Study of interfacial reactions in ionized metal plasma (IMP) deposited Al-0.5%wt Cu/Ti/SiO_2/Si structure

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Interfacial reactions in Al-0.5%wtCu/Ti/SiO_2/Si structure have been investigated up to the annealing temperature of 600°C for 30 min in Argon ambient. Annealing temperature at above 500°C, Al alloy and Ti start to react and produce Al_3Ti, which was already reported. Annealing at higher temperatures (550°C, and 600°C) made Al_3Ti transformed into Al_5Ti_2, which is thermodynamically more stable than Al_3Ti. The unreacted 52 nm thick Ti which existed underneath of Al_5Ti_2 might lead to retardation of the reaction between Al_5Ti_2 and the underlying SiO_2. Hence, the formation of ternary compound ($Al_xTi_ySi_z$) which is believed to be detrimental to the contact metallization layers was protected.

1. Introduction

Aluminum (Al) interconnections alloyed with a few percent of copper (Cu) have been widely used in Si integrated circuit (IC) interconnect metallization for their high reliability against electromigration and stress-induced migration [1]. The ease of processing, low resistivity, and process compatibility of this metal make it difficult to find better alternatives. There have been several hypotheses on the mechanism of Cu adding effect, such as the modification of grain size distribution, [2] and the suppression of vacancy electromigration at grain boundaries [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].

Ti has been used as a diffusion barrier/underlayer of Al alloy in its applications to 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 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 our Al-0.5%wt Cu/Ti/SiO_2/Si structure Ti is in direct contact with the overlaying Al alloy layer and reactions could occur during high temperature Al sputtering or reflow. Here, Al alloy/Ti interfacial reaction plays an important role. It was reported that the reaction products Al_3Ti and Al_5Ti_2 improve the electromigation (EM) resistance as a current bypass [10] when voids are formed in an Al alloy interconnection. In high temperature Al sputtering or reflow, temperature 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%wtCu/Ti/SiO_2/Si structure above 500°C has been investigated.

2. Experimental details

The Si substrates were cleaned in a dilute solution of HF to remove native oxide. For Al-0.5%wt Cu/Ti/SiO_2/Si structure, a 300 nm thick SiO_2 layer was deposited on Si wafer and then SiO_2/Si substrate were loaded into the IMP sputtering chamber for deposition of Ti (100 nm) and subsequently Al alloy (200 nm) without breaking the vacuum. The IMP deposition process has been described in detail elsewhere [11]. The samples were then annealed in a temperature range from 200 to 600°C for 30 min in Argon ambient. The sample sheet resistance was measured by the four-point

probe method to survey the overall reaction. The reaction products were identified by X-ray diffraction analysis (XRD). Surface morphology was examined by Scanning Electron Microscope (SEM). Rutherford Back Scattering Spectroscopy (RBS) measurements were carried out to evaluate the interaction between Al and Ti.

3. Result and discussion

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 is shown in Fig. 1. The measured sheet resistance is dominated by Al thin film since Al film (200 nm and 2.65 $\mu\Omega$ cm) is much thicker and has a much lower resistivity than Ti (100 nm and 42.0 $\mu\Omega$ cm) and any 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.

The sheet resistance increases slightly after annealing at 450°C and increases abruptly after annealing at 500°C where the interfacial reaction seems to proceed. Increase in sheet resistance is due to the combined effects of the positive temperature coefficients of resistivity of each of the layers, interlayer diffusion, and interfacial reactions resulting in the creation of new phases with higher resistivity.

To identify new phases formed during annealing, XRD was performed for Al-0.5%wtCu/Ti/SiO_2/Si structure. The XRD measurements were performed with a RIGAKU model RINT2000 diffractometer using a $\gamma = 1^\circ$ grazing incident angle geometry. The K_α Cu X-ray ($\lambda = 1.542$ A) detection was done from $2\theta = 20^\circ$ to $2\theta = 80^\circ$ with scan speed of 4°/min and scan step 0.05°. The grazing incident angle of 1° identified the intermixing and new phases formation for the structure Al-0.5%wtCu/Ti/SiO_2/Si annealed up to 600 °C. Fig. 2 shows the XRD spectra of the sample (a) as deposited, and (b) to (g) are annealed at 300 to 600°C respectively. The main observed peaks are for Ti at 62.95° (110) and 70.75° (103) and Al at 38.50° (111), 44.73° (200) and 65.13° (220) for as deposited sample. The small peak intensities at more than two crystallographic orientations were mainly due to rougher surfaces of Al and Ti films [12] deposited by IMP sputtering. All Al peaks gradually decreased and disappeared completely as the annealing temperature increased. The major change in the XRD spectra occurred after the 500°C annealing.

