



Superpolishing for Planarizing Copper Damascene Interconnects

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We demonstrate a superpolishing electrolyte, which consists of acid additives in conventional Cu polishing electrolytes (H_3PO_4), for efficiently planarizing Cu damascene features. The significant additive concentration gradient in features, resulting in a selective Cu dissolution rate within features, is explored as a major mechanism that yields such electrolytes with high planarization efficiency. Moreover, another additive, polyethylene glycol as a suppressor, is also employed to reduce oxygen bubbling on polished films. Consequently, a smooth surface with a complete step height elimination is obtained in a 70 μm trench after electropolishing.

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Chemical mechanical polishing (CMP) of Cu and barrier metals is widely recognized as the most promising technology for planarizing Cu damascene interconnects.¹⁻⁴ However, conventional Cu-CMP slurries contain mechanically hard abrasives that scratch and damage polished Cu surfaces. Recently, Cu electropolishing has been explored as a replacement of Cu-CMP due to its higher polishing rate, lower waste stream, no scratching, and no mechanical stress on substrates. TSMC company announced CMP-free and CMP-less approaches by integrating Cu electropolishing.⁵ Sony company announced a 25 μm wide line formed by soft polishing technology.⁶ They used a complexing agent to block Cu surface and introduced a soft pad to remove Cu complex outside of pattern, thereby producing selective electrochemical dissolution.

Cu electroplating generally produces a step on/between damascene features after deposition. Moreover, planarization efficiency (PE) of Cu electropolishing is a strong function of the feature size (also for Cu CMP).^{7,8} Those issues necessitate additional modifications to conventional polishing techniques. Because Cu dissolution rate depends on the pH value of polishing electrolytes and increases with solution conductivity, an addition of acid additives into polishing electrolytes can enhance Cu removal rate. Based on this mechanism and additive distributions controlled in diffusion limit, a presence of concentration gradient of additives in damascene features forms a selective electrochemical dissolution, thus enhancing step height reduction and improving PE of Cu electropolishing. In this article, we demonstrate a superpolishing electrolyte with high PE by adding acid additives into the polishing electrolyte (H_3PO_4). Additionally, oxygen formation during Cu electropolishing often causes severe etched pits on polished surfaces. With polyethylene glycol (PEG) as a suppressor in the electrolyte, the overpotential of oxygen formation is significantly elevated, thus leading to less damage on polished surfaces. A polishing electrolyte with those additives can planarize damascene interconnects even with feature sizes in several tens of micrometers.

Experimental

The patterned wafer used in PE measurements was composed of a 30 nm thick ionized metal plasma (IMP)-TaN layer as the diffusion barrier, a 200 nm thick IMP-Cu film as the seed layer, and a 1.7 μm electroplated Cu as the conduction layer, deposited in trenches with depth of 1.4 μm . The experiments on Cu electroplating and electropolishing were carried out in a tank of nonconducting material. The counter electrode was a platinum plate 6×6 cm and the

working electrode was a wafer 2×3 cm. In Cu electroplating, the electrolytes included copper sulfate, sulfuric acid, chloride ions, and filling promoters. The films were deposited under galvanostatic control at room temperature. In Cu electropolishing, the basic electrolyte was phosphoric acid (85% H_3PO_4) and the films were polished under potentiostatic control at room temperature.

Potentiodynamic and potentiostatic measurements performed on an EG&G potentiostat/galvanostat (model 273A) were used to analyze the electrochemical behaviors of electrolytes. The counter electrode was platinum and the working electrode was Cu with a constant surface area of 0.5 cm^2 . All potentials are reported relative to the Ag/AgCl electrode, which was used as the reference electrode. Current transient analyses were performed at constant applied voltage, and the cell current was recorded with a Keithley 196 digital multimeter. Cross-sectional profiles of Cu films were examined using a field-emission scanning electron microscope (FESEM).

Results and Discussion

To measure PE of the CMP process, Steigerwald *et al.* defined the following equation⁸

$$PE = [1 - (\Delta_{\text{down}}/\Delta_{\text{up}})] \times 100\% \quad [1]$$

where Δ_{down} and Δ_{up} are the thickness differences of the inside and outside of the feature after planarization processes, as shown in Fig. 1. In this article, we also apply Eq. 1 to monitor PE of Cu electropolishing. A better planarization ability is noted when the PE value is higher. Ideally, PE is equal to 1.

