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Letter

Interficial stability of Cu/Cu(Ru)/Si contact system for barrier-free copper metallization

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ABSTRACT

Films of Cu/Cu(Ru) and Cu(Ru) were deposited on Si substrates by magnetron sputtering. Samples were subsequently annealed and analyzed by four-point probe (FPP) measurement, X-ray diffraction (XRD), transmission electron microscopy (TEM) and Auger electron spectroscopy (AES). After annealing at 500 °C, resistivity values of both systems decrease, but the reduction is more significant for Cu(Ru). Moreover, the resistivity values of annealed Cu(Ru) film are still greater than those of annealed Cu/Cu(Ru) film. XRD data suggest that Cu/Cu(Ru) film has higher thermal stability and Cu silicide cannot be observed up to 500 °C. According to TEM results, after annealing at 500 °C, the grain size of the Cu(Ru) film is smaller than that of Cu/Cu(Ru) film. In conjunction with AES, XRD, TEM analyses and sheet resistance measurement, it indicates that Cu/Cu(Ru) seed layers are potentially good for advanced Cu interconnects from the views of interfacial stability and low resistivity.

1. Introduction

As the device dimension diminishes, the barrier structure plays a crucial role in the performance and reliability of the interconnect [1]. For example, the presence of the barrier layer increases the effective resistivity of the interconnect lines and sacrifices device performance. Therefore, the thickness of the barrier layer should be reduced to a minimum possible value. For instance, the desired barrier thickness is 3.3 and 2.4 nm, respectively, for the technology node of 45 and 32 nm [2]. However, a successful thin barrier layer (e.g., less than 5 nm in ULSI) with low electrical resistivity is often difficult to achieve. Hence, new material and processing techniques that can meet more rigorous requirements will inevitably be developed for future applications.

The Cu interconnect fabrication technique with self-formed thin barrier is very attractive to form low-resistance Cu interconnects. The self-formed thin barrier layers using Cu alloys with various low concentration solutes have been extensively studied by various authors [3–11]. The alloying of Cu, however, increases its resistivity by scattering of free electrons, which is the major drawback against using Cu alloys [12–14]. To minimize this increase, the alloy elements should segregate near the process temperature (400 °C) and maintain similar grain size compared to pure Cu [14,15]. But this will reduce the thermal stability of these contact systems. So, more intensive studies on the development of alloy films as future interconnect materials will be necessary. In this work, experimental studies have been designed to elucidate the performance of Cu/Cu(Ru) seed layer. Film characteristics such as resistivity, microstructure, and diffusion have been determined after annealing.

2. Experimental

Substrates of n-type (1 0 0) Si were progressively cleaned in an ultrasonic bath with acetone, methanol, isopropyl alcohol, and diluted HF solution and then rinsed in de-ionized water before the activation process, in order to remove organic contaminants and native oxide. To prepare the 100 nm Cu(Ru) films, Cu–Ru (0.3 at.%) alloy disk was used as the target. When the base pressure reached 2×10^{-5} Pa, Ar gas was channeled into the sputtering chamber. During the deposition, the sputtering power and working pressure were kept at 90 W and 0.3 Pa, respectively. The substrate holder was applied with a negative dc bias of 100 V. A 100 nm Cu layer was sequentially deposited on the 100 nm Cu(Ru)/Si multilayer samples by sputtering a Cu target at a sputtering power of 90 W and a negative substrate dc bias of 100 V. For comparison, a 200 nm Cu(Ru) film without top Cu layer was deposited on Si substrates under the same deposition conditions.

After deposition, Cu(Ru)/Si and Cu/Cu(Ru)/Si multilayer samples were vacuum-annealed at pressure of 2×10^{-3} Pa for 60 min between 400 and 500 °C. Four-point probe (FPP) measurements were used to measure the sheet resistances of these films. The crystallinity of the films was evaluated by X-ray diffraction (XRD) analysis and the depth profiles of the atomic distributions in Cu(Ru)/Si and Cu/Cu(Ru)/Si contact systems were investigated by Auger electron spectroscopy (AES). Transmission electron microscopy (TEM) was used to observe (plane view) the microstructures of the films.

