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Kinetics of Self-Formation of Ti-based Barrier Layers in Cu(Ti)/dielectric-layer Samples

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1. Introduction

We recently succeeded in forming Ti-based barrier layers using Cu(Ti) alloy films prepared on SiO₂/Si substrates after annealing at 400°C [1-3]. In our previous study [4], seven dielectric layers such as low-k1(SiO_xC_y), low-k2, low-k3, low-k4, SiCO, SiCN and SiO₂ layers were prepared and thin Ti-based barrier layers were found to be formed at the interface between the Cu(Ti) films and the dielectric-layer/Si substrates after annealing at elevated temperatures. The Ti-based interface layers formed in the Cu(10 at.%Ti) alloy films deposited on the dielectric layers after annealing at 500 and 600°C consisted of crystalline TiC or TiSi in addition to amorphous Ti oxides. The primary factor to control composition of the self-formed Ti-based interface layers was concluded to be the C concentration in the dielectric layers rather than the enthalpy of formation of the Ti compounds (TiC and TiSi).

In the present study, we investigated formation kinetics of the Ti-based interface layers fabricated at 400°C with a low content Ti (1 at.%). In order to understand the kinetics, the Cu(Ti)/dielectric-layer samples were annealed in ultra high vacuum (UHV). The microstructures were analyzed by transmission electron microscopy (TEM) and Rutherford backscattering spectrometry (RBS), and correlated with the electrical properties of the Cu(Ti) films. Based on the present results, the kinetics of formation of the Ti-based interface layers in the annealed Cu(Ti)/dielectric-layer samples is discussed.

2. Results and Discussion

Dielectric-layer dependence of resistivity decrease as a function of annealing time

Figure 1(a) shows electrical resistivities of the Cu(Ti)/dielectric-layer samples after annealing at 400°C as a function of annealing time. The electrical resistivities of the as-deposited Cu(Ti) alloy films were reduced significantly after annealing, because the Ti atoms in the Cu(Ti) alloy films segregated at the Cu(Ti)/dielectric-layer interfaces after annealing at 400°C. There were two tendencies in the resistivity decrease as a function of annealing time. The resistivities of Cu(Ti)/SiO₂ and Cu(Ti)/low-k4 samples were gradually reduced and continued to be reduced even

after annealing for 24 hours (broken lines in Fig. 1(a)). The resistivities of Cu(Ti)/low-k1 sample was quickly reduced to about 5 μΩ-cm after annealing for 24 hours and further resistivity decrease were not observed (a solid line in Fig. 1(a)). In the previous study [4], the Ti-based interface layers were found to consist of crystalline TiSi and amorphous Ti oxides when the dielectric layers were SiO₂ and low-k4, and found to consist of crystalline TiC and amorphous Ti oxides when the dielectric layer was low-k1. Thus, such the difference of resistivity decrease is in good agreement with difference of Ti compounds (TiSi or TiC) formed in the Ti-based interface layers. The electrical resistivities of the samples where the TiC formation was observed were lower than those of the annealed samples where the TiSi formation was observed. This indicates that the reaction of Ti atoms with the dielectric layers plays an important role in the formation kinetics of the Ti-based interface layers. The results show that kinetics of TiC formation was much faster than that of TiSi formation.

Formation kinetics of Ti-rich interface layers

In order to identify formation kinetics of the Ti-based interface layers, cross-sectional TEM observation of the annealed samples was carried out. About 10 nm-thick Ti-based interface layer was formed on the low-k1/Si substrate after annealing for 2 hours. Thickness of the Ti-based interface layers formed in the Cu(Ti)/low-k1 sample after annealing for 5 hours increased to be about 20 nm. There was a thickness deviation of about 25 % in all the annealed Cu(Ti)/low-k1 samples. The Ti-based interface layers were confirmed to consist of TiC by an electron diffraction analysis. Thickness data were plotted as a function of annealing time in Fig. 1(b). The thicknesses of the Ti-based interface layers in the Cu(Ti)/low-k1 samples increased with increasing annealing time and reached to about 40 nm after annealing for 24 hours. The thicknesses have not varied with annealing time for more than 24 hours. This corresponded with stopping the resistivity decrease of the annealed Cu(Ti)/low-k1 samples for more than 24 hours.

