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Study of diffusion barrier properties of ionized metal plasma (IMP) deposited tantalum (Ta) between Cu and SiO_2

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Abstract

The diffusion barrier properties of ionized metal plasma (IMP) deposited Ta between Cu and SiO_2 have been investigated in the Cu (200 nm)/Ta (30 nm)/SiO_2 (250 nm)/Si multi-layer structure. The IMP-Ta thin film shows better Cu diffusion barrier properties than CVD (chemical vapor deposition) and conventional PVD (physical vapor deposition) deposited Ta film. 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 XRD, scanning electron microscopy (SEM), secondary ion mass spectroscopy (SIMS) and Rutherford backscattering spectroscopy (RBS) in conjunction with electrical measurements. The 30 nm thick IMP-Ta was found to be stable up to 650°C for 35 min.

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

1. Introduction

Copper has drawn much attention as an interconnect material for deep sub-micron circuits due to its low resistivity and high electromigration and stress migration resistance superior to Al and Al-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, particularly, the diffusion of Cu into the 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 (Ta) is presently one of the most widely used copper diffusion barrier materials in copper metallization 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 physical vapor deposition (PVD) deposited Ta films to be excellent metallurgical diffusion barriers between copper and Si [6,7]. However, their processes have serious limitations owing to the poor step coverage caused by the shadowing effect for small feature sizes (< 0.35 μm) and high aspect ratio contact and via holes. Accordingly, Ta barriers deposited by chemical vapor deposition (CVD) have received much attention owing to their superior conformality compared to sputtered Ta barriers. However, it is well known that CVD-Ta has poor metallurgical stability and much higher resistivity than PVD-Ta.

In our present work, Ta barriers were prepared 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 metallurgical diffusion barrier properties. IMP deposition results in denser Ta film microstructures, particularly at grain boundaries. Hence, the diffusion and intermixing of Cu through Ta film can be blocked effectively due to the discontinuous grain boundaries, and it is expected that the barrier

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properties be much improved over those from CVD Ta films. The test sample structure is Cu (200 nm)/Ta (30 nm)/SiO_2 (250 nm)/Si and the diffusion barrier properties were evaluated by electrical measurements. Furthermore, X-ray diffracton (XRD), scanning electron microscopy (SEM), Secondary ion mass spectroscopy (SIMS) and Rutherford backscattering spectroscopy (RBS) were employed in conjunction with electrical measurements to examine the failure mechanism.

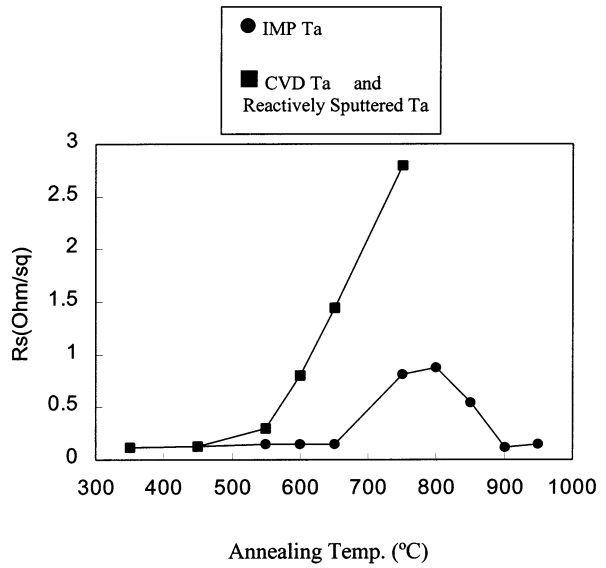

Fig. 1. Sheet resistance of Cu/IMP-Ta/SiO_2/Si structure as a function of annealing temperature (compared with CVD and reactively sputtered Ta).

