

Rutherford Backscattering Spectrometry Analysis of Growth of Ti-Rich Layer Formed at Cu(Ti)/Low-k Interfaces

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1. Introduction

In our previous studies, a new fabrication technique to prepare ultra-thin barrier layers for nano-scale Cu wires was proposed. Super-saturated Cu(Ti) alloy films deposited on dielectric layers such as SiO₂ and SiO_xC_y with low dielectric constants (low-k) were annealed at elevated temperatures, and thin Ti-rich layers were found to be formed at the interfaces[1,2]. The Ti-rich layers formed at the interfaces were found to consist of crystalline TiC or TiSi in addition to amorphous Ti oxides.

The growth of the Ti-rich layers consisting of TiC (Cu(1 at.%Ti)/low-k samples) was faster than those consisting of TiSi (Cu(1at.%Ti)/SiO₂ samples) after annealing at 400°C[3]. For systematic investigation of dependence of initial Ti contents in the Cu(Ti) alloy films and C concentrations in the dielectric layers on the Ti-rich interface layer growth, the Rutherford backscattering spectrometry (RBS) method was employed instead of TEM in this study.

2. Experimental Procedures

The Cu(1, 5 and 10at.%Ti) alloy films were deposited on SiO_xC_y (low-k1 and low-k4), SiO₂, SiCO, and SiCN dielectric layers by a radio frequency magnetron sputtering technique. Their dielectric constants (*k*) and compositions are shown in Tabel 1. The samples were annealed in ultra high vacuum (UHV) at 400°C-650°C for 2 h-72 h. The Ti segregation to the interface was investigated by RBS. For the RBS measurements, ⁴He²⁺ ion beams with energy of 2 MeV were impinged onto the film surfaces.

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

	<i>k</i>	C	O	Si	N
low-k1	3.0	17.0	24.9	18.8	-
low-k4	2.6	~14	~29	~18	-
SiO ₂	3.9	-	66.7	33.3	-
SiCO	4.5	20.8	16.6	24.6	-
SiCN	4.8	21.4	0.5	25.0	12.8

3. RBS Measurements and Criteria of Fit

The peak area (*A*) of an element in an RBS profile is the product of the incident beam dose (*Q*), the number of the element atoms in a unit of area (*N*), the scattering cross section of the element atom (σ), and the solid angle of the detector (Ω):[4]

$$A = QN\sigma\Omega. \quad (1)$$

The molar amount of Ti atoms segregated to the interface (*n*) was estimated by dividing the number (*N*) from eq. (1), above, by Avogadro's number *N_A*:

$$n = N/N_A = A/N_A Q\sigma\Omega. \quad (2)$$

In the present study, the values of *Q*, Ω and σ of Ti atoms were 3.12×10^{13} (10 μ C), 3×10^{-3} (steradian), and 6.28×10^{-29} m² (0.628 barn),

respectively. Figure 1 shows RBS spectrum profiles of Cu(10at.%Ti)/low-k1 samples after annealing in UHV. Ti peaks were observed only at the interfaces in all the samples, and those intensities increased with increasing annealing time and temperature. Similar RBS profiles were obtained in all the other samples after annealing. Each Ti peak was fitted by a Gaussian curve and an error function, and the *A* value was determined from the area under the fitted curve (e.g. Fig. 2). The fitted curve was refined using *S* value which is a measure of how well the fitted model accounts for the data[5]. The calculated *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. The *n* values could be estimated from the obtained *A* values (eq. (2)).

4. Results and Discussion

Growth Behaviors of the Ti-rich Interface Layers

Figures 3(a)-3(c) show the growth behaviors of the Ti-rich interface layers after annealing at 400 °C for initial Ti concentrations of 1, 5 and 10 at.%Ti, respectively. Growth behavior of the Ti-rich interface layers was exhibited by

$$n = Z \cdot \exp(-E/RT) \cdot t^m, \quad (3)$$

where *Z* is a preexponential factor and *E* the activation energy for the reaction. The plots of *n* vs *t* (Fig. 3) were changed to the plots of log *n* vs log *t*, and log *n* were found to be proportional to log *t*. The slopes of the log *n*-log *t* lines give the values of *m*, and they were almost similar for all the samples. The *m* values were around 0.2, lower than 0.5, suggesting that growth of the Ti-rich interface layers is not controlled by lattice diffusion, but controlled by grain-boundary and/or interface diffusion.

