JOURNAL OF MATERIALS SCIENCE 36 (2001) 5705–5712

Comparative study of copper films prepared by ionized metal plasma sputtering and chemical vapor deposition in the Cu/TaN/SiO_2/Si multilayer structure

KHIN MAUNG LATT*
Materials Engineering, School of Applied Science, Nanyang Technological University, Nanyang Avenue, Singapore 639798
E-mail: p101282@ntu.edu.sg

C. SHER-YI, T. OSIPOWICZ
Department of Physics, National University of Singapore, Lower Kent Ridge Road, Singapore 119260

K. LEE
Institute of Microelectronics, 11 Science Park Road, Singapore Science Park II, Singapore 117685

Y. K. LEE
Materials Engineering, School of Applied Science, Nanyang Technological University, Nanyang Avenue, Singapore 639798

This work investigated the properties of ionized metal plasma (IMP) deposited copper (Cu) and chemical vapor deposited (CVD) Cu on IMP-TaN (tantalum nitride) diffusion barrier in the Cu(200 nm)/TaN(30 nm)/SiO_2(250 nm)/Si multi-layer structure. The IMP-Cu film deposited on IMP-TaN had a preferred orientation (220) with a grain size of around 30 nm and roughness (RMS) of ~1.391 nm, while the CVD-Cu had a (111) preferred orientation with a grain size around 170 nm and roughness (RMS) of ~15.416 nm as determined by atomic force microscopy (AFM) and x-ray diffraction (XRD) analyses. Thermal stability study of the structures was also performed by sheet resistance measurements, scanning electron microscopy (SEM), XRD and Rutherford backscattering spectroscopy (RBS). These results revealed that IMP-Cu on IMP-TaN has higher thermal stability, less intermixing and/or agglomeration than CVD-Cu on IMP-TaN at the same annealing temperatures. The higher thermal stability of IMP-Cu than CVD-Cu can be accounted by their difference in microstructure. The failure mechanisms of IMP-Cu and CVD-Cu in multiplayer structure were also discussed.

1. Introduction

Copper has drawn attention as a new interconnect material for deep sub-micron circuits due to the low resistivity and high electromigration and stress migration resistance superior to the Al and its alloy based interconnecting metal [1, 2]. However, in order to successfully integrate Cu metallization into ICs, some problems such as an anisotropic etching, oxidation, corrosion, diffusion and adhesion to interlayer dielectric must be solved [3]. Among these Cu associated problems, particularly, Cu diffusion into dielectric and subsequently into silicon regions underneath is fatal because it can deteriorate the device operation [4, 5]. Clearly, a critical issue in the realization of structurally stable copper-based metallization architectures is the development of an appropriate diffusion barrier which prevent undesirable interactions between Cu and the semiconductor and dielectric regions of the computer chip. Tantalum and its nitrides are considered the most promising candidates because of they are highly refractory materials that are stable to extremely high temperatures. Additionally, they are known to be thermodynamically stable with respect to Cu, as documented by the absence of Cu-Ta or Cu-N compounds [6].

On the other hand, conventional forms of physical vapour deposition (PVD) of Cu including collimated sputtering are inherently incapable of conformal step coverage in aggressive trench and via structures, given their "line of sight" type approach. Alternative processing techniques are thus required for producing

*Author to whom all correspondence should be addressed.

Cu metallization for incorporation in subquarter micron device technologies. In this respect, ionized metal plasma (IMP) and chemical vapour deposition (CVD) are the most promising techniques.

However, it has not been demonstrated yet on the effect of Cu deposition method (IMP and CVD) on the thermal stability of IMP-TaN diffusion barrier. Hence, in our present work, we focus on the effect of the type of Cu (deposited by IMP or CVD) on the thermal stability of IMP-TaN diffusion barrier. The test sample structures are IMP-Cu(200 nm)/IMP-TaN(30 nm)/SiO_2(250 nm)/Si and CVD-Cu(200 nm)/IMP-TaN(30 nm)/SiO_2(250 nm)/Si. The basic properties of the IMP-Cu and the CVD-Cu were characterized by atomic force microscopy (AFM) and secondary ion mass spectroscopy (SIMS) measurements. Electrical

