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Study of electroplated copper thin film and its interfacial reactions in the EPCu/IMPCu/IMPTaN/SiO_2/Si multilayer structure

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Rather than depositing a blanket layer of Al and patterning by reactive ion etching (RIE), Cu interconnects are being formed by deposition into prepatterned (damascene) trenches and vias, followed by chemical mechanical polishing (CMP). In a significant departure from the trend towards dry processing, electroplating is emerging as the methods of choice for the Cu deposition [1]. This choice is based on a combination of factors including the ability to fill dual damascene architectures without voids and lower cost as compared to other techniques such as physical vapor deposition (PVD) and chemical vapor deposition (CVD) [2]. Another important reason for the selection of electroplating is the large grained microstructure that can be obtained to further improve the electromigration resistance. In addition to grain size, another important influence on electromigration resistance may be the crystallographic texture of the Cu. The crystallographic orientations of PVD diffusion barrier and Cu seed layer have also been shown to influence the texture of the EP-Cu [3, 4]. In our present work, a TaN diffusion barrier and a seed Cu layer were deposited by ionized metal plasma (IMP) sputtering as a deposition technique. The IMP process can affect film properties such as crystal orientation, roughness and atomic composition of the EP-Cu film.

On the other hand, integration of electroplating into the manufacturing of advanced microelectronic devices will require an additional low temperature anneal step to guarantee a stable microstructure of the EP-Cu [5]. In this letter, we present an analysis of the evolution of the crystallographic texture, grain growth and intermixing/reactions of the blanket EP-Cu film before and after annealing up to 950 °C in the EPCu (1 μm)/IMPCu (150 nm)/IMPTaN (25 nm)/SiO_2 (500 nm)/Si multilayer structure.

Si wafers were cleaned in 10 : 1 diluted HF solution and rinsed in deionized water before SiO_2 deposition. First, a 500 nm thick plasma enhanced chemical vapor deposited (PECVD) SiO_2 film was deposited on 6″ Si wafers. Tantalum nitride (TaN) films of 25 nm thickness were deposited onto PECVD-SiO_2/Si substrates by using IMP sputtering in a gas mixture of Ar and N_2. Without breaking the vacuum, a 150 nm Cu seed layer was then deposited. It is important to know the microstructure of the Cu-seed layer and diffusion barrier because they play an important role on the texture of the plated films. Surface roughness and morphology of the IMP deposited TaN barrier layer and seed Cu were characterized using atomic force microscopy (AFM). The AFM results show that the IMP-TaN diffusion barrier was an amorphous phase (Fig. 1) with the roughness (RMS) of ∼0.369 nm and the seed IMP-Cu layer has a grain size about 30 nm and the roughness (RMS) of ∼1.4 nm (Fig. 2). This IMP-Cu layer acts as the anode in the electrochemical deposition of the Cu layer of 1.0 μm thickness. Electroplated Cu was deposited using a commercially available Cu plating bath with Cu sulfate/sulfuric acid plating chemistry and a pulse waveform with a current of 5 A cycled at 95 ms on/35 ms off. As a result, when the grain size of the seed layer was smaller, a larger number of nucleation

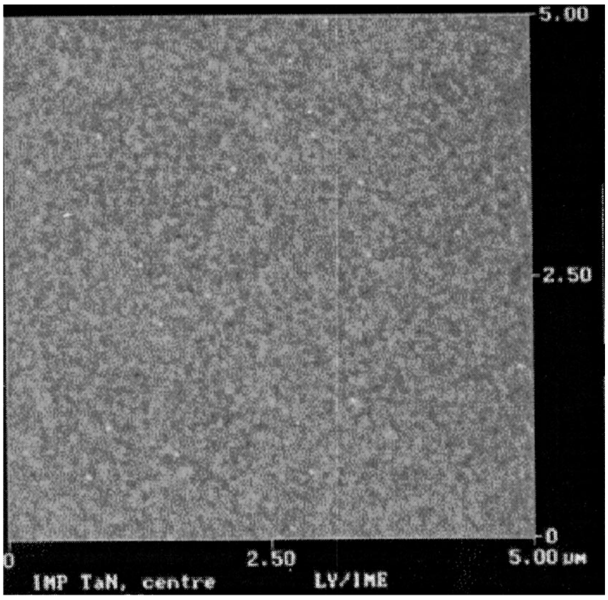

Figure 1 AFM measurement results for IMP-TaN diffusion barrier (Amorphous). Roughness (RMS) = 0.369 nm.