The square of thicknesses of the Ti-based interface layers in the annealed Cu(Ti)/low-k1 samples was proportional to annealing time. Thus, the formation kinetics of the Ti-based interface layers was determined by diffusion. The

Ti bulk diffusion length in Cu(Ti) alloy films at 400°C was estimated to be about 0.4nm/s and thus it takes 15 minutes for Ti atoms to diffuse from the surface of the Cu(Ti) alloy film to the Cu(Ti)/low-k1 interface. At 400°C, grain boundary diffusion should be faster than the bulk diffusion and thus diffusion of Ti atoms in the Cu(Ti) alloy films must not determine the formation kinetics of the Ti-based interface layers. Thus, Ti diffusion in the Ti-based interface layers could determine the kinetics of formation of the Ti-based interface layers.

The thicknesses of the Ti-based interface layers of the Cu(Ti)/SiO₂ sample after annealing for 5 hours was much thinner than that of the Cu(Ti)/low-k1 sample. Thus, the reaction of Ti atoms with low-k1 films was the stronger than that with the SiO₂ film. In other words, the TiC formation observed in the annealed Cu(Ti)/low-k1 samples was faster than the TiSi formation observed in the annealed Cu(Ti)/SiO₂ samples. This is in good agreement with the electrical resistivity results.

3. Conclusions

The Cu(1at.%Ti) alloy films were deposited on the low-k1, low-k4 and SiO₂ dielectric layers in order to understand the kinetics of formation of the Ti-based interface layers after annealing at 400°C. The Ti-based layers were formed only at the Cu(Ti)/dielectric-layer interface in all the samples after annealing in UHV at 400°C. Electrical resistivities were reduced with increasing annealing time in all the samples. However, there were two tendencies in the resistivity decrease at 400°C as a function of annealing temperature: slow resistivity decrease in the Cu(Ti)/SiO₂ and Cu(Ti)/low-k4 samples and fast resistivity decrease in the Cu(Ti)/low-k1 sample. The difference of resistivity decrease is in good agreement with difference of Ti compound formation (TiSi or TiC) in the Ti-based interface layers. The kinetics of TiC formation found to be faster than that of TiSi formation at 400°C. The square of thicknesses of the Ti-based interface layers was proportional to annealing time in the Cu(Ti)/low-k1 samples after annealing at 400°C. Thus, the kinetics of formation of the Ti-based interface layers was determined by diffusion. Ti diffusion in the Ti-based interface layers could determine the kinetics of formation of the Ti-based interface layers. Whether TiC or TiSi was formed in the Ti-based interface layers after annealing at elevated temperature was reported to be determined by the C concentration in the dielectric layers rather than the enthalpy of formation of the Ti compounds [4]. Thus, the composition of the dielectric layers was concluded to play an important role in the kinetics of formation of the Ti-based interface layers.

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References

- [1] S. Tsukimoto, T. Morita, M. Moriyama, K. Ito and M. Murakami, *J. Elec. Mater.* **34** (2005) 592.
- [2] S. Tsukimoto, T. Kabe, K. Ito and M. Murakami, *J. Elec. Mater.* **36** (2007) 258.
- [3] K. Ito, S. Tsukimoto, T. Kabe, K. Tada and M. Murakami, *J. Elec. Mater.* **36** (2007) 606.
- [4] K. Kohama, K. Ito, S. Tsukimoto, K. Mori, K. Maekawa and M. Murakami, *J. Elec. Mater.* in press.

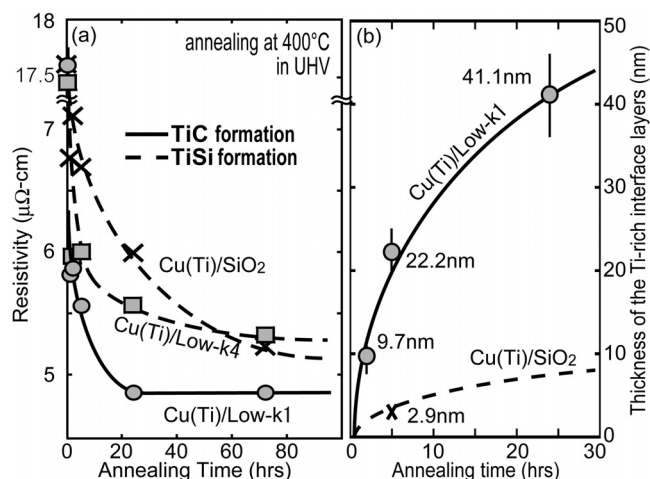


Fig. 1 (a) Electrical resistivities after annealing at 400°C for Cu(Ti)/low-k1, Cu(Ti)/low-k4 and Cu(Ti)/SiO₂ samples and (b) thickness of the Ti-based interface layers of the Cu(Ti)/low-k1 and Cu(Ti)/SiO₂ samples as a function of annealing time.