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

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Electroplated Cu film on a thin seed layer of IMP deposited Cu has been investigated in the EPCu (1 μm)/IMPCu (150 nm)/TaN (25 nm)/SiO_2 (500 nm)/Si multi-layer structure. The characteristics of Electroplated-Cu films before and after annealing were investigated by means of sheet resistance, X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), and Rutherford Backscattering Spectroscopy (RBS). Annealing at temperatures of higher than 750°C resulted in slightly higher sheet resistance, larger grain sizes and rougher surface. SEM micrograph showed that the agglomeration of EP-Cu film occurred only at annealing temperatures higher than 850°C. During annealing, the EP-Cu grain grew normally and their sizes increased to about five times larger than the thickness of the EP-Cu film but the (111) preferred orientation was maintained up to 950°C. Furthermore, the interfacial reactions between Cu layer and IMP-TaN diffusion barrier were also detected at annealing temperatures of higher than 750°C.

1. Introduction

The rapidly accelerating interest in Copper to replace Aluminium and its alloy for advanced interconnects in multilevel integrated circuits is being driven by the lower resistivity and improved electromigration resistance of the Cu. 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 vapour deposition (PVD) and chemical vapour 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. Whereas the texture of Al interconnects has been shown to influence electromigration resistance, [3, 4] the limited data on the relationship between texture and electromigration performance of electroplated damascene Cu are less clear [5–7]. The crystallographic orientations of PVD diffusion barrier and Cu seed layer have also been shown to influence the texture of the EP-Cu [8, 9]. In our present work, TaN diffusion barrier and seed Cu layer were 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 EP-Cu film. Integration of electroplating into manufacturing of advanced microelectronic devices will require an additional low temperature anneal step to guarantee a stable microstructure of the EP-Cu [10]. In this report, we present an analysis of the evolution of the crystallographic texture, grain growth, intermixing and/or 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.

2. Experimental details

For all sample preparation and experiments described in this study used 6″ Si (100) wafers. 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 dielectric was deposited on 6″ Si wafers. Tantalum nitride (TaN) films of 25 nm thickness, which act as a diffusion barrier and adhesion layer for the highly conductive Cu atoms, were deposited onto PECVD-SiO_2 (500 nm)/Si substrates by using ionized metal plasma (IMP) sputtering of a Ta target in a gas mixture of Ar and N_2. Without breaking the vacuum, a 150 nm Cu seed layer was then deposited by IMP sputtering. Detailed IMP deposition process has been described elsewhere [11]. This IMP-Cu layer acts as the anode in the electrochemical deposition of the Cu layer of 1.0 μm thickness. During this process the wafer was submerged in a commercially available copper platting bath. The bath is sulfate based ($CuSO_4$ is one of the constituents), but also contains some proprietary organic additives, designed to improve the filling of deep trenches with Cu during the electroplating process. At four points on the edge of the wafer an electrical connection was made to the Cu seed layer. The applied potential between the Cu seed layer and a Cu cathode then results in a flux of Cu atoms to the wafer surface. Deposition was done at 35°C through a pulse waveform with a current of 5 A cycled at 90 ms on/ 40 ms off. The samples were then annealed for 35 min in nitrogen ambient up to 950°C from 350°C with 100°C interval. The sheet resistance for as-deposited and annealed samples was measured by four-point probe to survey the overall reaction involving Cu. XRD was used for the analysis of reaction product phases and the interdiffusion of the elements across the interfaces.

3. Results and discussion

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. Hence, surface roughness and morphology of the IMP deposited TaN barrier layer and seed were characterized using AFM. Fig. 1 shows the AFM image of the diffusion barrier TaN deposited by IMP method. IMP-TaN on PECVD SiO_2 grow as an amorphous phase, with the roughness of ~0.369 nm. Consequently, seed IMP-Cu is composed of more compact grains with grain sizes of around 30 nm and with surface roughness (RMS) of ~1.4 nm (Fig. 2). The SEM observation results [Fig. 5a] show that the average EP-Cu grains after self-annealing were around 1.0 μm and much lager than IMP-Cu seed materials grains, indicating the growth of the EP-Cu grains strongly depends on the grain size of the seed materials. This result suggests that the Cu ions attached themselves at certain preferred sites, forming bonds with the cathode surface, were partially neutralized. These adions diffused rapidly on to various surface absorption sites such as kinks, edges and steps, [12] where they were incorporated into the lattice of the seed layer. As a result, when the grain size of the seed layer was smaller, more number of nucleation 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.