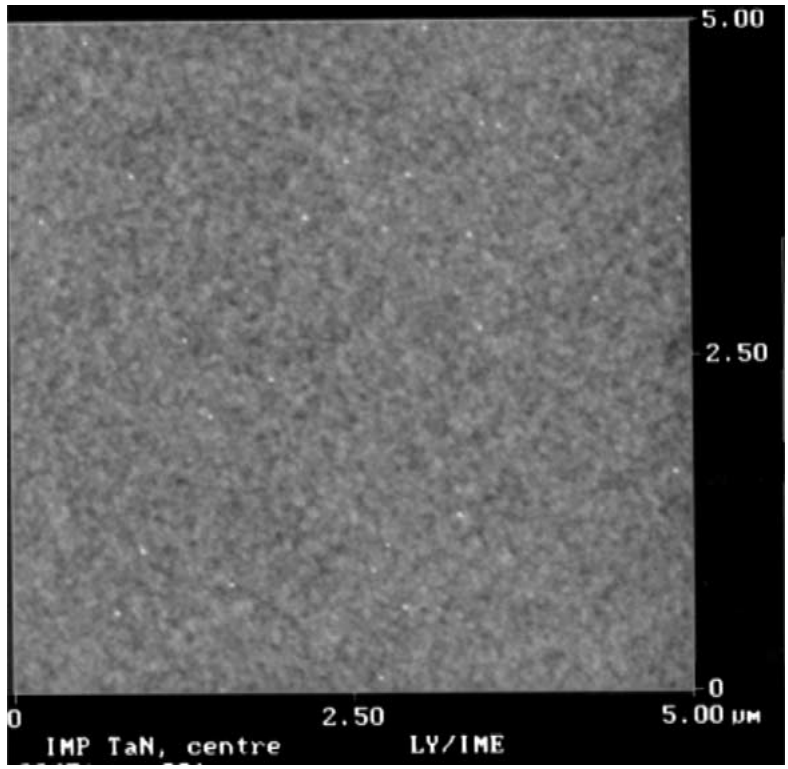

Figure 1 AFM measurement result for IMP-TaN (amorphous).

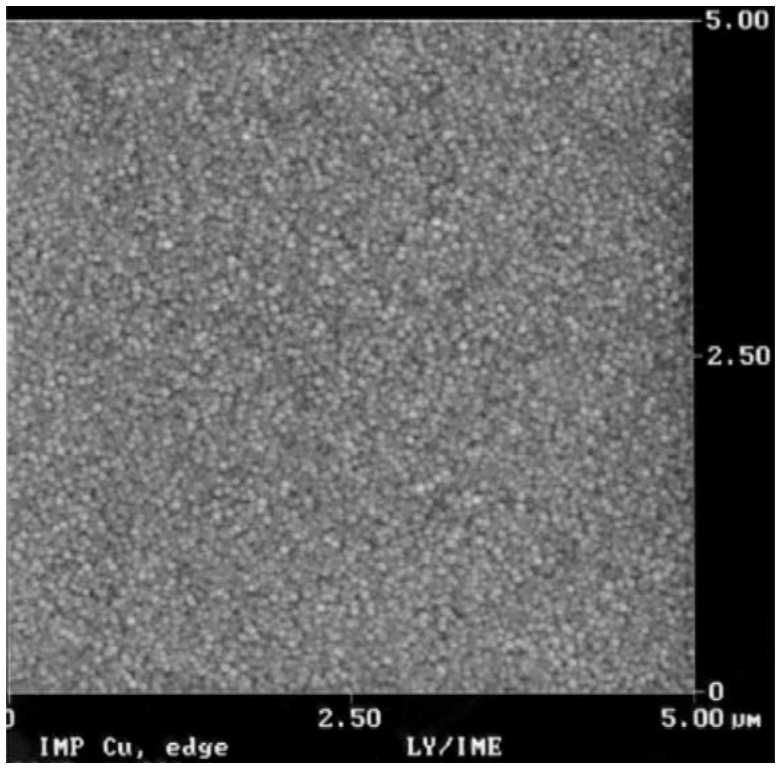

Figure 2 AFM measurement result for IMP-Cu film deposited on IMP-TaN diffusion barrier.

measurement, x-ray diffraction (XRD), scanning electron microscopy (SEM) and Rutherford backscattering spectroscopy (RBS) were used to evaluate the diffusion barrier properties and the effect of the type of Cu (deposited by IMP or CVD).

2. Experimental details

For all sample preparation and experiments described in this study used 6-inches 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-inches wafers. Tantalum nitride (TaN) films of 30 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 200 nm Cu layer was then deposited in the same setup for IMP-Cu or the CVD-Cu deposition was carried out by the disproportionate of [hfac Cu(I) tmvs] also known as CupraSelect, using a specially designed vaporizer. Ar/He mixture was used as carrier gas. A very thin layer, ∼200 Å thick, of Cu (referred to as a *flash*) was also sputtered prior to the CVD Cu deposition. Detailed of IMP and CVD deposition processes have been described elsewhere [7, 8].

AFM images were taken to compare the grain sizes and the surface roughness obtained from the different deposition techniques (IMP-Cu and CVD-Cu) and the diffusion barrier TaN. SIMS was used to determine the C and O contamination in the as deposited test structures. To investigate thermal stability of the CVD-Cu/IMP-TaN/SiO_2/Si and IMP-Cu/IMP-TaN/SiO_2/Si structures, the samples were annealed at temperatures ranging from 350°C to 950°C for 35 min in N_2 ambient. The sheet resistance of the annealed samples was measured by a four-point probe to survey the overall reaction involving Cu. Reactions and microstructural analysis of the samples, before and after annealing, were carried out by XRD and RBS. A computer controlled RIGAKU model RINT2000 diffractometer using Cu K_α radiation ($\lambda = 1.542$ Å), operated at 50 KV and 20 mA, was used for phase identification with the glancing angle of 2.5° (for IMP-Cu structure) and 1.5° (for CVD-Cu structure). 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 13.5 KeV resolution.