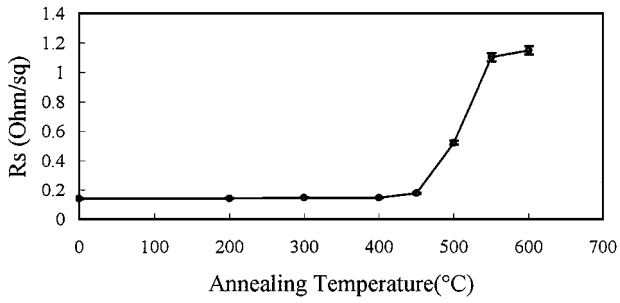


Figure 1 Variation of sheet resistance in Al-0.5%wtCu/Ti/SiO_2/Si structure as a function of annealing temperature.

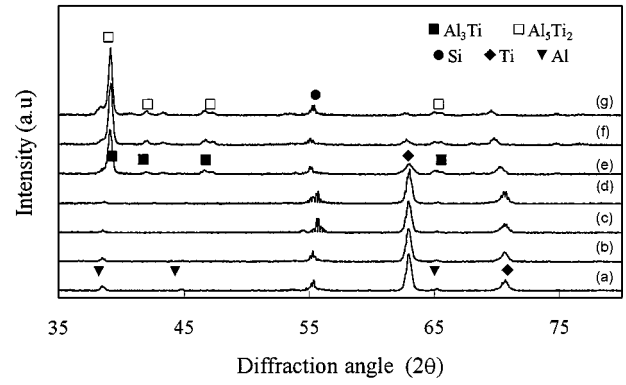


Figure 2 The XRD spectra from Al- 0.5%wtCu/Ti/SiO_2/Si structure before (a) and after annealing at (b) 300 °C, (c) 400 °C, (d) 450 °C, (e) 500 °C, (f) 550 °C, (g) 600 °C for 30 min in Ar ambient.

New peaks at 2θ angles 39.1°, 41.95°, 47.2° and 65° have appeared which are mainly due to the formation of Al_3Ti (112), (103), (200) and (204) respectively. A significant decrease in the 2θ angle 62.95° Ti peak intensity is observed after 500°C annealing. These changes are caused by a complete intermixing of Al and Ti which could lead to the formation of Al_3Ti compound and the reaction progressed drastically at 550°C, followed by the rapid increase in sheet resistance as shown in Fig. 1. With annealing 550°C and above, the new Al rich compound namely Al_5Ti_2 turns up and becomes dominant over Al_3Ti. It results in the loss of conductive Al atoms in the Al alloy layer, and since Al_3Ti and Al_5Ti_2 have the resistivity 15 times greater than Al [13] that can explain the escalation of sheet resistance at 550°C.

In order to examine the mechanism in which the intermixing occurs, X-ray diffraction measurements with different grazing incident angles from $\gamma = 0.5^\circ$ to 1.5° were performed on the intermixed sample (annealed at 500 °C). The penetration depth (t) of X-ray, perpendicular to the film surface, can be determined by the absorption coefficient μ of the film and grazing incident angle γ [14]. The penetration depth, t is;

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

The XRD represents the whole thickness of the Al Alloy film in the case of $\gamma = 0.5^\circ$, and $t > 200$ nm in the

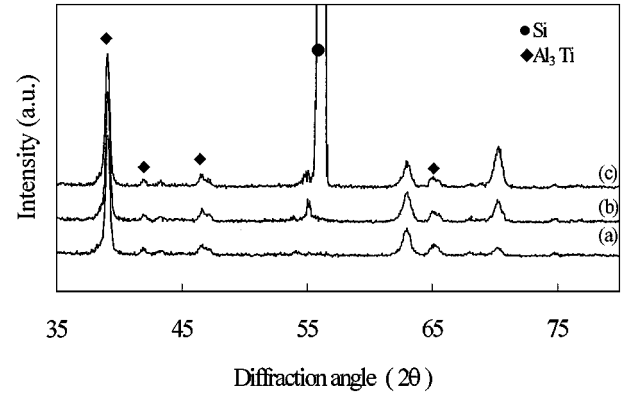


Figure 3 The XRD spectra from Al-0.5%wtCu/Ti/SiO_2/Si structure annealed at 500°C for 30 min in Ar ambient with different grazing incident angles (a) 0.5°, (b) 1.0° and (c) 1.5°.

