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Oxidation Resistance of Ti Oxide Self-Formed Barrier in Cu Interconnects

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1. Introduction

As a Cu wire width reduces to a deep sub-micron scale in ultra-large scale integrated devices, a large resistance-capacitance delay is one of critical material-related issues. One of the primary factors for the increase in electrical resistivity of the Cu wires is reducing a Cu cross-sectional area due to increase of barrier volume fraction in the wire. We have recently proposed a new fabrication technique to prepare ultrathin TiO_x self-formed barrier (SFB) for nanoscale Cu wires [1-3]. The TiO_x SFB using Cu(Ti) alloy seed was applied to 45 nm-node dual-damascene interconnects and its performance has been evaluated [4]. Compared with conventional Ta/TaN barrier interconnects, resistance of the vias and narrow lines was about 70% and 30% lower, respectively, and their distributions were dramatically improved. Also, breakdown voltage and TDDB performance were similar, indicating that the TiO_x SFB has sufficient barrier strength to prevent Cu diffusion into dielectrics. However, EM reliability was worse than that for the Ta/TaN barrier, probably because of Cu oxidation at the interface due to moisture from pores in the low-k dielectrics [5]. Thus, in this study, oxygen-induced change of barrier structure and barrier strength to prevent Cu diffusion into SiO_2 for Cu/Ta/TaN and Cu/TiO_x samples was investigated.

2. Experimental Procedures

Ta/TaN barriers with 20 nm in thickness of each layer were deposited on SiO_2/Si substrates in a radio frequency magnetron sputter system, and followed by about 80 nm-thick Cu films without breaking the vacuum. The TiO_x SFB was prepared after annealing Cu(Ti)/SiO_2 samples at 500°C for 10 h or at 600°C for 3 h in ultra high vacuum. Those samples with the two types of barriers were annealed at 400°C for 1 h with oxygen contents (2~40 $ppmO_2$). In addition, the samples with the TiO_x SFB were annealed at 500°C for 1 h. The resistivity of the Cu films was measured by van der Pauw method. To investigate stability of the barrier structure and Cu diffusion into SiO_2 as a function of oxygen contents, we employed the Rutherford backscattering spectrometry (RBS) technique, cross-sectional transmission electron microscopy (TEM) observation, and an X-ray Photoelectron spectroscopy (XPS) technique with simultaneous Ar etching.

3. Results and Discussion

I. Oxidation Resistance of Barriers in Cu Interconnects

Figure 1 shows oxygen-induced resistivity change of Cu films on the two-types of barriers at 400°C. The significant resistivity increase was observed in the Cu films on the Ta/TaN barrier after annealing with oxygen contents more than 10 ppm. In contrast, the resistivity of the Cu films on the TiO_x SFB did not increase in all oxygen contents (about 3μΩcm). Figure 2 shows typical RBS spectra of the Cu/Ta/TaN samples after annealing with oxygen contents of 2 and 10 ppm, for comparison, with those before annealing. The RBS spectra before and after annealing in 2 $ppmO_2$ overlapped each other, indicating a stable barrier and no Cu diffusion into SiO_2 (Fig. 2(a)). Similar spectra were observed in Cu/TiOx samples in all oxygen contents (not shown). In contrast, penetration of both Ta and Cu atoms beneath each layer was observed after annealing at 10 $ppmO_2$ (Fig. 2(b)). The Ta peak intensity significantly decreased, and the peak width increased to about one and a half as thick as the original. Those suggest that almost of the Ta/TaN layer were oxidized. Figure 3 shows cross-sectional TEM images of the as-deposited and annealed Cu/Ta/TaN samples. Although the RBS spectra for the samples before and after annealing in 2 $ppmO_2$ was not obviously different, lens-like reactants with contrast in-between Cu and Ta layers were found to form at the interface (Fig. 3(b)). After annealing in 10 $ppmO_2$, lateral growth of reactants and layer formation with about 45 nm in thickness was observed (Fig. 3(c)). The oxygen-induced change of the barrier thickness is consistent with the RBS result. The smooth Cu surface was lost, probably induced by significant Cu oxidation. Thus, oxidation resistance of the Ta/TaN barrier was worse than that of the TiO_x SFB. A part of the Ta/TaN barrier was started to be collapsed at 400°C even in 2 $ppmO_2$, and its barrier strength to prevent Cu diffusion into SiO_2 was losing in more than 10 $ppmO_2$.