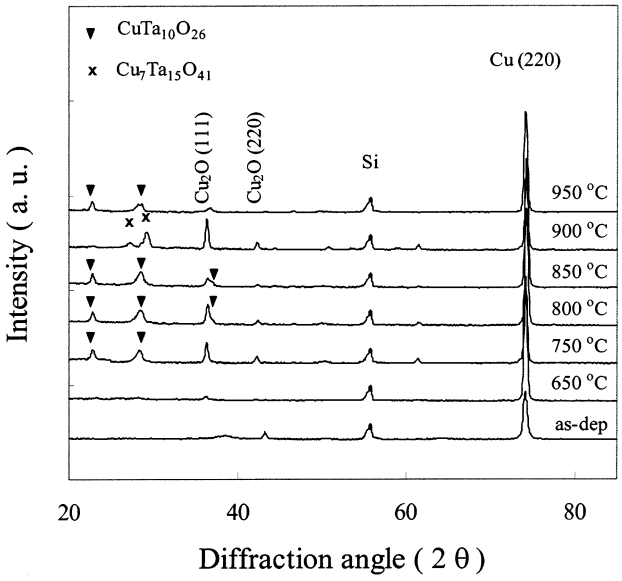

Fig. 2. XRD patterns of the Cu/IMP-Ta (30 nm)/SiO_2/Si structure annealed at various temperatures.

2. Experimental procedure

Tantalum films of 30 nm thickness were deposited onto SiO_2 (250 nm)/Si substrates by using IMP sputtering in Ar 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 substrates were loaded into the IMP sputtering chamber for the deposition of Ta (30 nm) and subsequently Cu (200nm) without breaking the vacuum. The IMP deposition process has been described in detail elsewhere [8]. The samples were annealed in Ar ambient up to 950 from 350 with 100°C intervals. The resistivities of as-deposited and annealed samples were measured by four-point probe to survey the overall reactions involving Cu. XRD was used for the analysis of reaction product phases and the interdiffusion of the elements across the interface, respectively. XRD, SEM, 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/Ta/SiO_2/Si structure as a function of annealing temperature in Ar 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 μm) is much thicker and has a markedly lower resistivity than Ta film and any reaction products. Since the top Cu layer of 100 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 350°C due to the reduction of crystal defects and grain growth in the copper film, and then remains constant up to 650°C. The abrupt rise in sheet resistance after 650°C indicates that there is a significant intermixing and reactions involving the Cu layer and the underneath films. A similar behavior was observed for CVD or reactively sputtered Ta between Cu and SiO_2 while the IMP-Ta has a much higher thermal stability than that of CVD or reactive sputtered Ta. This is most likely due to the extension and densification of the Ta grain boundaries and the reduced carbon and oxygen concentrations in the IMP Ta film. It was reported [9] that when Ta film is deposited by IMP sputtering, the individual grains are tightly packed and hence the packing density of Ta films increases considerably, leading to a good matching and densification of the grain boundaries of Ta film. In the dense microstructure, particularly, in the grain boundaries, the diffusion and intermixing of Cu, Ta, O, and Si atoms can be blocked effectively due to the discontinuous grain boundaries. Hence, Ta microstructure in smaller grain