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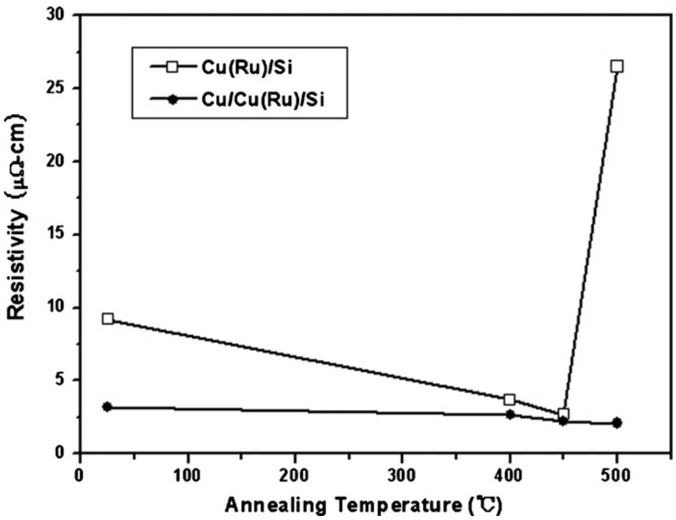

Fig. 1. Resistivity of Cu/Cu(Ru) and Cu(Ru) alloy films as a function of annealing temperature.

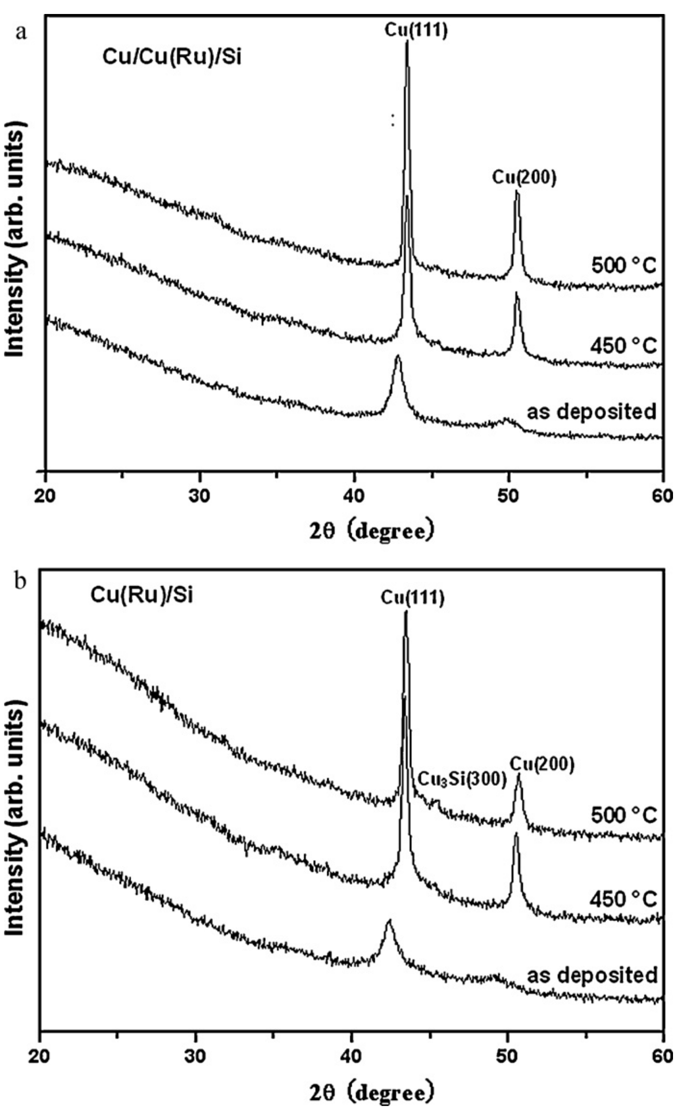

Fig. 2. XRD spectra of (a) Cu/Cu(Ru)/Si and (b) Cu(Ru)/Si samples, as deposited and after annealing at 450 °C and 500 °C.