II. Oxidation Resistance of the TiO_x Self-formed Barrier

Although the TiO_x SFB exhibited superior barrier stability at 400°C even in 40 $ppmO_2$, the barrier strength was losing at 500°C with increasing oxygen content. The oxygen-induced resistivity increase for the Cu films on the TiO_x SFB was not observed at 400°C, while resistivity increase with increasing oxygen content was observed at 500°C (Fig. 4). Figure 5 shows typical RBS spectra of the Cu/TiO_x samples after annealing at 500°C with oxygen contents of 2, 5, and 10 ppm. The TiO_x SFB was corresponding to the Ti peaks beneath channel 700, and oxygen-induced increase of the Ti peak width such as that in the oxidized Ta/TaN barrier was not clear in all oxygen contents. However, the RBS spectrum intensity in channel between 550 and 750 in 5 and 10 $ppmO_2$ was obviously higher than that before annealing, indicating Cu diffusion below the TiO_x SFB. Thus, the barrier strength of the TiO_x SFB was losing in more than 5 $ppmO_2$ at 500°C. Figure 6 shows cross-sectional TEM images of the Cu/TiO_x samples after annealing at 500°C in 2 and 5 $ppmO_2$. The continuous and very thin TiO_x SFB was preserved in 2 $ppmO_2$, in contrast, was not preserved well in 5 $ppmO_2$. The interface including the TiO_x SFB became wavy, and the barrier may be not continuous, suggesting lost of the barrier strength. Figures 6(c) and 6(d) were selected area diffraction images obtained in the white circles in Fig. 6(a) and 6(b), respectively. In addition to Cu diffraction spots, more Cu_2O spots were observed in 5 $ppmO_2$ than in 2 $ppmO_2$. The oxygen-induced Cu oxidation was suggested to facilitate near the interface in 5 $ppmO_2$, resulting in collapse of barrier continuity. Those were confirmed in XPS measurements (Fig. 7). The Ti depth distribution spread and Cu_2O formed near the interface at 500°C in 5 $ppmO_2$, although the Cu_2O formation near the interface was not observed in 2 $ppmO_2$. Such the Cu oxidation near the interface induced the collapse of barrier continuity. A volume fraction of Ti_2O_3 decreased and that of TiO increased in 5 $ppmO_2$, comparing with those in 2 $ppmO_2$. The decrease of oxygen content in the TiO_x SFB could facilitate Cu oxidation near the TiO_x SFB.

4. Conclusions

Oxygen-induced change of barrier structure and barrier strength

to prevent Cu diffusion into SiO_2 for Cu/Ta/TaN and Cu/TiO_x samples was investigated. Oxidation resistance of the Ta/TaN barrier was worse than that of the TiO_x SFB. The lens-like reactant with contrast in-between Cu and Ta layers formed at the interface at 400°C even in 2 ppmO_2, and grew into a thicker layer than original barrier in 10 ppmO_2. Significant Cu diffusion below the original Ta/TaN layer was observed in more than 10 ppmO_2. On the other hand, the TiO_x SFB exhibited superior barrier strength at 400°C even in 40 ppmO_2. However, the TiO_x SFB became not continuous due to Cu oxidation near the interface, and its barrier strength was losing at 500°C in more than 5 ppmO_2.

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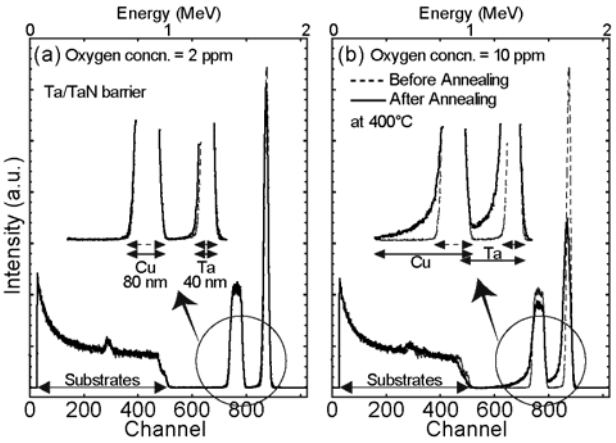

Fig. 2 RBS spectra for Cu/Ta/TaN samples before and after annealing at 400°C for 1h in 2 and 10 ppmO_2. Inset figures are enlargements in the circle areas.