3. Results and discussion

It is important to know the microstructure of the IMP-TaN diffusion barrier because they play an important role on the texture of the to be deposited films. Fig. 1 shows the AFM image of the diffusion barrier TaN deposited by IMP method. IMP-TaN grow as an amorphous phase, with the roughness of ∼0.369 nm. Consequently, 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). AFM images also revealed that the grain sizes of CVD-Cu distributed uniformly between 167 to 187 nm with surface roughness (RMS) of ∼15 nm (Fig. 3).

TABLE I The relevant properties of IMP-Cu and CVD-Cu deposited on IMP-TaN

Relevant properties	IMP-Cu	CVD-Cu
Pull tester	608.2 ± 70.7 Kg cm^{-2}	466.1 ± 161.4 Kg cm^{-2}
Scoth test	Pass	Pass
Grain size	∼30 nm (center)	∼166.67 nm (center)
	∼30 nm (edge)	∼187.50 nm (edge)
Roughness (RMS)	1.361 nm (center)	15.416 nm (center)
	1.464 nm (edge)	15.890 nm (edge)
Texture	(220)	(111)
Resistivity	1.72 $\mu\Omega$-cm	2.4 $\mu\Omega$-cm

Both IMP and CVD Cu have almost the same concentrations and depth profiles of carbon and oxygen being examined by SIMS as shown in Figs 4 and 5. The relevant properties of IMP-Cu and CVD-Cu are listed in Table I.

Fig. 6 shows the sheet resistance of the IMP-Cu/IMP-TaN/SiO_2/Si and CVD-Cu/IMP-TaN/SiO_2/Si structures as a function of annealing temperature in N_2 ambient for 35 min. The measured sheet resistance was dominated by the copper thin film since the copper film (200 nm and 1.72 $\mu\Omega$-cm for IMP-Cu and 2.4 $\mu\Omega$-cm for CVD-Cu) is much thicker and has a markedly lower bulk resistivity than TaN film (30 nm and 380 $\mu\Omega$-cm) or any other reaction products. Since the top Cu layer of 200 nm carries almost all the current, the sheet resistance measurements monitor the condition and the quality of the Cu overlayer. For IMP-Cu/IMP-TaN/SiO_2/Si sample, the sheet resistance gradually decreases with increasing annealing temperature up to 550°C due to the reduction of crystal defects and grain growth in the copper film and then remains constant up to 800°C. However, after annealing at 850°C, the color of the sample was observed to change from Cu color to gray, and the sheet resistance of the sample underwent an abrupt raise indicating the severe intermixing and/or reaction between Cu and TaN thin film.

Compared to IMP-Cu/IMP-TaN/SiO_2/Si sample, CVD-Cu/IMP-TaN/SiO_2/Si sample shows the similar behavior but in the lower temperature region. The sheet resistance undergoes an abrupt rise at 650°C, much lower than 850°C for IMP-Cu/TaN/SiO_2/Si. As for the difference of sheet resistance profile, firstly, the amounts of carbon and oxygen residing in as deposited CVD-Cu and IMP-Cu were examined and compared by SIMS analysis. Since it was reported that the higher the carbon and oxygen concentration the higher the film resistivity [9]. However, in our case, it must be excluded as the main cause because both IMP and CVD Cu have almost the same concentrations and depth profiles of carbon and oxygen. Secondly, the grain sizes and roughness were examined with AFM and compared as shown in Figs 2 and 3. In the dense microstructure, the interdiffusion and/or intermixing of Cu, Ta, O, and Si atoms can be blocked effectively due to the discontinuous grain boundaries. Hence, IMP-Cu microstructure