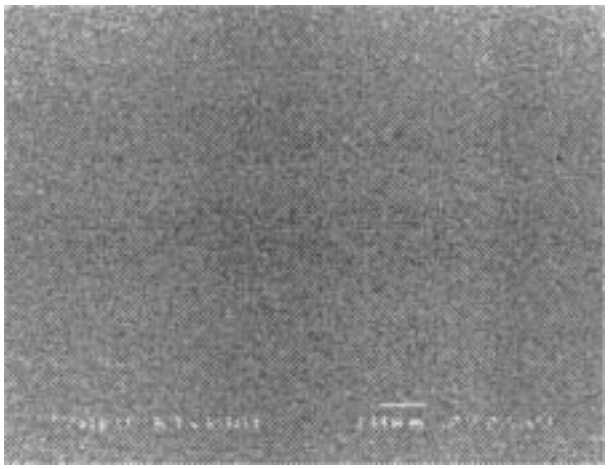
case of $\gamma = 1^\circ$ and 1.5°. With more than 0.5° incident angles, the contribution comes not only from the whole layer of 200 nm Al alloy film but also from the interface and underneath layer. As shown in Fig. 3, the peak intensities of Al_3Ti remain more or less constant at all grazing incident angles. It can be concluded that Al_xTi_y was uniformly formed through out Al layer.

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 explained later, might work as a diffusion barrier effectively.

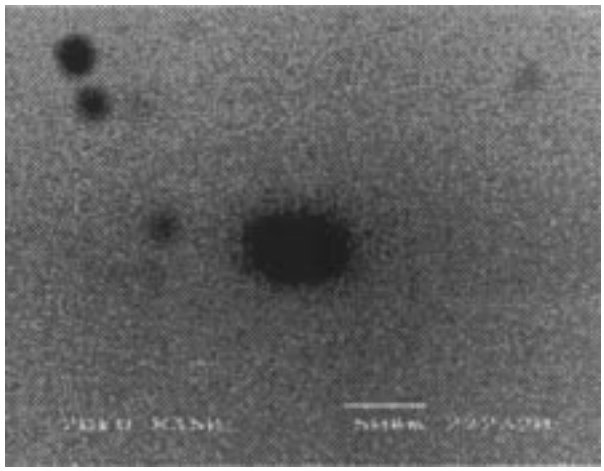
The surface morphology examined by SEM micrograph of the Al-0.5%wtCu/Ti/SiO_2/Si structure before and after annealing was shown in Fig. 4. Any noticeable change can not be observed until it is annealed at the temperatures lower than 450°C and pinholes were observed thereafter. Increasing the annealing temperature to 550°C results in the surface shown in Fig. 4c. The dark areas in the image are thought to be Al_xTi_y compound. Apparently, the reaction has proceeded sufficiently for Ti to consume the Al film all the way to the surface. This is consistent with RBS results at 550°C (see the following text).

Rutherford Back Scattering (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 5 and 6 show the RBS spectra for the Al-0.5%wt Cu/Ti/SiO_2/Si structure after 450°C, 500°C, 550°C 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. 5. At 450°C, the RBS spectra shows 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.

