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Interfacial Characteristics of Copper/Diffusion Barrier/Low Dielectric Constant Material Systems at Elevated Temperatures

J. S. CHEN※, J. S. JENG and C. C. CHANG

Dept. Materials Science and Engineering, National Cheng Kung University
Tainan, Taiwan
*jenschen@mail.ncku.edu.tw

Thermal reactions of sputtered Cu films on the fluorinated silicon oxide (FSG) and organosilicate glass (OSG) layers, with and without TiN or TaN diffusion barrier, were investigated. The sheet resistance, surface morphology, phase formation and compositional depth profile of the mutilayer structures after vacuum annealing at 400 to 800 °C were examined. It is found that the sheet resistance values of all samples decreased after annealing at 400 to 600 °C and increased after annealing at 700 or 800 °C. Without the barrier layer, the increase of sheet resistance was accompanied with the dewetting of Cu films and the carbon outdiffusion for Cu/OSG sample or the Cu indiffusion of the Cu/FSG sample. When a TiN/Ti or a TaN/Ta barrier layer was interposed between Cu and the dielectric layer, the degree of dewetting of Cu film was significantly reduced for both systems. The reaction characteristics of the two dielectric systems upon vacuum annealing, with and without the barrier layer, are discussed.

Key words: Low dielectric constant, copper, diffusion barrier, integrated circuits

1. Introduction

Aluminum-based alloys are the conventional interconnect materials used for integrated circuits. At the same time, plasma-enhanced chemical vapor deposition (PECVD) SiO_2 has been used as the interlevel (or intermetal) dielectric material. The continuous down-scaling of device dimensions in integrated circuits produces several problems for circuit operation, such as the rapid increase of interconnect resistance-capacitance (RC) delay [1]. To reduce the RC delay, copper will substitute for aluminum to be the new conduction material because of its lower electrical resistivity; on the other hand, replacement of SiO_2 with low dielectric constant (low-k; $k<k_{SiO2}\approx3.9$) materials as the intermetal dielectrics is also indispensable. Fluorinated silicon oxide (FSG) produced by PECVD has been a widely accepted low-k material [2]. However, it is difficult to make the dielectric constant of FSG lower than 3. Organosilicate glass (OSG), also produced by PECVD [3], is one of the promising candidates of low-k ($k\approx2.5$-3) materials in next generation integrated circuits. Because copper is a fast diffusion species in silicon and silicon dioxide [4], it is expected to diffuse rapidly into FSG or OSG It is therefore important to characterize the interfacial diffusion and/or reaction between copper and low-k materials. On the other hand, in order to resist copper diffusion into low-k materials, it is necessary to interpose a barrier layer between copper and low dielectric constant layers. TiN and TaN are two of the popularly used diffusion barriers for copper metallizations [5,6]. In this work, we had prepared the Cu/FSG and Cu/OSG layers on bare Si, with and without the TiN/Ti or TaN/Ta barrier layer, and the samples were then annealed in vacuum at 400 °C to 800 °C. The material characteristics of these samples were examined to understand the thermal reactions of the Cu-FSG and Cu-OSG systems.

2. Experimental

The FSG and OSG films, 280 nm in thickness, were deposited on Si wafer in a single wafer CVD chamber. All wafers with dielectric films had been baked at 400 °C in N_2 atmosphere before Cu or barrier layer deposition (to ensure no moisture remaining on the film surface during the transportation). The Cu films (220 nm) were prepared using d.c. magnetron sputtering with a Cu target and at a negative substrate bias. Ti (10 nm) and TiN (50 nm) layers were deposited by r.f. sputtering from a Ti metal target, while Ta (10 nm) and TaN (50 nm) layers were deposited by r.f. sputtering from a Ta metal target. Both barrier layers were deposited at a negative substrate bias. After deposition, the Cu/FSG/<Si>, Cu/OSG/<Si>, Cu/TiN/Ti/FSG/<Si>, Cu/TiN /Ti/OSG/<Si>, Cu/TaN/Ta/FSG/<Si>, Cu/TaN/Ta/OSG/<Si> (the symbol of "<Si>" represents the single-crystalline silicon substrate) samples were annealed in vacuum (with Ti foils to reduce the residual oxygen) at temperatures ranging from 400 °C to 800 °C, with an interval of 100 °C, at 2×10^{-5} Torr for 1 hr to investigate their thermal reactions.