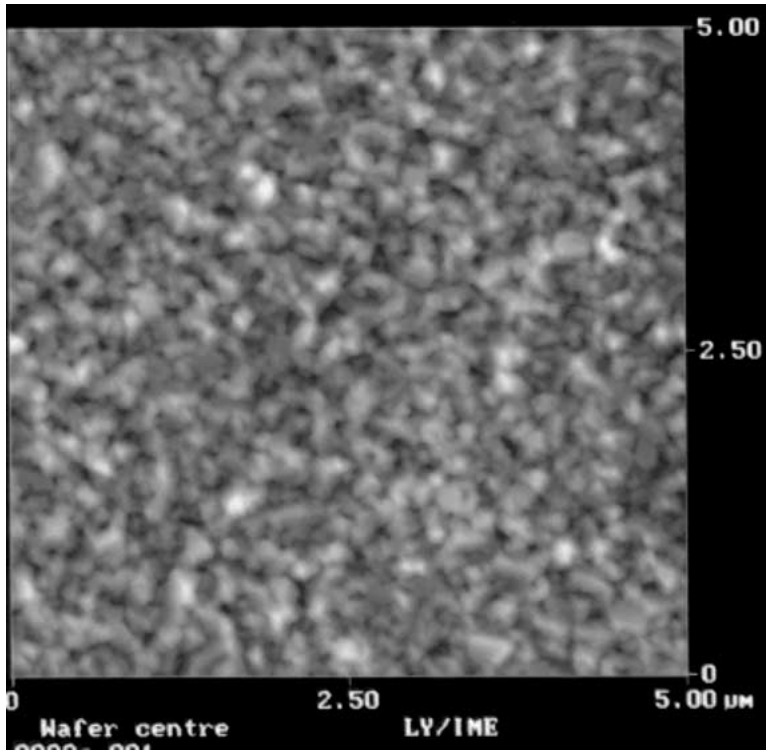

Figure 3 AFM measurement result for CVD-Cu film deposited on IMP-TaN diffusion barrier.

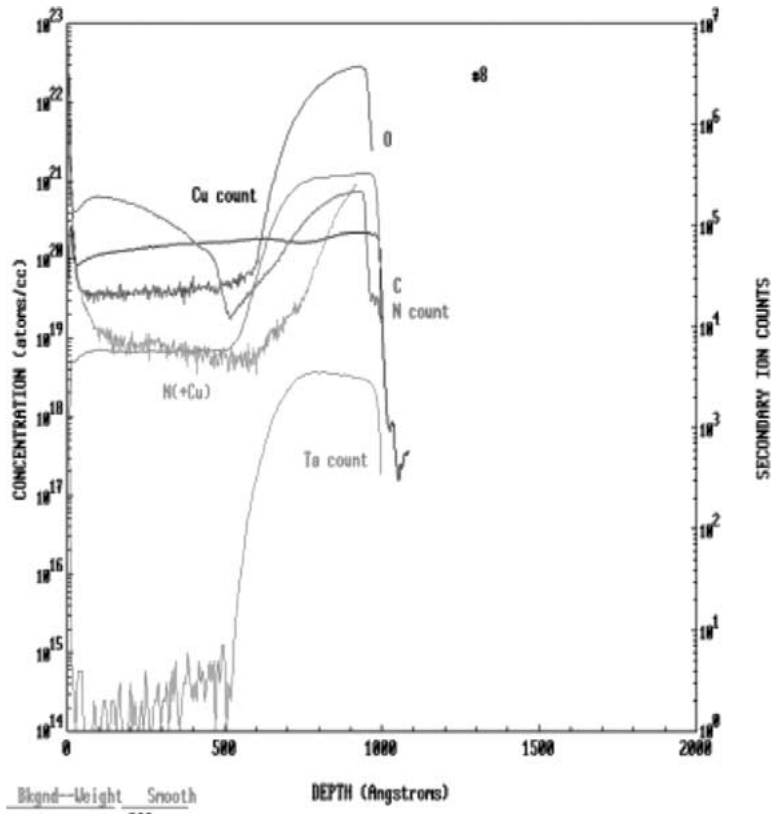

Figure 4 SIMS depth profile for oxygen and carbon atoms for IMP-Cu deposited on IMP-TaN diffusion barrier.

with smaller grain sizes, in other words, with denser grain boundaries than CVD-Cu in conjunction with a fine IMP-TaN diffusion barrier can retard the interdiffusion and/or intermixing of elements effectively, which can be accounted for a higher thermal stability of IMP-Cu/IMP-TaN/SiO_2/Si sample.

XRD analysis identified the intermixing and new phase formation in both the IMP-Cu/IMP-TaN/SiO_2/Si and CVD-Cu/IMP-TaN/SiO_2/Si structures annealed up to 950°C and 750°C respectively. The as deposited CVD-Cu film deposited on IMP-TaN diffusion barrier layer has a predominantly (111) texture at 2θ angle of 43.0° while IMP-Cu film deposited on IMP-TaN has a strong (220) at 74.05° as shown in Figs 7 and 8. Other small Cu peaks (200), (311), (222) and (400) were also observed at 50.45°, 89.9°, 95.05° and 116.8°

