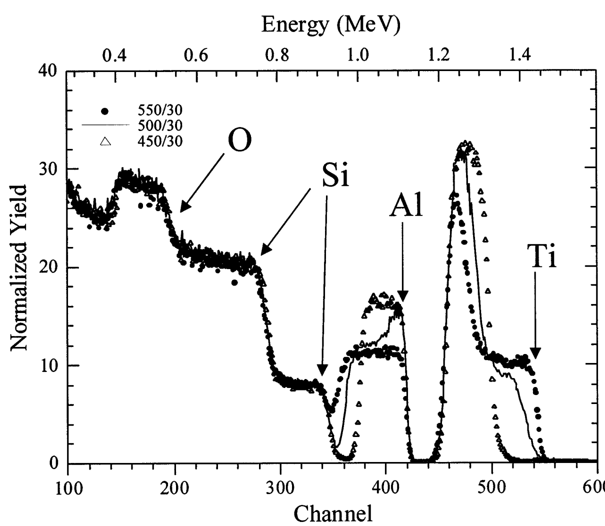

Fig. 6. RBS spectra of Al–0.5 wt.% $Cu/Ti/SiO_2/Si$ structure after annealing at 450, 500 and 550°C for 30 min in Ar ambient.

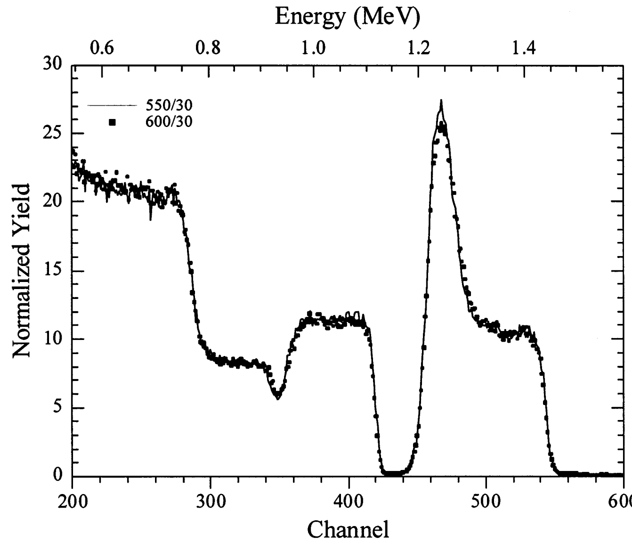

Fig. 7. RBS spectra of Al–0.5 wt.% $Cu/Ti/SiO_2/Si$ structure after annealing at 550 and 600°C for 30 min in Ar ambient.

Al_5Ti_2. It is believed that the Al_3Ti and Al_5Ti_2 phases formation is the cause for the drastic increase in sheet resistance. Because the resistivities of Al_3Ti and Al_5Ti_2 are 15 times greater than that of Al [13]. On the other hand, the intermixing of Al_3Ti and Al_5Ti_2 results in the loss of the conductive Al atoms in the Al alloy layer that can explain the escalation of sheet resistance above 500°C.

Fig. 5 shows the XRD spectra of the sample annealed at 500°C with different grazing incident angles. It can be seen that the intensities of Al_3Ti peaks remain constant at all grazing incident angles. It could be considered that Al_xTi_y was formed uniformly throughout the Al layer.

In the present work, formation of the ternary compounds such as $Al_xTi_ySi_z$ was also monitored for sample annealed above 500°C because it was reported that the ternary compounds such as $Al_xTi_ySi_z$ could be formed from Al_xTi_y and SiO_2 at 500°C and became detrimental to the contact metallization layers [9]. However, in our case, any ternary compounds ($Al_xTi_ySi_z$) was observed in XRD spectra because the unreacted Ti layer between Al_5Ti_2 and SiO_2, which was verified by RBS and will be explained later, might work as a diffusion barrier effectively.

RBS spectra were taken with 2 MeV He^+ ions at a scattering angle of 160° using a 50 mm^2 passivated implanted planar silicon (PIPS) detector of 14 keV resolution. The purpose was to evaluate the interaction between the Al and Ti layers. Figs. 6 and 7 show the RBS spectra for the Al–0.5 wt.% $Cu/Ti/SiO_2/Si$ structure after 450, 500, 550 and 600°C annealing. The surface scattering energies of Al and Ti have been indicated. The Si and O signals are also marked in Fig. 6. At 450°C, the RBS spectra show a sharp layer structure. At 500°C, the shape of the Ti and Al peaks begin to change. The Ti peak moves to higher energies and tailing of the Al is observed. This is indicative that intermixing/reaction of Al and Ti has started. At 550°C annealing, interdiffusion between Al and Ti proceeds and Ti is now present on the surface. The Ti peak exhibits a high energy "shelf" with a flat top. The Al peak has also broadened into a lower but wider shape, again with a flat top. This is strong indication that a new Al_xTi_y compound has been formed. No significant changes were observed between the samples annealed at 550 and 600°C (Fig. 7).

The unreacted Ti thickness was 52 nm as determined from the RBS spectrum. This unreacted Ti layer separates the Al_5Ti_2 compound and SiO_2 layer so that the reaction between these two is not detected. The properties of the Al_5Ti_2 compound are not yet clear. It can also be seen from the spectra that there is no change to the O signal from the SiO_2 layer after the 550°C anneal. This indicates that O has not moved out of the SiO_2 layer.

4. Conclusion

The interfacial reactions in Al–0.5 wt.% Cu/Ti/SiO_2/Si structure annealed at various temperatures have been investigated in detail. The results show that no reaction occurs in the samples annealed below 450°C and the 100 nm thick IMP–Ti was found to be stable up to 450°C. Annealing the samples at temperatures above 500°C, the reaction between Al alloy and Ti takes place and forms Al_3Ti. At the higher annealing temperature, Al_3Ti transforms to the thermodynamic stable phase — Al_5Ti_2. However, there is a layer of unreacted Ti in 52 nm thickness between Al_5Ti_2 and SiO_2. This layer can effectively retard the reaction between these two compounds to form the ternary compound ($Al_xTi_ySi_z$), which is detrimental to the contact metallization layers.

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