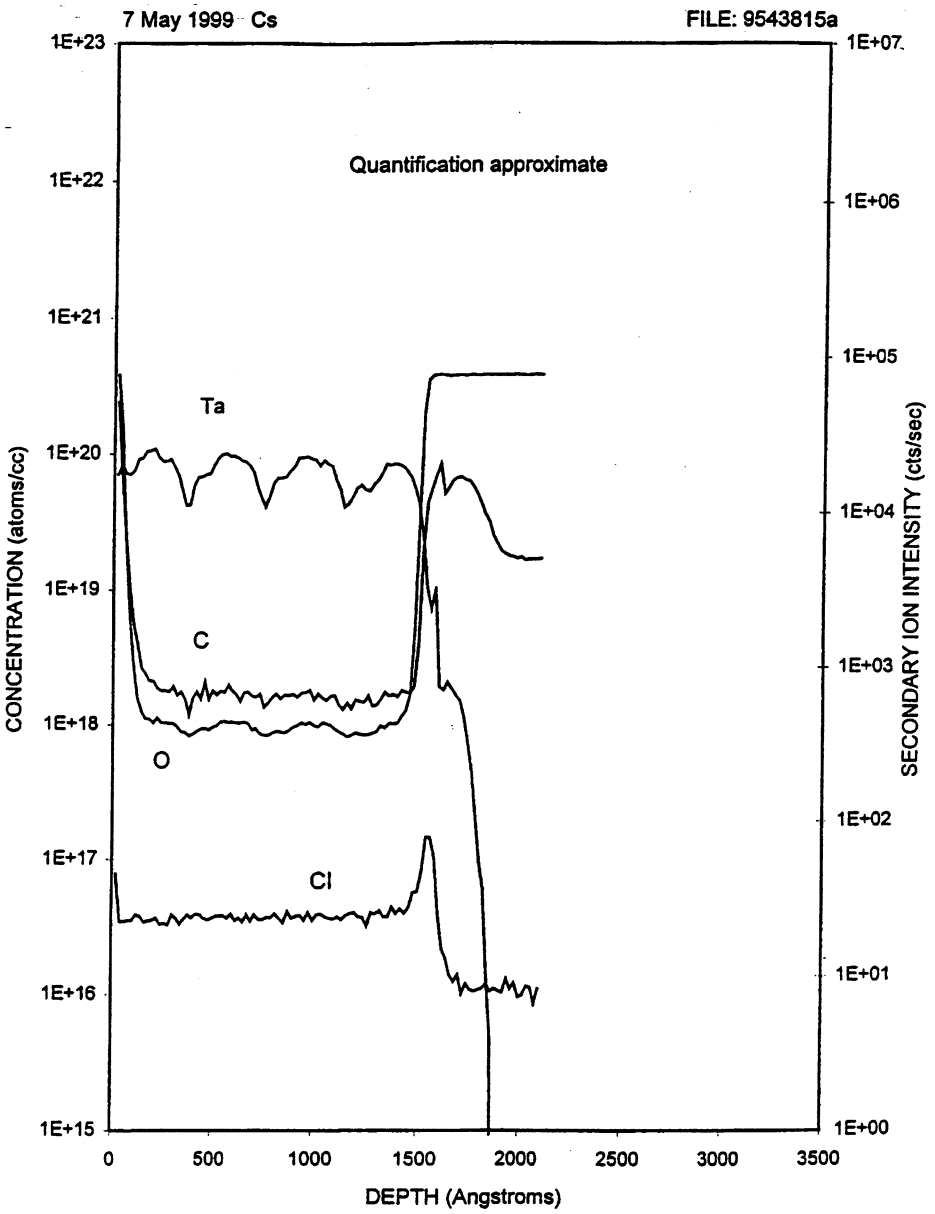

Fig. 3. SIMS depth profile for oxygen and carbon atoms for IMP-Ta.

sizes, in other words, in denser grain boundaries, can retard the intermixing and diffusion of Cu, Ta, O, and Si atoms due to blocking of the fast pathway through grain boundaries, which can account for a higher thermal stability of Cu/IMP-TaN/SiO_2/Si.

The X-ray diffraction measurements were performed with a RIGAKU model RINT2000 diffractometer using a $\gamma = 2.5°$ grazing incident angle geometry. The K_α Cu X-ray ($\lambda = 1.542$ A) detection was done from $2\theta =$ 20 to $2\theta = 85°$ with scan speed of 4° min^{-1} and scan step 0.05°. The grazing incident angle of 2.5° identified the intermixing and new phase formation for the Cu/Ta/SiO_2/Si structure annealed up to 950°C. As shown in Fig. 2, 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°. Any reaction involving Cu, Ta, O or Si was not observed. Distinctly, at 750°C, several new peaks are found at around 23 and 29°, which were identified as $CuTa_{10}O_{26}$ (001) and $CuTa_{10}O_{26}$ (200), respectively. Also, you can see the small peak of $CuTa_{10}O_{26}$ (201) at 37° after annealing at 800°C. Here, three sources of oxygen atoms forming $CuTa_{10}O_{26}$ will be considered. Firstly, oxygen atoms from the SiO_2, which is very likely to happen, but were excluded by the following reasons. Jang et al. [6] and Wang et al. [10] reported that the integrity of SiO_2 in the Cu/Ta/SiO_2/Si structure was maintained up to 800°C, being examined by 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 incorporated in the Ta metal film from the deposition ambient during the Ta deposition and decorating the grain boundaries [11]. Fig. 3 shows the oxygen and carbon concentration and the depth profile in IMP-Ta, being examined by SIMS analysis. Lastly, oxygen atoms can be incorporated from the annealing ambient, but this mechanism was excluded because it cannot explain the sudden emergence of Cu_2O at 750°C annealing, based on the report by Yang et al. [10] that Cu doesn't react with O_2 anymore once the amount of Cu_2O on the surface reaches some critical value.

