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The Effects of Boron in the Cu(B)/Ti/SiO$_2$ System on the Cu-Ti Reaction, Resistivity, and Diffusion Barrier Properties

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The behavior of boron in Cu(4.8at.%B)/Ti/SiO$_2$ was investigated as a function of temperature, and its influences on the Cu-Ti interaction, resistivity, and diffusion barrier properties were also studied. The results showed the formation of a titanium boride layer at the Cu-Ti interface, after heating the Cu(B)/Ti/SiO$_2$ at 400°C and higher, effectively served as a barrier for the Cu and Ti diffusion, and significantly enhanced the Cu (111) texture. The resistivity dropped from 16.3 to 2.33 μΩ-cm after heating at 600°C, and continued to decrease up to 800°C. As a result, the Cu, in the form of B(O)$_x$/Cu/TiB$_2$/Ti(O)$_x$/SiO$_2$ multilayers, obtained by heating the Cu(B)/Ti/SiO$_2$, showed high thermal stability with low resistivity and, thus, can be used as interconnections in advanced integrated circuits. Since the Cu, in the form of B(O)$_x$/Cu/TiB$_2$/Ti(O)$_x$/SiO$_2$ multilayers, obtained by heating the Cu(B)/Ti/SiO$_2$, showed high thermal stability with low resistivity, it can be used as interconnections in advanced integrated circuits.

Key words: Boron, TiB$_2$, Cu-Ti interaction, resistivity, Cu(B) alloy

INTRODUCTION

The dual-damascene Cu integration scheme is replacing the conventional Al metallization system for deep submicron integrated circuits, as Cu exhibits lower resistivity, superior electromigration resistance, and higher resistance to stress-induced voids. However, copper is known to diffuse rapidly through SiO$_2$.[1–6] Thus, it is necessary to introduce a diffusion barrier between the Cu and the dielectrics. In addition, Cu also suffers from poor adhesion to SiO$_2$ dielectrics, due to its inability to reduce SiO$_2$, which causes a rapid mass diffusion along the interface and surfaces, resulting in degraded reliability.[7,8] Titanium can be an excellent adhesion promoter, because of its ability to reduce SiO$_2$, producing titanium oxide at the interface, and also because it reacts with Cu, to form intermetallic compounds,[9] resulting in good adhesion between Cu and SiO$_2$. However, titanium cannot serve as a diffusion barrier for Cu metallization, as significant amounts of titanium can dissolve into the Cu layer during annealing at about 400°C.[10,11] In addition, the Ti-SiO$_2$ reaction occurring at the SiO$_2$ surface, upon annealing at 550°C and higher, causes a serious decomposition of SiO$_2$, leading to thinning of the SiO$_2$ layer; thus, resulting in the further decrease of the failure temperature for the Cu/Ti/SiO$_2$/Si multilayers.[12]

In this study, the doping of Cu, with immiscible, reactive elements, has been studied to address these issues. Among the various immiscible elements, boron was chosen as an additive, due to its strong affinity with Ti, and the TiB$_2$ produced can act as a diffusion barrier for Cu metallization, due to its high melting point (3,225°C), which also shows a low resistivity of 7 μΩ-cm.[13–15] In addition, the consumption of Ti in the formation of titanium boride can limit its supply for the Ti-SiO$_2$ reaction, effectively suppressing SiO$_2$ decomposition.[18] Further, the boron added to Cu can passivate the copper surface, possibly due to the formation of surface boron oxide. Therefore, the Cu(B) alloy/Ti/SiO$_2$ structures have been annealed to investigate the behavior of boron, and its resultant effects on Cu-Ti

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inter-diffusion, resistivity, texture, and diffusion barrier properties.[16]

