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Roles of copper mechanical characteristics in electropolishing

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We investigated the effect of film stress, hardness, and grain size of copper films on copper electropolishing, which was considered as a next-generation technique in copper multilevel interconnects. The copper electropolishing rate was found to increase with an increase in the tensile stress of copper films. It was suggested that the tensile stress weakened metallic bonds between copper atoms and assisted the copper electropolishing rate, whereas the hardness and grain size of polished copper films did not relate directly to the copper electropolishing rate due to a negligible etching effect and no mechanical stress applied during copper electropolishing in a concentrated phosphoric acid electrolyte. [DOI: 10.1116/1.1633775]

I. INTRODUCTION

Chemical–mechanical polishing (CMP) of copper and barrier metals was widely recognized as a most promising technology for planarizing copper damascene interconnects.[1–3] However, conventional copper CMP slurries contained mechanically hard abrasives that scratched and damaged polished copper surfaces resulting in reliability problems. Therefore, alternative planarization approaches, compatible with electroplating, were attractive to pursue. Recently, copper electropolishing has received much attention in multilevel interconnects mainly due to its advantages of not scratching polished surfaces and not imposing mechanical stress on substrates.[4–6] The stress-free characteristic of copper electropolishing was especially beneficial to the integration of super low dielectric constant ($k<2$) materials into multilevel interconnects in next-generation technology. Replacing copper CMP with copper electropolishing was demonstrated by Contolini *et al.*[4] in 1994. In following works, TSMC and SONY companies have demonstrated fabrications of multilevel interconnects using copper electropolishing.[5,6]

During copper electropolishing, the oxidation of Cu to be Cu^{2+} from breaking metallic bonds between copper atoms was achieved by the input of an anodic current. The mechanical properties of copper films, therefore, were thought to have great influences on the copper electropolishing rate. However, various plating baths, substrate materials, annealing processes, etc., affected the mechanical properties of deposited copper films.[7–9] For example, our previous study[7] has reported that various plating baths resulted in copper films with different impurity levels, thus leading to plated copper with a different activation energy of grain growth. Nevertheless, a few studies have reported the relationship between the mechanical characteristic of copper films and copper electropolishing. This article elucidates the roles of film stress, hardness, and grain size in the copper removal during the electropolishing process.

II. EXPERIMENT

To eliminate the impurity effect of copper films on the copper electropolishing rate, 1-μm-thick copper films were deposited by sputtering on $TaN/SiO_2/Si$ substrates (6 in.) and then annealed by a furnace with various temperatures for 30 min in a high vacuum (5×10^{-5} Torr) to change the mechanical properties of copper films. After being annealed, the film stress of copper films was determined by a TENCOR FLX 2320 through measuring a difference of wafer curvature between before and after the deposition of copper films. A nanoindenter XP system was used to measure nanoscale hardness. The phase and crystal structure of copper films were identified by x-ray diffractometry (XRD). The resistivity of copper films was measured by a four-point probe. The measurements before copper electropolishing were performed near the center of 6 in. wafers. The experiments on copper electropolishing were carried out in a tank of nonconducting material, in which the counterelectrode was a platinum plate with a size of 6 cm×6 cm and the working elec-

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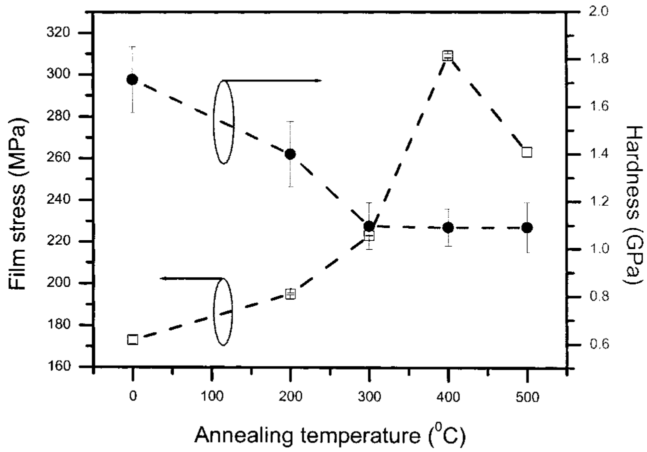

FIG. 1. Variation of film stress and hardness of copper films with the annealing temperature.