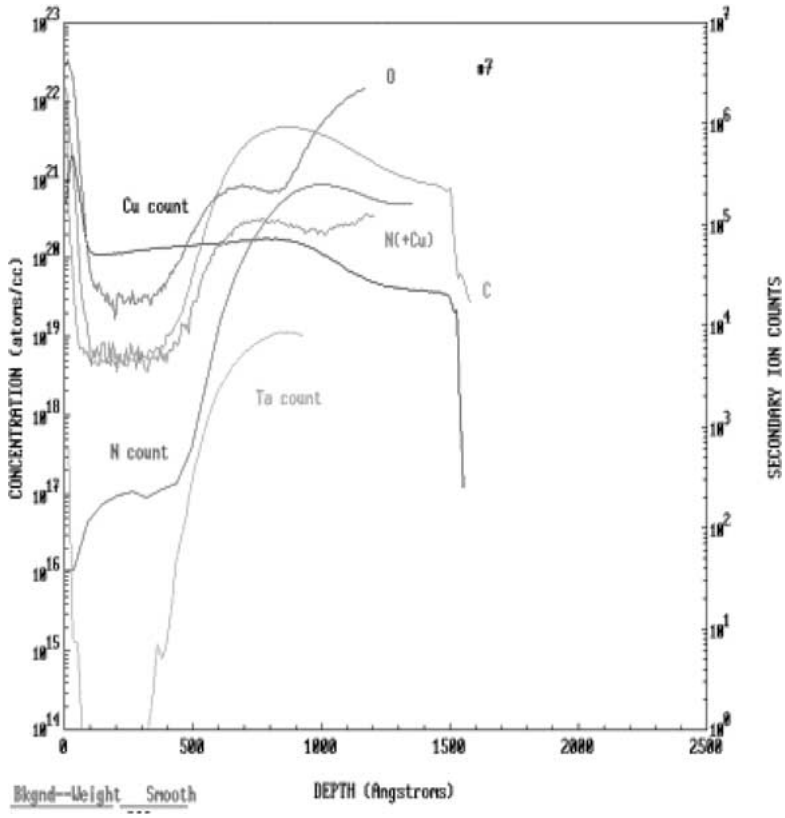

Figure 5 SIMS depth profile for oxygen and carbon atoms for CVD-Cu deposited on IMP-TaN diffusion barrier.

respectively. Only a broad peak of TaN appeared at 36° indicates IMP-TaN is an amorphous phase (see also AFM result in Fig. 1). But after annealing at 550°C a-TaN became crystalline Ta_xN_y.

As shown in Fig. 7, the IMP-Cu/IMP-TaN/SiO_2/Si structure has 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 around 23°, 29° and 36°, which were identified as TaO (001), Ta_2O_5 (100) and Cu_2O (111), respectively. The intensity of Cu (200) peaks was slightly reduced due to the formation of Cu_2O. Annealing at temperatures higher than 750°C makes Cu and weakly bonded Ta_xN_y and/or Ta 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. At 800°C annealing, a new peak of $CuTa_{10}O_{26}$ appeared, probably due to the reaction among Cu_2O, Ta_2O_5, Ta and Cu at the interface of Cu/TaN [10]. At 900°C annealing, small peaks of $Cu_5Ta_{11}O_{30}$ start to appear and becomes dominant over $CuTa_{10}O_{26}$ at 900°C. 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).

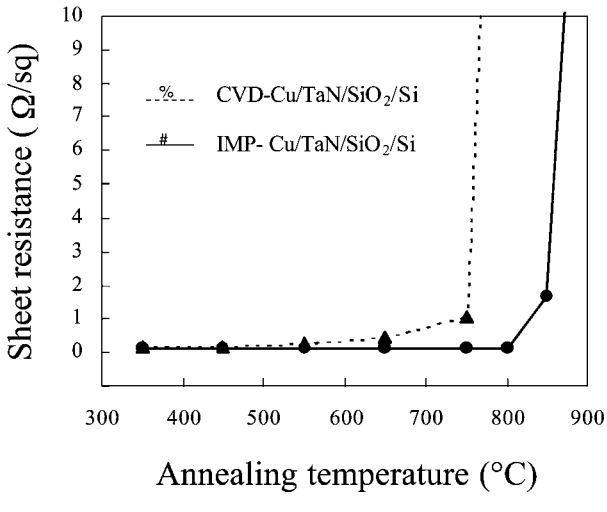

Figure 6

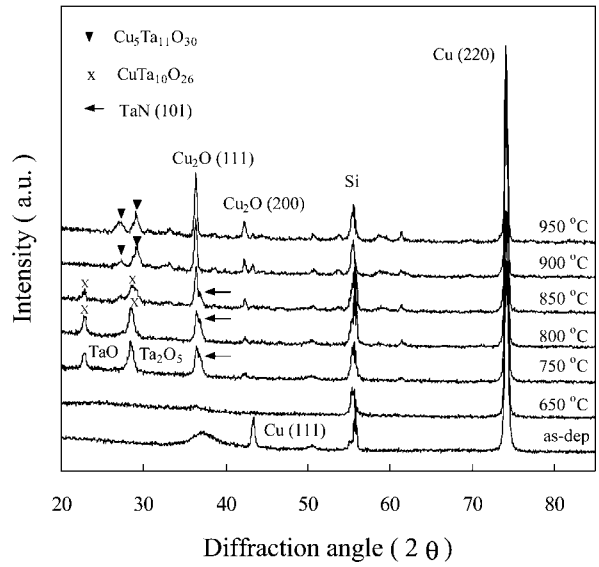

Figure 7 XRD patterns of the IMP-Cu/IMP-TaN/SiO_2/Si structure annealed at various temperatures for 35 min in N_2 ambient.