EXPERIMENTAL

Titanium and Cu(B) films were successively magnetron-sputter deposited on 100-nm-thick SiO_2 films, which were thermally grown on (100) Si wafers, from Ti and Cu(4.8at.%B) targets, with a purity level of 6 N, in one chamber. Two different thicknesses, 20 nm and 35 nm, were deposited for the Ti films, with a thickness of 200 nm for the Cu(B) films. For comparison, 200-nm-thick Cu films were deposited onto Ti/SiO_2/Si wafers. The sputtering conditions were as follows: base pressure in the chamber 2×10^{-6} Torr, substrate temperature equal to room temperature, and Ar pressure and sputtering power for Ti and Cu (or Cu(B)) deposition equal to 6 mTorr and 130 W and 3 mTorr and 180 W, respectively. Annealing of these Cu(B) (or Cu)/Ti/SiO_2/Si samples was performed at a vacuum level of 3×10^{-6} Torr, at temperatures between 100°C and 900°C, for 30 min. The sheet resistance was measured using a four-point probe, and the distribution of elements, such as Ti, Cu, B, Si, and O, in the as-deposited and as-annealed samples, identified using Auger electron spectroscopy (AES). In addition, a θ-2 θ x-ray diffractometer, equipped with a Cu tube, operated at 50 KV and 200 mA, with a monochromatic wavelength (Cu K_α) of 0.154 nm, was used to identify the phases of the reaction products and the intensity of the Cu (111) texture and the shift of the x-ray diffraction spectra. Since the spectrum shift in Cu(111) is proportional to the lattice distortion ratio, the temperature dependence of the stress in a Cu film can be determined by measuring the spectrum shift.[17]

RESULTS AND DISCUSSION

Two systems, Cu/Ti/SiO_2 and Cu(4.5at.%B)/Ti/SiO_2, have been annealed at temperatures between 100°C and 900°C, in a vacuum, to investigate the effects of boron on the Cu-Ti interdiffusion. The x-ray spectra of the Cu/Ti(35 nm)/SiO_2 samples, as-deposited and as-annealed, for 30 min at 100–800°C, are shown in Fig. 1a. The as-deposited film showed peaks corresponding to Cu and Ti. Annealing at 400°C produced a metastable Cu_3Ti phase and a shift of the α-Ti (002) peak to a higher d spacing, indicating the expansion of the c-axis of the Ti film, due to the increased amount of oxygen into the unreacted Ti film, as the formed Cu_3Ti layer moved the oxygen into the Ti. In addition, the peaks corresponding to Cu_3Ti disappeared, with a strongly increased intensity of the Cu (111) peak.

In the case of Cu(B)/Ti(20nm)/SiO_2, as shown in Fig. 1b, the Cu (111) texture significantly improved with increases in the temperature. Note that no intermetallics, such as CuTi, Cu_3Ti, and Cu_4Ti, can be seen at temperatures between 100°C and 800°C, indicating that negligible interdiffusions occurred between the Cu and Ti, due to the formation of a titanium boride layer at the Ti surface. Also, a relatively abrupt shift of the Cu (111) spectrum, to 2θ lower, was seen above 300°C, possibly due to the relaxation in the compressive stress of the supersaturated solid solution as the boron precipitates along the grain boundaries.[18,19]

Figure 2 shows the AES depth profiles of the as-deposited Cu/Ti/SiO_2 and of those annealed at 300–600°C. Annealing at 400°C allowed for interdiffusion between the Cu and Ti, and for outdiffusion of Ti to the Cu surface. At 500°C, the intermetallic compounds resulting from the Cu-Ti reactions further grew into the Cu layer, with an increased amount of Ti dissolving into the Cu. Also, significant amounts of Ti outdiffused to the Cu surface, forming a mixture of titanium oxide and Cu. Annealing at 600°C further increased the Ti outdiffused to the surface, forming a thicker titanium oxide layer, which also left the Cu layer free of titanium. Note that significant amounts of oxygen and silicon can be seen in the Ti glue layer at 600°C. According to Zeng et al., the heating of Ti/SiO_2 structures at 550°C and higher produce a mixture of oxygen-rich titanium (e.g., stable titanium oxide) and Ti_5Si_3 compounds, via the reaction with Ti-SiO_2.[12]

Figure 3 shows the AES depth profiles of the as-deposited Cu(B)/Ti/SiO_2 structure and those annealed at 300–800°C. Annealing at 300°C allowed for the