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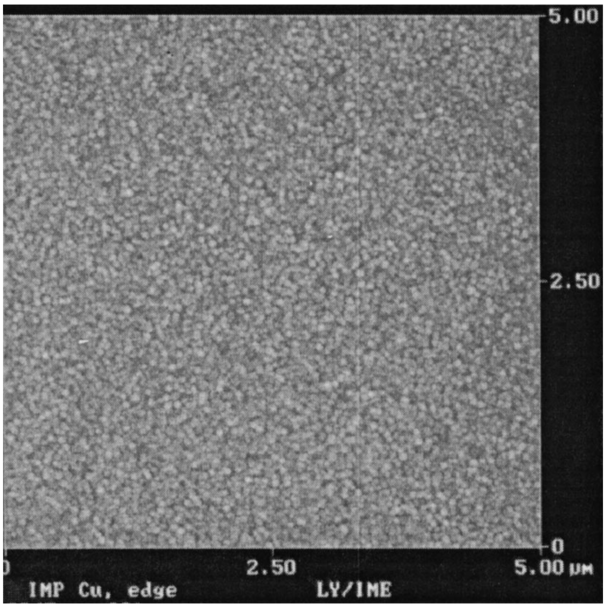


Figure 2 AFM measurement results for IMP-Cu seed layer. Grain size = 30 nm. Roughness (RMS) = 1.4 nm.

sites occurred due to the presence of more surface irregularities, giving rise to the electroplating of small Cu grains that coalesced after completion of electroplating and produced larger grains as shown in Fig. 5a.

The samples were then annealed for 35 min in a nitrogen ambient up to 950 °C from 350 °C with 100 °C intervals. The sheet resistance for the as-deposited and annealed samples was measured by four-point probe to survey the overall reaction involving Cu. X-ray diffraction analysis (XRD) was used for the analysis of the reaction product phases and the interdiffusion of the elements across the interface.

Fig. 3 shows the sheet resistance of the EPCu/IMPCu/IMPTaN/SiO_2/Si structure as a function of annealing temperature in N_2 ambient for 35 min. The measured sheet resistance was dominated by the EP-Cu thin film since the copper film (1.0 μm and 1.72 $\mu\Omega$ cm) is much thicker and has a markedly lower resistivity than that of TaN film (25 nm and 265 $\mu\Omega$ cm) and any reaction products. Since the top EP-Cu layer of 1.0 μm thickness carries nearly all the sensor current, the sheet resistance measurements monitor the condition and the quality of the EP-Cu overlayer. The sheet resistance gradually increases with increasing annealing temperature up to 750 °C. However, after annealing at 750 °C, the sheet resistance of the sample undergoes an abrupt rise (~200%).

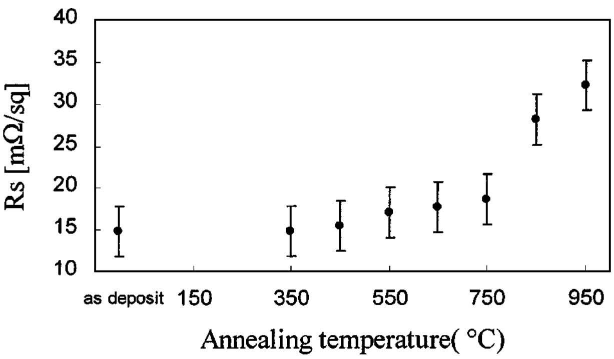


Figure 3 Variation of sheet resistance in EPCu/IMPCu/IMPTaN/SiO_2/Si structure as a function of annealing temperature.