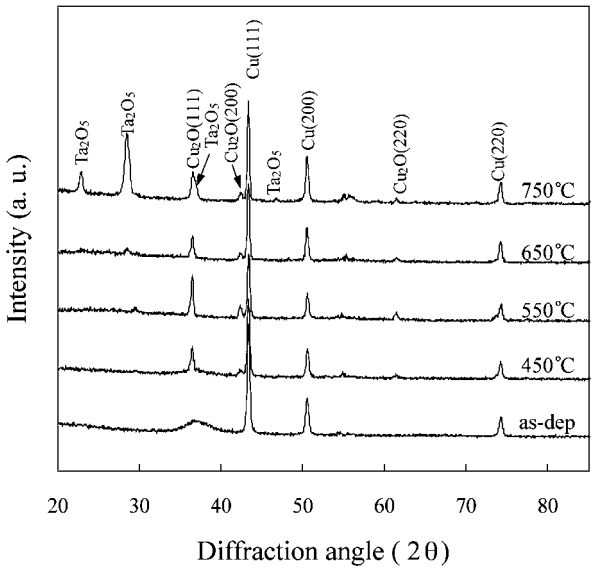

Figure 8 XRD patterns of the CVD-Cu/IMP-TaN/SiO_2/Si structure annealed at various temperatures for 35 min in N_2 ambient.

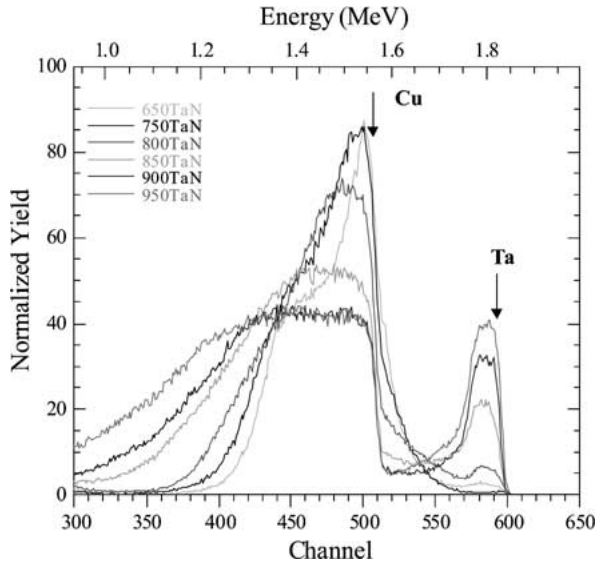

Figure 9 RBS spectra of the IMP-Cu/IMP-TaN/SiO_2/Si structure after annealing at various temperatures for 35 min.

Fig. 8 shows the XRD spectra of CVD-Cu/IMP-TaN/SiO_2/Si structure annealed at various temperatures. CVD-Cu structure shows similar XRD spectra to IMP-Cu structure except for the orientation of Cu (111). However, in contrast to the IMP-Cu/IMP-TaN/SiO_2/Si structure, Ta_2O_5 seems to be directly related to the increase of sheet resistance at 750°C annealing in the CVD-Cu/IMP-TaN/SiO_2/Si structure. Ta_2O_5 starts to form at below 650°C annealing, affecting the sheet resistance at 650°C annealing, and then lead to the escalation of sheet resistance value in the structure at 750°C annealing. The comparison of the two XRD spectra (Figs 7 and 8) leads to a conclusion that (111) oriented CVD-Cu with larger gain size in CVD-Cu/IMP-TaN/SiO_2/Si structure showed lower thermal stability than (220) oriented with smaller grain size IMP-Cu/IMP-TaN/SiO_2/Si structure. Although an interfacial reaction and the formation of Cu_2O, Ta_2O_5 occurred in our structures, no evidence of diffusion of Cu through the barrier was detected even after annealing at 950°C(IMP-Cu) and 750°C(CVD-Cu) for 35 min respectively.

Fig. 9 shows the RBS depth profile of the IMP-Cu/IMP-TaN/SiO_2/Si sample annealed for 35 min at various temperatures. At 650°C, RBS spectra shows that the gradient of the trailing edge of the Cu signal changes and a small amount of Ta appear at the higher energy levels. This implies that intermixing of Cu and Ta begins to occur. When the temperature reaches 850°C, a new Ta peak appears at an energy level of 1.836 MeV and grows as increasing temperature. This seems to imply that Ta has reached and accumulated at the surfaces of Cu film. A strong tailing is indicative for agglomeration process. The severe intermixing of the constituent elements occurs after annealing at 850°C, which can account for the abrupt rise of the sheet resistance at 850°C and thereafter.