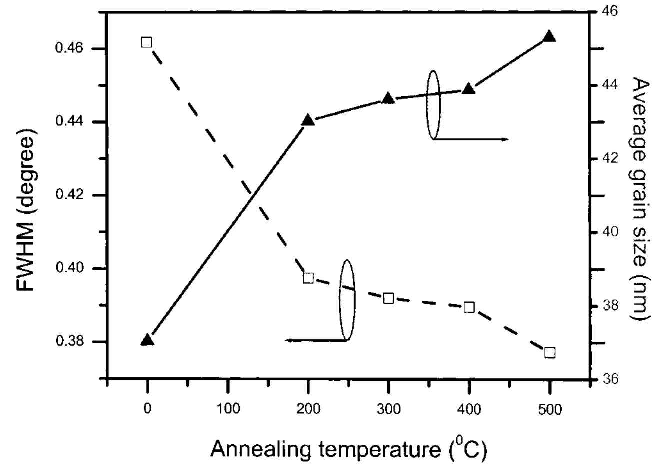

FIG. 3. Annealing temperature dependence of the FWHM of the (111) diffraction peaks of annealed copper films. Crystalline sizes for those annealed copper films were calculated as the Scherrer equation.

trode was a sliced wafer with a size of 2 cm×3 cm. Contacting to the electrode was implemented outside of the electrolyte with an alligator clip. The polishing electrolyte was phosphoric acid (~16 M H_3PO_4, purchased from Fluka) and the copper films were polished under potentiostatic control (1.75 V) at room temperature. The polishing rate was calculated from the thickness difference of copper films (measured near the center of sliced wafers) before and after copper electropolishing. The film thickness was examined using a field emission scanning electron microscope. The data of the polishing rate were on average from one film to another.

III. RESULTS AND DISCUSSION

Figure 1 depicts that the magnitude of tensile stress in copper films increased gradually from 173 MPa to 309 MPa as the annealing temperature was elevated to 400 °C, whereas a higher annealing temperature of 500 °C inversely resulted in a decrease of tensile stress. Meanwhile, the hardness of the annealed films decreased to a stable value of ~1.1 GPa as the annealing temperature increased.

Figure 2 shows the XRD spectra for as-deposited and annealed copper films with the annealing temperatures of 200, 300, 400, and 500 °C. Two peaks on XRD spectra corresponded to the (111) and (200) planes and indicated annealed copper films with face-centered-cubic structures. By fitting the (111) peaks with Gaussian profiles, the full width at half maximum (FWHM) of those peaks in Fig. 2 was shown in Fig. 3. The average grain size (D) of copper films was determined using the Scherrer equation:[10]

$$D = 0.9\lambda/\Delta \cos \theta, \tag{1}$$

where λ was the x-ray wavelength, Δ was the FWHM of XRD peaks in 2θ units, and θ was the Bragg diffraction angle. Figure 3 thus depicts that the grain size of annealed copper films increased by increasing the annealing temperature.