The sheet resistances of all samples, before and after annealing, were measured with a four-point probe. Surface morphology of the samples was characterized by scanning electron microscopy (SEM). The characteristic phases were identified by θ-2θ X-ray diffraction (XRD) with Cu K_α radiation. Compositional depth profiles analysis was performed with Auger electron spectroscopy (AES).

3. Results and Discussion

3.1 Cu/FSG/<Si> and Cu/OSG/<Si>

Figure 1 shows the sheet resistances of Cu/FSG/<Si> and Cu/OSG/<Si> samples as a function of annealing temperature. Compared with the value of the as-deposited sample, the sheet resistance values of both systems were significantly lowered after annealing at 400-500 °C. The sheet resistance values of the samples after annealing at 600 and 700 °C are about the same as those of 500 °C-annealed samples. According to our previous study on the Cu/SiO_2 systems [7], the reduction of sheet resistance shall be mainly attributed to the grain growth and defect annihilation in the copper films. Slight increase in sheet resistance of both systems was observed after annealing at 800 °C. Furthermore, the degree of increase is more evident for Cu/FSG/<Si> than Cu/OSG/<Si>. The difference in the change of sheet resistance with annealing temperature for the two systems suggests unlike behaviors for Cu/FSG and Cu/OSG systems upon annealing.

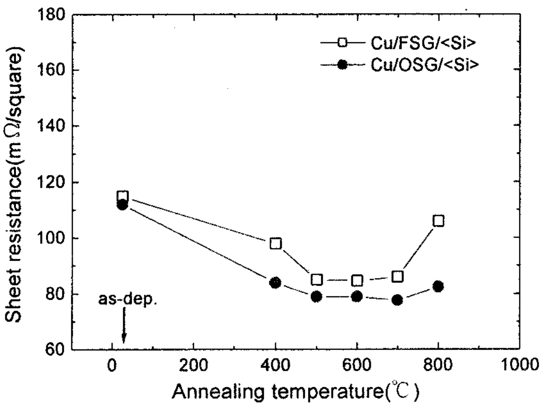

Fig. 1 Dependence of sheet resistances of Cu/FSG/<Si> and Cu/OSG/<Si> as a function of annealing temperature.

The phases presented in the samples before and after annealing were examined by XRD. Only diffraction peaks of Cu were revealed by XRD. Therefore, no significant chemical reaction had occurred in either system upon annealing. The increase of sheet resistance must relate with some minute structural change in the samples. Figure 2 gives the SEM micrographs on the surfaces of the 800 °C annealed Cu/FSG/<Si> and Cu/OSG/<Si> samples. The photographs show that there are large flower-liked broken regions on the surface of Cu/FSG/<Si> sample. The broken regions shall be formed simply due to the dewetting of the Cu films during high temperature annealing, since no reaction was detected by XRD and the sample surface still appeared to be the normal copper color. The dewetted region may extend to be as wide as 40 μm. Similar flower-liked dewetted regions are also seen on the surface of the Cu/OSG/<Si> sample, but with smaller sizes (about 5 μm). The different sizes of the dewetted regions shall be attribute to the difference in the interface energy or the stress developed in the Cu/FSG and Cu/OSG systems.

