Study of diffusion barrier properties of ionized metal plasma (IMP) deposited TaN between Cu and SiO$_2$

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Abstract

The diffusion barrier properties of IMP deposited TaN between Cu and SiO$_2$ have been investigated in the Cu (200 nm)/TaN (30 nm)/SiO$_2$ (250 nm)/Si multi-layer structure. The IMP-TaN thin film shows better Cu diffusion barrier properties than chemical vapor deposition (CVD) and conventional physical vapor deposition (PVD) deposited TaN films. The thermal stability was evaluated by electrical measurement and X-ray diffraction (XRD) analysis. As a main part of thermal stability studies, the atomic intermixing, new compound formation and phase transitions in the test structure were also studied. Furthermore, a failure mechanism was also examined by X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), secondary ion mass spectroscopy (SIMS) and Rutherford backscattering spectroscopy (RBS) in conjunction with electrical measurements. The 30 nm thick IMP-TaN was found to be stable up to 800°C for 35 min. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Tantalum nitride (TaN); Ionized metal plasma (IMP); Diffusion barrier

1. Introduction

Copper has drawn attention as an interconnect material for deep sub-micron circuits due to the low resistivity, high electromigration and stress migration resistance superior to the Al and its alloy based interconnecting metals [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, in particular, 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.

Tantalum nitride (TaN) is presently one of the most widely used copper barrier materials in copper metallization because it shows not only a relatively high melting temperature but also is known to be thermodynamically stable with respect to Cu. Previous studies have revealed reactive sputtered TaN and Ta$_2$N films to be excellent mutallurgical diffusion barriers between copper and Si [6,7], and between aluminum and Si substrates [8,9]. However, the reactive sputtering process has serious limitations owing to the poor step coverage caused by the shadowing effect in the small feature sizes (less than 0.35 μm) and high aspect ratio contact and via holes. Accordingly, TaN barrier metals deposited by chemical vapor deposition (CVD) have received much attention owing to their superior conformality over sputtered ones. However, it was reported by Tsai et al. [10] that CVD-TaN (60 nm thickness) has poor metallurgical stability (550°C) and much higher resistivity (920 μΩ cm) than physical vapor deposited (PVD) TaN (650°C and 380 μΩ cm) due to a higher carbon and oxygen concentration in it.

In our present work, TaN barriers were deposited by ionized metal plasma (IMP) sputtering as a deposition technique. It will overcome the generic PVD processing

limitations such as the poor step coverage without losing the excellent mutallurgical diffusion barrier properties. In addition, IMP deposition makes the TaN film microstructure denser, in particular, in grain boundaries. Hence, the diffusion and intermixing of Cu through TaN film can be blocked effectively due to the discontinuous grain boundaries, which is expected to improve the barrier properties much better than reactive sputtered TaN. The test sample structure is Cu (200 nm)/ TaN (30 nm)/SiO$_2$ (250 nm)/Si and the diffusion barrier properties were evaluated by electrical measurement. Furthermore, XRD, SIMS, AFM and RBS were employed in conjunction with electrical measurements to examine the failure mechanism.

2. Experimental procedure

TaN films of 30 nm thickness were deposited onto SiO$_2$ (250 nm)/Si substrates by using IMP sputtering at N$_2$ ambient. Si wafers were cleaned in 10:1 diluted HF solution and rinsed in deionized water before SiO$_2$ deposition. The SiO$_2$ deposited Si substrate was loaded into an IMP sputtering chamber for deposition of TaN (30 nm) and subsequently Cu (200 nm) without breaking the vacuum. A detailed IMP deposition process has been described elsewhere [11]. The sample was annealed in nitrogen ambient up to 950°C from 350°C with 100°C intervals. 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 the reaction product phases and the interdiffusion of the elements across the interface, respectively. XRD, SEM, AFM, SIMS and RBS were employed in conjunction with electrical measurements to examine the failure mechanism.