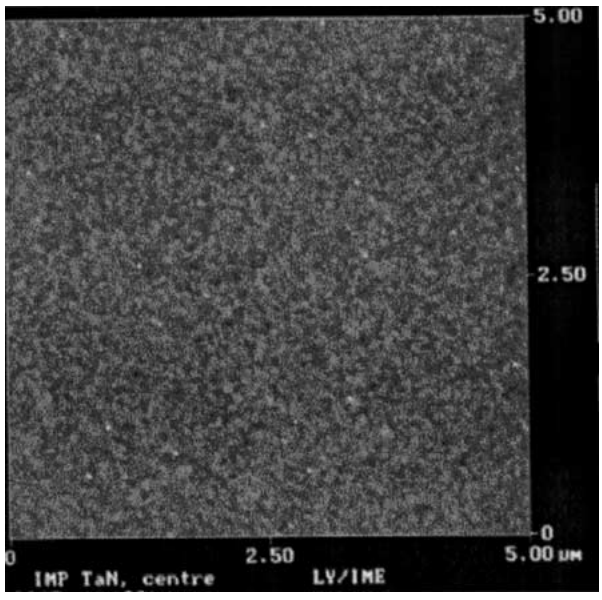

Figure 1 AFM measurement result for IMP-TaN diffusion barrier (Amorphous).

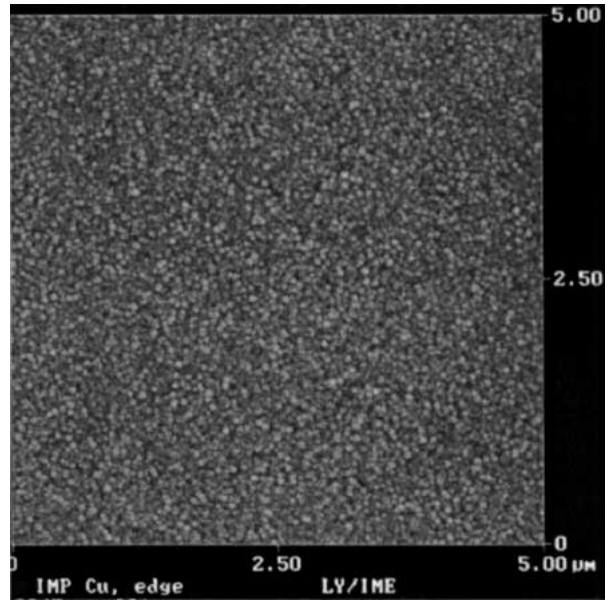

Figure 2 AFM measurement result for IMP-Cu seed layer.

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

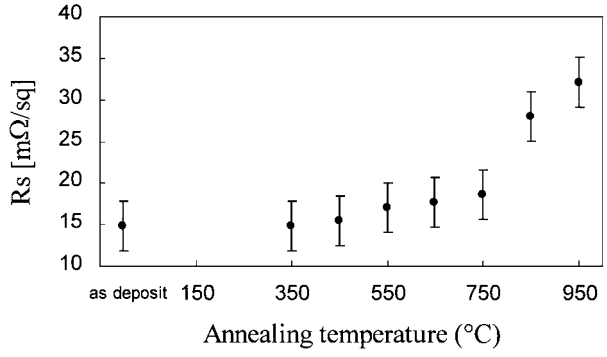

Figure 3 Variation of sheet resistance in EPCu/IMPCu/IMPTaN/SiO_2/Si structure as a function of annealing temperatures.

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 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%). To identify the new phases formed during the annealing, X-ray diffraction analysis (XRD) was carried out to evaluate the interaction between layers. XRD measurements were performed with the grazing incident angle (5°) attachment in RIGAKU RINT-2000 diffractometer, using Cu K_α X-ray at 50 KV and 20 mA from 10° to 120° with 0.05° step and 1°/min scanning rate.

The blanket EP-Cu film deposited on IMP-Cu seed layer has a predominantly (111) texture at 2θ angle of 43.0° while IMP-Cu film deposited on typical barrier IMP-TaN has a strong (220) at 74.05° [13] 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° indicates IMP-TaN is an amorphous phase (see AFM result in Fig. 1). But after annealing at 550°C a-TaN became crystalline Ta_xN_y.