Figure 4 reveals the effect of annealing temperature on the copper electropolishing rates. With increasing annealing temperature up to 400 °C, the electropolishing rate of annealed copper films increased gradually to ~910 nm/min. A further increase in annealing temperature to 500 °C, however, re-

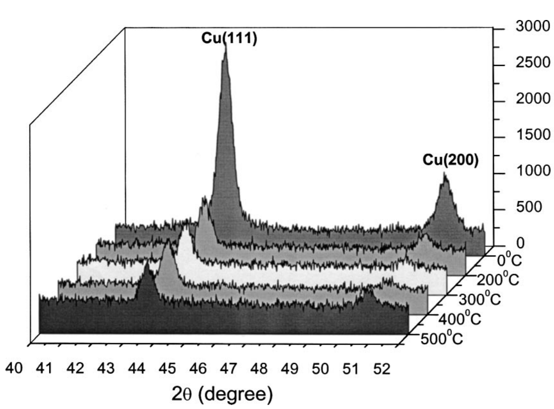

FIG. 2. X-ray diffraction patterns for as-deposited copper films and copper films annealed at the temperatures of 200, 300, 400, and 500 °C.

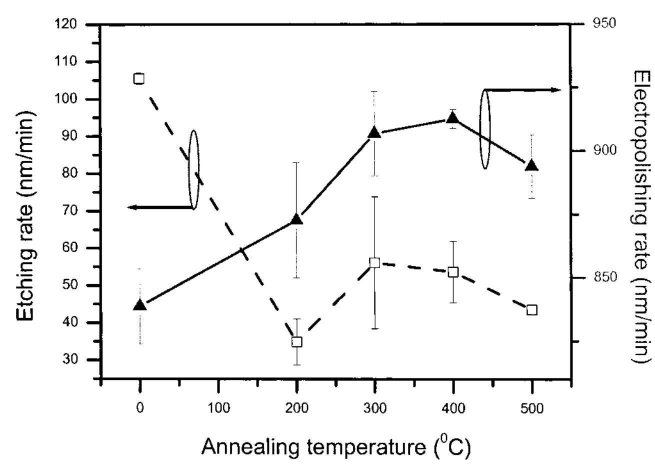

FIG. 4. Variation of the chemically etching rate (in ~0.22 M HNO_3) and the electropolishing rate (in ~16 M H_3PO_4) of copper films with various annealing temperatures.

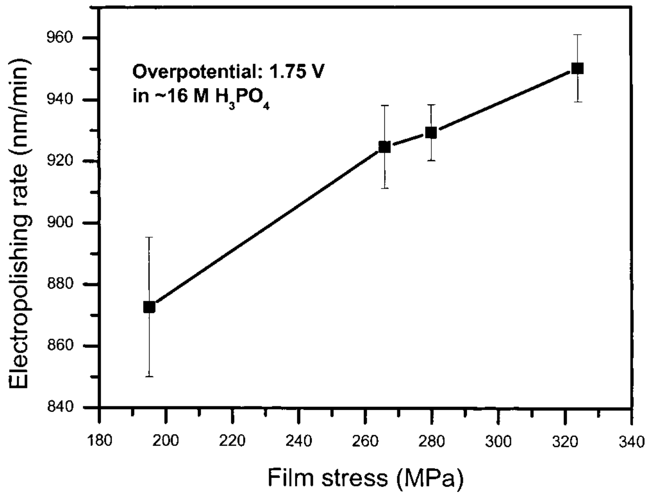

FIG. 5. Copper electropolishing rate for copper films with various stresses but with the same hardness and grain size.

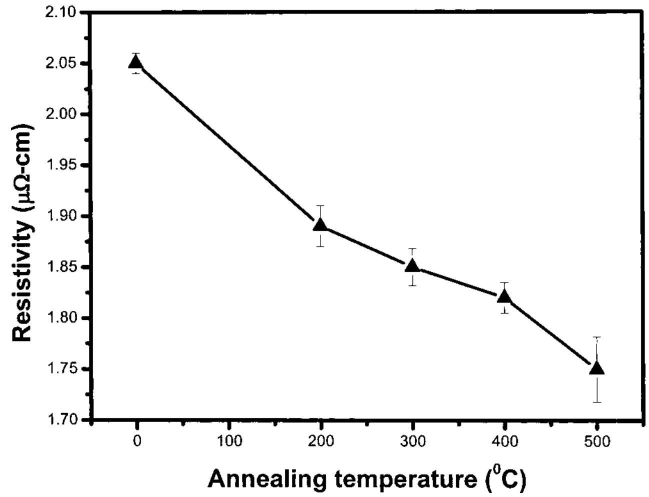

FIG. 6. Evolution of copper resistivity with the annealing temperatures.

