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Self-Formation of Ti-Based Barrier Layers in Cu(Ti)/Porous-Low-k Samples

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1. Introduction

Our previous studies proposed a new fabrication technique to prepare ultra-thin barrier layers: Supersaturated Cu(Ti) alloy films deposited on dielectric layers with low dielectric constants (low-k) were annealed at elevated temperatures, and thin Ti-rich layers were found to be formed at the interface [1-3]. The Ti-rich interface layers were found to consist of polycrystalline TiSi or TiC in addition to amorphous Ti oxides. The primary factor to control composition of the Ti-rich 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) [2]. Also growth of the Ti-rich interface layers was controlled by chemical reaction, represented by the preexponential factor and activation energy, of the Ti atoms with the dielectric layers, although there are a few diffusion processes possible [3].

In the present study, we investigated formation of the Ti-rich interface layers on low-k dielectric layers containing pores with/without about 6.5nm-thick SiCN pore-seals. 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, effect of pores and pore-seals on self-formation of Ti-rich interface layers is discussed.

2. Results and discussion

Self-formation of Ti-rich interface layers on porous low-k layers

Figure 1 shows RBS profiles of Cu(1at.%Ti)/low-k samples before and after annealing in Ar for 2h. The low-k layers contained pores without (Fig. 1(a)) and with a pore-seal (Fig. 1(b)). Ti peaks were obtained at the surface and interfaces after annealing at 400-600°C. Cu edges at the interface (around channel 600) remained sharp after annealing, indicating that Cu interdiffusion was prevented by self-formed Ti-rich interface layers. The Ti-peak intensities increased with annealing temperature. Those are similar to self-formation of the Ti-rich interface layers on low-k layers not containing pores [2, 3].

Figure 2 shows portions (around the Ti peaks at the interface) of the RBS profiles of the samples after annealing at 400°C for 2h (Fig. 1), and refinement plots (solid lines) were placed upon the observed data. The refinement plots consisted of components: Ti segregation at the interface, Ti atoms in the alloy film, and a Cu edge above the Ti segregation at the interface. The refinement plots were obtained by refinement of parameters until the residuals were minimized in some sense (the smallest *S* indicators) [3]. The *S* values were in the range of 1.0 to 1.3 in all the samples, which were low enough to indicate an adequate model.

A single Ti peak was observed around channel 540 in the sample without a pore-seal (Fig. 2(a)). This is similar to previous results for Cu(Ti)/dielectric-layer samples after annealing at elevated temperatures [1-3]. In contrast, Two Ti peaks were observed around channels 536 and 560 in the sample with a pore-seal (Fig. 2(b)). Similar Ti peaks were observed in all samples with a pore-seal after annealing at 400-600°C for 2h. This indicates that two Ti-rich interface layers were formed, and that Ti atoms reacted with a pore-seal and a low-k layer containing pores in order.

Cross-sectional TEM images and selected-area diffraction (SAD) patterns for Cu(1at.%Ti)/porous-low-k samples after annealing at 600°C in Ar for 2h without and with a

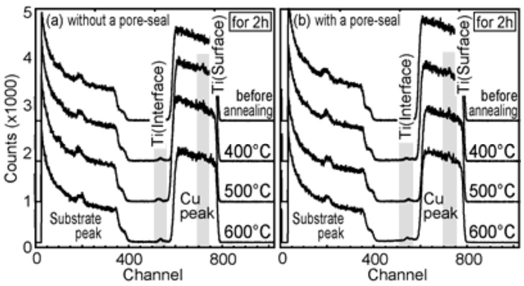

Fig. 1 RBS spectrum profiles of the Cu(1at.%Ti)/porous-low-k samples before and after annealing in Ar for 2h (a) without and (b) with a pore-seal.

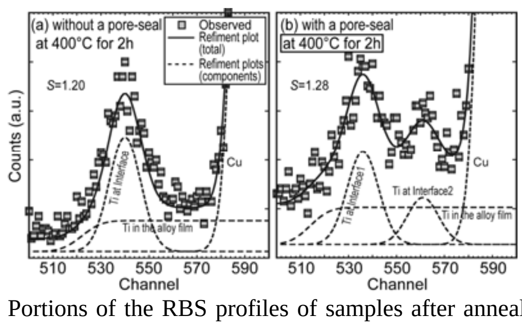

Fig. 2 Portions of the RBS profiles of samples after annealing at 400°C for 2h (Fig. 1) and refinement plots (solid line) placed upon the observed data. The refinement plots consisted of components: Ti segregation at the interface, Ti atoms in the alloy film, and a Cu edge above the Ti segregation at the interface.

pore-seal are shown in Fig. 3(a) and (b), and Fig. 3(c), respectively. Thin interface layers were observed in both annealed samples. The sample without a pore-seal had rough interface, indicating that Ti atoms reacted with the low-k layers at the pore surfaces (Fig. 3(a)). In contrast, the sample with a pore-seal had smooth interface (Fig. 3(c)). The SAD pattern shows the Ti-rich interface layer consisted of fine polycrystalline TiC (Fig. 3(b)). The C concentration of the porous low-k layer is higher than 17 at.%. This is agreement with the rule that TiC is formed in the Ti-rich interface layers when C concentration of dielectric layers is higher than 17 at.% [2]. Columnar structures were observed in both samples (Figs. 3(a) and 3(b)). The columnar grains in the sample with a pore-seal were coarser than those in the sample without a pore-seal. This suggests that amount of the residual Ti atoms in the Cu alloy films in the sample with a pore-seal was smaller than that without a pore-seal, and that low residual Ti atoms in the alloy films enhanced Cu grain growth.