As shown in Fig. 4, there is a distinction in XRD spectra between samples annealed below and above 750°C. 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 and Ta_2O_5 are the main cause for the jump in sheet resistance value after 750°C annealing as shown in Fig. 3. Here, three sources of oxygen atoms forming Cu_2O and Ta_2O_5 will be considered. Firstly, oxygen atoms from the SiO_2, which would diffuse into and/or react with the TaN layer, as the annealing temperature increased since Lance *et al*. reported the possible reactions between SiO_2 and TaN and the formation of

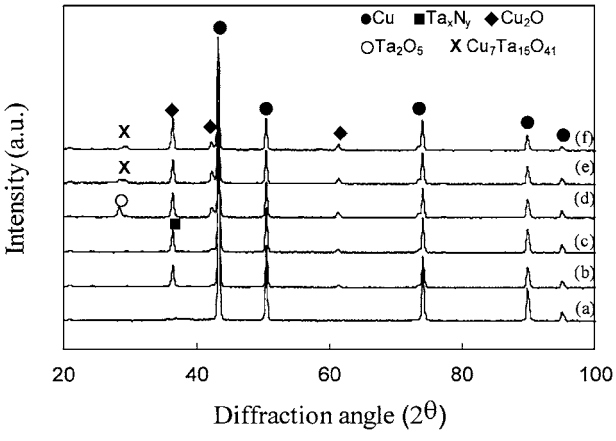

Figure 4 The XRD spectra from EPCu/IMPCu/IMPTaN/SiO_2/Si structure before (a) and after annealing at (b) 550°C, (c) 650°C, (d) 750°C, (e) 850°C, (f) 950°C for 30 min in N_2 ambient.

Ta_2O_5 [14]. The second source is oxygen atoms incorporated with Cu and Ta metal film from the deposition ambient during the Cu and Ta deposition and decorating the grain boundaries of each film [15]. 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 Cu_2O and Ta_2O_5 [13]. Lastly, oxygen atoms incorporated from annealing ambient, but were excluded because all the samples were annealed in an "inert" nitrogen atmosphere. However, the formation of Cu_2O and/or Ta_2O_5 cannot be fully prevented. This reveals the fact that formation of Cu oxide and Ta oxide in the structure is mainly due to the oxygen incorporated during the deposition process and form SiO_2. The intensity of 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 Ta_xN_y start to react with the O_2 existing in the grain boundaries of Cu as well as TaN resulted 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 [16]. As a result, a slightly reduced in 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 tantalum oxide peaks (Ta_2O_5). 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 was detected even after annealing at 950°C for 35 min.

Fig. 5 shows the surface morphologies of EP-Cu film annealed at various temperatures in N_2 ambient for 35 min. The grain size of an as deposited EP-Cu was about 1.0 μm and it grew as annealing temperature increased. Average grain size after annealing at 750 and 850°C was 5 times larger than the film thickness as shown in Fig. 5f and g. Annealing temperatures higher than 850°C, Cu film starts to agglomerate due to the accelerated grain growth in EP-Cu film. At 950°C, Cu grains agglomerated each other disclosing the underneath seed Cu and/or TaN to the ambient.

Besides grains boundary energy reduction, surface energy and strain energy reductions are the driving forces for grains growth in thin films [17, 18]. 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 [19, 20]. Zielinski *et al*. reported that if 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 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 Cu film was observed during thermal annealing. As shown in Fig. 4, a (111) preferred orientation