Fig. 10 shows the RBS spectra of CVD-Cu/IMP-TaN/SiO_2/Si films as deposited, and when annealed to 450°C, 550°C and 650°C for 35 min. The surface

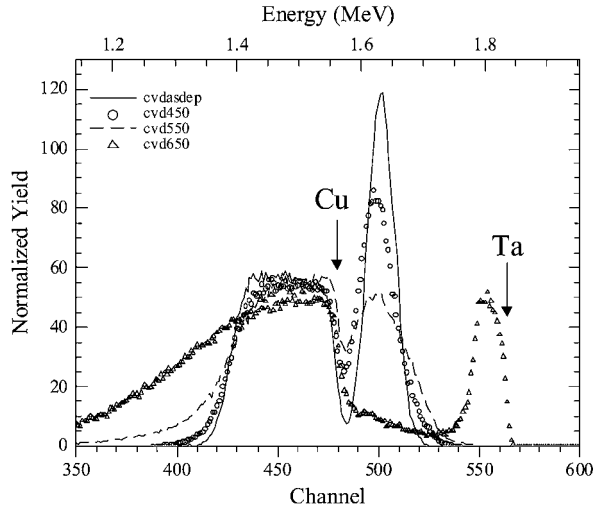

Figure 10 RBS spectra of the CVD-Cu/IMP-TaN/SiO_2/Si structure after annealing at various temperatures for 35 min.

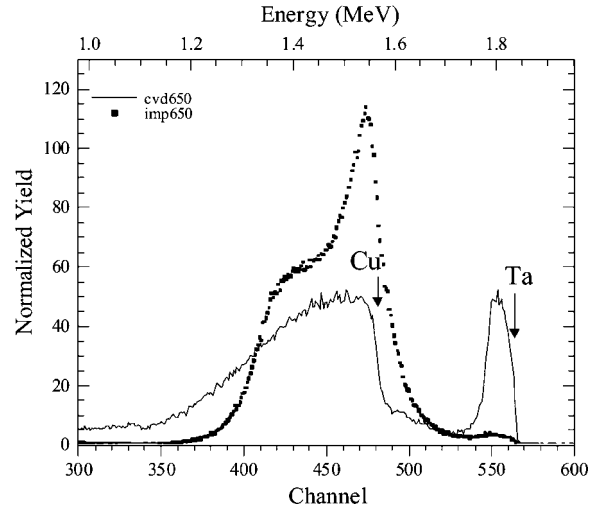

Figure 11 RBS spectra of the IMP-Cu/IMP-TaN/SiO_2/Si and CVD-Cu/IMP-TaN/SiO_2/Si structures after annealing at 650°C for 35 min.

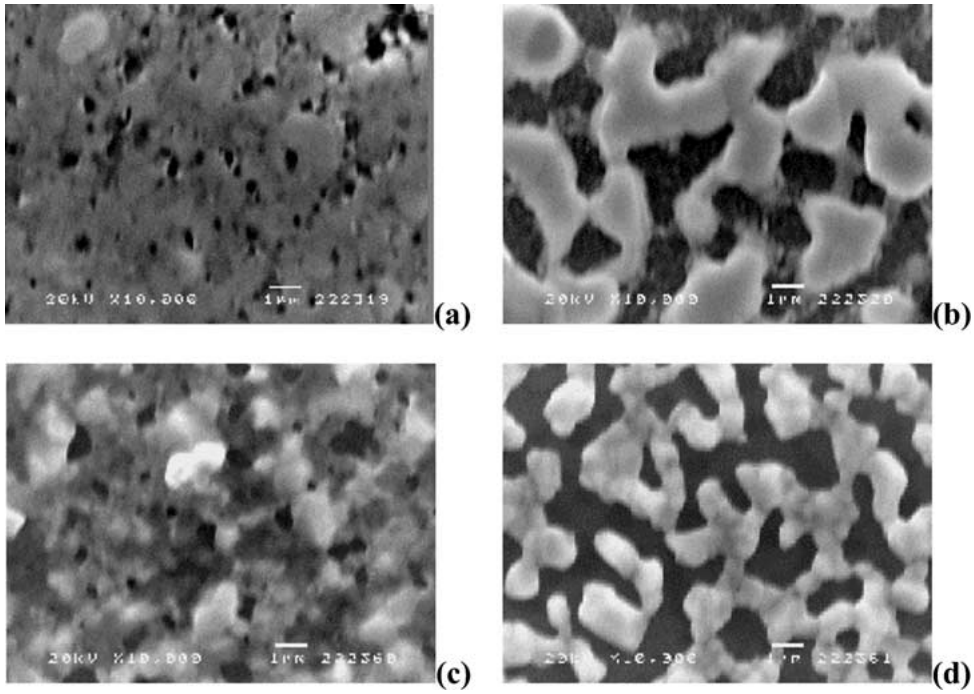

Figure 12 SEM image of IMP-Cu/IMP-TaN/SiO_2/Si structure after annealing at (a) 850°C and (b) 950°C and CVD-Cu/IMP-TaN/SiO_2/Si structure after annealing at (c) 650°C and (d) 750°C for 35 min.

scattering energies of Ta and Cu are indicated. At 450°C and 550°C, the trailing edge of the Cu peak and the leading edge of the Ta peak show decreasing gradient. This indicates intermixing and/or agglomeration of the Cu and Ta. At 650°C, a new peak appears at the surface scattering energy of Ta, indicating that Ta is present on and has accumulated on the surface. This result indicates that the quality of the Cu overlayer has deteriorated and is consistent with the abrupt rise in sheet resistance at this temperature.

