Structure Analyses of Ti-Based Self-Formed Barrier Layers

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1. Introduction

Self-formed Ti-based barrier layer using Cu(Ti) alloy seed was applied to 45nm-node dual-damascene interconnects and has been evaluated its performance [1]. Thin Ti-based barrier layer was successfully formed along the interface between Cu(Ti) and dielectrics. Compared with conventional Ta/TaN barrier interconnects, resistance of the via and narrow line decreased to about 70% and 30%, respectively, and their distributions were drastically improved, Also breakdown voltage and TDDB performance were similar, indicating that the self-formed Ti-based barrier has enough barrier properties against Cu diffusion into dielectrics.

In our previous studies based on transmission electron microscopy (TEM)/selected area diffraction (SAD) observation, the self-formed Ti-based barrier layers consist of amorphous Ti oxides (TiO_x) with crystalline Ti compounds (TiC, TiSi or TiN). The composition of the self-formed Ti-based barrier layers depended on dielectrics [2, 3]. However, the barrier structure and amorphous phases in the barrier layer were not directly identified. In this study, we employed an X-ray Photoelectron Spectroscopy (XPS) technique with simultaneous Ar etching, to investigate the structure and composites (Ti compounds) of the self-formed Ti-based barrier layers systematically with dielectrics.

2. Experimental Procedures

70nm-thick Cu(5at.%Ti) alloy films were deposited on SiOCH with low dielectric constants (low-k), SiO₂, and SiCN dielectric layers by a radio frequency magnetron sputtering technique. Their thickness (t), dielectric constants (k), and compositions are shown in Table 1. The samples were annealed in ultra high vacuum (UHV) at 600°C for 2h. In order to obtain depth dependence of composition of the Ti-based barrier layers, Ar etching and the XPS measurements were simultaneously carried out in the same vacuum chamber. In addition, cross-sectional TEM observations were also carried out for the annealed samples.

3. Results and Discussion

Figure 1 shows typical elemental depth profiles of the $Cu(5at.\%Ti)/SiO_2$ sample after annealing in UHV at 600°C for 2h, obtained by simultaneous Ar etching and XPS measurements. Ti segregation was observed around etch times between 18000 s and 25000 s, indicating that the Ti-based barrier layer formed at the interface between the Cu(Ti) alloy film and the SiO₂ layer. Similarly, Ti segregation at the interfaces was observed in all the other samples.

Figure 2 shows portions of the XPS profiles around the binding energies of Ti 2p, C 1s, Si 2p, and N 1s, obtained from the middle of Ti-based barrier layers (etch time of about 21600 s) formed in the annealed Cu(5at.%Ti)/dielectric-layer samples. As shown in Fig. 2(a),

the XPS profiles around the Ti 2p binding energy (460 eV [4, 5]) were fitted by the sum of the XPS profiles of TiC, TiO₂, Ti₂O₃, TiO, and a background. Similarly, the XPS profiles around C 1s (284 eV [4]), Si 2p (99eV [6, 7]), and N 1s (398eV [8, 9]) were fitted as shown in Figs. 2(b), 2(c), and 2(d), respectively. Note that it was difficult to determine a volume fraction of TiSi in the annealed Cu(Ti)/SiO₂ sample due to a thin SiO₂ layer. Peak positions of Si 2p derived from TiSi and Si substrates are similar. The crystalline TiSi was identified by TEM/SAD in the Ti-based barrier layers formed on SiO₂ (Fig. 3). The TiSi peak area could be estimated from the XPS profile around Si 2p obtained in the Ti-based barrier layers formed beneath Cu(Ti) alloy films, although Si 2p peak intensity from a Si substrate increased with increasing etching time (Fig. 4).

Based on the peak area estimation from the XPS profile obtained in a certain depth of the Ti-based barrier layers, volume fractions of TiC, TiSi, TiN, TiO₂, Ti₂O₃, and TiO phases were determined by a ratio of each peak area to sum of peak areas. Figure 5 shows depth dependence of composition of the Ti-based barrier layers in the annealed Cu(Ti)/dielectric-layer samples. In the Cu(Ti)/SiO₂ sample, Ti-based barrier layer mainly consisted of Ti oxides (Fig. 5(a)). The Ti oxides were in amorphous state, since crystalline Ti oxides were not detected by TEM/SAD analyses (Fig. 3). Similarly, Ti-based barrier layers in the other samples (low-k1, low-k4, SiCN) consisted of a large amount of amorphous Ti oxides (50 ~ 75%), as shown in Fig. 5(b)-(d).