Figure 4(a) shows molar amounts of Ti atoms segregated at the interface. Those increased with increasing annealing temperature. Note that total amounts of Ti atoms segregated at the interface in the samples with a pore-seal are higher than those without a pore-seal. This is in agreement with Cu columnar microstructures after annealing samples (Fig. 3). In the sample with a pore-seal, a molar amount of Ti atoms at the interface 2 is smaller than that at the interface 1. The Ti segregation at the interface 1 and 2 indicates reactions of Ti atoms with low-k layers with pores and a pore-seal (SiCN), respectively. The resistivity of the annealed samples with a pore-seal was lower than that without a pore-seal. This is due to low residual Ti atoms in the alloy films and coarse Cu columnar grains.

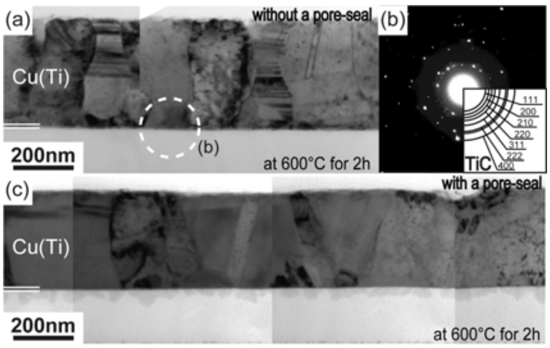

Fig. 3 Cross-sectional TEM images and a SAD pattern for Cu(1at.%Ti)/porous-low-k samples after annealing at 600°C in Ar for 2h (a) and (b) without and (c) with a pore-seal.

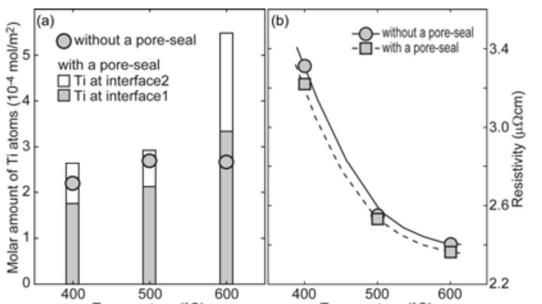

Fig. 4 (a) Molar amounts of Ti atoms segregated at the interface and (b) resistivity in samples without/with a pore-seal after annealing at 400-600°C in Ar for 2h.

Comparison of self-formation of Ti-rich interface layers on low-k layers between with and without pores

In order to understand the effect of pores in the low-k layers on self-formation of Ti-rich interface layers, Cu(1at.%Ti) alloy films deposited on four kinds of low-k dielectric layers, and the samples were simultaneously annealed at 400°C in Ar for 2h. Ti segregation was observed at the interface as well as the surface in all the samples (Fig. 5(a)). Resistivity for annealed Cu alloy films deposited on porous low-k layers is lower than that on low-k layers not containing pores, although molar amounts of Ti atoms segregated at the interface was not significantly different in all the samples (Fig. 5(b)).

3. Conclusions

The Cu(1at.%Ti) alloy films were deposited on the porous low-k dielectric layers without/with a pore-seal. Self-formed Ti-rich interface layers were formed on the porous low-k layers after annealing at 400-600°C in Ar for 2h. The Ti-rich interface layers consisted of polycrystalline TiC, which is agreement with the rule as mentioned in the previous study [2]. In the annealed samples with a pore-seal, two Ti-rich interface layers were formed, and a total molar amount of Ti atoms segregated at the interface is larger than that in the samples without a pore-seal. Resistivity of the sample with a pore-seal is lower than that without a pore-seal because of low residual Ti atoms in the alloy films and coarse Cu columnar grains.

Acknowledgements

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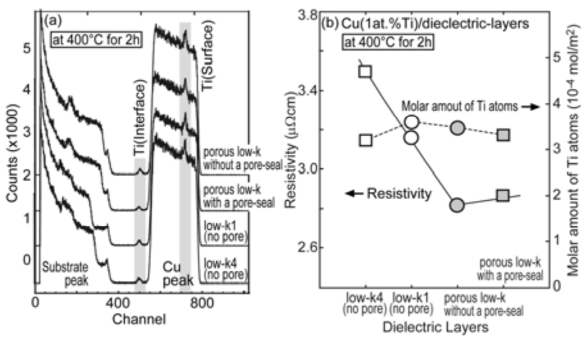

Fig. 5 (a) RBS profiles and (b) resistivities and molar amounts of Ti atoms segregated at the interface for the Cu(1at.%Ti)/dielectric-layer samples after annealing at 400°C in Ar for 2h.