

Diffusion Barrier Property of an Interface Layer Formed with Cu-Mn, Al and Mg Alloy Films on SiO₂

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1. Introduction

Cu has been accepted as an advanced interconnect material. TaN or Ta has been widely employed as a conventional barrier layer to prevent interdiffusion between Cu and Si atoms. However, the barrier layer formation has become increasingly difficult as the technology node is reduced from 90 to 65 and to 45 nm. An alternative to the conventional barrier process is a “self-forming” barrier process. Cu-X alloy is deposited directly on SiO₂ by sputtering method. During subsequent heat treatment, an oxide layer is formed at the interface and acts as a diffusion barrier layer.

Earlier works have shown the possibility of Mg or Al as an alloying element in Cu. Frederick *et al.* revealed in the Cu-(5-12) at.% Mg alloy films the sequence of solute segregation, microstructure evolution, and reaction kinetics at the film-SiO₂ interface annealed at 400 or 600 °C [1-3]. Shepherd *et al.* indicated that aluminum alloyed with copper at the SiO₂ interface serves as an effective adhesion promoter and thermal diffusion barrier [4]. Recently, Cu-Mn alloy process was proposed by Koike *et al.*. An excellent barrier layer could be self-formed by the use of Cu-Mn alloy annealed at 450 °C [5]. Using this alloy as a seed layer of dual-damascene interconnect structure, Usui *et al.* reported that a self-formed barrier layer was successfully fabricated without a barrier at the via bottom. They also demonstrated excellent resistance against stress-induced voiding and electromigration [6].

However, it is necessary to compare the Cu-Mn alloy with previously reported alloys under the same experimental conditions and to examine the difference and advantages of the Cu-Mn alloy. In the present work, we investigated barrier morphology and barrier property in the three alloys of Cu-4 at. % Mn, Al, Mg alloy under the same experimental condition.

2. Experiment

Alloy films of Cu-4 at. % Mn were deposited directly on SiO₂ substrates to a thickness of 150 nm by sputtering of Cu-4%Mn targets. Alloy films of Cu-4 at. % Al, Mg were deposited by simultaneous sputtering of Cu, Al and Mg targets. Substrates were n-type Si wafers having a plasma TEOS oxide of 100 nm in thickness. Resistivity change was measured in situ with a standard two-point probe during heat treatment in a mixed gas atmosphere of Ar+O₂ at 220

°C. Depth profile along the thickness direction was measured by secondary ion mass spectrometry (SIMS) by etching from the SiO₂ side. Microstructure was investigated by observing cross-sectional images with a transmission electron microscope (TEM). TEM and SIMS investigations were performed on samples annealed in a mixed gas atmosphere of Ar+3%H₂ at 450 °C for 30 min.

3. Results and Discussion

Figure 1 shows the relative resistivity change ρ/ρ_0 with annealing time for each sample in a mixed gas atmosphere of Ar+O₂ at 220 °C. Here ρ_0 is the resistivity of the as-deposited samples, and ρ is the resistivity of samples after annealing. The relative resistivity of Cu-Mn sample decreases rapidly with annealing time, and is found to almost saturate after 600 sec. This result suggests the reduction of the Mn content from the Cu-Mn alloy layer. The decrease of the relative resistivity of Cu-Al sample is far less than the Cu-Mn sample. In contrast, the relative resistivity change of Cu-Mg is found to increase with time because an oxide layer is formed on the surface of the alloy film. The observed difference in reduction tendency of residual alloying elements can be explained by the activity coefficient concept. The activity coefficient γ of a substance A in a liquid or solid mixture is a dimensionless quantity defined in terms of the chemical potential μ_a of A in the mixture. The activity coefficient of 4 at. % Mn in Cu is nearly equal to 1 [7], while that of 4 at. % Al and Mg in Cu is much less than 1.[8, 9]. This indicates that Mn can be easily expelled from Cu. In contrast, Mg and Al tend to remain in Cu because of their strong chemical interaction with Cu.

Figure 2 shows cross-sectional TEM images for (a) the Cu-Mn, (b) the Cu-Al, and (c) the Cu-Mg samples annealed at 450 °C for 30 min. A uniform interfacial layer (see arrow) is self-formed between Cu-Mn alloy and SiO₂ having approximate thickness of 4 nm in Fig. 2 (a). It is noted that inhomogeneous diffraction contrast is not observed in SiO₂ layer. We suppose this interfacial layer consists of segregated Mn atom or Mn oxide, which can be identified in the next SIMS profile. Fig. 2 (b) shows the uniform formation of a 10-nm thick layer on the alloy-film side of the interface. In addition, regions of dark contrast extending out from the film into the SiO₂ are observed. Fig. 2 (c) shows a 30-nm thick interface layer together with a

dark contrast in the SiO₂ layer. In the case of Cu-Al and Cu-Mg, a thicker interface layer is formed as compared to Cu-Mn.