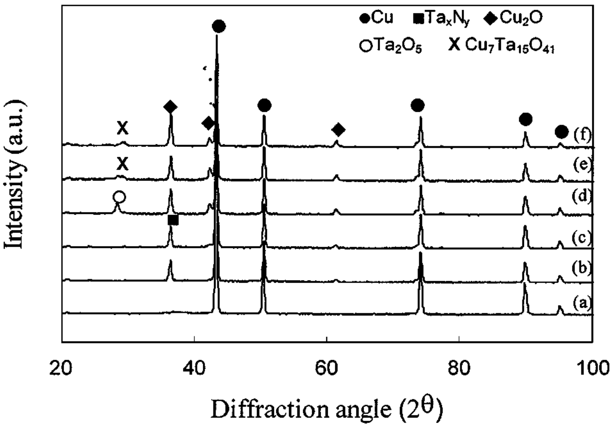
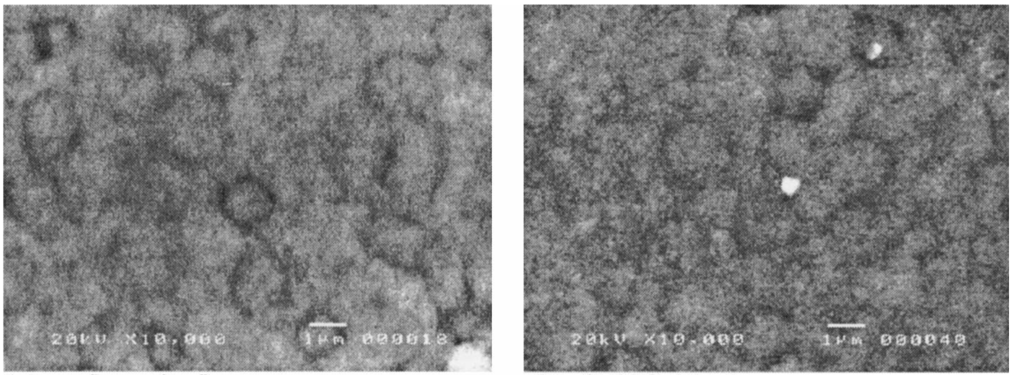


Figure 4 The XRD spectra from EPCu/IMPCu/IMPTaN/SiO_2/Si structure before (a) and after annealing at (b) 550 °C, (c) 650 °C, (d) 750 °C, (e) 850 °C, (f) 950 °C, for 35 min in N_2 ambient.

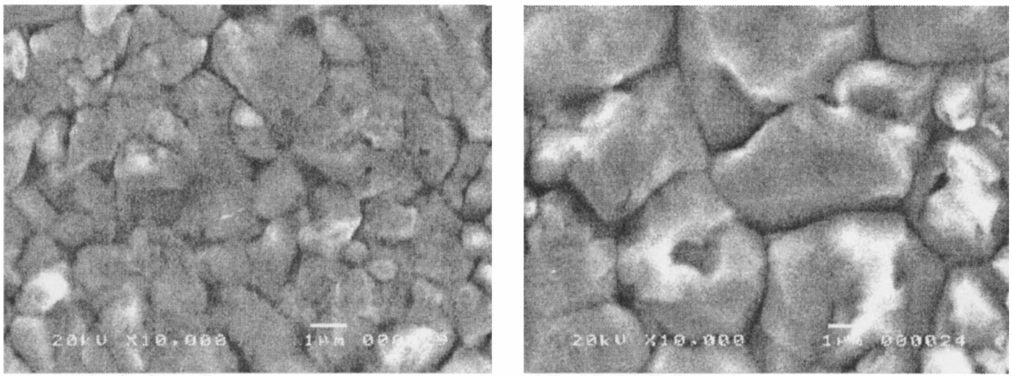
To identify the new phases formed during the annealing, XRD was carried out to evaluate the interaction between layers. The blanket EP-Cu film deposited on IMP-Cu seed layer has a predominantly (111) texture at a 2θ angle of 43.0 ° while the IMP-Cu film deposited on a typical barrier IMP-TaN has a strong (220) at 74.05° [6] as shown in Fig. 4. Other small Cu peaks (200), (311), (222) and (400) were also observed at 50.45°, 89.9°, 95.05° and 116.8° respectively. Only a broad peak of TaN appeared at 36° indicating that IMP-TaN is an amorphous phase. But after annealing at 550 °C a-TaN became crystalline Ta_xN_y.

As shown in Fig. 4, there is a distinction in the XRD spectra between samples annealed below and above 750 °C. At all annealing temperatures below 750 °C, Ta_xN_y peak and Cu peaks were observed. Distinctly, at 750 °C, several new peaks were found at 28.35°, 36.35°, 42.36° and 61.30°. They were identified as Ta_2O_5 (001), Cu_2O (111), (200), and (220) respectively. Cu_2O (111) appeared very close to the peak of Ta_xN_y. Probably, the formation of Cu_2O is the main cause for the jump in sheet resistance value after the 750 °C annealing as shown in Fig. 3. We also reported the oxygen and carbon concentration and the depth profile in IMP-TaN and IMP-Cu, being examined by SIMS analysis and the formation of Ta_2O_5 and Cu_2O [6].