In addition to the amorphous Ti oxides, TiC were observed in the three samples except the Cu(Ti)/SiO₂ sample. The three dielectric layers such as low-k1, low-k4, SiCN consisted of carbon. The crystalline TiC was observed in the annealed Cu(Ti)/low-k1 and Cu(Ti)/SiCN samples, but not observed in the annealed Cu(Ti)/low-k4 sample [3]. This indicates that the TiC phase in the Cu(Ti)/low-k4 sample is in amorphous state. TiN was also observed in the Cu(Ti)/SiCN sample. The crystalline TiN was not observed in the Cu(Ti)/SiCN sample in the previous study [3], and thus the TiN phase is indicated to be in amorphous state. The volume fractions of TiC and TiN were estimated to be about 20%, and both phases occupied a small part of the Ti-based barrier layers. While, TiSi was observed in the Cu(Ti)/SiO₂ and Cu(Ti)/low-k4 samples, but not observed in the other samples. This is in good agreement with the previous study [3].

The crystalline Ti compounds such as TiC and TiSi tended to be formed beneath the Cu(Ti) alloy films. Some SAD patterns obtained in Cu(Ti)/low-k1 and Cu(Ti)/SiCN samples showed that orientation relationship between crystalline TiC and Cu grains (not shown). This is one of the evidences that TiC was formed beneath the Cu(Ti) alloy films. On the other hand, the amorphous phases such as TiO_x tended to be formed above the dielectric layers. The amorphous phases were believed to be formed continuously above the dielectric layers as shown in Fig. 6, and play an important role to prevent Cu diffusion into the dielectric layers.

4. Conclusions

XPS analyses identified the structure and component of the self-formed Ti-based barrier layers. The Ti-based barrier layers mainly consisted of amorphous Ti oxides such as TiO_2 , Ti_2O_3 , and TiO, regardless of dielectrics. In addition to the Ti oxides, the barrier layers consisted of Ti compounds such as TiC, TiSi, and TiN, depending on dielectrics. The Ti compounds such as TiC and TiSi were in crystalline state. They were formed beneath the Cu(Ti) alloy films, and had orientation relationship with the Cu(Ti) alloy films. The amorphous Ti oxides were formed above the dielectric layers. The amorphous Ti oxides are believed to be formed continuously above the dielectric layers and prevent Cu diffusion into the dielectric layers.

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Table 1 Thickness t (nm) and dielectric constants k of the dielectric layers and their compositions of C, O, Si and N (at.%).

| | t | k | С | 0 | Si | Ν |
|---------|-----|-----|------|------|------|------|
| Low-k1 | 440 | 3.0 | 17.0 | 24.9 | 18.8 | - |
| Low-k4 | 450 | 2.6 | ~14 | ~29 | ~18 | - |
| SiO_2 | 100 | 3.9 | - | 66.7 | 33.3 | - |
| SiCN | 200 | 4.8 | 21.4 | 0.5 | 25.0 | 12.8 |



Fig. 5 Depth dependence of volume fractions of Ti compounds in the Ti-based barrier layers formed on the $(a)SiO_2$, (b)low-k1, (c)low-k4, (d)SiCN layers after annealing.



15 110 Into Finding Energy (eV) 95 90 415 410 405 400 Binding Energy (eV) Fig. 2 Portions of the XPS profiles around the binding energies of (a)Ti 2p [4, 5], (b)C 1s [4], (c)Si 2p [6, 7], and (d)N 1s [9], obtained from the middle of the Ti-based barrier layers (etch time of about 21600 s) formed in the annealed Cu(5at.%Ti)/dielectric-layer samples.

(a) Surface (b) Cu(Ti) SiO₂ (b)



Fig. 3 (a)A cross-sectional TEM image of the annealed Cu(5at.%Ti)/SiO₂ sample. (b)An SAD image taken from the area marked with a broken circle in (a).

| Cu(Ti) | Cu(Ti) | | |
|-------------------------------------------|----------------------------------|--|--|
| Crystalline TiSi 🗄 | Crystalline TiSi 🖞 | | |
| | Amorphous TiČ | | |
| Amorphous TiOx | Amorphous TiOx | | |
| SiO ₂ C Cocentration 0 at.% | Low-k4 C Cocentration 14 at.% | | |
| | | | |
| Cu(Ti) | Cu(Ti) | | |
| Crystalline TiC ↓ | Crystalline TiC | | |
| | | | |
| Amorphous TiOx | Amorphous TiOx, TiN | | |
| Low-k1 C Cocentration | SiCN C Cocentration | | |

Fig. 4 Portions of the XPS profiles around the binding energies of the Si 2p peaks obtained in the annealed Cu(5at.%Ti)/SiO₂ sample, for the etch time of (a)19800 s, (b)21600 s, (c)23400 s.

Fig. 6 Schematic illustrations of the Cu(5at.%Ti)/dielectric-layer samples after annealing.