The Effect of Plating Current Densities on Self-Annealing Behaviors of Electroplated Copper Films

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In this study, the effect of plating current densities on self-annealing behaviors of electroplated Cu films was found to be relevant to the polarization resistance of electroplating systems. Porous films with defects occurred at low plating current density or at low polarization resistance. In contrast, dense films with small grains occurred at higher plating current density or at higher polarization resistance. However, when more current was further supplied, Cu aggregation occurred and deposited films became spongy or dendritic. We suggest that both the defects within porous films and the underlying energy of fine-grained deposits accelerated self-annealing. These two characteristics competed with each other to determine the resistivity drop by self-annealing. On the other hand, the (111) texture evolutions of deposited Cu films with an increase of plating current densities were consistent with the evolutions of resistivity and surface morphology.

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Experimental

The blanket wafer for this study was prepared by depositing a 50 nm sputtered TaN diffusion barrier and a 50 nm sputtered Cu conductive layer on a SiO2/Si substrate. In Cu electroplating processes, the films were deposited under galvanostatic control at room temperature. The crystallographic texture of Cu films was analyzed by X-ray diffraction (XRD). The morphology and the thickness of deposited films were examined by field emission scanning electron microscope (FESEM). The sheet resistance of Cu deposits was measured by a four-point probe measurement. The grain size and surface roughness were measured by atomic force microscope (AFM) of DI Nanoscope.

Results and Discussion

The behavior of electroplated Cu differs from the usual behavior of sputtered Cu, in which no dramatic changes occur at room temperature unless additional stored energy is present. Electroplated Cu thin films can undergo spontaneous abnormal grain growth at room temperature. Microstructure evolution occurs during a transient period of hours following deposition, and includes an increase in grain size, changes in preferred crystallographic texture, and decreases in resistivity, hardness, and compressive stress.11-15 One reasonable model was based on grain boundary energy in the fine-grained as-deposited films providing the underlying energy that drives abnormal grain growth.16,17 A number of studies13-15 have reported on the effect of the bath temperature, current density, bath concentration, etc., on morphologies and textures, but the effect of plating current densities on textures and self-annealing behaviors has not been well understood.

In our previous work,18 we demonstrated the polarization effect on microstructure evolution and filling capability with an increase of plating current density. According to the range of the current density, the electroplating process can be divided into two regions of mechanisms. When electroplating is under a lower current regime, the electrocrystallization process is a charge-transfer controlled dominant reaction. As the bias current is increased, a mass-transfer controlled dominant reaction takes over until the limiting current density is reached; finally, the reaction is pure mass transfer controlled. In this study, we suggest that the polarization resistance also influences the rate of self-annealing. Figure 1 displays the proposed model of a microstructure evolution with an increase of plating current densities and polarization resistance. Porous or less dense films with defects occurred at low plating current density or at low polarization resistance, as shown in Fig. 1a, then the defects of porous films accelerated resistivity drop. When the defects within porous films decreased with an increase of plating current densities and...
The resistivity evolution with time and comparison of the films containing Cu sulfate plated at different plating current densities in the electrolyte-fig-2 curves a-c of Fig. 2 represent resistivity drops of Cu deposited at 1, 3.33, 6.67, 10, and 16.67 mA/cm², respectively. It can be seen that the resistivity drop by self-annealing was largest at the lowest current density (curve a of Fig. 2), and it decreased to a minimum value with an increase of plating current densities (curve a-c of Fig. 2). In general, porosity in a film is associated with defects generated during deposition and porous films occur at low plating current density or at low polarization resistance. Therefore, the defects of porosities drove self-annealing and promoted resistivity drop. However, when the defects within porous films decreased with plating current densities, the self-annealing velocity was slow down. Therefore, the quantity of defects eventually responds to the resistivity of as-deposited films. Figure 3 shows the resistivity and average surface roughness (Ra) evolutions of as-deposited films with plating current densities. We found that the abrupt drop of resistivity (7.70 to 2.86 μΩ cm) and average surface roughness (56.10 to 31.43 nm) when the plating current density increased from 1 to 3.33 mA/cm². The assistant evidence of decreasing porosity with plating currents was obtained in Fig. 3. This phenomenon was first observed and seen to be different from accelerating self-annealing as an increase of the bias current density, which was mentioned by several groups. On the other hand, the perfect gap-filling performance of Cu electroplating in high aspect ratio gaps was usually operated at lower plating current densities. In our previous study, we demonstrated that a higher filling capability was operating in a lower current regime and the filling capability was inversely proportional to the plating current densities (0.33-6.67 mA/cm²). So far, this finding was valuable for optimizing the super-filling abilities and electrical characteristics of plated Cu.

