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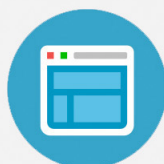
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# Microleveling mechanisms and applications of electropolishing on planarization of copper metallization

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The optimization of Cu electropolishing processes was explored to be in the mass-transfer-limited plateau with a stable limiting current density and in concentrated phosphoric acid by elucidating surface morphologies and potentiodynamic polarization. After electropolishing, the average roughness of polished surfaces achieved to 1.1 nm. Both the x-ray photoelectron spectroscopy and the electrochemical impedance spectroscopy suggest that the existence of a passivation film on the polished surface contributed to the microleveling effect of Cu electropolishing. Moreover, this passivation layer also induces an application of end point in electropolishing. © 2002 American Vacuum Society. [DOI: 10.1116/1.1511218]

## I. INTRODUCTION

Chemical mechanical polishing (CMP) of Cu and barrier metals is widely recognized as the most promising technology for planarizing Cu damascene interconnects.<sup>1-3</sup> However, conventional Cu-CMP slurries contain mechanically hard abrasives that can scratch and damage polished Cu surfaces. Therefore, alternative planarization approaches, compatible with electroplating, are attractive to pursue. Traditional electropolishing is an important technology in surface treatment, which can uniformly dissolve a metallic film and produce a smooth and bright surface. Furthermore, electropolishing has the potential advantages of a reduced waste stream, fewer consumable ingredients, and no mechanical stress applied to the substrate. The latter represents a benefit with low dielectric constant interlayers. Electrochemical planarization (ECP) of Cu was initially demonstrated by Contolini and co-workers in 1994.<sup>4,5</sup> Wang and colleagues have designed a commercial tool for electropolishing,<sup>6,7</sup> and Cheung has proposed a process for Cu electropolishing to enhance CMP throughput.<sup>8</sup> Recently, TSMC and SONY companies further demonstrated completely new planarization approaches by integrating Cu electropolishing (removal of

electroplated Cu to barrier layer) with CMP or dry etching (removal of remaining Cu and the barrier metal).<sup>9,10</sup>

However, only a few studies have addressed the issues regarding the electropolishing electrolyte concentration and applied voltage dependence of surface roughness of polished films and polishing rates and the optimum controls of electropolishing.<sup>11-13</sup> In this work, electrochemical techniques, including primarily anodic potentiodynamic polarization measurement and the electrochemical impedance spectroscopy, were employed to evaluate the dissolution mechanism of Cu electropolishing. Experimental results indicated that the existence of the passivation film on the anodic surface contributes to microleveling and maintains the smoothness of the polished surface. Moreover, this inert layer (passivation layer) is relevant to the plateau region defined in potentiodynamic (PD) polarization curves and induces an application of end point in electropolishing.

## II. EXPERIMENT

A blanket wafer was prepared by depositing a 50 nm sputtered TaN diffusion barrier and a 1  $\mu\text{m}$  sputtered or electroplated Cu conduction layer on a  $\text{SiO}_2/\text{Si}$  substrate. A patterned wafer was composed of a 30-nm-thick ionized metal plasma (IMP)-TaN layer as the diffusion barrier and a 200-nm-thick IMP-Cu film as the seed layer, deposited into trenches with a depth of 1.4  $\mu\text{m}$ . The experiments on Cu

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electroplating and electropolishing were carried out in a tank of nonconducting material. The counter electrode was a platinum plate and the working electrode was a 2 cm × 3 cm wafer. During integrated electrochemical planarization (ECP), 6 in. wafers for Cu electroplating and electropolishing were placed in a homemade apparatus. Chemical mechanical polishing (CMP) was performed on a Westech 372M polisher with a Rodel IC1400 polish pad, and a H<sub>2</sub>O<sub>2</sub>-based final-step slurry to remove remaining metals. The polishing parameters, such as down pressure, back pressure, platen and carrier rotation speeds, and the slurry flow rate, were set to 3.0 psi, 1.5 psi, 60 rpm, 65 rpm, and 150 cm<sup>3</sup>/min, respectively. In Cu electroplating, the electrolytes included CuSO<sub>4</sub>·5H<sub>2</sub>O (30 g/l), H<sub>2</sub>SO<sub>4</sub> (275 g/l), chloride ions (50–100 ppm), polyethylene glycol with the degree of polymerization of 6000 (40–2000 ppm) and 2-aminobenzothiazole (10–100 ppm).<sup>14</sup> The films were deposited under galvanostatic control. In Cu electropolishing, the electrolyte was phosphoric acid (85% ortho-phosphoric acid) and the films were polished under potentiostatic control.

