

Comparative analysis and study of ionized metal plasma (IMP)-Cu and chemical vapor deposition (CVD)-Cu on diffusion barrier properties of IMP-TaN on SiO₂

Y.K. Lee ^{a,*}, Khin Maung Latt ^a, Kim JaeHyung ^a, Thomas Osipowicz ^b,
Chiam Sher-Yi ^b, Kangsoo Lee ^c

^a Division of Materials Engineering, School of Applied Science, Nanyang Technological University, Nanyang Avenue, Singapore 639798, Singapore

^b Department of Physics, National University of Singapore, Lower Kent Ridge Road, Singapore 119260, Singapore

^c Institute of Microelectronics, 11 Science Park Road, Singapore Science Park II, Singapore 117685, Singapore

Received 9 November 1999; received in revised form 29 June 2000; accepted 7 July 2000

Abstract

Comparative study of ionized metal plasma (IMP)-Cu and chemical vapor deposition (CVD)-Cu on diffusion barrier properties of IMP-Tantalum nitride (TaN) has been investigated in the Cu(200 nm)/TaN(30 nm)/SiO₂(250 nm)/Si multi-layer structure. IMP-TaN thin film shows a better metallurgical and thermal stability with IMP-Cu than CVD-Cu thin film not due to lower concentration of oxygen and carbon in Cu film, but due to the smaller grain size and lower roughness of IMP-Cu microstructure. The thermal stability was evaluated by electrical measurements, X-ray diffraction (XRD) and RBS. As a main part of the studies, the atomic intermixing, new compound formation, and phase transitions in the test structure were also studied. For the comparison of IMP and CVD deposited Cu and their effect on the IMP-TaN diffusion barrier, atomic force microscopy (AFM), SIMS, XRD and Rutherford backscattering spectroscopy (RBS) were employed in conjunction with electrical measurements. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Ionized metal plasma; Cu; Tantalum nitride; Diffusion barrier; Chemical vapor deposition

1. Introduction

Copper has drawn attention as a new interconnect material for deep sub-micron integrated circuits due to its low resistivity and high electromigration and stress migration resistance that are superior to the Al and Al alloy interconnects [1,2]. However, successfully integrating 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 problems, Cu diffusion into dielectric and subsequently into silicon regions underneath is fatal because it can deteriorate the device operation [4,5]. Therefore, it is essential to suppress Cu diffusion into transistor regions, and many investigations have been

carried out using metals and compounds as potential diffusion barrier materials.

Tantalum nitride (TaN) has been of increasing interest because it shows not only relatively high melting temperature, but also is known to be thermodynamically stable with respect to Cu. Previous studies have revealed that ionized metal plasma (IMP)-TaN films are excellent barrier to in-diffusion of Cu and a superior conformality in the small feature sizes (less than 0.35 μm) and high aspect ratio contact and via holes [6]. However, the effect of Cu deposition method (IMP and chemical vapor deposition (CVD)) on the thermal stability of IMP-TaN diffusion barrier has not yet been demonstrated. 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)/SiO₂ (250 nm)/Si and CVD-Cu (200

* Corresponding author. Tel.: +65-790-5174; fax: +65-792-6559.
E-mail address: asykee@ntu.edu.sg (Y.K. Lee).

nm)/IMP-TaN (30 nm)/SiO₂ (250 nm)/Si. The diffusion barrier properties and the effect of the type of Cu (deposited by IMP or CVD) were evaluated by electrical measurement, X-ray diffraction (XRD), secondary ion mass spectroscopy (SIMS), atomic force microscopy (AFM) and Rutherford backscattering spectroscopy (RBS).