sulted in a decrease of copper electropolishing rate. In particular, the transformation of copper electropolishing rate with increasing annealing temperature was found to be consistent with that of the film stress of annealed copper films. Film stress, therefore, was suggested to be involved in the mechanism of copper electropolishing. During electropolishing, Cu was oxidized to be Cu^{2+} by the applied overpotential. The copper electropolishing rate depended on the strength of copper metallic bonds. The bond stretching or contraction resulted from tensile or compressive stresses, respectively, in the polished copper films either assisted with or impeded the copper removal. In order to clarify the influence of film stress on the copper electropolishing rate, silicon nitride films with different thicknesses were deposited on the wafer back side by a plasma-enhanced chemical vapor deposition system. Then, wafers were annealed at the same temperature of 200 °C for 30 min to change the film stress, while maintaining copper films with the same hardness (~1.4 GPa) and grain size (~43.0 nm). Figure 5 reveals that the copper electropolishing rate increased by increasing the tensile stress of polished copper films. The result confirms that the film stress contributed to the copper electropolishing rate.

Figure 6 shows the evolution of copper resistivity with annealing temperatures. It was found that the resistivity of copper films decreased as the annealing temperature increased. When the copper films with different thicknesses of silicon nitride films on the wafer back side were annealed at the same temperature of 200 °C to maintain copper films with a similar hardness and grain size, the copper resistivity nearly remained unchanged. Therefore, the reduction of copper resistivity was suggested to be dominated by the grain size of copper films.

By etching copper films with ~0.22 M HNO_3, which could provide directly copper dissolution without the passivation effect on copper surfaces, a slower etching rate was found for the copper films annealed at higher temperatures, as shown in Fig. 4. This result suggested that an increase in the grain size of the annealed copper films led to fewer active surfaces or grain boundaries in the films as compared with that of as-deposited copper films, and thus resulted in a slower etching rate. Moreover, the chemically etching rate of annealed copper films in 16 M phosphoric acid was about 2–5 nm/min, which was almost negligible as compared with the electropolishing rate of 800–950 nm/min (at the applied voltage of 1.75 V). The slight etching effect of copper electropolishing in concentrated phosphoric acid may be due to the passivation effect on copper surfaces.[12] Therefore, we propose that the grain size (grain boundaries) of copper films was not a dominant factor in the copper electropolishing rate.

Hardness was the resistance of materials to plastic deformation. In CMP studies, the removal rate of some dielectric materials was found to be inversely proportional to the film hardness due to the dominant mechanical polishing.[8,11] However, copper electropolishing was a nonmechanical-stress process and our previous work reported that the optimization of copper electropolishing processes was explored to be in the mass-transfer-limited plateau with a stable limiting current density.[12,13] The existence of a passivation film on the polished surface also contributed to the microleveling effect of copper electropolishing.[14] In a previous study, Padhi *et al.*[15] demonstrated that with optimal process parameters, the local topography was reduced from 5500 to 2000 Å while global nonuniformity after electropolishing on a 200 mm wafer was 1.3%. Due to the slight etching effect and lack of mechanical stress applied during the electropolishing process, the grain size (the former mechanism) and hardness (the latter mechanism) of polished copper films were suggested to be exclusive factors for removing copper metal.

IV. CONCLUSION

In this study, the copper electropolishing rate was explored to ascertain the dependence on the film stress of polished copper films, and the increase by increasing tensile stress due to tensile-stress-induced weaker copper metallic bonds. The passivation effect on copper surfaces with a negligible etching rate and no mechanical stress applied on polished copper films resulted in the grain size and hardness of copper films being the exclusive factors contributing to the copper removal.

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