The unreacted Ti thickness was 52 nm as determined from the RBS spectrum. This unreacted Ti layer



(a)



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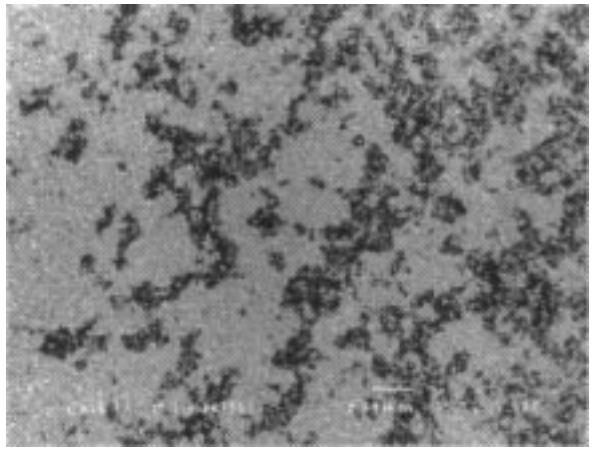

(c)

Figure 4 The SEM images of Al-0.5%wtCu/Ti/SiO_2/Si structure before (a) and after annealing at (b) 500 °C, (c) 550 °C for 30 min in Ar ambient.

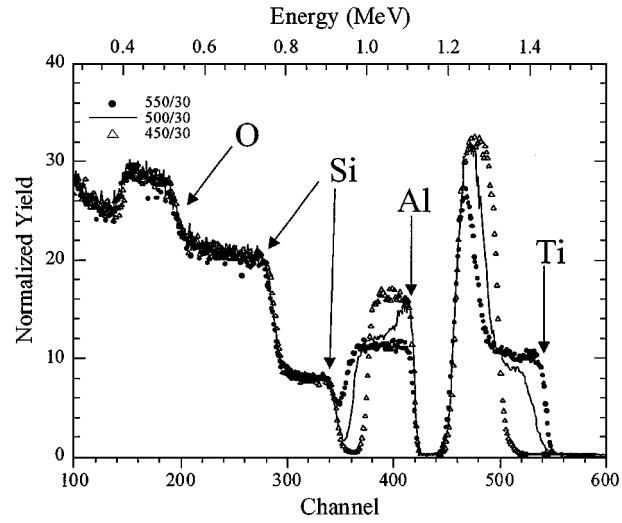

Figure 5 RBS spectra of Al-0.5%wt Cu/Ti/SiO_2/Si structure after annealing at 450°C, 500 °C and 550 °C for 30 min in Ar ambient.

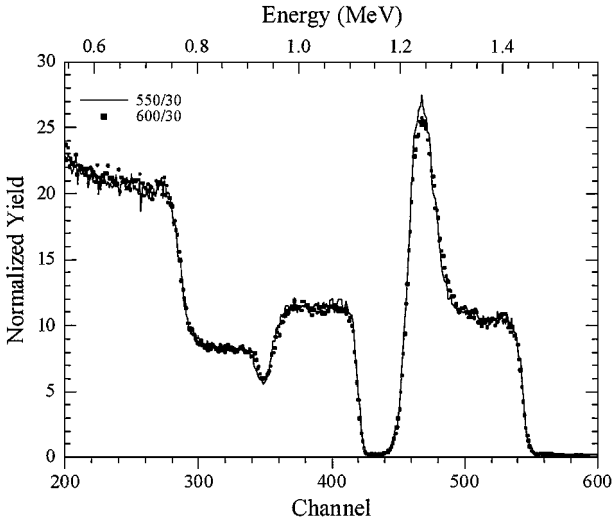

Figure 6 RBS spectra of Al-0.5%wt Cu/Ti/SiO_2/Si structure after annealing at 550 °C and 600 °C for 30 min in Ar ambient.

separates the compound Al_5Ti_2 and SiO_2 layer so that the reaction between these two is not observed. The properties of the compound Al_5Ti_2 are not yet clear. It can 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 annealed Al-0.5%wt Cu /Ti/SiO_2/Si structure have been investigated up to 600°C. The 100 nm thick IMP-Ti was found to be stable up to 450 °C. Annealing temperature at above 500°C, Al alloy and Ti start to react and produce Al_3Ti In this structure, the Al_3Ti compound easily transformed to a new, Al rich compound, Al_5Ti_2 at annealing temperature higher than 500°C. The 52 nm thick unreacted Ti layer between Al_5Ti_2 and SiO_2 can effectively retard the reaction between these two layers. Therefore, the formation of ternary compound ($Al_xTi_ySi_z$) which can become a junction spiking and is believed to be detrimental to the contact metallization layers was protected.

Acknowledgments

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