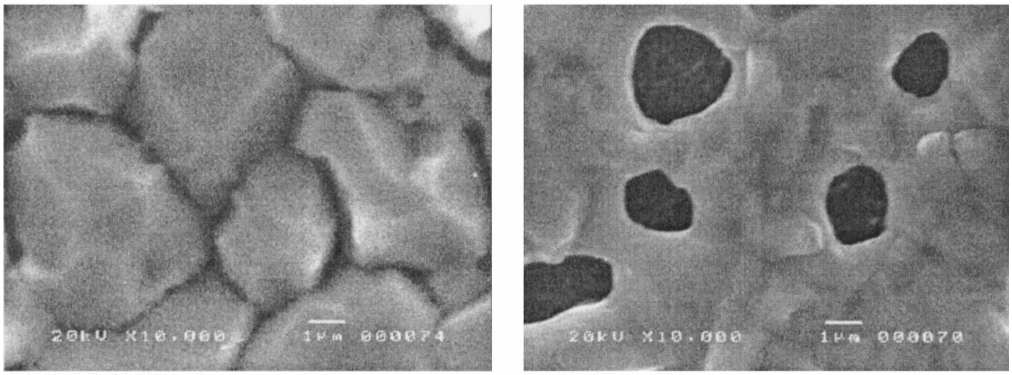
The intensity of the EP-Cu (111) and Cu (200) peaks were slightly reduced due to the formation of Cu_2O. Annealing at temperatures higher than 750 °C makes seed Cu and weakly bonded TaN start to react with the O_2 existing in the grain boundaries of Cu as well as TaN resulting in the formation of Cu_2O and Ta_2O_5. By annealing at 850 °C, a new peak of $Cu_7Ta_{15}O_{41}$ appeared at 28.35°, probably due to the reaction among Cu_2O, Ta_2O_5, Ta and Cu at the interface of Cu/TaN [7]. As a result, a slightly reduced intensity of Cu (220) and Ta_xN_y peaks was also observed due to the formation of Cu_2O, Ta_2O_5, and $Cu_7Ta_{15}O_{41}$. The peak of a new compound was observed very close to the tantalum oxide (Ta_2O_5) peaks. Although an interfacial reaction and the formation of Cu_2O, Ta_2O_5 occurred in our structure, no evidence of diffusion of Cu through the barrier



(a) as deposited **(b) 350°C-35min**



(c) 650°C-35min **(d) 750°C-35min**



(e) 850°C-35min **(f) 950°C-35min**

Figure 5 The SEM images of 1 μm thick EP-Cu surfaces annealed at various temperatures in N_2 ambient for 35 min.

was detected even after annealing at 950 °C for 35 min. Fig. 5 shows the surface morphologies of the EP-Cu film annealed at various temperatures in a N_2 ambient for 35 min. The grain size of an as-deposited EP-Cu was about 1 μm and it grew as annealing temperature increased. The average grain size after annealing at 750 and 850 °C was 5 times larger than the film thickness as shown in Fig. 5d and e. At annealing temperatures higher than 850 °C, the Cu film starts to agglomerate due to the accelerated grain growth in EP-Cu film. At 950 °C, Cu grains agglomerated with each other disclosing the underneath seed Cu and/or TaN to the ambient.

Besides grain boundary energy reduction, surface energy and strain energy reductions are the driving forces for grains growth in thin film [8, 9]. Due to the thin oxide (copper oxides) formed on EP-Cu surfaces, the surface energy of Cu grains or the stress of the film will change, and these variations may cause the accelerated grain growth. It was reported that normal grain growth occurs until the nominal grain size of the film becomes 2–5 times larger than the film thickness, while abnormal grain growth gives a preferential growth of some grains [10, 11]. Zielinski *et al.* reported that if the surface energy and stress variation were significantly different with different orientations of grains, some specially oriented grains would grow abnormally to reduce the total system energy. Conversely, if the surface energy and stress variation are uniform with the orientation of the grains, abnormal grain growth will not be observed. In our present work, no evidence of abnormal grain growth in the Cu film was observed during thermal annealing. As shown in Fig. 4, a (111) preferred orientation was maintained throughout the annealing process, and no abnormal grains were observed in the SEM images. These facts reveal that normal grain growth occurs in EP-Cu during the annealing process. On the other hand, the uniform variation of surface energy in the thin film is not likely [12]. Since the volume of grain boundaries reduces during the grain growth, tensile stress is produced in film. As a consequence, only a compressive stress condition can be relaxed by grain growth [12, 13]. Halliday *et al*. also reported that the oxidation of Cu increased the compressive stress in the film due to the formation of a superficial oxide layer [14]. This suggests the fact that compressive stress induced from the oxidation of Cu becomes the driving forces for the normal grain growth of the EP-Cu thin film. However, all the above results, an increase in sheet resistance by four points probe, the formation of Cu_2O by XRD, and the accelerated grain growth observed by SEM agree well and simultaneously occur at around 750 °C.

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