At 750°C annealing temperature the Cu and the Ta start to react with the O_2 existing in the grain boundaries of Ta. This results in the loss of conductive copper atoms in the copper layer, which can explain the escalation of sheet resistance at 750°C shown in Fig. 4. Hence, it can be concluded that the loss of copper by forming Cu–Ta–O compound brought about the abrupt rise of sheet resistance at 750°C. In order to examine the mechanism in which the intermixing occurs, X-ray diffraction measurements with different grazing incident angles from $\gamma = 0.5$ to 2.5° were performed on the samples (annealed at 800°C). The penetration depth t of X-ray, perpendicular to the film surface, can be determined by the absorption coefficient μ of the film (for Cu, $\mu = 460.25\ cm^{-1}$) and grazing incident angle γ [12]. The penetration depth, t is;

$$t = \frac{\sin \gamma}{\mu}$$

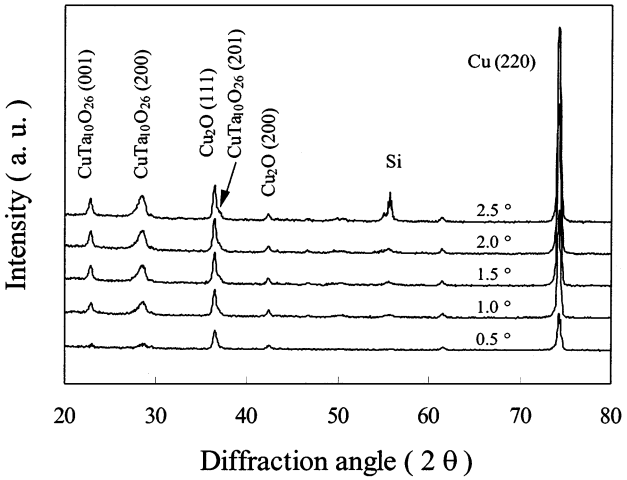

Fig. 4. XRD patterns of the Cu/IMP-Ta (30 nm)/SiO_2/Si structure annealed at 800°C for 35 min with various X-ray incident angles.

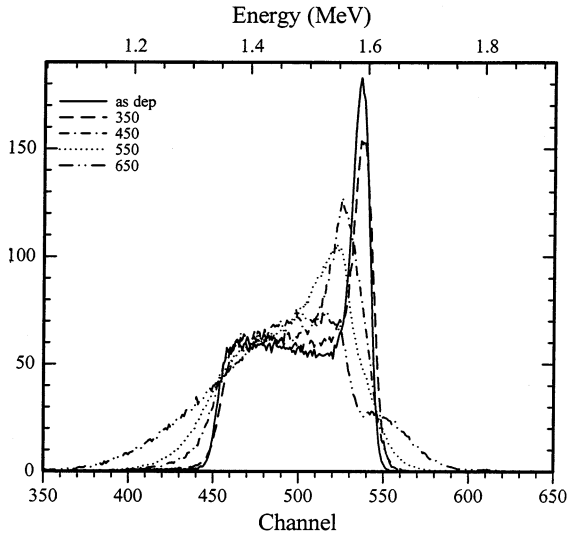

Fig. 5. RBS depth profiles of the Cu/IMP-Ta/SiO_2/Si structure annealed for 30 min at 350, 450, 550, and 650°C.