Figure 3 presents the AES compositional depth profiles of Cu/FSG/<Si> and Cu/OSG/<Si> samples, after annealing at 800 °C. The AES depth profiles were taken by probing the area covered with copper, so that the profiles would not be complicated by the presence of dewetted regions. Fig. 3(a) shows that AES profiles for the 800 °C

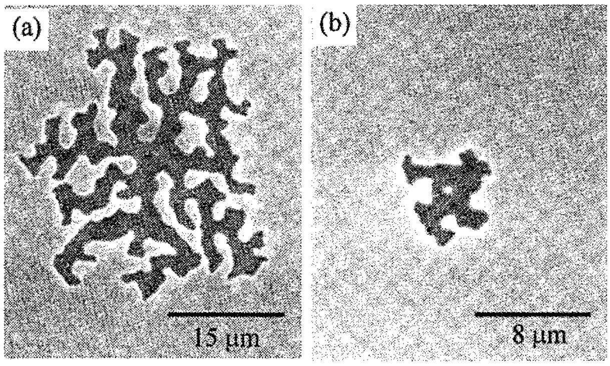

Fig. 2 SEM micrographs on the surfaces of 800 °C annealed (a) Cu/FSG/<Si> and (b) Cu/OSG/<Si>.

annealed Cu/FSG/<Si> sample. The Cu, O, and Si profiles at the Cu/FSG interface of the 800 °C annealed sample are quite similar to that of as-deposited sample, indicating that no apparent reaction had occurred in the sample. We had not observed the extension of F profile into the Cu layer in Cu/FSG/<Si> sample after annealing at 800 °C. However, Fig. 3(a) reveals a slight penetration of Cu profile into FSG layer (in the range of sputtering time of ~1200 sec.), which indicates that Cu diffused easily into FSG when annealing at 800 °C. Therefore, FSG is not a proper dielectric material for direct contact with copper.

Fig. 3(b) presents the AES compositional profiles of Cu/OSG/<Si> after annealing at 800 °C. In comparison with AES spectra of the as-deposited sample (not shown here), the slopes of Cu, O and Si profiles at Cu/OSG

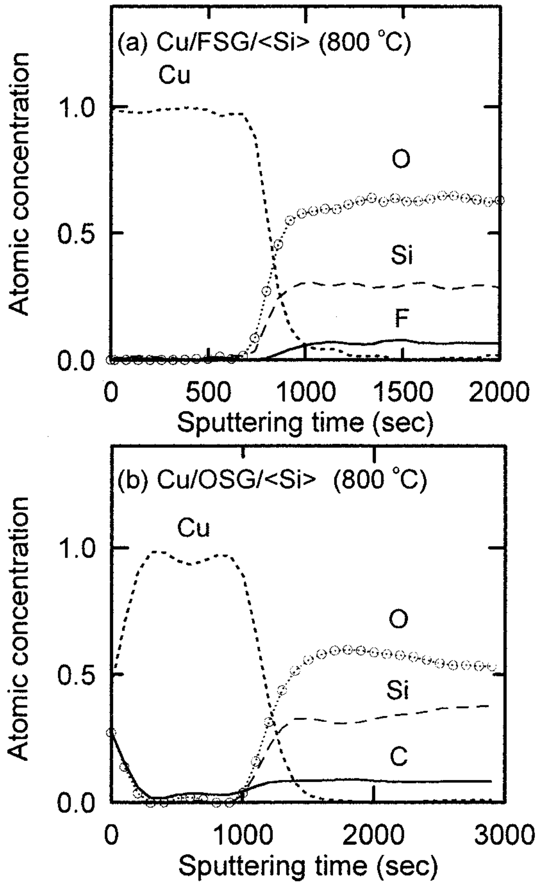

Fig. 3 AES compositional depth profiles of 800 °C annealed (a) Cu/FSG/<Si>, and (b) Cu/OSG/<Si>.

interface were almost unchanged after annealing at 800 °C, except that the carbon profile had penetrated into the Cu region. The slight increase in the sheet resistance for Cu/OSG/<Si> sample after annealing at 800 °C may be related with the diffusion of carbon into the copper layer.