Potentiodynamic (PD) polarization was employed to analyze electrochemical behavior of Cu electropolishing. In these analytical experiments, the counter electrode was platinum and the working electrode was Cu with a constant surface area of 0.5 cm<sup>2</sup>. All potentials were reported relative to the Ag/AgCl electrode, which was used as the reference electrode. Potentiodynamic polarization measurement and electrochemical impedance spectroscopy were performed on an EG&G potentiostat/galvanostat (model 273A) and an EG&G frequency response detector (model 1025A), with a Pentium PC. X-ray photoelectron spectroscopy (XPS) was utilized to determine the interfacial structure of Cu films. XPS analyses were performed using a VG ESCA 210 instrument, with excitation by Mg *K*α radiation ( $h\nu = 1253.6$  eV). Cross-section profiles of Cu films were examined using a field emission scanning electron microscope (SEM) and the surface roughness was measured using an atomic force microscope.

### III. RESULTS AND DISCUSSION

Figure 1(a) shows that a defect-free filling was generated by an acid cupric sulfate electrolyte that contains chloride ions (Cl), polyethylene glycol (PEG), and 2-aminobenzothiazole (2ABT). The combined action of Cl-PEG-2ABT provided an inhibitive gradient between the opening and the bottom of submicron features to yield obviously selective deposition and bottom-up filling. Following Cu electroplating by this plating chemistry, neither “overplate” nor “dishing” phenomena occur in small features, nor even in 0.15 μm vias.<sup>14</sup> A clean and scratch-free surface was produced by electropolishing in the phosphoric acid (85% ortho-phosphoric acid) electrolyte, as shown in Fig. 1(b). The polishing rate of electroplated Cu films was lower than that of sputtered Cu films, due to high contents of organic additives in electroplated Cu films. In this study, the polishing rate of electroplated Cu films was approximately 500 nm/min, compared with 600 nm/min for sputtered Cu films.

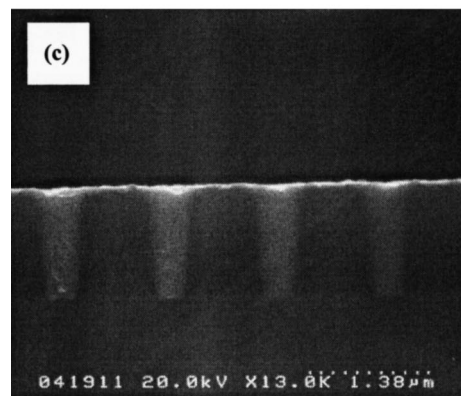
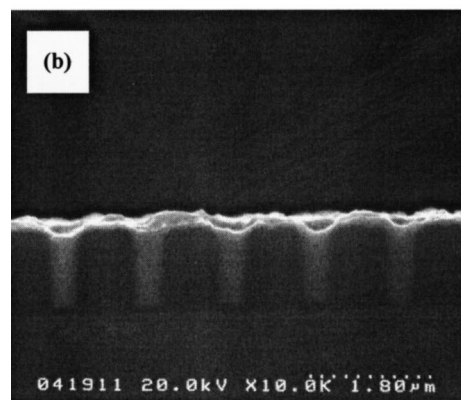
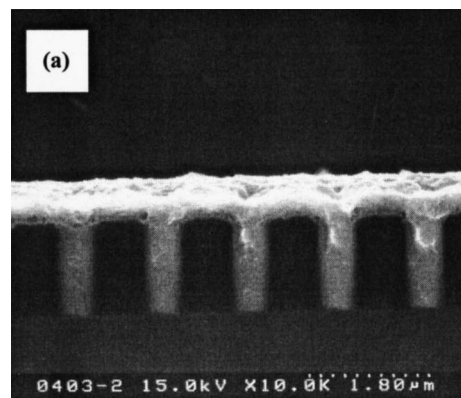


Fig. 1. SEM cross sections of 0.35 μm, 1.4-μm-deep trenches: (a) after electroplating, (b) after electropolishing, (c) after CMP.

The remaining Cu and barrier metal were finally removed by a single-step CMP process, as depicted in Fig. 1(c). The final-step CMP process used the H<sub>2</sub>O<sub>2</sub>-based slurry, which removed TaN more rapidly than Cu.