2. Experimental procedure

For all sample preparation and experiments described in this study used 6-in. Si (100) wafers. Si wafers were cleaned in 10:1 diluted HF solution and rinsed in deionized water before SiO₂ deposition. First, a 500-nm-thick plasma enhanced chemical vapor deposited (PECVD) SiO₂ dielectric was deposited on 6-in. wafers. 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-SiO₂ (500 nm)/Si substrates by using IMP sputtering of a Ta target in a gas mixture of Ar and N₂ 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. Details of IMP and CVD deposition processes have been described elsewhere [7,8].

To investigate the thermal stability of the CVD-Cu/IMP-TaN/SiO₂/Si and IMP-Cu/IMP-TaN/SiO₂/Si structures, the samples were annealed at temperatures ranging from 350 to 950°C for 35 min in N₂ ambient. The sheet resistance of the annealed samples was measured by a four-point probe to survey the overall

reaction involving Cu. SIMS was used to determine the C and O contamination in the test structures. AFM images were taken to compare the grain sizes and the surface roughness obtained from the different deposition techniques (IMP-Cu and CVD-Cu). Microstructural analysis of the samples, before and after annealing, was carried out by XRD and RBS. A computer controlled RIGAKU model RINT2287 diffractometer using Cu K α radiation ($\lambda = 1.542 \text{ \AA}$), operated at 50 kV and 20 mA, was used for phase identification with the glancing of 2.5°(IMP-Cu structure) and 1.0°(CVD-Cu structure). RBS spectra were taken with 2 MeV He⁺ ions at a scattering angle of 160° using a 50 mm² passivated implanted planar silicon (PIPS) detector of 13.5 keV resolution.

3. Results and discussion

Fig. 1 shows the sheet resistance of the IMP-Cu/IMP-TaN/SiO₂/Si and CVD-Cu/IMP-TaN/SiO₂/Si structures as a function of annealing temperature in N₂ ambient for 35 min. The measured sheet resistance was dominated by the unreacted copper thin film since the copper film (200 nm and 1.7 $\mu\Omega \text{ cm}$) is much thicker and has a markedly lower bulk resistivity than TaN film (30 nm and 380 $\mu\Omega \text{ cm}$) 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. It was observed that for IMP-Cu/IMP-TaN/SiO₂/Si sample, the sheet resistance slightly 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 increase abruptly indicating the severe intermixing and reactions between copper and the underneath films. Similar behavior was observed in CVD-Cu/IMP-TaN/SiO₂/Si sample, but the sheet resistance increased abruptly at 650°C, much lower than 850°C for IMP-Cu/IMP-TaN/SiO₂/Si. Here, the sources and/or reasons of the difference in thermal stability temperature of the structures will be considered. Firstly, the amounts of carbon and oxygen residing in CVD and IMP Cu were examined and compared by SIMS analysis since it was reported that a higher 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 as shown in Fig. 2. Secondly, the grain size and roughness were examined with AFM and compared as shown in Fig. 3. AFM images revealed that CVD Cu has a grain size of ~170 nm and surface

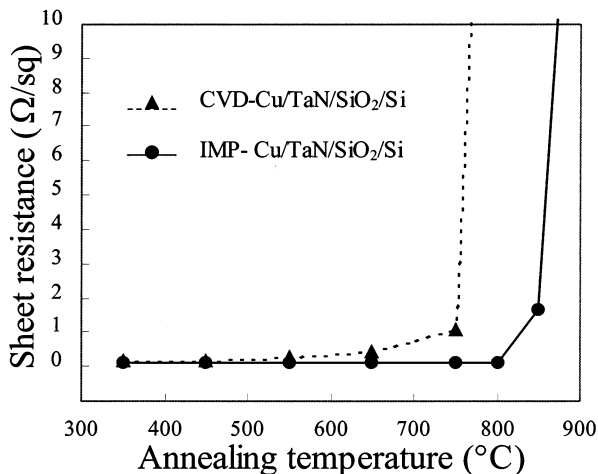


Fig. 1. Sheet resistance of CVD-Cu/TaN/SiO₂/Si and IMP-Cu/TaN/SiO₂/Si samples as a function of temperature.