Arrhenius plots of log *n* vs 1/*T* in Cu(Ti)/dielectric-layer samples for the initial Ti concentrations of 1, 5 and 10 at.%Ti are shown in Figs. 4(a)-4 (c), respectively. They show a linear relationship, and this suggests that the formation of the Ti-rich interface layers is controlled by a thermally-activated process.

The *E* and *Z* values were estimated from the slopes and the intercepts of the log *n*-1/*T* lines, respectively. The values of *E* and *Z* were plotted as a function of C concentration in the dielectric layers, as shown in Fig. 5. Both the *E* and *Z* values for the 1at.%Ti were lower than those of 5at.%Ti and 10at.%Ti, which were similar. This suggests that reducing the initial Ti concentration can reduce effective activation energies and preexponential factors. On the other hand, the *E* and *Z* values for the samples consisted of dielectric layers with carbon tended to decrease with decreasing the C concentration, and those without carbon (SiO₂) were much higher than others. This suggests that composition of the dielectric layers plays an important role in the reaction, and the carbon may be a key element to control the reaction. This is similar to the formation rule of Ti compounds (TiC or TiSi) in the Ti-rich interface layers [2].

Potential for Low Temperature Fabrication Technique

The reaction rate was defined as $Z \cdot \exp(-E/RT)$. Figure 6 shows the calculated ratio of $Z \cdot \exp(-E/RT)$ to $Z \cdot \exp(-E/R \cdot 673)$ ($T=400^\circ\text{C}$) for the Cu(Ti)/dielectric-layer samples as a function of annealing temperature. The reaction rate was large in the samples with low-k, and was small in the samples with SiO_2 at less than 400°C . Furthermore, reducing the initial Ti concentration in the alloy films can increase the reaction rate due to a decrease in effective activation energy. Thus, combination of the low initial Ti concentration in the alloy films and low-k layers is concluded to contribute to a low temperature fabrication technique to prepare low-resistivity Cu wires with ultra-thin self-formed barrier layers.

5. Conclusions

For systematic investigation of growth of the Ti-rich interface layers, the RBS technique was employed.

The $\log n$ values were found to be proportional to $\log t$ values. The similar slopes of the $\log n$ vs $\log t$ lines suggest that a growth mechanism is similar. In addition, the E and Z values were significantly sensitive to the C concentration in the dielectric layers. These results suggest that growth of the Ti-rich interface layers is believed to be controlled by chemical reactions, represented by the E and Z values, of the Ti atoms with the dielectric layers, although there are a few diffusion processes possible. Furthermore, combination of the low initial Ti concentration in the alloy films and low-k layers is concluded to contribute to a low temperature fabrication technique.

Acknowledgements

This work was supported by Research Fellowships of the Japan Society for the Promotion of Science for Young Scientists (Kohama).

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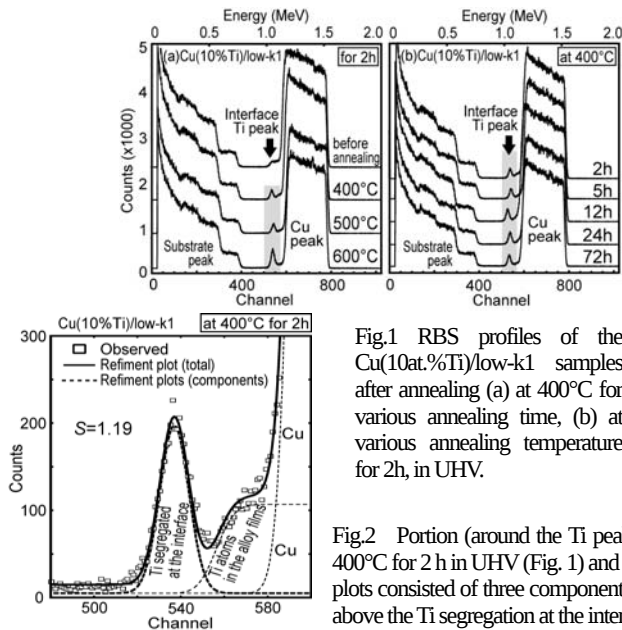


Fig.1 RBS profiles of the Cu(10at.%Ti)/low-k1 samples after annealing (a) at 400°C for various annealing time, (b) at various annealing temperature for 2h, in UHV.

