Formation of Copper Interconnects by Reflow of Sputtered Copper Films

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Formation of Cu interconnects using conventional sputtering and reflow processes has been developed for the first time. On W, Mo and TiN underlayers, Cu film easily agglomerates because of its low wettability. On the other hand, on TiW and Ta underlayers, Cu film does not agglomerate. These results reflect the filling characteristics. The employment of underlying materials such as W, Mo and TiN is necessary to achieve Cu filling in trenches at a reflow temperature of less than 500 °C. By combining CMP process, Cu interconnects down to 0.6 μ m wide were successfully formed in reflowed samples.

I. INTRODUCTION

In the trend of ever increasing packing density of VLSI's, Al interconnects have become more critical in terms of electromigraiton (EM) performance and stressinduced migration. Some refractory metal lines are considered to be candidates for future devices. Copper (Cu) interconnects that has advantages of low resistivity and high resistance to EM¹⁾ is one of these candidates to achieve high speed and high reliable devices. The formation of Cu interconnects using reactive ion etching (RIE) is, however, difficult because of low vapor pressure of Cu halides that are produced during etching process, and the substrate heating higher than 220 °C during etching is necessary to volatilize Cu chloride²⁾³⁾. In recent years, Damascene process using Chemical Mechanical Polishing (CMP) has been developed for etching free pattern formation to avoid this problem⁴⁾⁻⁶⁾. CVD Cu films are generally used in Damascene process because excellent step coverage is necessary for the process⁷). Cu CVD is, however, not a mature process for ULSI fabrication compared with Cu sputtering.

In this work, we have tried Cu filling using conventional sputtering and reflow processes, and it is shown for the first time that the sputtered Cu film can be filled in the trenches at a reflow temperature of less than 500 °C.

II. EXPERIMENTAL

600 nm thick CVD SiO₂ films were grown on 6-inch silicon wafers, and Cu/Ta, Cu/TiW, Cu/W, Cu/Mo and Cu/TiN structures on SiO₂ films were prepared using DC magnetron sputtering. Cu deposition was carried out after the underlying refractory films were deposited and exposed to air. Thickness of the Cu film and the underlying films such as TiW, Ta, W, Mo and TiN is 15-100 nm and 100 nm, respectively. After Cu deposition, the samples were annealed successively in a same vacuum at 450 °C for 30 min. The base pressure in an annealing chamber was 8×10^{-7} Torr. After annealing, agglomeration properties of the Cu films were evaluated by optical microscope. Furthermore, the interfacial reactions between the Cu and the underlying metals were evaluated by Rutherford backscattering spectrometry (RBS), and Cu crystallization was measured by X-ray diffraction (XRD). The shape of the Cu heaps was observed by cross-sectional secondary electron microscopy (SEM).

In other samples, trenches were formed in 1000 nm thick CVD SiO₂ layer on Si substrates by RIE. The depth and the width of a trench were 0.5 μ m and 0.6 μ m, respectively. Cu/Ta, Cu/TiW, Cu/W, Cu/Mo and Cu/TiN structures on trench-patterned SiO₂ samples were fabricated as the same manner described above. After breaking a vacuum, Cu films of 700 nm thickness were deposited on the various metals of 100 nm thickness. The samples were then in-situ annealed at 450 °C for 30 min in the vacuum. For Cu filled trench-patterned samples, CMP was carried out. The Cu and the underlying metals were polished away from the top of SiO₂ surface, forming interconnects inlaid into the trenches. The Cu filling and buried Cu interconnects were observed by cross-sectional SEM.

III. RESULTS AND DISCUSSION

It is well known that Cu films agglomerate in high temperature annealing, although agglomeration properties of Cu films are not clear. The effect of the underlying materials on Cu agglomeration was evaluated. Figure 1 shows optical photographs of Cu film(100 nm) on various metal films after annealing at 450 °C for 30 min. On Ta and TiW films, the surface of Cu film is smooth. On the other hand, on W, Mo and TiN films, holes are formed in Cu film. The hole formation in Cu films is considered to be one process of agglomeration caused by Cu atom mobility. Therefore, it appears that Cu atoms move easily on W, Mo and TiN films compared with TiW and Ta films.

On a basis of above results, Cu filling characteristics in trenches were examined. Figure 2 shows cross-sectional SEM photographs of Cu stacked structures after annealing at 450 °C for 30 min. In Cu/Ta and Cu/TiW layered structures, the step coverage of Cu films do not change before and after annealing. In the Cu/W, Cu/Mo and Cu/TiN layered structures, however, the trenches are completely filled with Cu, and Cu is perfectly planarized. These results indicate that the Cu filling has a close relation to Cu agglomeration. For the realization of the Cu filling, the underlying material on which Cu easily agglomerates is necessary.