Figures 3(a)-(c) show the SIMS depth profiles for the Cu-Mn, Cu-Al and Cu-Mg samples annealed at 450 °C for 30 min, respectively. Since Ar ion etching was performed from the SiO₂ side to the surface of Cu alloys, Si and O atoms were injected into the Cu alloy, leading to an apparent presence of these atoms in the Cu alloy layer. Alloying elements are concentrated at interface between the Cu alloy layer and the SiO₂ layer. The Mn and Al signals are also concentrated at surface area. On the other hand, the Mg signal is not observed at surface area, which indicates that Mg atoms still remain in the Cu alloy layer. These results correspond to the relative resistivity change in Fig. 1 and the TEM images in Fig.2.

Concentration distribution near the Cu/SiO₂ interface is different among the three alloying elements. In the case of the Cu-Mn alloy, Cu is located on the alloy-film side while Mn is located on the SiO₂ side. In contrast, in the case of the Cu-Al and the Cu-Mg alloys, Cu is located on the SiO₂

side with noticeable intensity even in the interior of the SiO₂ layer. These results indicate that the Mn containing diffusion barrier prevents Cu from diffusing into the SiO₂ layer while the interface layers formed by Mg and Al allow Cu to diffuse into the SiO₂ layer.

4. Conclusions

The relative resistivity of Cu-Mn sample decreases rapidly with annealing time by annealing treatment. On the other hand, the relative resistivity of Cu-Al remains at nearly the initial value and that of Cu-Mg increases substantially. The diffusion barrier property was excellent in the Cu-Mn alloy after annealing at 450 °C for 30min, whereas it was very poor in the Cu-Al and the Cu-Mg alloy as confirmed by SIMS depth profiles and TEM images. An advantage of Mn over Al and Mg is demonstrated as an alloying element for the self-forming barrier process.

Acknowledgements

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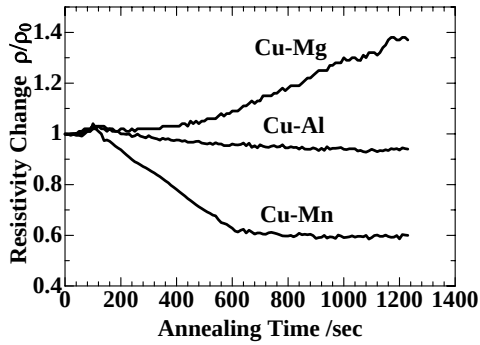


FIG. 1. Relative resistivity change ρ/ρ_0 with annealing time for each sample in a mixed gas atmosphere of Ar+O₂ at 220 °C

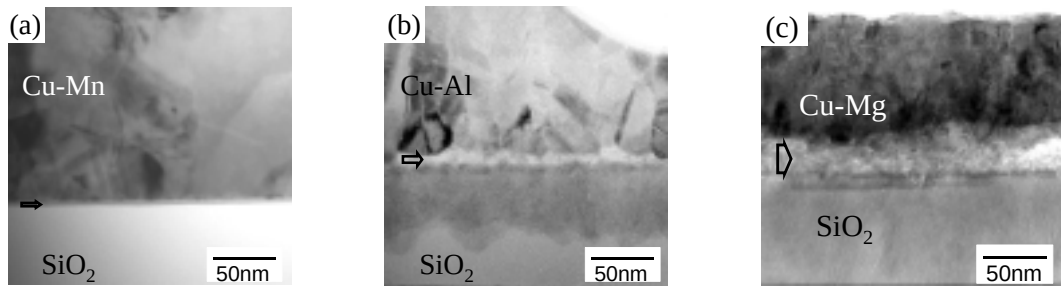


FIG. 2. TEM images for the samples of (a) Cu-Mn, (b) Cu-Al and (c) Cu-Mg annealed at 450 °C for 30 min.

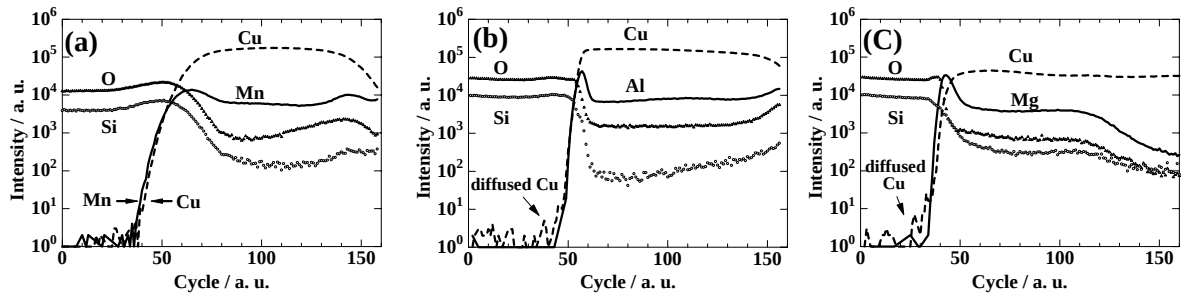


FIG. 3. SIMS depth profiles for the samples of (a) Cu-Mn, (b) Cu-Al and (c) Cu-Mg samples annealed at 450 °C for 30 min.