Fig.2 Portion (around the Ti peaks) of the RBS profile of Cu(10at.%Ti)/low-k1 sample after annealing at 400°C for 2h in UHV (Fig. 1) and refinement plots (solid line) placed upon the observed data. The refinement plots consisted of three components: Ti segregation at the interface, Ti atoms in the alloy film, and a Cu edge above the Ti segregation at the interface.

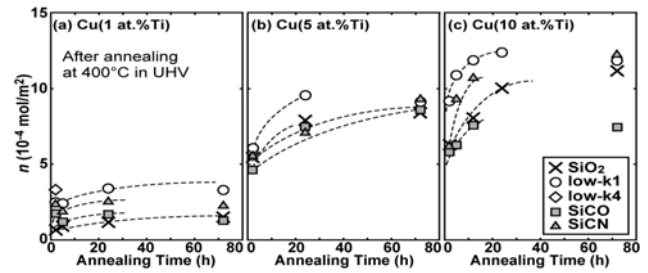


Fig.3 Plots of n vs t for Cu(Ti)/dielectric-layer samples after annealing at 400°C in UHV. The initial Ti concentrations are (a) 1 at.%, (b) 5 at.%, and (c) 10 at.%.

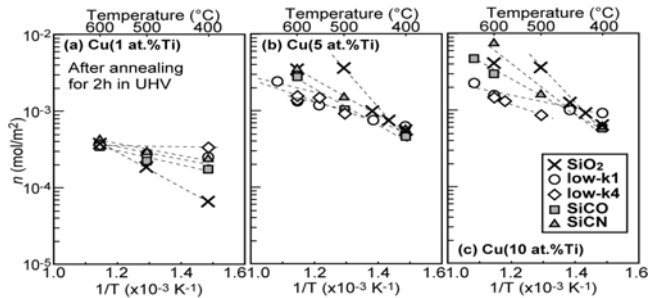


Fig.4 Arrhenius plots of $\log n$ vs $1/T$ for Cu(Ti)/dielectric-layer samples after annealing for 2h in UHV. The initial Ti concentrations are (a) 1 at.%, (b) 5 at.%, and (c) 10 at.%.

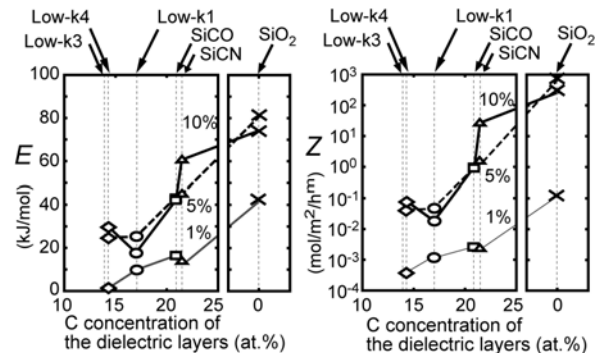


Fig.5 Activation energies of E and preexponential factors Z of the Cu(Ti)/dielectric-layer samples, as a function of C concentration of the dielectric layers.

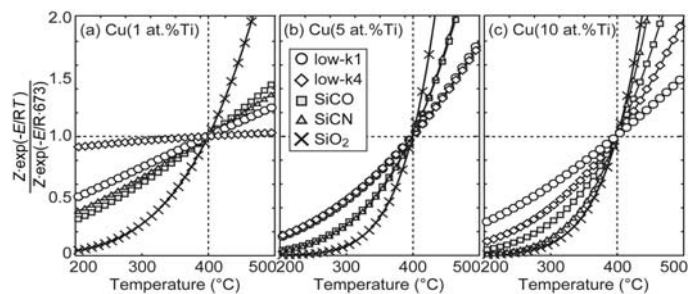


Fig.6 The ratio of $Z \cdot \exp(-E/RT)$ to $Z \cdot \exp(-E/R \cdot 673)$ ($T=400^\circ\text{C}$) for the Cu(Ti)/dielectric-layer samples as a function of annealing temperature. The initial Ti concentrations are (a) 1 at.%, (b) 5 at.%, and (c) 10 at.%.