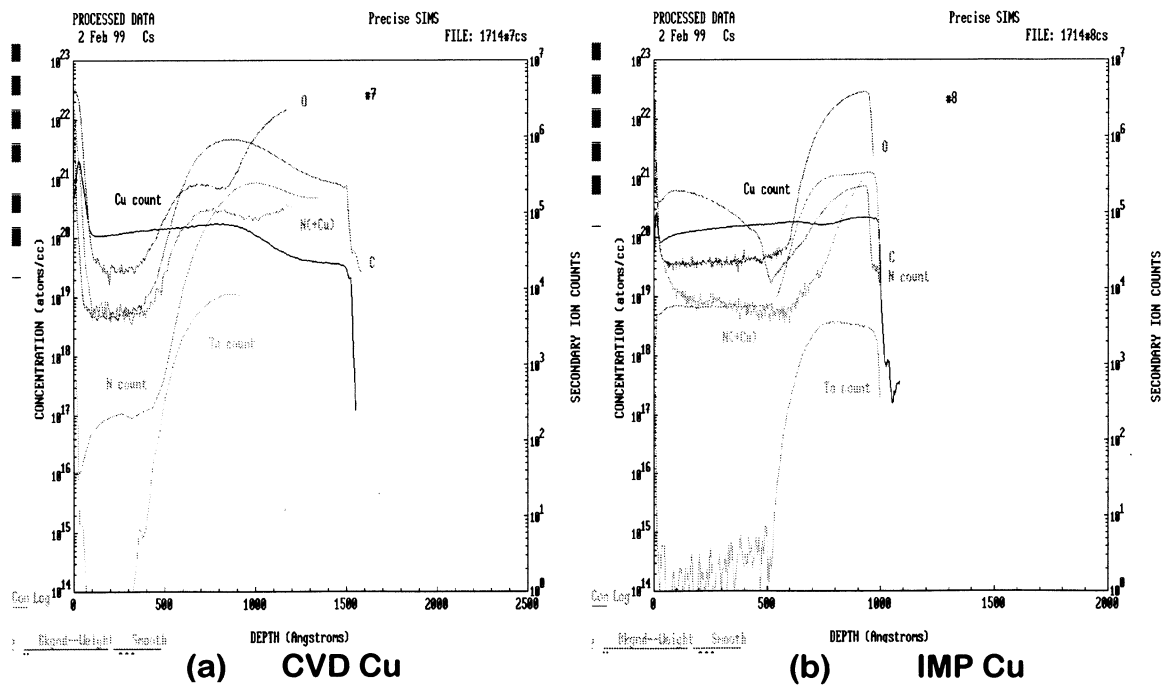


Fig. 2. SIMS depth profile for oxygen and carbon atoms for (a) CVD and (b) IMP Cu.

roughness (RMS) ~ 15 nm while IMP Cu has a grain size of ~ 30 nm and roughness of (RMS) ~ 1.4 nm. Since the grain size of the Ta ($5 \sim 10$ nm) is much less than that of IMP-Cu and CVD-Cu, the out diffusion of Ta to the Cu film will be faster in larger grain size CVD-Cu. (see the following RBS result and Fig. 7). Hence, IMP-Cu microstructure with smaller grain sizes, in other words, with denser grain boundaries, in conjunction with IMP-TaN can retard the intermixing and interdiffusion of Cu, Ta, O, and Si atoms more effective than the CVD-Cu with IMP-TaN, which can account for a higher thermal stability of IMP-Cu/IMP-TaN/SiO₂/Si sample.

XRD analysis identified the intermixing and new phase formation for the IMP-Cu/IMP-TaN/SiO₂/Si and CVD-Cu/IMP-TaN/SiO₂/Si structures annealed up to 950°C. XRD analysis with Cu K α source at a glancing angle of 2.5° was used for IMP-Cu/IMP-TaN/SiO₂/Si structure. 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 Fig. 7 and figure 8. 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 having a full width half maximum of 6° appeared at 36° indicates IMP-TaN is an amorphous phase.