3. Results and discussion

Fig. 1 shows the sheet resistance of the Cu/TaN/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 unreacted copper thin film since the copper film (250 nm and 1.7 μΩ cm) is much thicker and has a markedly lower resistivity than that of the TaN film (30 nm and 380 μΩ cm) and any reaction products. Since the top Cu layer of 200 nm carries nearly all the current, the sheet resistance measurements monitor the condition and the quality of the Cu overlayer. 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 to 800°C. However, after annealing at 850°C, the color of the sample is observed to change from Cu color to gray, and the sheet resistance of the

sample undergoes an abrupt rise because of the breakdown of the diffusion barrier. It results from the severe intermixing and reactions between copper and the underneath films. A similar behavior was observed by Kim et al. [3] and Tsai et al. [10] in CVD and PVD deposited TaN and Ta$_2$N between Cu and SiO$_2$, while the IMP-TaN has a much higher thermal stability than that of CVD deposited or reactive sputtered TaN. It is most probably due to the extension and densification of TaN grain boundaries and the less carbon and oxygen concentrations in IMP TaN than PVD and CVD films. When TaN is deposited by IMP sputtering, the individual grains are tightly packed and hence the packing density of TaN films increases considerably, leading to a good matching and densification of the grain boundaries of TaN films as shown in Fig. 2. Correspondingly, the effectiveness of TaN film as a Cu diffusion barrier is enhanced by suppressing the fast diffusion and intermixing of Cu through TaN film.

XRD analysis identified the intermixing and new phase formation for the Cu/TaN/SiO$_2$/Si structure annealed up to 950°C. As shown in Fig. 3, there is a distinction in XRD spectra between samples annealed below and above 750°C. Below 750°C, only a strong pure Cu (200) peak is observed at 74°, except for as deposited sample which has Cu (200) and Cu (111) peak at 43°. Any reaction involving Cu, Ta, O or Si was not observed. Distinctly, at 750°C, several new peaks are found at around 23, 29 and 36° and identified as TaO (001), Ta$_2$O$_5$ (100) and, Cu$_2$O (111) respectively. Here, three sources of oxygen atoms forming Cu$_2$O, TaO and Ta$_2$O$_5$ will be considered. Firstly, oxygen atoms from the SiO$_2$, which is very likely to happen, but were excluded for the following reasons. Jang et al. [12] and Wang et al. [13] reported that the integrity of SiO$_2$ in the Cu/Ta/SiO$_2$/Si structure was maintained up to 800°C,
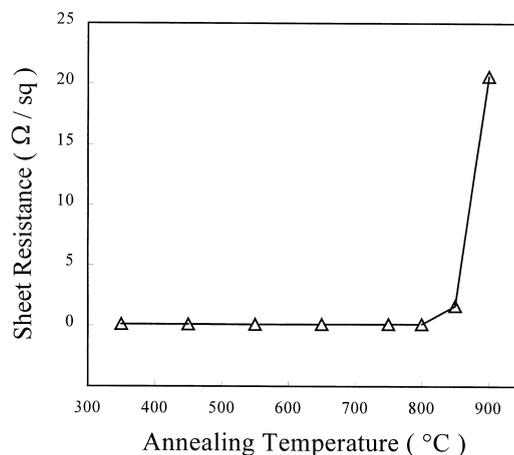

Fig. 1. Sheet resistance of Cu/IMP-TaN/SiO$_2$/Si structure as a function of annealing temperature.

being examined by the AES depth analysis, and the SiO_2/Ta system is free from any reaction for anneals below 900°C. The second source is oxygen atoms were incorporated with Ta metal film from the deposition ambient during the Ta deposition and decorating the grain boundaries [6]. Fig. 4 shows the oxygen and
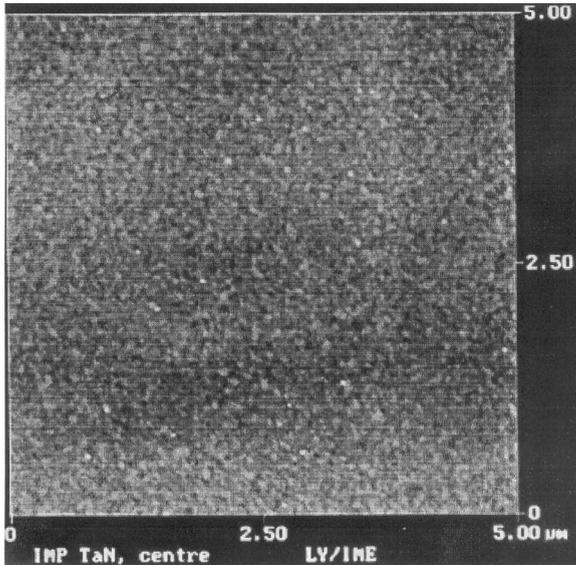
carbon concentration and the depth profile in IMP-TaN, being examined by SIMS analysis. Lastly, oxygen atoms were incorporated from the annealing ambient, but this was excluded because it cannot explain the sudden emergence of Cu_2O at 750°C annealing, based on the report by Yang et al. [14] that Cu doesn't react with O_2 any more once the amount of Cu_2O on the surface reaches some critical value.