First, we add citric acid into H_3PO_4 to improve PE of Cu electropolishing. Citric acid was usually employed as a complexing agent in manufacturing printed circuit board (PCB) for electroless Cu plating and in metal finishing industries. It has been introduced into the HNO_3 -based slurry for Cu-CMP to enhance surface planarity.⁹ Additionally, it can act as a chelating agent to complex Cu^{2+} and to inhibit the redeposition of Cu.⁹ Figure 2a shows the change of conductivity and pH values of electrolytes with increasing citric acid concentration in the H_3PO_4 electrolyte. When the concentration of citric acid increases, the solution conductivity increases to a maximum value at citric acid concentration of 1000 ppm and then falls down; and pH values of the electrolytes become saturated. By measuring PE and polishing rate for those electrolytes in Fig. 2a, Fig. 2b shows that maximum values for those two factors also occur at the same citric acid concentration. We suggest that the triacid, citric acid, can release hydrogen ion (H^+) into the H_3PO_4 electrolyte and increase the acidity and conductivity of the solution. However, the amount of undissolved citric acid increases when the con-

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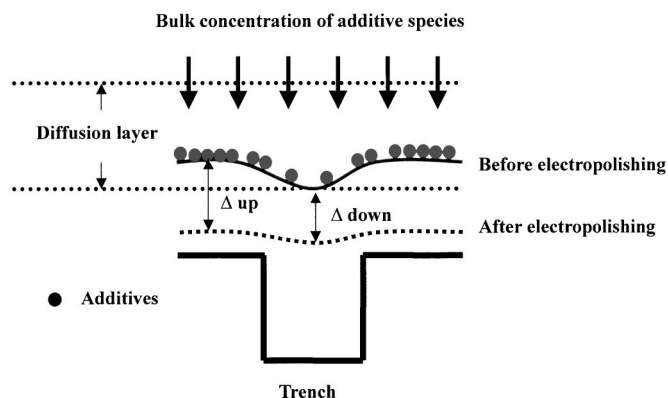


Figure 1. Definition of PE of Cu electropolishing, where Δ_{down} and Δ_{up} are the thickness differences of inside and outside of the feature after planarization processes. Proposed model of additive contribution within damascene features during Cu electropolishing is also shown.

centration of citric acid increases, then the pH value reaches a saturated value and the undissolved citric acid lessens the solution conductivity.

Notably, the PE value for the electrolyte containing citric acid with 1000 ppm is almost two times larger than that for electrolytes without additives, as shown in Fig. 2b. Results from Fig. 2a and b mean that the improvement in step height reduction of polished

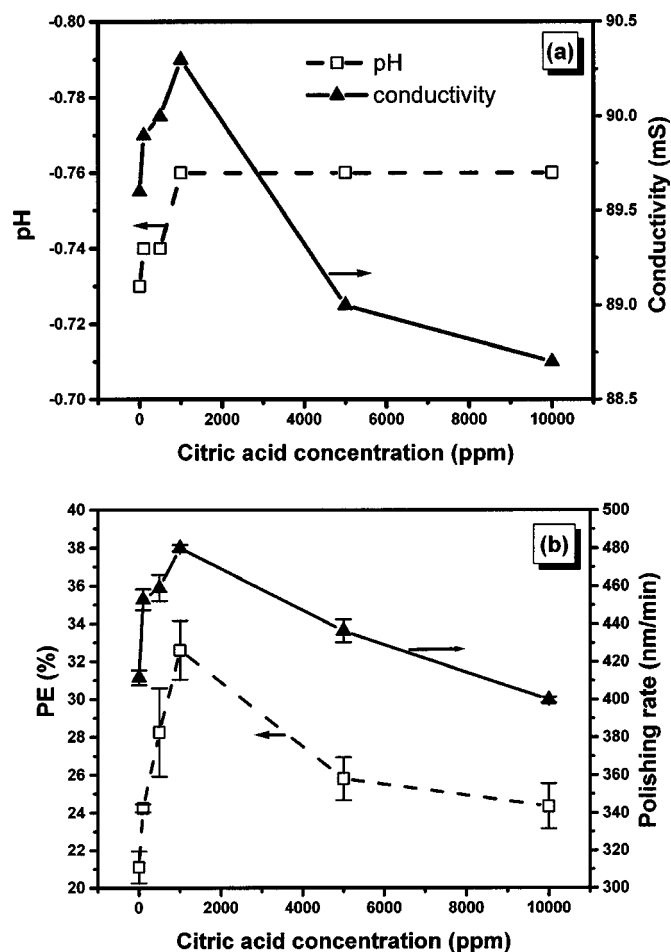


Figure 2. (a) Conductivity and pH value and (b) polishing rate and PE as a function of citric acid concentration in the H_3PO_4 electrolyte.