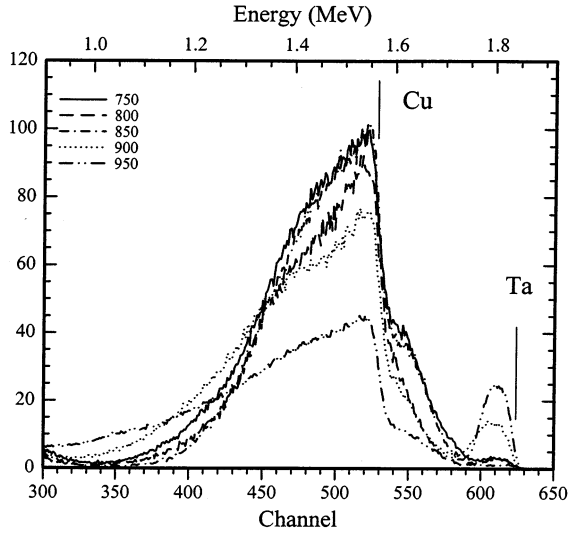

Fig. 6. RBS depth prifile of the Cu/IMP-Ta/SiO_2/Si structure annealed for 30 min at 750, 800, 850, 900, and 950°C.

The XRD represents the upper 189 nm of the Cu film in the case of $\gamma = 0.5°$, and $t > 200$nm in the case of $\gamma = 1$, 1.5, 2, and 2.5°. With more than 1.0° incident angles, the contribution comes not only from the whole layer of 200 nm Cu film but also from the interfaces and underneath layer. As shown in Fig. 5, the peak intensity of $CuTa_{10}O_{26}$ at the grazing angle of $\gamma = 1°$ is much higher than that of $\gamma = 0.5°$ and remains more or less constant with increasing grazing angles ($\gamma = 1.5$, 2, and 2.5°). It indicates that the $CuTa_{10}O_{26}$ formed and stayed near the initial interface of Cu and Ta layer.

SEM micrographs show (not shown here) that the copper surface did not exhibit any change up to 650°C and circular dots were observed at beyond 650°C and grew with the increasing temperature. These dots might be the part of Ta film exposed to the ambient due to Cu film agglomeration. Similar phenomena were observed by Holloway et al. [11] using Ta as a diffusion barrier of Cu. EDX (energy dispersive X-ray) analysis was performed on the circular dots and the agglomerated Cu film for the sample annealed at and beyond 800°C. It revealed that the circular dot had much lower Cu

concentration than the other area, supporting that the circular dot might be the part of Ta film exposed to the ambient due to Cu film agglomeration.

Fig. 5 and Fig. 6 show the RBS depth profile of the $Cu/Ta/SiO_2/Si$ sample annealed for 30 min at various temperatures. For the sample annealed at 550°C, the RBS spectra show 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 750°C, a new Ta peak appears at the energy level of 1.836 MeV and grows, and the back edge of the Cu signal becomes more graded with increasing temperature, implying that Cu film starts to agglomerate, thus exposing part of the Ta film to the ambient.

4. Conclusion

The diffusion barrier properties of IMP deposited Ta film between Cu and SiO_2 have been investigated in the Cu (200 nm)/Ta (30 nm)/SiO_2 (250 nm)/Si multi-layer structure. The 30 nm thick IMP-Ta was found to be stable up to 650°C, which is much better than CVD and conventional PVD deposited Ta films. We concluded that it is because IMP sputtering of Ta made the individual grains tightly packed and hence increased the packing density of Ta film considerably, leading to a good matching and densification of the grain boundaries of Ta film. Correspondingly, the effectiveness of Ta film as a Cu diffusion barrier was enhanced by suppressing fast diffusion and intermixing of Cu through Ta film. The abrupt rise of the sheet resistance was attributed to the loss of copper by forming $CuTa_{10}O_{26}$ compound at 750°C annealing.

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