In summary, without employing any diffusion barrier, Cu will not react with FSG or OSG. However, the Cu layer becomes dewetted after high temperature annealing. Cu will diffused into FSG after annealing at 800 °C. On the other hand, no apparent diffusion of Cu into OSG was observed but the C atoms in OSG will diffuse into the Cu layer.

3.2 Cu/TiN/Ti/FSG/<Si> and Cu/TiN/Ti/OSG/<Si>

Sheet resistances of Cu/TiN/Ti/FSG/<Si> and Cu/TiN/Ti/OSG/<Si> samples as a function of annealing temperature are show in Fig. 4. When interposing the TiN/Ti barrier layer between copper and FSG or OSG, we observed that the sheet resistance also decreases after annealing the samples at 400-600 °C. The sheet resistance value of the 700 °C annealed Cu/TiN/Ti/FSG/<Si> and Cu/TiN/Ti/OSG/<Si> sample increased, as compared to that of 600 °C annealed sample. Sheet resistances of both systems increase further after annealing at 800 °C. The change in the sheet resistance of FSG system is a little larger than that of the OSG system. However, similar to the systems without TiN/Ti barrier, XRD did not detect any new phase in the annealed samples. Accordingly, no reaction had occurred in the Cu/TiN/Ti/ FSG/<Si> and Cu/TiN/Ti/OSG/<Si> samples after heat treatments.

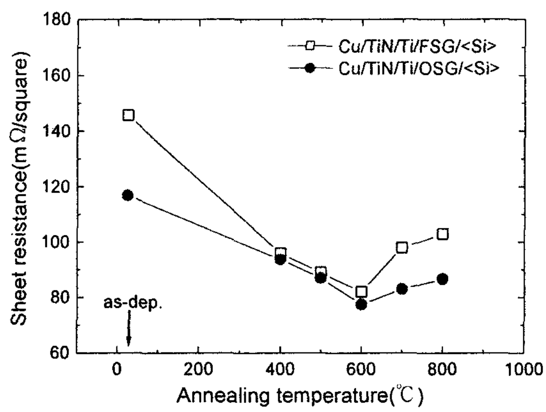

Fig. 4 Sheet resistances of Cu/TiN/Ti/FSG/<Si> and Cu/TiN/Ti/OSG/<Si> vs. annealing temperature.

As for the surface morphology, small-size voids were revealed on the Cu/TiN/Ti/FSG/<Si> and Cu/TiN/Ti/OSG/<Si> samples after annealing at 800 °C (Fig. 5). The TiN/Ti barrier layer of Cu/TiN/Ti/FSG(or OSG)/<Si> samples therefore could modify the interface energy and/or film stress so that it would reduce the dewetting of copper.

Regarding the interdiffusion phenomenon, figure 6 shows the AES compositional profiles of Cu/TiN/Ti/FSG/<Si> and Cu/TiN/Ti/OSG/<Si> samples after annealing at 800 °C. In the FSG sample, Cu had diffused into the TiN/Ti barrier after annealing at 800 °C. However, Cu will not diffuse into TiN/Ti for the OSG sample. The FSG layer acts as a "sink" to Cu; therefore Cu will diffuse towards to FSG, even with a TiN/Ti barrier in between. Also, for the 800 °C annealed Cu/TiN/Ti/OSG/<Si> sample, the carbon profile was stopped at Ti/OSG interface, which implies that TiN/Ti barrier layer can sufficiently resist the outdiffusion of carbon atoms. However, the O profile extended into Ti layer, and even into the TiN layer. Although TiN/Ti barrier will effectively retard the outdiffusion of carbon from OSG, it will be oxidized during annealing. Oxidation of TiN/Ti barrer layer shall contribute to the increase of sheet resistance of the system.