Figure 2(a) displays the potentiodynamic (PD) curve of Cu electropolishing in 85% H<sub>3</sub>PO<sub>4</sub> solution. The metal surface became active at anodic potentials in the AB range. A passivation layer may start to form on the anodic surface when the anodic potential increased from the value at point B into the BC range. The formation of this layer is discussed later. A wide passivation (0.71–1.62 V vs Ag/AgCl) existed

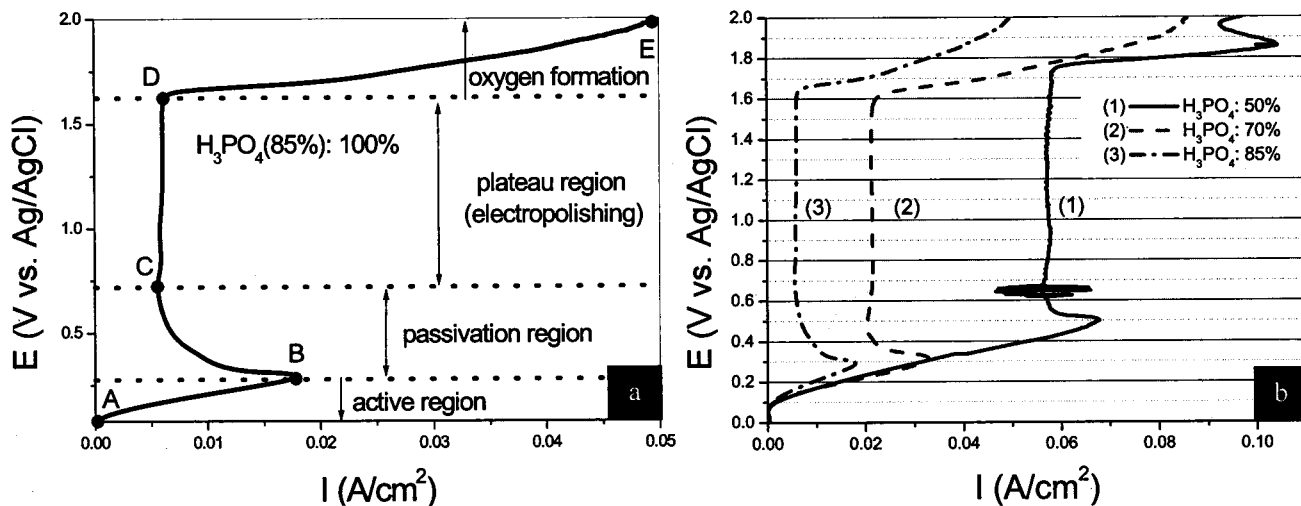


FIG. 2. PD curve for Cu electropolishing.

within the CD range, called the “plateau region;” electropolishing occurred with hardly any change in the current density as the applied voltage was increased. In this plateau region, an almost constant current density of 6 mA/cm<sup>2</sup> maintained stable electropolishing.

Figure 3 shows potentiostatic (PS) curves at various applied voltages. When the voltages were set to 1.0, 1.3, and 1.6 V, the corresponding PS [ $I(t)_v$ ] curves almost overlapped and fixed at a constant equilibrium current density of 6 mA/cm<sup>2</sup>, which was consistent with the anodic-limiting current plateau in the PD polarization measurement. The limiting current density was independent of applied voltages in the plateau region. The current  $I(t)_{350\text{ mV}}$ , which fell within the passivation region of Fig. 2(a), in the initial stages of the process, was higher than  $I(t)_{1.0\text{ V}}$ ,  $I(t)_{1.3\text{ V}}$ , and  $I(t)_{1.6\text{ V}}$ . However, the PS curve saturated at a value equal to that for the biased voltages in the plateau region. A reasonable explanation is that a passivation film gradually formed on a pol-

ished surface and this inert layer for 350 mV needed more process time (more than 50 s) to become stable than that for other voltages in the plateau region. When the voltage was set to 2.0 V [in the DE range of Fig. 2(a)], the steady-state current density was much higher than that at the biased voltage in the plateau region. An increase in current in this stage increased the rate of oxygen formation, owing to the breakdown of water in the electrolyte by increased potentials. This oxygen formation causes severe etch pits on the Cu surface, confirmed by the optical microscope images in Fig. 3. In comparison, a smoother surface was obtained by setting the potential to 1.3 V. Thus, excellent polishing is usually obtained over the plateau region with a stable limiting current.<sup>4,5,11–13</sup>