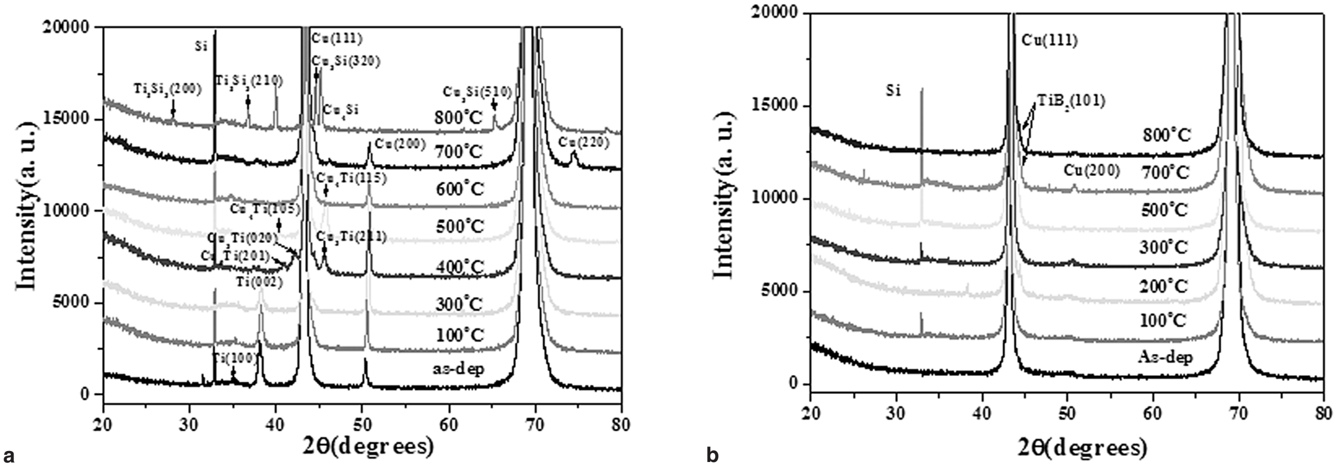
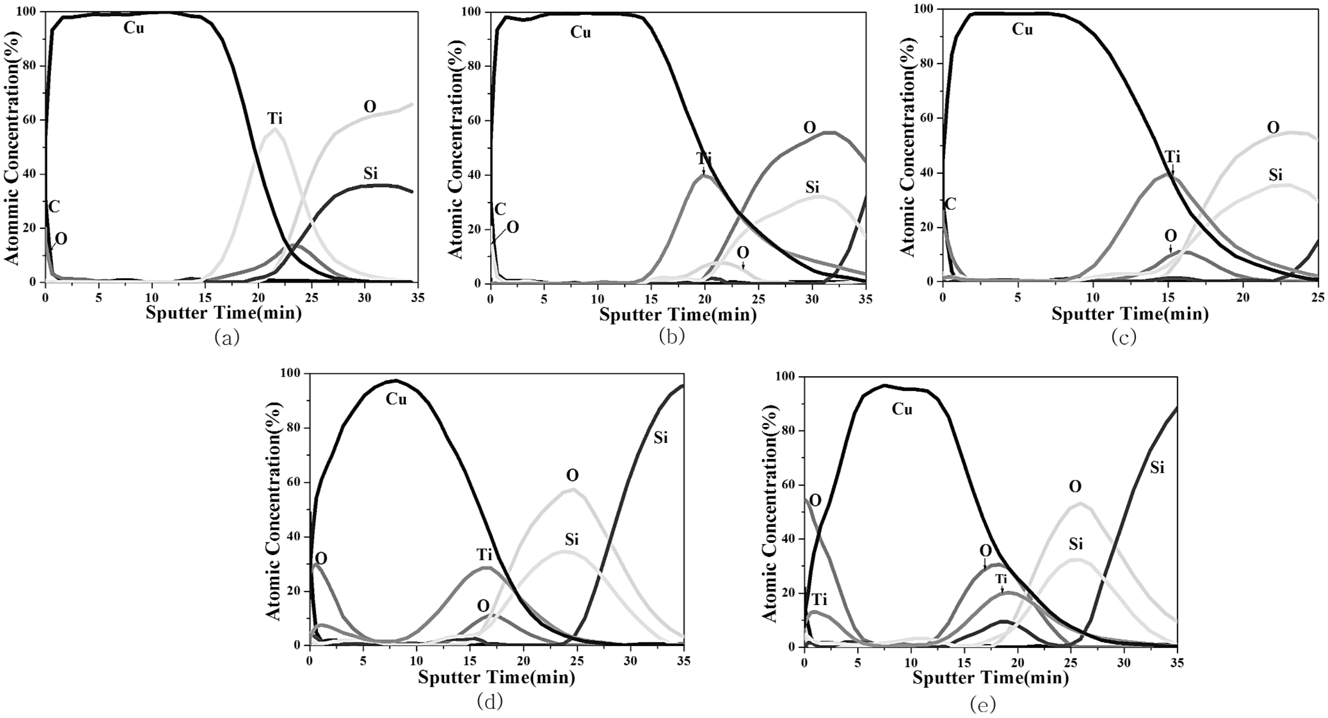