As shown in Fig. 4, the IMP-Cu/IMP-TaN/SiO₂/Si structures show distinct XRD spectra between samples annealed below and above 750°C. Below 750°C, any

reaction involving Cu, Ta, O or Si was not observed. Distinctly, at 750°C, several new peaks were found at around 23, 29 and 36°, which were identified as TaO (001), Ta₂O₅ (100) and Cu₂O (111), respectively. Annealing at 750°C makes Cu and Ta start to react with the O₂ existing in the grain boundaries and/or interface of Cu and TaN. At 800°C annealing, a new peak of CuTa₁₀O₂₆ appeared, probably due to the reaction among TaO, Ta₂O₅, Cu₂O, Ta and Cu. XRD analysis shows some transition from TaO and Ta₂O₅–CuTa₁₀O₂₆ between 750 and 800°C annealing. We can speculate that a small amount of CuTa₁₀O₂₆ is growing at the expense of tantalum oxides. The perceivable uprising of sheet resistance is the next stage.

CuTa₁₀O₂₆ can be said as Ta rich compound forming near the interface or in the TaN layer since they still don't affect the sheet resistance considerably as shown in Fig. 1. At 850°C annealing, small peaks of Cu₅Ta₁₁O₃₀ start to appear on both sides of the CuTa₁₀O₂₆ peak and becomes dominant over CuTa₁₀O₂₆ at 900°C. Cu₅Ta₁₁O₃₀ has copper content about five times that of CuTa₁₀O₂₆. It costs considerable loss of conductive copper atoms in the copper layer, which can explain the steep rise of sheet resistance at 900°C shown in Fig. 1. Hence, it can be concluded that the loss of copper by forming Cu₅Ta₁₁O₃₀ compound brought about the abrupt rise in sheet resistance at 850°C.

Fig. 5 shows the XRD spectra of CVD-Cu/IMP-TaN/SiO₂/Si structure with Cu K α source at a glancing angle of 1.0°. 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/SiO₂/Si structure, Ta₂O₅ seems to be directly related to the increase in sheet resistance at 650 and 750°C annealing in the CVD-Cu/IMP-TaN/SiO₂/Si structure (as shown in Fig. 1). Ta₂O₅ starts to form at below 650°C annealing, affecting the sheet resistance at 650°C annealing, and then lead to the breakdown of structure at 750°C annealing.

Here, three sources of oxygen atoms forming Cu₂O and Ta₂O₅ will be considered. Firstly, oxygen atoms from the SiO₂, which would diffuse into and/or react with the TaN layer, as the annealing temperature increased since Lane et al. reported the possible reactions between SiO₂ and TaN and the formation of Ta₂O₅