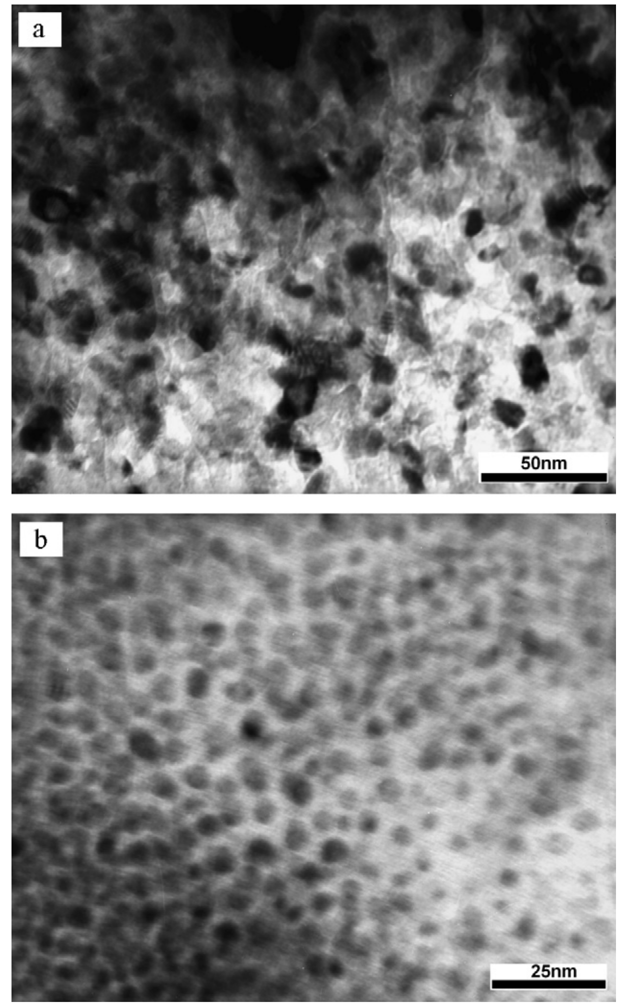

Fig. 3. TEM micrographs for the (a) Cu/Cu(Ru)/Si and (b) Cu(Ru)/Si samples annealed at 500 °C for an hour.

3. Results and discussion

Fig. 1 presents the changes in the resistivity of the Cu(Ru) and Cu/Cu(Ru) films as a function of the annealing temperature. Compared with the Cu/Cu(Ru) film, the resistivity of as-deposited Cu(Ru) alloy film is higher. The reason is that the Cu(Ru) alloy films have fine grains and there are many Ru atoms embedded in Cu grains. After annealing in a range from 400 to 500 °C, the resistivity became lower than the as-deposited values. Comparing to the annealed Cu/Cu(Ru) films, the resistivity of annealed Cu(Ru) films decreases dramatically. It indicates that the segregation of Ru additives shall have the major inference on the lowering of resistivity. However, the resistivity values of annealed Cu(Ru) film are still greater than that of annealed Cu/Cu(Ru) film. This suggests the residual Ru atoms remaining inside the films would increase the resistivity. On the other hand, a drastic increase in resistivity for Cu(Ru) film after annealing at 500 °C is primarily caused by the formation of high resistivity copper silicide phase.

In order to further investigate the source of the changes in resistivity discussed in the previous section, XRD analyses of the as-deposited and annealed structures were carried out. As shown in Fig. 2a and b, the XRD patterns of all annealed samples show an increasing intensity of Cu peaks in the annealed structures when compared with those of the as-deposited samples. It is likely due to the grain growth and densification of Cu film as a result of annealing. No diffraction peaks corresponding to Ru precipitates