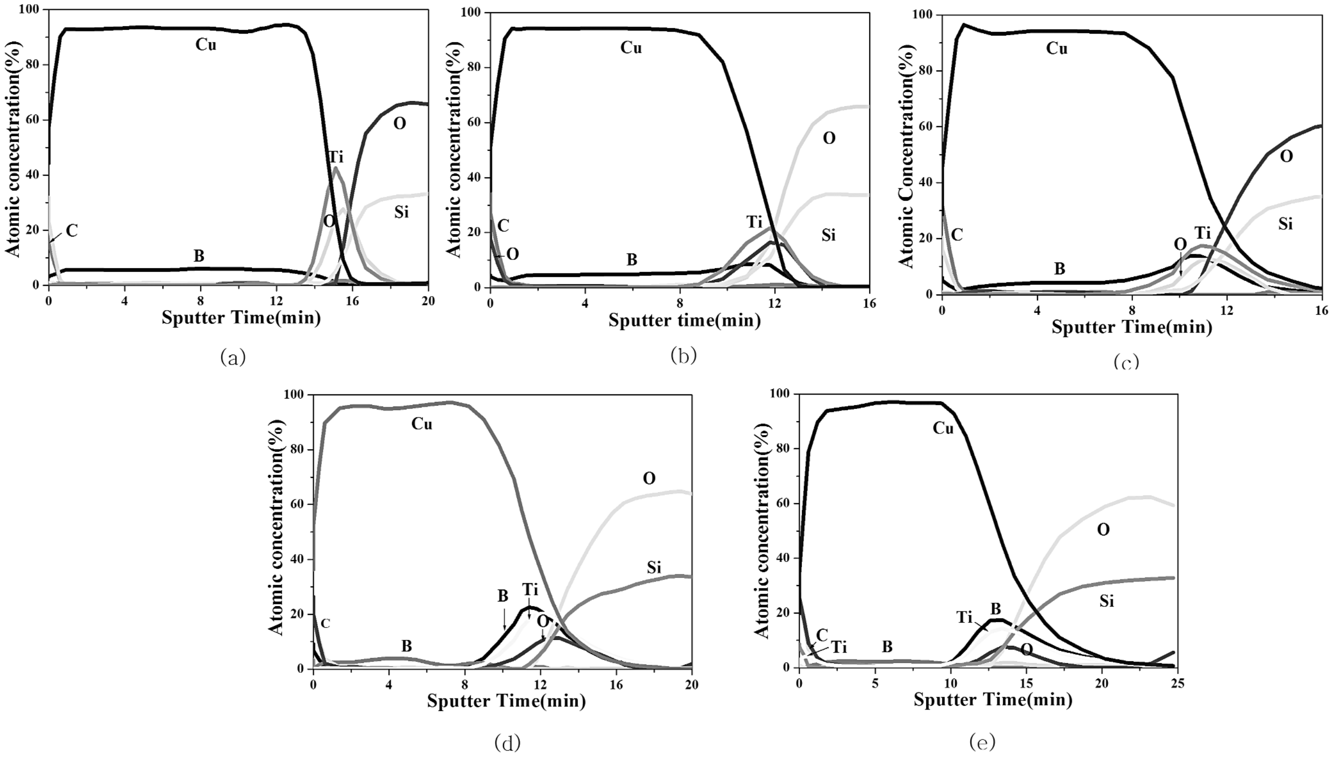