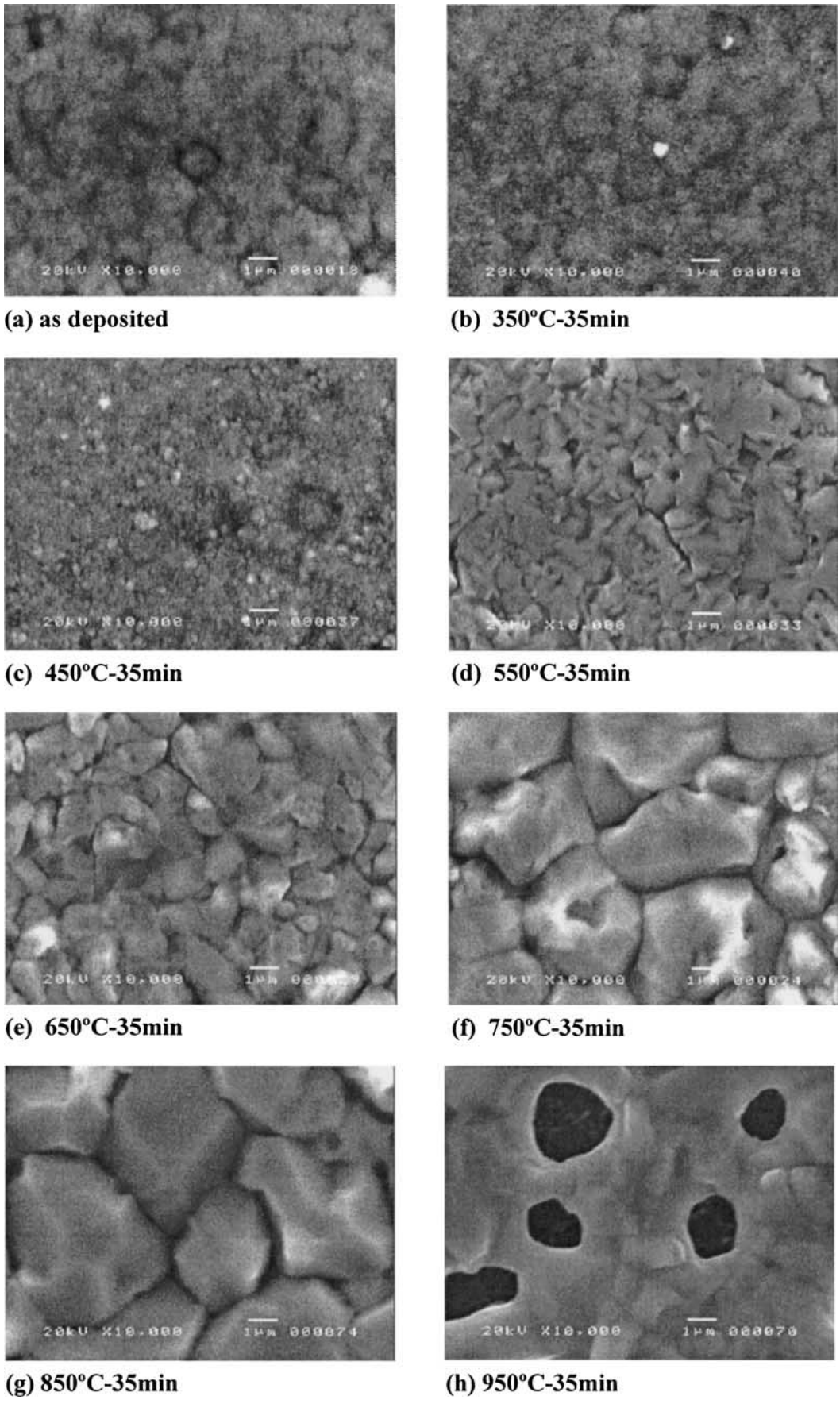

Figure 5 The SEM images of 1.0 μm thick EP-Cu surfaces annealed at various temperatures in N_2 ambient for 35 min.

was maintained through out the annealing process, and no abnormal grains were observed in SEM images. These facts reveal that normal grain growth occurs in this EP-Cu during the annealing process. On the other hand, it is not likely that the uniform variation of surface energy with grain orientation induces the grain growth in thin films [21]. 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

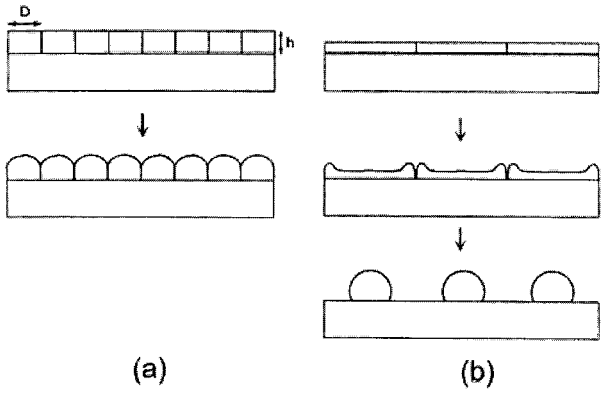

Figure 6 Relation between thin film stability and h/D ratio.

[21, 22]. 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 [23]. This suggests the fact that compressive stress induced from the oxidation of Cu becomes the driving forces for the normal grain growth of EP-Cu thin film.