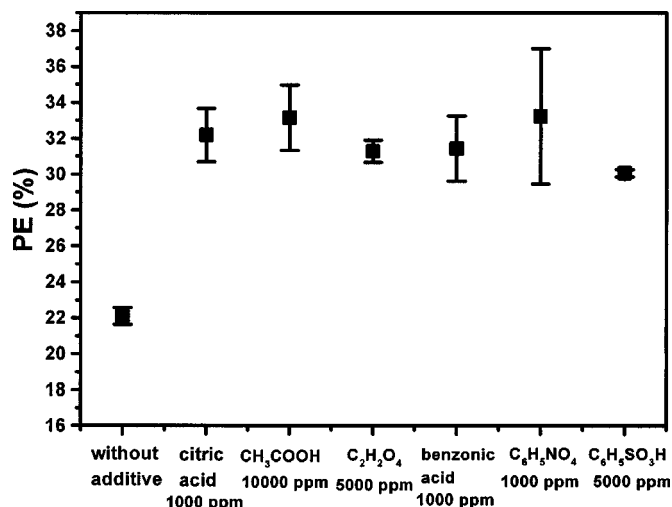


Figure 3. PE for the H_3PO_4 electrolyte with various organic acid additives.

damascene patterns is attributed to additives in polishing electrolytes and depends on their concentrations. Generally, we can infer that this phenomenon is owing to the formation of a significant gradient of Cu removal rate within damascene features. Due to the mass-transfer-limited transportation of citric acid with a low concentration, the Cu dissolution rate on the outside of features with more citric acid is higher than that on the inside of features with less citric acid. Then a dissolution gradient forms and reduces the step height of profiles. The proposed superpolishing model is shown in Fig. 1. Figure 3 further shows that various organic acid additives with their optimum concentration achieve improvement of PE.

During Cu electropolishing, oxygen formation causes severe etched pits on Cu surfaces.^{6,7} We add PEG with molecular weight of 6000 (PEG6000: 1000 ppm) into the electrolyte to increase the overpotential of oxygen formation, as shown in the potentiodynamic curves of Fig. 4. PEG is usually used as an inhibitor or a wetting agent in Cu electroplating.¹⁰ The interaction between the PEG molecules and electrolytes may retard the electrolytic dissociation of oxygen. The inset of Fig. 4 reveals that adding PEG6000 decreases the polishing current from 50.6 to 13.7 mA/cm^2 at the overpotential of 2.0 V, and optical images (magnified 500 times) display that the damages on polished Cu surface are reduced by PEG6000.

Figure 5a shows a cross-sectional profile with a step of 200 nm

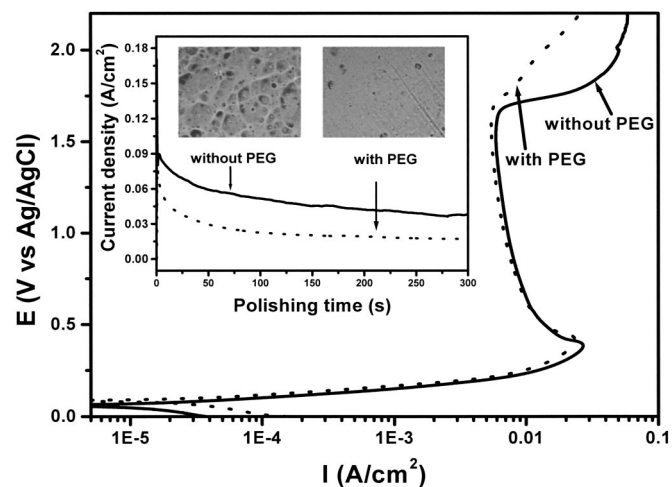


Figure 4. Potentiodynamic curves of various electrolytes. Potentiostatic curves and optical images are also shown in the inset.

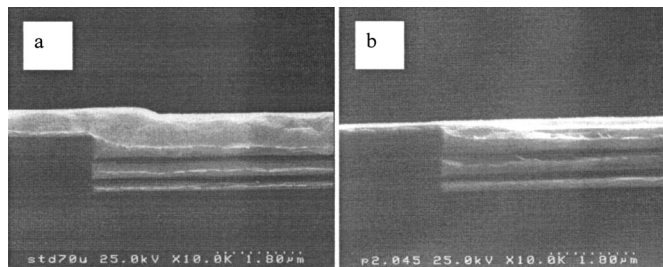


Figure 5. SEM cross-sectional profiles of (a) 70 μm trench completely filled by Cu electroplating and (b) patterns of (a) electropolished using the H_3PO_4 electrolyte containing 1000 ppm citric acid and 1000 ppm PEG.

in a 70 μm trench completely filled by Cu electroplating. Figure 5b displays a smooth profile with full step height elimination by Cu electropolishing using the H_3PO_4 electrolyte with 1000 ppm citric acid and 1000 ppm PEG6000. The polishing rate for this novel polishing electrolyte is about 480 nm/min at the overpotential of 2.0 V.

Conclusion

In this study, we find that adding acid additives into the H_3PO_4 electrolyte enhances planarization efficiency of Cu electropolishing because those additives produce a gradient of dissolution rate between the outside and inside of features. Furthermore, adding a suppressor, PEG6000, into the H_3PO_4 electrolyte increases the overpo-

tential of oxygen formation, thus leading to less damage on polished surfaces. Using this novel polishing electrolyte, a smooth profile with full step height elimination is obtained.

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