Several attempts have been made to address the microleveling effect of the passivation layer in electropolishing. However, evidence concerning this inert layer needs more investigation. Figure 4 presents the x-ray photoelectron spectroscopy (XPS) spectra of the Cu films before and after electropolishing. The presence of phosphorus (P) on the polished anodic surface indicates the formation of a passivation

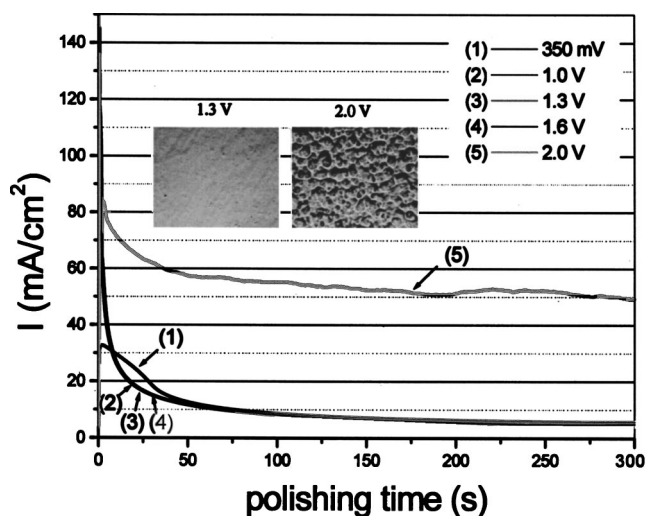


FIG. 3. Effect of applied voltage on PS curves for Cu electropolishing in 85% H<sub>3</sub>PO<sub>4</sub> electrolyte. The optical microscope images (200×) depict surface morphologies of Cu electropolished at 1.3 and 2.0 V.

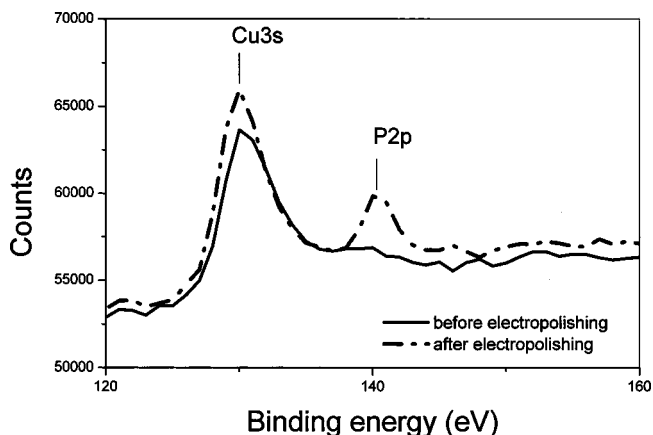


FIG. 4. XPS analyses of surfaces of Cu films, before and after electropolishing in 85% H<sub>3</sub>PO<sub>4</sub> electrolyte.



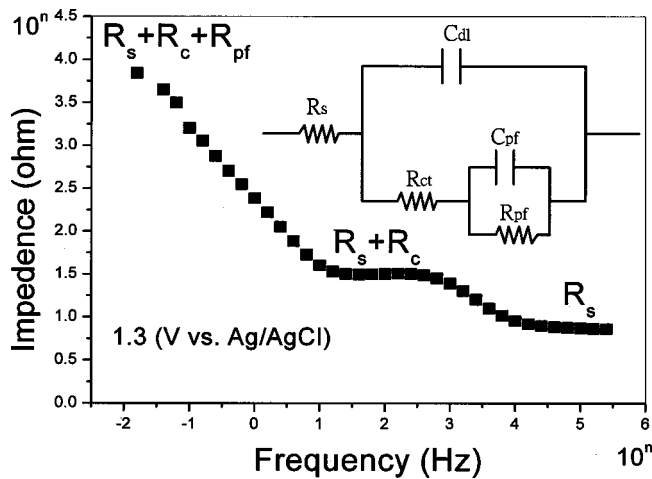


FIG. 5. Bode plot of Cu electropolishing at an applied voltage of 1.3 V (with respect to the Ag/AgCl reference electrode) in 85%  $\text{H}_3\text{PO}_4$  electrolyte. The proposed equivalent circuit diagram shows the electrochemical characteristics of Cu electropolishing in 85%  $\text{H}_3\text{PO}_4$  electrolyte.

layer. The Bode plot in Fig. 5 reveals the existence of two capacitance elements in the Cu/electrolyte interface. In addition to the double layer capacitance, the second capacitance was derived from the existence of the passivation film. An applied voltage of 1.3 V in 85%  $\text{H}_3\text{PO}_4$  solution was used for this measurement.