In contrast, the ratio of the film thickness (h) to the grain size (D) is the important factor in determining the possibility of agglomeration [24]. If h/D ratio is large (Fig. 6a), the free surface will become a circular cap before the thermal groove reaches the underlayer so that the continuity of the film is maintained. However, if h/D ratio is small (Fig. 6b), the thermal groove will be able to reach the under layer, which will result in the agglomeration of the film [25]. Therefore, in the two films with the same thickness and different grain sizes, the film with larger grains agglomerates to become a discontinuous morphology during thermal annealing. 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 occurs at around 750°C.

Fig. 7 shows the RBS spectra for EPCu/IMPCu/IMPTaN/SiO_2/Si multilayer structure at various temperatures. A 2 MeV H^+ beam was used with normal sample incidence and 160° scattering angle using a 50 mm^2 Passivated Implanted Planar Silicon (PIPS) detector of 14 KeV resolution and proton beam backscattering was employed to determine depth profiles of the samples. The surface scattering energies for O, Si, Cu and Ta are indicated. The Ta layer appears to remain largely intact up to 650°C. At higher temperatures, the back edge of the Cu signal is increasingly graded and a small amount of Ta appears at the Ta surface energy. It is likely that Cu film starts to agglomerate at higher temperatures, thus exposing part of the Ta film to the ambient. The Oxygen peak clearly visible on top of the slowly varying Si signal also remains unchanged until 650°C, at higher temperatures it broadens, also indicating mixing of the different layers. The N concentration is too low to be detected using proton beam backscattering.

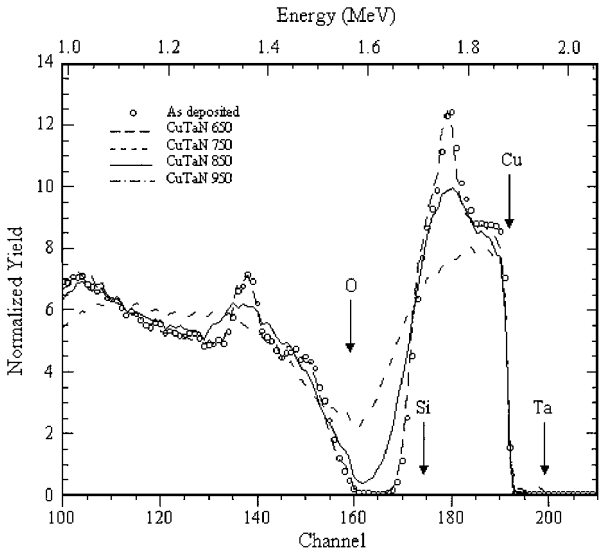

Figure 7 RBS spectra from EP-Cu/TaN/SiO_2/Si structure before and after annealing at 650°C, 750°C, 850°C, and 950°C for 30 min in N_2 ambient.

According to RBS and SEM results, Ta has reached and accumulated on the Cu surface since Ta had migrated to the Cu surface, giving a peak in RBS signal at the surface energy expected for Ta. The out diffusion of the Ta that accumulates on the surface has been reported earlier [26, 27]. However, in our structure the as deposited TaN diffusion barrier is an amorphous phase. It is though that, the a-TaN then transits from amorphous phase to a mixture of TaN and Ta_2N up on thermal annealing (does not alter the resistivity of the film). But Ta_2N is unstable and dissociates into body center cubic (α-phase) Ta and a Ta_2N phase [28]. That α-Ta atoms are the main agents, which out diffused to the Cu layer and on the way to the Cu surface it were reacted with the oxygen resided in the grain boundaries of Cu film, Cu atoms and/or Cu_2O and formed Ta_xO_y and $Cu_xTa_yO_z$. By compare to Ta, Cu that has larger grain size, in other words, the widely open grain structure will serve the fast diffusion paths for Ta (grain size 10–20 nm) to migrate to the Cu surface.

4. Conclusion

The growth morphology of EP-Cu film on IMP-Cu seed layer was found to be more uniform and gave lower RMS values, resulting in a lower resistivity of EP-Cu film. Up on post annealing at higher than 750°C in N_2 ambient, the normal grain growth and agglomeration of EP-Cu started to occur simultaneously which was attributed to stress produced during the oxidation of Cu. Furthermore, the interfacial reactions between Cu layer and IMP-TaN diffusion barrier were also detected at annealing temperatures of higher than 750°C. However, a strong (111) preferred orientation of EP-Cu was maintained through out the annealing process.

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