Fig. 11 shows a comparison of the RBS spectra of CVD-Cu/IMP-TaN/SiO_2/Si and IMP-Cu/IMP-TaN/SiO_2/Si films annealed to 650°C for 35 min. The CVD-Cu spectrum has a peak at the surface scattering energy of Ta, showing Ta accumulation on the surface. Heavy tailing of the Cu peak is also observed. These features are less significant in the IMP-Cu spectrum, indicating that intermixing and/or agglomeration of the constituent elements is far more severe in the sample with CVD-Cu.

In both case, 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 [11, 12]. However, in our structures the as deposited TaN diffusion barrier is an amorphous phase.

Which 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 [13]. 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 and formed Ta_xO_y. By compare to IMP-Cu, CVD-Cu that has larger grain size, in other words, the widely open grain structure will serve the fast diffusion paths for Ta (grain size $10 \sim 20$ nm) to migrate to the Cu surface. Surface morphology examined by SEM micrograph of the both structures at annealing temperature lower than 450°C (CVD-Cu) and 750°C (IMP-Cu) revealed no obvious changes and pinholes were observed thereafter. Increasing the annealing temperature to 750°C (for CVD-Cu) and 950°C (for IMP-Cu) results in the surfaces shown in Fig. 12. The highly agglomeration of Cu films were clearly seen in both types and exposing part of Ta and/or TaN to the ambient.

4. Conclusions

The effect of Cu deposition method (IMP and CVD) on the thermal stability of IMP-TaN diffusion barrier was investigated in the Cu(200 nm)/TaN(30 nm)/SiO_2(250 nm)/Si structure. The IMP-Cu/IMP-TaN structure was found to be stable up to 800°C, which is much higher than 550°C of CVD-Cu/IMP-TaN structure. It was found that IMP sputtering of Cu made the individual grains tightly packed and hence increased the packing density. Correspondingly, IMP Cu deposition method enhanced the IMP-TaN diffusion barrier property by suppressing the interdiffusion and intermixing between Cu and TaN film. Both structures have a similar failure mechanism. Ta has out diffused through Cu in a local site and react with oxygen residing in the grain boundaries of Cu and formed Ta_xO_y. In the case of IMP-Cu the reaction occurred between Cu_2O, Ta_2O_5, Cu and Ta formed $Cu_5Ta_{11}O_{30}$ compound after 850°C annealing, which leads to loss of conducting Cu layer.

References

1. T. NITTA, T. OHMI, T. HOSHI, S. SAKAI, K. SAKAIBARA, S. IMAI and T. SHIBATA, *J. Electrochem. Soc.* **140** (1993) 1131.

2. J. TAO and N. W. CHEUNG, *IEEE Electron Device Lett.* **14** (1993) 249.
3. KYUNG-HOON MIN, KYU-CHANG CHUN and KI-BUM KIM, *J. Vac. Sci. Technol. B* **14** (1996) 3263.
4. M. O. ABELFOTOH and B. G. STEVENSSON, *Phy. Rev.* **44** (1991) 12742.
5. A. BRONIAUOWSKI, *Phys. Rev. Lett.* **62** (1989) 3074.
6. K. HOLLOWAY, P. M. FRYER, C. CABRAL, J. M. E. HARPER, P. J. BAILEY and K. H. KELLEHER, *J. Appl. Phys.* **71** (1992) 5433.
7. S. M. ROSSNAGEL and J. HOPWOOD, *J. Vac. Sci. Technol. B* **12** (1994) 499.
8. PACSCAL DOPPELT and THOMAS H. BAUM, *MRS Bulletin* August 1994 (1994) 41.
9. S. C. SUN, M. H. CHIU, S. H. CHUANG and C. E. TSAI, *IEEE IEDM.* **95** (1995) 461.
10. H.-J. LEE, K. W. KWON, C. RYU and R. SCINLAIR, *Acta Mater.* **47**(15) (1999) 3965.
11. C. K. HU, S. CHANG, M. B. SMALL and J. E. LEWIS, in Proceeding of the Third International VLSI Multilevel Interconnection Conference, IEEE Electron Devices Society, June 9, 1986, Santa Clara, CA.
12. K. HOLLOWAY and P. M. FRYER, *Appl. Phys. Lett.* **57** (1990) 1738.
13. X. SUN, E. KOLAWA, J. S. CHEN, J. S. REID and M. A. NICOLET, *Thin Solid Film* **236** (1993) 347.

Received 1 June 2000
and accepted 31 May 2001