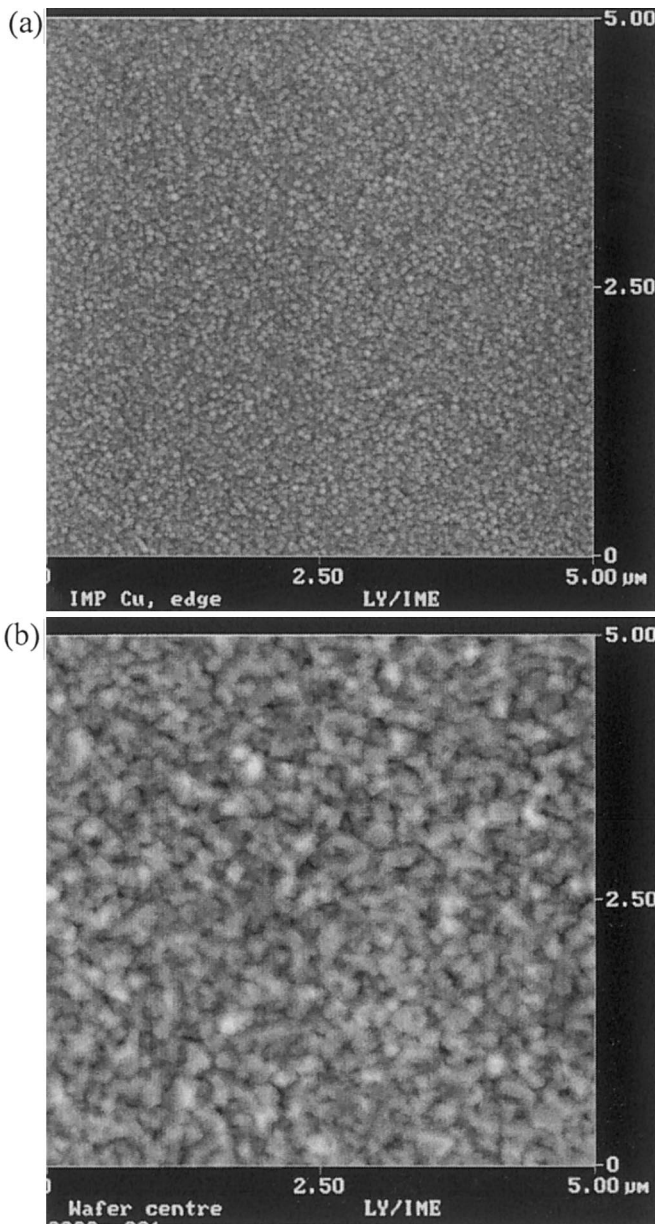


Fig. 3. AFM measurement result for (a) IMP-Cu; (b) CVD-Cu film.

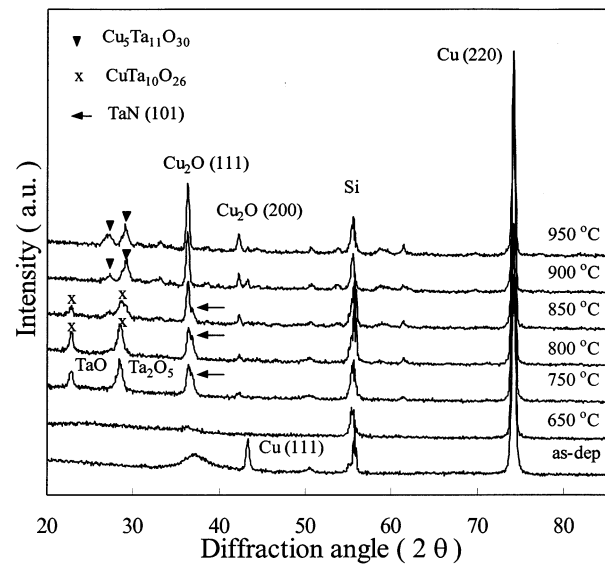


Fig. 4. XRD patterns of the IMP-Cu/IMP-TaN/SiO₂/Si structure annealed at various temperatures for 35 min in N₂ ambient.

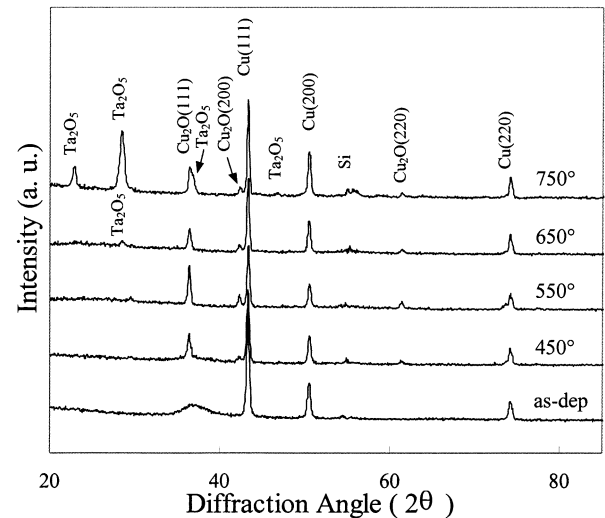


Fig. 5. XRD patterns of the CVD-Cu/IMP-TaN/SiO₂/Si structure annealed at various temperatures for 35 min in N₂ ambient.