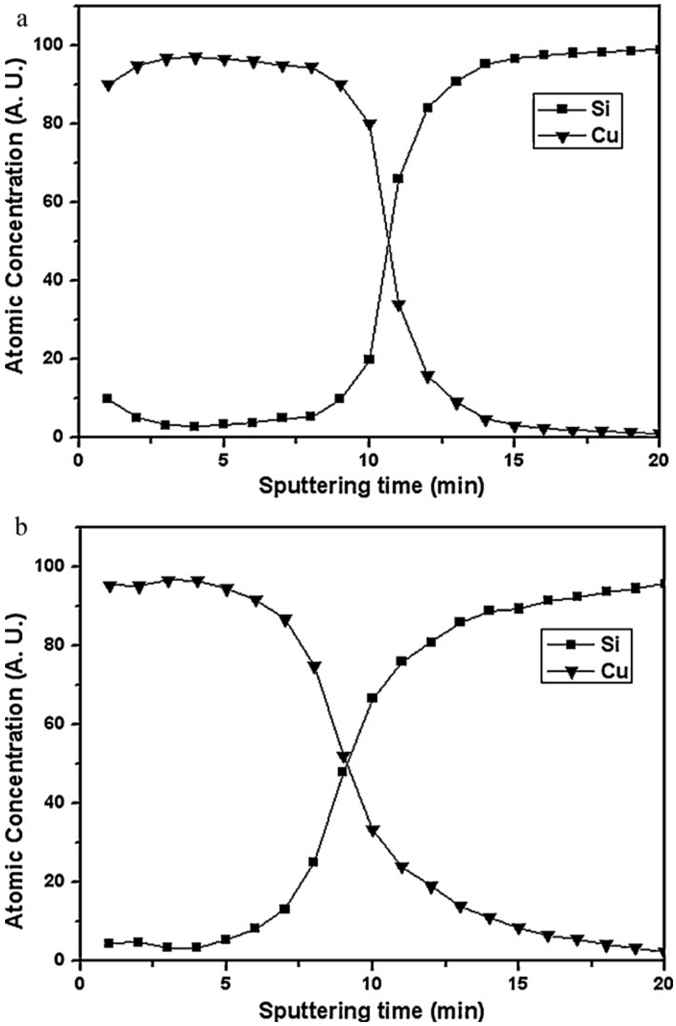

Fig. 4. AES depth profiles of (a) Cu/Cu(Ru)/Si and (b) Cu(Ru)/Si samples annealed at 500 °C for an hour.

are observed due to the small alloying content. The Cu diffraction peaks shifts toward higher diffraction angles with annealing temperature increasing. When annealed at 500 °C for Cu/Cu(Ru) film, Cu remains as the major phase without detectable copper silicide in the films. However, the peaks due to the formation of Cu silicide appear after annealing at 500 °C for the Cu(Ru)/Si structure (Fig. 2b). The formation of copper silicide is related to the presence of residual oxygen in the annealing ambient [15]. Since the grain boundaries that often provide as oxygen diffusion paths are reduced in the structures, the higher thermal stability of Cu/Cu(Ru)/Si samples is considered to be attributed to the top Cu layer that acts as a protecting layer to keep the Cu(Ru) from contacting with residual oxygen [16]. Thus, Cu/Cu(Ru) films have a high thermal stability and tolerates annealing at 500 °C, satisfying temperatures for post metallization processes to keep the Cu layer as a reliable interconnect metal.

Fig. 3 shows the plan-view transmission electron microscopy (TEM) micrographs of Cu/Cu(Ru) and Cu(Ru) film, respectively. According to Fig. 3a and b, after annealing at 500 °C, the grain size of the Cu(Ru) film is smaller than that of Cu/Cu(Ru) film. It indicates that Ru atoms may segregate to the grain boundaries and hinder the movement of grain boundaries. Consequently, the degree of grain growth is less in the Cu(Ru) films. The fine grain and alloy element in grain all can increase the resistivity of Cu film, which has been proved by the four-point probe measurement as well. Fig. 4a and b presents the AES compositional depth profiles of Cu/Cu(Ru)/Si and Cu(Ru)/Si samples after annealing at 500 °C. Any Ru signal is not detected in the 500 °C annealed sample due to the low Ru content. By doping Ru into pure copper, some of the Ru atoms precipitate at the grain boundaries, which can block the path of diffusion between copper and silicon, and inhibit the interaction between copper and silicon. In case of the Cu(Ru)/Si sample of Fig. 4b, no severe interdiffusion is observed between the original Cu(Ru) layer and the Si substrate, but the tail of Cu peak into the barrier layer is longer than that of Cu/Cu(Ru)/Si of Fig. 4a. This implies that the thermal stability of the Cu(Ru)/Si system is inferior to that of the Cu/Cu(Ru)/Si system. These results observed by AES are consistent with those obtained from XRD and resistivity measurements. Although there is no conclusive evidence supporting the presence of a self-formation barrier layer, obvious increasing stability of interface for Cu/Cu(Ru)/Si contact system is obtained. And further investigations are required to understand the phase development at the Cu(Ru)/Si interface during annealing.

4. Conclusions

The application of Cu/Cu(Ru) films on barrierless Si substrates for Cu metallization has been investigated. FPP, XRD, AES, and TEM have been used to characterize the films. After annealing at 450 °C, resistivity values of both systems decrease, but the reduction is more significant for Cu(Ru). However, the resistivity values of annealed Cu(Ru) film are still greater than that of annealed Cu/Cu(Ru) film. XRD data suggest that Cu/Cu(Ru) film has higher thermal stability and Cu silicide cannot be observed up to 500 °C. According to TEM results, after annealing at 500 °C, the grain size of the Cu(Ru) film is smaller than that of Cu/Cu(Ru) film. In conjunction with AES, XRD, TEM analyses and sheet resistance measurement discussed above, it implies that Cu/Cu(Ru) seed layers are potentially good for advanced Cu interconnects where both interfacial stability and low resistivity are required.

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