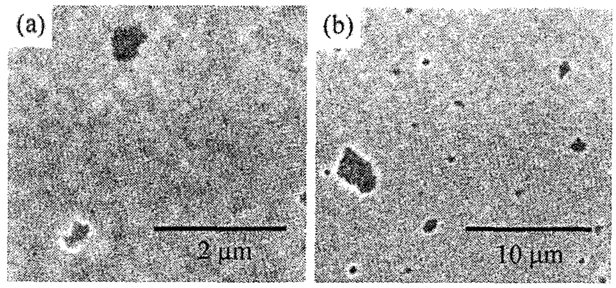

Fig. 5 SEM micrographs on the surfaces of 800 °C annealed (a) Cu/TiN/Ti/FSG/<Si> and (b) Cu/TiN/Ti/OSG/<Si>.

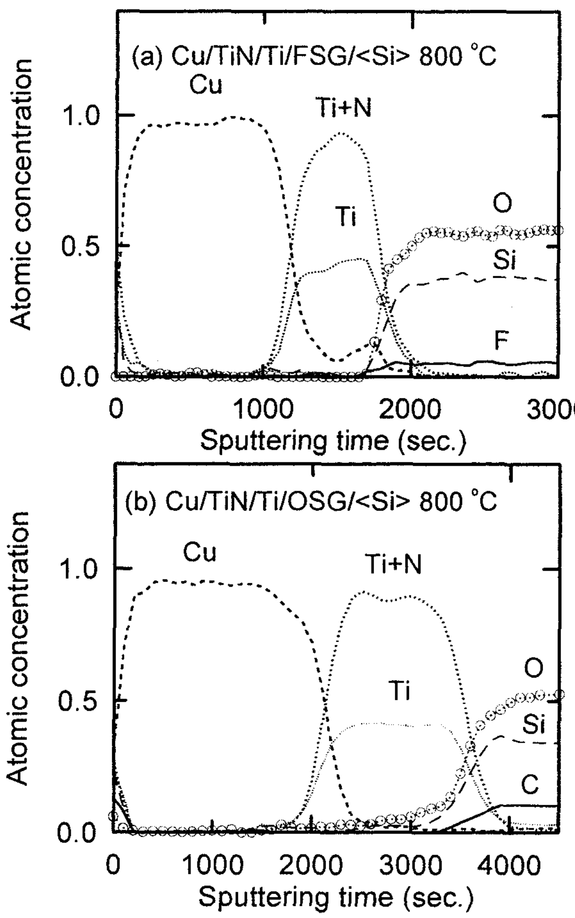

Fig. 6 AES compositional depth profiles of 800 °C annealed (a) Cu/TiN/Ti/FSG/<Si> and (b) Cu/TiN/Ti/OSG/<Si>.

3.3 Cu/TaN/Ta/FSG/<Si> and Cu/TaN/Ta/OSG/<Si>

Since TiN barrier will be oxidized when contacting with the dielectric layer, an oxidation-resistant material, TaN [8], is employed as the diffusion barrier. Variation of sheet resistances of Cu/TaN/Ta/FSG/<Si> and Cu/TaN/Ta/OSG/<Si> samples with the annealing temperature is show in Fig. 7. The minimum resistance is reached after annealing at 600°C, for both FSG and OSG systems. As the annealing temperature increased to 700 °C and 800 °C, the sheet resistances are raised again. Since the values of sheet resistance for both systems are almost the same after annealing at 500-800°C, the TaN/Ta barrier shall be effective in preventing the reaction between Cu and FSG or OSG; therefore, the sheet resistance becomes independent of the dielectric layers been used. When comparing Fig. 4 and Fig. 7, one sees that the sheet resistance values of the FSG system are more stable with the TaN/Ta barrier than with the TiN/Ti barrier. TaN thus shall be a superior barrier to TiN for the Cu-FSG system.