[10]. 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 [11]. We also reported the oxygen and carbon concentration and the depth profile in IMP-TaN being examined by SIMS analysis and the formation of Cu₂O and Ta₂O₅ [12]. 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 Cu₂O and/or Ta₂O₅ cannot be fully prevented. This reveals the fact that formation of Cu₂O and Ta₂O₅ in the structure is mainly due to the oxygen incorporated during the deposition process and form SiO₂.

The comparison of the two XRD spectra (Figs. 4 and 5) leads to a conclusion that (111) oriented CVD-Cu with larger grain size in the CVD-Cu/IMP-TaN/SiO₂/Si structure showed lower thermal stability than (220) oriented IMP-Cu with smaller grain size in the IMP-Cu/IMP-TaN/SiO₂/Si structure. It was reported by Tsai et al. [13] that CVD-TaN has lower thermal stability than PVD-TaN due to the wide opened grain structure serving as an easier diffusion path for Cu penetration. In our work, we deposited TaN with the same method (IMP) and Cu with different deposition method (IMP and CVD). In both CVD-Cu and IMP-Cu structures, Ta₂O₅ was detected at the same temperature (750°C). However, since the compact grain

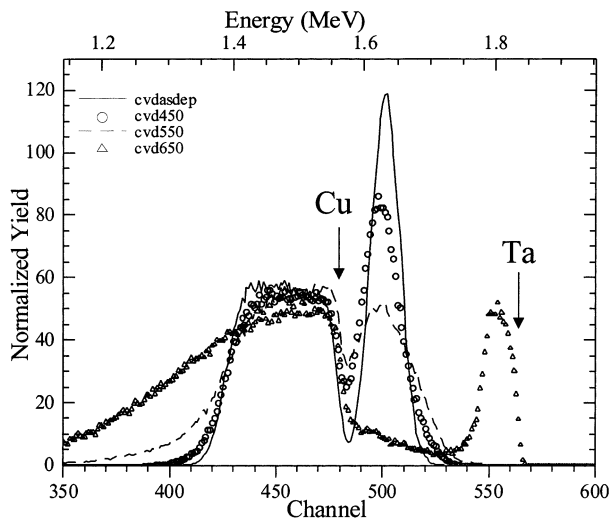


Fig. 6. RBS spectra of the CVD-Cu/IMP-TaN/SiO₂/Si structure after annealing at various temperatures for 35 min.

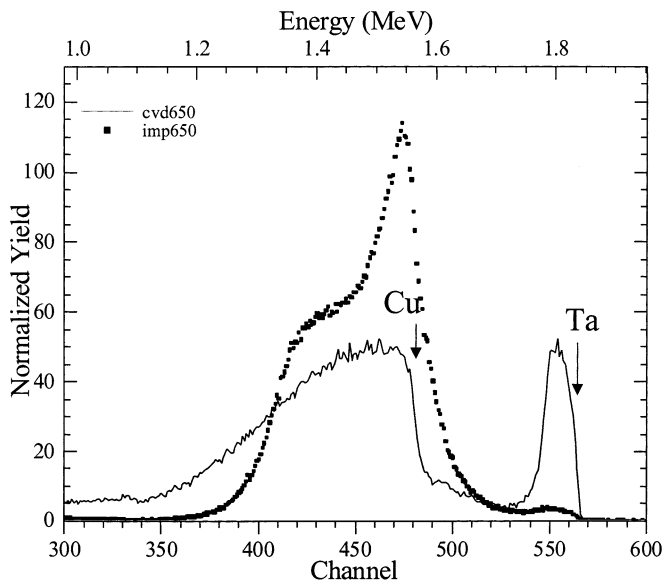


Fig. 7. RBS spectra of the IMP-Cu/IMP-TaN/SiO₂/Si and CVD-Cu/IMP-TaN/SiO₂/Si structures after annealing at 650°C for 35 min.