Fig. 1. XRD patterns of (a) Cu/Ti(35 nm)/SiO_2 and (b) Cu(B)/Ti(20 nm)/SiO_2 structures, as a function of the annealing temperature.



(a) (b) (c) (d) (e)

Fig. 2. AES depth profiles of Cu/Ti(35 nm)/SiO$_2$ films (a) as-deposited and annealed at (b) 300°C, (c) 400°C, (d) 500°C, and (e) 600°C.



(a) (b) (c) (d) (e)

Fig. 3. AES depth profiles of Cu(B)/Ti(20 nm)/SiO$_2$ films (a) as-deposited and annealed at (b) 300°C, (c) 400°C, (d) 500°C, and (e) 800°C.

diffusion of boron to the Cu-Ti interface, or Cu surface, with the accompanying reduction in the B concentration. As the temperature increased to 400°C, the boron continued to diffuse to the Ti surface, and formed titanium boride, with further diffusion of boron to the Cu surface.

At 500°C, significant amounts of boron segregated to the Ti surface, producing a much thicker titanium boride layer, with the oxygen snowplowed into the remaining Ti layer. It can be seen clearly that no dissolution of Ti into the Cu layer occurred, implying the formation of a titanium boride layer effectively prevented the dissolution of Ti into the Cu layer, across the titanium boride layer. Note that the boron diffused to the surface of the $Ti(O)_x$ glue layer, thus producing a bilayer of titanium boride/oxygen-rich titanium, instead of a mixture of TiB_2 and B_2O_3, even though the TiB_2 and B_2O_3 compounds show Gibbs free energies of -65.7 Kcal/mol and -285 Kcal/mol, respectively.[20] From these facts, it is proposed that the initially formed CuTi intermetallics, at the Cu-Ti interface, were converted into TiB_2 and free Cu, via the following reaction:

$$CuTi + 2B \rightarrow TiB_2 + Cu, \quad \Delta G_f^\circ = -55 \text{ Kcal/mol} \qquad (1)$$

As the CuTi grew into the Ti layer, the dissolved oxygen was snowplowed to the unreacted Ti at the initial annealing stage; the conversion of the CuTi layer, via the above reaction, resulted in a bilayer of $TiB_2/Ti(O)_x$.

Figure 4 shows the variation in the resistivities of the Cu(B) alloy and pure Cu films, as a function of the annealing temperature. With the Cu(B)/Ti(20nm)/SiO_2, the resistivity of the Cu(4.5at.%B) alloy film continued to decrease, as the temperature was increased, from 100°C to 800°C, to 2.3 μΩ-cm, approximately that of a pure Cu film. Also, it abruptly increased after heating at 900°C.

For the pure Cu film in the Cu/Ti/SiO_2 structure, the resistivity began to increase at about 400°C, and continued to increase up to 500°C. It also showed a sharp decrease between 500°C and 600°C, and then increased significantly after heating at 700°C. Therefore, it could be concluded that the increased resistivity of the pure Cu film, at temperatures between 400°C to 500°C, was due to the formation of intermetallic compounds as a result of the Cu-Ti and Ti-O reactions and the Ti dissolved in the Cu. Also, the abruptly decreased resistivity at 600°C was a consequence of the formation of a titanium-free Cu layer, as the Ti was completely consumed in the formation of the surface and interface titanium oxide layers.

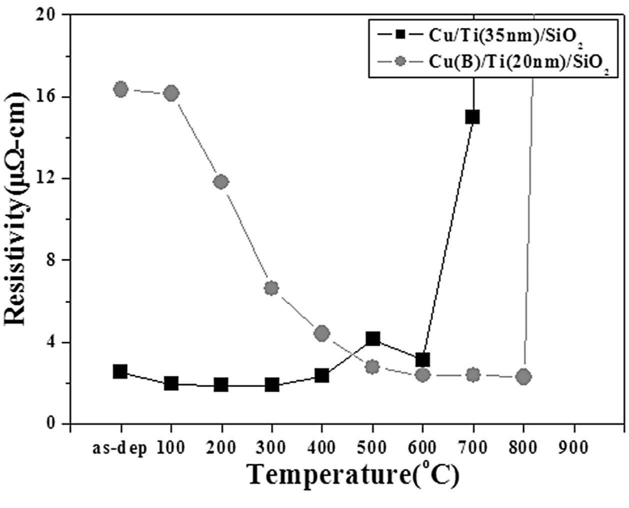


Fig. 4. Resistivity variation of the Cu/Ti(35 nm)/SiO_2 and Cu(B)/Ti(20 nm)/SiO_2 structures, as a function of the annealing temperature.

CONCLUSIONS

Annealing of the Cu(B)/Ti/SiO_2 structure, at 100–900°C, in a vacuum, has been carried out to investigate the effects of boron on the Cu-Ti reaction, resistivity, texture evolution, and thermal stability. Because of the low solubility of boron in copper, and its high affinities with titanium and oxygen, annealing allowed for the out-diffusion of boron to the Cu surface, producing a surface boron oxide layer; the boron also diffused to the Ti surface, reacting with the Ti, forming a bilayer of $TiB_2/Ti(O)_x$, which acted as an effective barrier to Cu and Ti diffusion. This also resulted in a low resistivity, close to that of a pure copper film. In addition, a highly developed Cu (111) texture was obtained by heat treatment of Cu(B)/Ti/SiO_2 above 400°C. Consequently, Cu, in the form $B(O)_x/Cu/TiB_2/Ti(O)_x/SiO_2$, was obtained by annealing, and the simple structure, Cu(B)/Ti/SiO_2, could be implemented as an advanced metallization for silicon technology devices.

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