Annealing at 750°C makes Cu and Ta start to react with the O_2 existing in the grain boundaries of TaN [15]. Cu atoms that diffuse into TaN via local defects react with O_2 and form Cu_2O around the Cu/TaN interface and in the TaN grain boundaries. As per TaO and Ta_2O_5, the amount is not likely to be crucial since the thermal energy of 750°C is not sufficient to break the Ta–N bonding [16]. Some unstable Ta in the TaN layer, which is probably near the surface or local defects, react with adjoining O_2 to make TaO or Ta_2O_5. By annealing at 800°C, a new peak of $CuTa_{10}O_{26}$ appeared, probably due to the reaction among TaO, Ta_2O_5, Cu_2O, Ta and Cu at the interface of Cu/TaN. The peaks of a new compound were observed very close to tantalum oxide peaks. We can speculate that this new compound coexists with tantalum oxides, reacting each other. The perceivable uprising of sheet resistance is the next stage.

$CuTa_{10}O_{26}$ can be described as Ta rich compound being formed near the interface or in the TaN layer. With annealing at 850°C and above, the new compound ($Cu_5Ta_{11}O_{30}$) turns up at 850°C and becomes dominant

Fig. 2. AFM measurement result for IMP-TaN (amorphous): surface roughness (RMS ~ 0.369 nm).
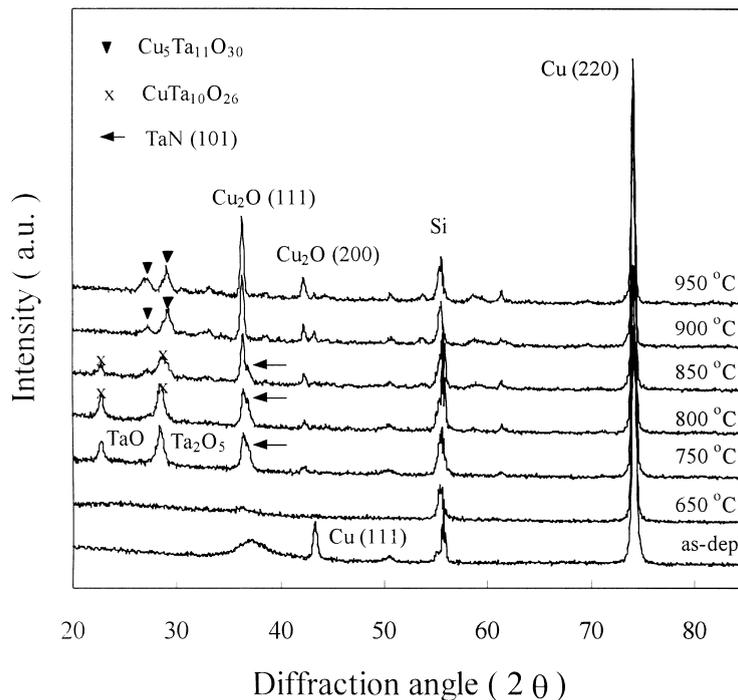

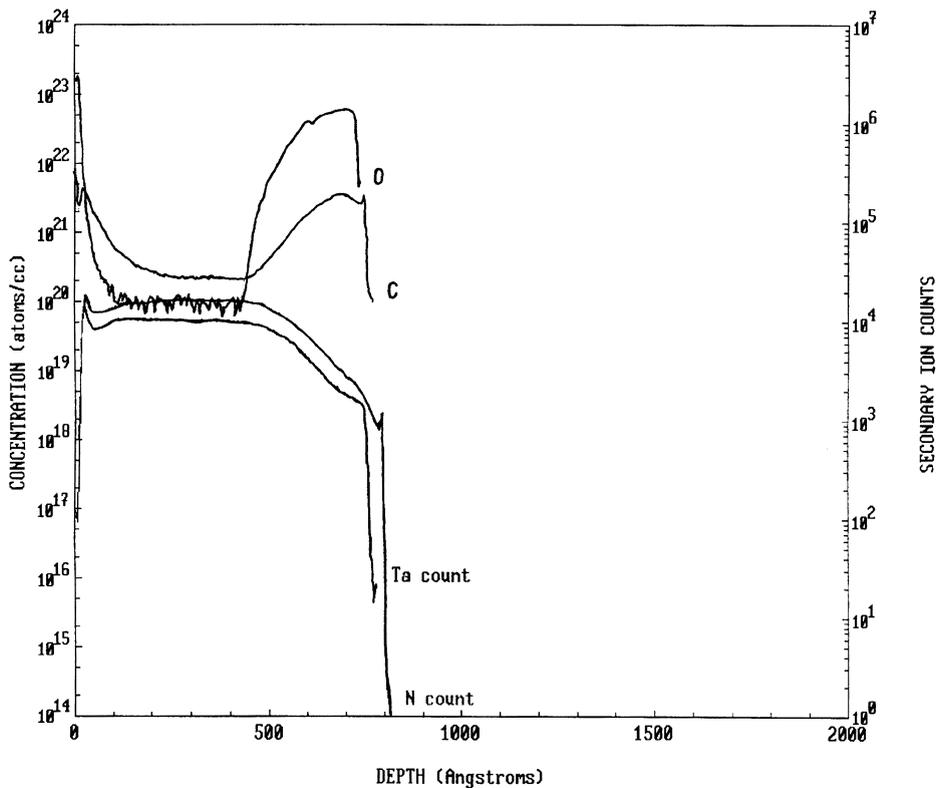Fig. 3. XRD patterns of the Cu/IMP-TaN (30 nm)/SiO_2/Si structure annealed at various temperatures.