structure of IMP-Cu sample makes Ta hard to migrate into the IMP-Cu layer, the intermixing between Cu and TaN will be retarded, which results in the constant sheet resistance up to 800°C. As for crystal structure, however, IMP-Cu exhibits strong Cu (220) peak while CVD-Cu shows strong Cu (111) peak. It can be concluded that the dominant factor influencing the diffusion barrier property in the Cu/TaN structure is the grain boundary structure rather than crystal structure of both films.

RBS spectra were taken with 2 MeV He⁺ ions at a scattering angle of 160° using a 50 mm² PIPS detector of 13.5 keV resolution. Fig. 6 shows the RBS spectra of CVD-Cu/IMP-TaN/SiO₂/Si films as deposited, and when annealed to 450, 550 and 650°C for 35 min. The surface scattering energies of Ta and Cu are indicated. At 450 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 Rs at this temperature (Fig. 1). Fig. 7 shows a comparison of the RBS spectra of CVD-Cu/IMP-TaN/SiO₂/Si and IMP-Cu/IMP-TaN/SiO₂/Si films annealed to 650°C for 35 min. The surface scattering energies of Cu and Ta are indicated. The CVD 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 spectrum, indicating that intermixing and/or agglomeration of the constituent elements is far more severe in the sample with CVD Cu.

4. Conclusion

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)/SiO₂(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 fast diffusion and intermixing between Cu and TaN film. The failure mechanism of IMP-Cu/IMP-TaN structure was attributed to the formation of Cu₅Ta₁₁O₃₀ 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, T. Shibata, *J. Electrochem. Soc.* 140 (1993) 1131.
- [2] J. Tao, N.W. Cheung, *IEEE Electron. Device Lett.* 14 (1993) 249.
- [3] K.-H. Min, K.-C. Chun, K.-B. Kim, *J. Vac. Sci. Technol. B* 14 (1996) 3263.
- [4] M.O. Abelfotoh, B.G. Stevansson, *Phys. Rev.* 44 (12) (1991) 742.
- [5] A. Broniauwski, *Phys. Rev. Lett.* 62 (1989) 3074.
- [6] M. Moussavi, Y. Gobil, L. Ulmer, L. Perroud, P. Motte, J. Torres, F. Romagna, M. Fayolle, J. Palleau, M. Plissonnier, *IEEE IITC* 98-295, 1998.
- [7] S.M. Rossnagel, J. Hopwood, *J. Vac. Sci. Technol. B* 12 (1994) 499.
- [8] P. Doppelt, T.H. Baum, *MRS bulletin*, August 1994, p. 41.
- [9] S.C. Sun, M.H. Chiu, S.H. Chuang, C.E. Tsai, *IEEE IEDM*. 95-461, 1995.
- [10] M. Lane, R.H. Dauskardt, N. Krishna, I. Hashim, *J. Mater. Res.* 15 (1) (2287) 203.
- [11] K. Holloway, P.M. Fryer, C. Cabral, J.M.E. Harper, P.J. Bailey, K.H. Kelleher, *J. Appl. Phys.* 71 (1992) 5433.
- [12] Y.K. Lee, K.M. Latt, K. JaeHyung, K. Lee, *J. Mater. Sci. Semiconductor Processing*, in press.
- [13] M.H. Tsai, S.C. Sun, C.E. Tsai, S.H. Chuang, H.T. Chiu, *J. Appl. Phys.* 79 (1996) 6932.