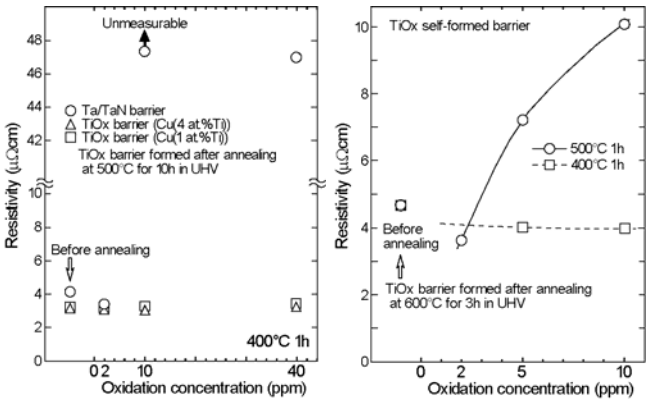

Fig. 1 Resistivity variation with oxygen contents for Cu films on the Ta/TaN and TiO_x barriers after annealing at 400°C for 1h.

Fig. 4 Resistivity variation with oxygen contents for Cu films on the TiO_x barriers after annealing at 400°C and 500°C for 1h.

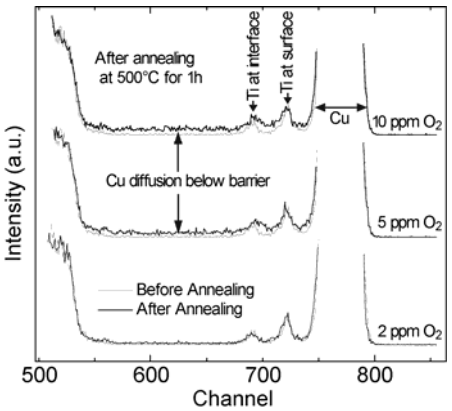

Fig. 5 RBS spectra for Cu/TiO_x samples before and after annealing at 500°C for 1h in 2, 5, and 10 ppmO_2..

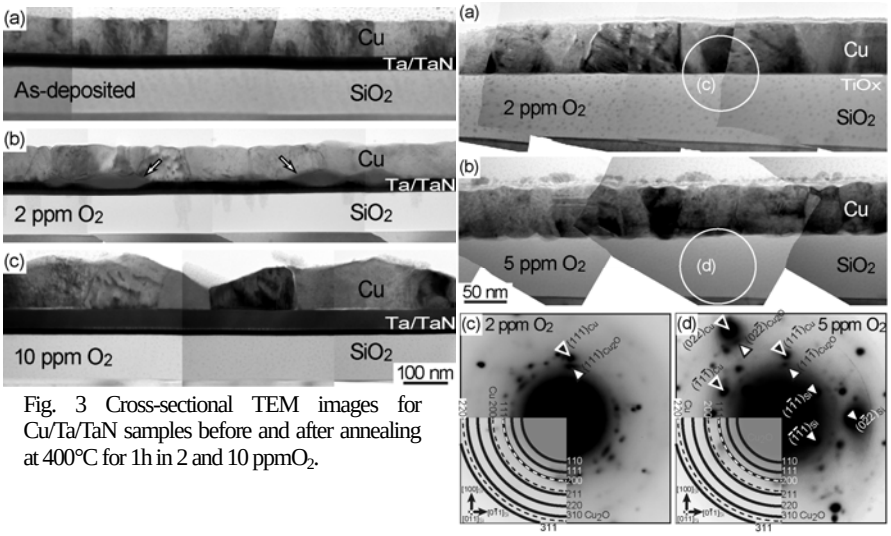

Fig. 3 Cross-sectional TEM images for Cu/Ta/TaN samples before and after annealing at 400°C for 1h in 2 and 10 ppmO_2.

Fig. 6 (a), (b) Cross-sectional TEM images for Cu/TiO_x samples after annealing at 500°C for 1h in 2 and 5 ppmO_2. (c), (d) SAD images obtained in white circle areas.

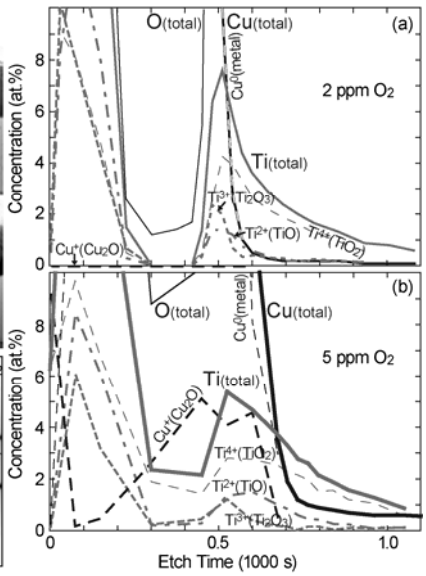

Fig. 7 Elemental depth profiles of Cu/TiO_x samples after annealing at 500°C for 1 h in 2 and 5 ppmO_2, obtained by simultaneous Ar etching and XPS measurements.