Continuously, when further high current density was supplied (curve c to d of Fig. 2), the resistivity drop increased again. This can be understood as an increase of the current density enforced the polarization effect and thus enhanced the Cu nucleation process, which promotes the formation of denser Cu films and gives uniform grain distribution, resulting in a lower resistivity Cu film, as shown in Fig. 3. Therefore, the underlying energy of the finer-grained deposits (curve d vs. curve c) enhanced self annealing. This observation was similar to the investigations of Haebum et al. According to the principles of electrocrystallization, the rate of formation of new nuclei on the electrode surface increases exponentially as the cathodic polarization increases.

\[
\omega = B \exp \left( -\frac{K}{\eta} \right) \tag{1}
\]

where the constants B and K are specific for a given metal and temperature. If all other factors remain constant, the increase of cathodic polarization will result in a larger number of newly formed nuclei and a smoother deposit. Figure 3 displays that the resistivity and Ra of as-deposited Cu films decreased with an increase of plating current densities until a threshold current density was reached, and then increased with an increase of plating current densities.

The SEM cross section of Fig. 4 also shows that the Cu film deposited at 10 mA/cm² was denser than the film deposited at 3.33 mA/cm². But a porous film occurred again when the plating current density was increased to 16.67 mA/cm². Furthermore, the mean grain size measured by atomic force microscopy (AFM) also decreased with an increase of plating current densities, but increased when more current was supplied, as can be seen in Fig. 5. For grain

Figure 1. The proposed model of the relationship between self-annealing with polarization effect.

Figure 2. The resistivity evolution with time and comparison of the films plated at different dc densities for the electrolyte containing Cu sulfate (30 g/L), sulfuric acid (275 g/L), and chloride ion (100 ppm).

Figure 3. The effect of plating current densities on surface roughness and resistivity of as-deposited Cu films.
growth, the stored energy decreases with an increase of the growing grain size, and the grain boundary velocity is inversely proportional to the average grain size.\textsuperscript{17} This also can explain the phenomenon that the self-annealing effect of the film deposited at 10 mA/cm\textsuperscript{2} was faster than the film deposited at 6.67 mA/cm\textsuperscript{2}, as shown in Fig. 2.

When more current was further supplied, the depletion of cupric ions in the diffusion layer near the cathode surface became severe. Therefore, cupric ions were more difficult to replenish instantly from the solution into the diffusion layer.\textsuperscript{13,14} In addition, since cupric ions were reduced very fast and Cu aggregation occurred around the protrusion on the surface under higher electric field, the morphology of deposits became spongy or dendritic. Concurrently, the crystalline defects accelerated self-annealing. In a previous study,\textsuperscript{9} Haebum and co-workers found the visible evidence of those defects, and they demonstrated that the density of dislocation loops, which could accelerate the self-annealing process, increased with plating current densities \( \sim 3.5 \) to \( 40 \) mA/cm\textsuperscript{2}.

According to the above discussion, we suggest that both the defects of less dense packing deposits and the underlying energy of fine-grained deposits accelerated self-annealing. Therefore, there were two characteristics competing with each other to determine the velocity of self-annealing. Figure 6 also shows the rate of resistivity evolution with time and compares this rate for the films deposited at an equal number of coulombs (average film thickness was about 450 nm). The results are consistent with the trend of Fig. 2.

The crystallographic texture of Cu is face-centered-cubic (fcc) and (111) is the closed packed plane in fcc structures. Therefore, (111) has higher electromigration resistance than other planes of the fcc structure. In fcc thin films, the (111) texture is favored by the surface and interfacial energy minimization, whereas the (200) texture is favored by the strain energy minimization.\textsuperscript{17} The observed textures may result from a competition between these mechanisms as mentioned. In Fig. 7, X-ray diffraction (XRD) analyses show the textures of deposits varied with plating current densities. We see that electroplated Cu films had a strongly preferred orientation of (111). In Fig. 5, we also can find that the intensities of Cu(111) peaks increased with an increase of plating current densities, then decreased when more current was supplied. This is because when the deposit plane is oriented normal to the electric field direction, its texture or preferred orientation is symmetrical to the field direction or its growth direction. Lee and co-workers demonstrated that the texture of electrodeposits changes from the orientation that places the lowest energy crystal facets parallel to the substrate under a condition of the lower ion concentration adjacent to the deposit, to the orientation that places the higher energy crystal facets parallel to the substrate as the higher ion concentration adjacent to the deposit increases.\textsuperscript{13,14} An increase of plating current densities decreases the cupric ion concentration adjacent to the cathode, because the depletion rate of cupric ion due to reduction at the cathode is higher than the diffusion rate of cupric ion to the cathode, as can be seen in Fig. 1. Since the (111) plane is the lowest surface energy plane for Cu, an
adequate increase of plating current with sufficient polarization enhances Cu (111) intensities. However, when more current is supplied, the less dense packing deposits reduce the (111) peaks. The texture evolutions of Cu films with an increase of plating current densities were consistent with previous discussions on resistivity and surface morphology. Therefore, we suggest that the textures of deposits also correspond to polarization effects.

Conclusions

We investigated the microstructure evolution of the electroplated copper with different plating current densities and found that there were two mechanisms competing with each other to determine the resistivity drop by self-annealing. One is the defects of less dense packing deposits and the other is the underlying energy of the fine-grained deposits. The intensities of Cu(111) peaks increased with an increase of plating current densities, then decreased when more current was supplied. The texture evolution of Cu films with plating current densities is consistent with the evolutions of resistivity and surface morphology. Therefore, the texture of deposits may correspond to polarization effects of Cu electroplating.

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