Similar to the situation of using TiN/Ti barrier, small voids are observed on the surfaces of the Cu/TaN/Ta/FSG/<Si> sample after annealing at 800 °C. However, on the surface of the 800 °C annealed Cu/TaN/Ta/OSG/<Si> sample, voids are very few and scattered. By comparing Fig. 5 and Fig. 8, we are aware that the surface voids are more significantly reduced when using TaN/Ta barrier. Therefore, the TaN/Ta barrier is not only beneficial for stabilizing the sheet resistance, it may also improve the surface morphology of the Cu films at high temperatures.

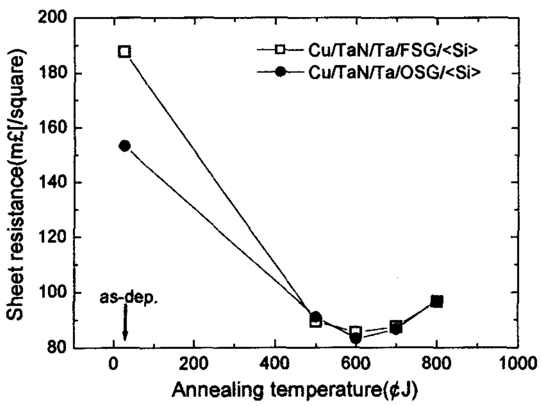

Fig. 7 Sheet resistances of Cu/TaN/Ta/FSG/<Si> and Cu/TaN/Ta/OSG/<Si> vs. annealing temperature.

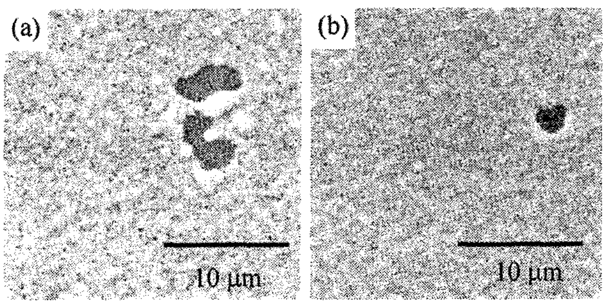

Fig. 8 SEM micrographs on the surfaces of 800 °C annealed (a) Cu/TaN/Ta/FSG/<Si> and (b) Cu/TaN/Ta/OSG/<Si>.

4. Conclusions

Sheet resistances of all systems are significantly lowered after annealing at 400 to 600 °C, for both FSG and OSG systems, either with or without the barrier layers. As the annealing temperature increased to 700 °C, the sheet resistances of samples without diffusion barrier stay at about the same values. In contrast, the sheet resistances of samples with either TiN/Ti or TaN/Ta diffusion barrier increase slightly. However, the stability of the sheet resistance (the change upon annealing) of the Cu-low k systems becomes thermally more stable with the TaN/Ta barrier, particularly for the FSG systems.

The variation of sheet resistance is not attributed to the chemical reaction because XRD analysis reveals no new phase formed upon annealing. Cu films beome dewetted of on both systems after annealing at 800 °C. However, the degree of Cu dewetting is significantly reduced when the TaN/Ta barrier is interposed. Regarding the interdiffusion, diffusion of Cu (into the FSG layer) and diffusion of C (from OSG to Cu) are observed in the 800 °C annealed Cu/FSG/<Si> and Cu/OSG/<Si> systems, respectively. With the TiN/Ti barrier, the inward diffusion of Cu cannot be prevented in the FSG system, but the outward diffusion of C in the OSG system is retarded. The significant increase in the sheet resistance of the 800 °C annealed Cu/FSG/<Si> and Cu/TiN/Ti/FSG/<Si> systems is thus related with the Cu diffusion and Cu dewetting. These phenomena shall be prevented when the TaN/Ta barrier is interposed between Cu and FSG. Additionally, the thermal stability of the OSG system is superior to that of the FSG system and it can be further improved with the TaN/Ta barrier.

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