Fig. 4. SIMS depth profile for oxygen and carbon atoms for IMP-TaN.
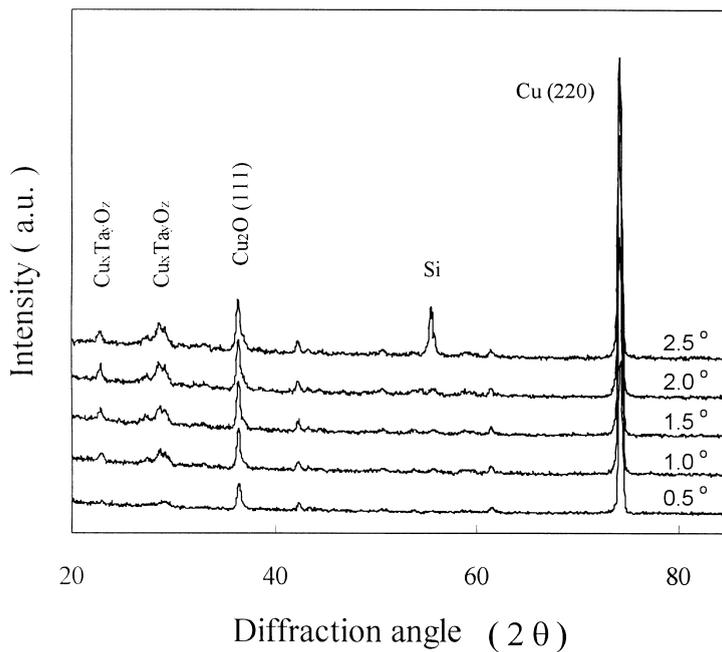

Fig. 5. XRD patterns of the Cu/IMP-Ta/SiO$_2$/Si sample annealed at 850°C for 35 min with various X-ray incident angles.

over $CuTa_{10}O_{26}$ at 900°C. $Cu_5Ta_{11}O_{30}$ has a copper content about five times as much as that of $CuTa_{10}O_{26}$. It costs the loss of conductive copper atoms in the copper layer, which can explain the escalation of sheet resistance at 900°C shown in Fig. 1. Hence, it can be concluded that the loss of copper by forming the

$Cu_5Ta_{11}O_{30}$ compound brought about the abrupt rise of sheet resistance at 900°C.

In order to examine the mechanism in which the intermixing occurs, the intermixed samples (annealed at 850°C) were scanned with increasing scan angles from 0.5 to 2.5° and two Cu compounds ($CuTa_{10}O_{26}$ and
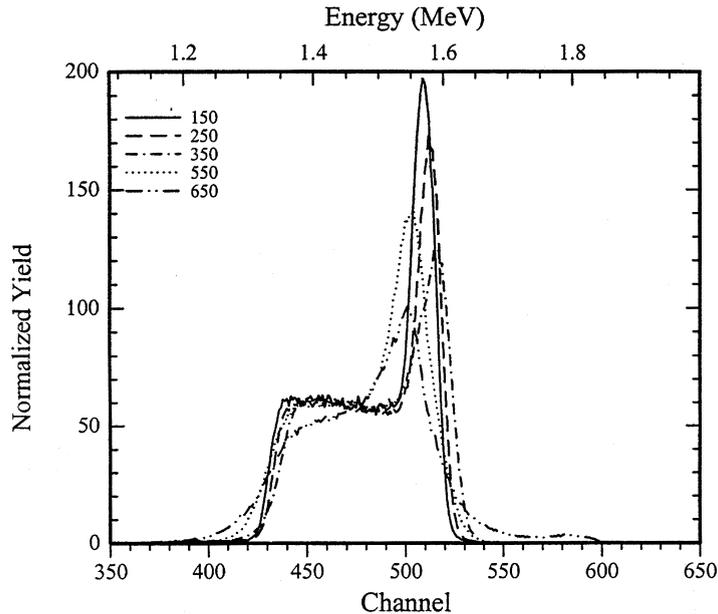