In order to understand the phenomenon of the Cu agglomeration, Cu/W and Cu/Ta structures are especially used in the following experiments as two extremes. In both structures, there is a great difference in Cu agglomeration as shown in Fig.1. It is considered that the interfacial reaction, the crystalline connection and the wettability between Cu and the underlying materials would have effects on Cu agglomeration. M.Hansen and K.Anderko⁸⁾ reported that Cu-W and Cu-Ta systems form immiscible mixtures. However, the reaction of these systems is not clear in thin film. Figure 3 shows RBS spectra for (a) Cu(300 nm)/W structure and (b) Cu(300 nm)/Ta structure before and after in-situ annealing of 500 °C for 30 min. The samples deposited Cu film of 300 nm thick were used for RBS, since Cu film having 300 nm thick did not agglomerate on W and Ta underlayers after annealing. In the both Cu/W and Cu/ Ta structures, the backscattering spectra before and after annealing do not change. From these results, it is clarified that Cu does not react with W or Ta at all. Next, the effect of the underlayer on Cu orientation was evaluated by XRD. If crystal continuity between Cu and the underlying metals suppresses the movement of Cu atoms, Cu agglomeration would be suppressed. Figure 4 shows XRD patterns from Cu/W and Cu/Ta structures. In both structures, Cu films preferentially orient (111) direction which is the most stable for face-centered cubic (fcc) metals, and the intensity of Cu (111) peak decreases compared to SiO₂ underlayer due to the crystallographic effect from the underlayer. However, Cu (111) peak height is almost same on Cu/W and Cu/Ta structures. So, it is considered that the difference of Cu agglomeration is not caused by the crystalline effect. The wettability between Cu and underlying metals was observed by SEM. Copper film thickness of 15 nm was deposited on W and Ta underlayers because noticeable difference of Cu agglomeration occurs. Figure 5 shows that SEM photographs of Cu surface morphology on W and Ta underlayers after in-situ annealing at 450 °C for 30 min. After annealing, Cu film agglomerates in hemisphere shape on W underlayer. On the other hand, Cu film does not agglomerate on Ta underlayer and only some cavities are seen. It seems that these phenomenon can be elucidated by wettability because the interfacial reaction, the crystalline connection between Cu and the underlying materials do not have relation to Cu agglomeration. The wettability of Cu film is low on W underlayer compared with Ta underlayer. In classical theory, the wettability of the liquid on the solid is commonly expressed by Young's equation as illustrated Fig.6;

$\cos\theta = (\sigma_s - \sigma_{sl})/\sigma_l$

where σ_s and σ_l are surface energy of solid and surface energy of liquid, σ_{sl} is interfacial energy between solid and liquid, and θ is contact angle. Table1 shows the surface energy of various materials such as W,Ta and Cu⁹. The surface energy of W and Ta is 2400 ergs/cm² and 2150 ergs/cm², respectively. The value of the surface energy in both materials is close. From these results and Young's equation, $\cos\theta$ is determined by σ_{sl} . Therefore, it is considered that the surface state on W or Ta underlayer has effect on the mobility of Cu atoms, and Cu agglomeration is distinct due to the difference of the surface state. Further evaluation is now under investigation.

In final, Cu interconnects was fabricated by CMP. The polishing rate of Cu and W is 100 and 200 nm/min. Figure 7 shows the cross-sectional SEM photographs of Cu/W layered structure after CMP process. Cu interconnects down to 0.6 μ m wide with dishing and recess-free were successfully formed by combining conventional sputtering, reflow and CMP processes.

IV. CONCLUSION

The trench filling using reflow of sputtered Cu films was realized for the first time. On W, Mo and TiN underlayers, Cu film easily agglomerates because of its low wettability. On the other hand, on TiW and Ta underlayers, Cu film does not agglomerate. These results reflect the filling characteristics. In the Cu/W, Cu/Mo and Cu/TiN layered structures, the trenches are completely filled with Cu, and Cu is perfectly planarized. The proper choice of underlayer metals was found to be essential to achieve low temperature reflow of Cu films and void-free Cu filling. By combining CMP process, Cu interconnects down to 0.6 μ m wide were successfully formed in reflowed samples.

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Cu(100 nm)/W(100 nm) Cu(100 nm)/Mo(100 nm) Cu(100 nm)/TiN(100 nm)





Cu(100 nm)/TiW(100 nm) Cu(100 nm)/Ta(100 nm)

Fig.1 Optical photographs of Cu film (100 nm) on various metal films after annealing at 450 °C for 30 min.







1µm

400

500

10µm

Cu(700 nm)/W(100 nm) Cu(700 nm)/Mo(100 nm) Cu(700 nm)/TiN(100 nm)





Cu(700 nm)/TiW(100 nm) Cu(700 nm)/Ta(100 nm)

Fig.2 Cross-sectional SEM photographs of Cu stacked structures after annealing at 450 °C for 30 min.



Fig.3 RBS spectra for (a) Cu(300 nm)/W structure and (b) Cu(300 nm)/Ta structure before and after annealing at 500 °C for 30 min.



Fig.4 XRD patterns from (a) Cu/W structure and (b) Cu/Ta structure after annealing at 450°C for 30min.





Cu(15 nm)/W(100 nm)

Cu(15 nm)/Ta(100 nm)

0.5µm

Fig.5 SEM photographs of Cu surface morphology on W and Ta underlayers.



Os surface energy of solid

Osl interfacial energy between solid and liquid

σ1 surface energy of liquid

θ contact angle

Fig.6 Schematic diagram of Young's equation model.

Table 1 The surface energy of various materials.

Metal	Surface Energy (ergs/cm2)	
AI	866	
Cu	1300	
W	2400	
Мо	2250	
Та	2150	
SiO ₂	663	