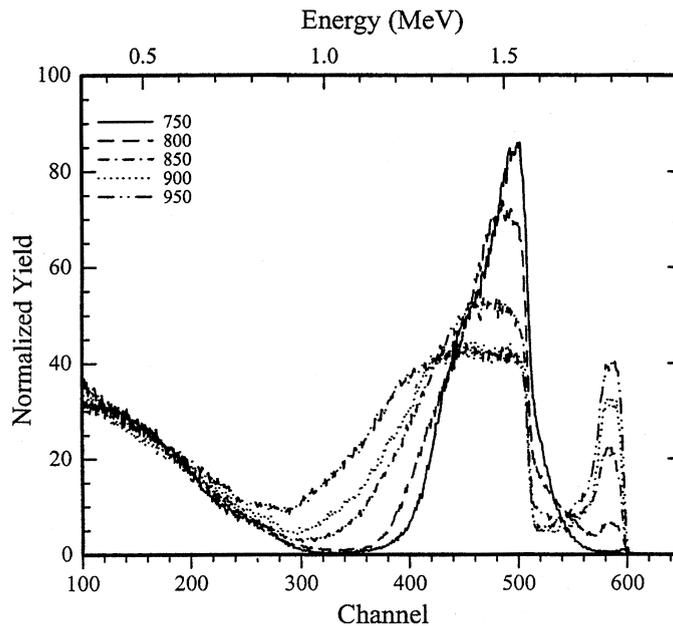Fig. 6. RBS depth profile of the Cu/IMP-TaN/SiO$_2$/Si structure annealed for 35 min at 150, 250, 350, 550 and 650°C.

Fig. 7. RBS depth profile of the Cu/IMP-TaN/SiO$_2$/Si structure annealed for 35 min at 750, 800, 850, 900 and 950°C.

$Cu_5Ta_{11}O_{30}$) formed by the intermixing were closely monitored. As shown in Fig. 5, the peak intensities do not change significantly with the scan angles of 1, 1.5, 2 and 2.5° except for 0.5°, showing that Cu, Ta, and O atoms were intermixed well except for the top surface of copper layer. An appearance of small TaN peaks at 750°C shows that the crystallization temperature of amorphous IMP-TaN is higher than that of Sun et al. [17] who reported that a mixture of amorphous and crystalline Ta_2N film crystallized after annealing at 600°C for 65 min.

SEM micrographs show (not shown here) that the copper surface did not exhibit any change up to 750°C and circular dots were observed thereafter. These dots might be the sites of the initial copper compounds formed by any interdiffusion mechanism. Similar phenomena were observed by Holloway et al. [6] using Ta and Wang et al. [18] using TiN as the diffusion barriers.

Figs. 6 and 7 show the RBS depth profile of the Cu/ $TaN/SiO_2/Si$ sample annealed for 30 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 appears 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 with 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.

4. Conclusion

The diffusion barrier properties of IMP deposited TaN between Cu and SiO_2 have been investigated in the Cu (200 nm)/TaN (30 nm)/SiO_2 (250 nm)/Si multi-layer structure. The 30 nm thick IMP-TaN was found to be stable up to 800°C, which is much better than CVD and conventional PVD deposited TaN films. It was found that IMP sputtering of TaN made the individual grains tightly packed and hence increased the packing density of the TaN film considerably, leading to a good matching and densification of the grain boundaries of the TaN film. Correspondingly, the effectiveness of the TaN film as a Cu diffusion barrier was enhanced by suppressing the fast diffusion and intermixing of Cu through TaN film. The abrupt rise of the sheet resistance was attributed to the loss of copper by forming the $Cu_5Ta_{11}O_{30}$ compound at 900°C annealing.

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