Figure 5 displays an equivalent circuit used to simulate the electrochemical behavior of this system, where  $C_{dl}$  was capacitance of the double layer capacitance and  $C_{pf}$  that of the passivation film. Nested circuits, rather than circuits in series, were considered to indicate that no clear interface existed between the double layer and the passivation film: a porous passivation film was suggested, instead. In this Bode spectrum, the impedance in the high frequency range was attributable to the solution resistance ( $R_s$ ) of 7.5  $\Omega$ ; the impedance in the low frequency range was a function of the total impedance, which includes the solution resistance, the charge-transfer impedance ( $R_{ct}=22.2 \Omega$ ) and the impedance of the passivation film ( $R_{pf}=4010.4 \Omega$ ). Figure 2(a) reveals that the slope of region AB (before forming the passivation layer) was around 9.2  $\Omega$  and that of region CD was around 4000  $\Omega$  (after forming the passivation layer). This result correlates well with results from the Bode plot. Furthermore, the large passivation range (0.71–1.62 V vs Ag/AgCl) of the PD polarization curve in Fig. 2(a) confirms that a stable passivation film was formed during Cu electropolishing.

One theory relates the limiting current to the formation of a salt film (passivation film).<sup>13,15</sup> A passivation film is assumed to form on the anodic surface and limit the rate at which metal ions leave the surface. This mass-transport-controlled feature determines the polishing rate. The magnitude of the limiting current in an electropolishing process generally corresponds to the saturation concentration of  $\text{Cu}^{2+}$  near the anodic surface.

Figure 6 shows PS curves and conductivities of various acid concentrations. When the applied voltages were set to 1.3 V, the magnitude of the limiting current density increased

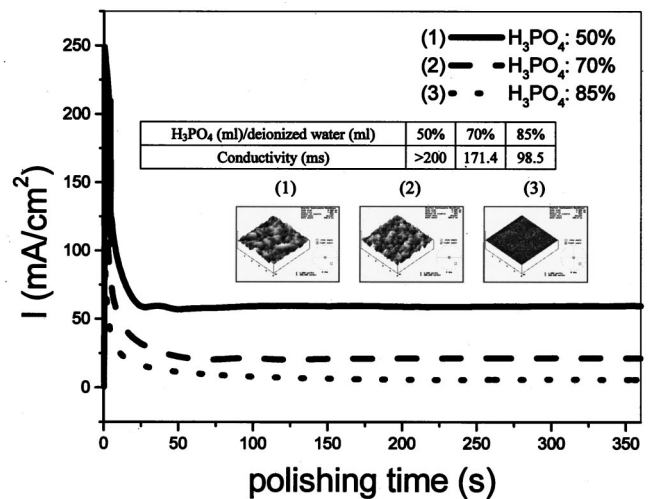


FIG. 6. Surface morphologies, PS curves and conductivities of various acid concentrations.

as the  $\text{H}_3\text{PO}_4$  concentration declined. This effect may be due to a decrease in the concentration of  $\text{H}_3\text{PO}_4$  that increased the conductivity of electrolytes, promoting the dissolved metal ions' diffusion into the bulk electrolyte and enhancing the limiting current. The saturation currents of PS curves in Fig. 6 agree with results from their corresponding PD curves in the plateau region, as shown in Fig. 2(b). Figure 6 also displays the surface roughness of polished surfaces increased as the acid concentration decreased, and shows the polishing rate for the electrolyte with low acid concentration is too high to produce a uniform electropolishing. The polishing rates of electroplated Cu were about 500, 1000, and 1500 nm/min for 85% (vol.), 70% (vol.), and 50% (vol.)  $\text{H}_3\text{PO}_4$  electrolytes, respectively. Therefore, a concentrated acid electrolyte is chosen in this study because it provided not only a significant polishing rate but also a smoothly polished surface. After electropolishing at 1.3 V in 85% (vol.)  $\text{H}_3\text{PO}_4$  electrolyte, the average roughness ( $R_a$ ) of the polished sur-

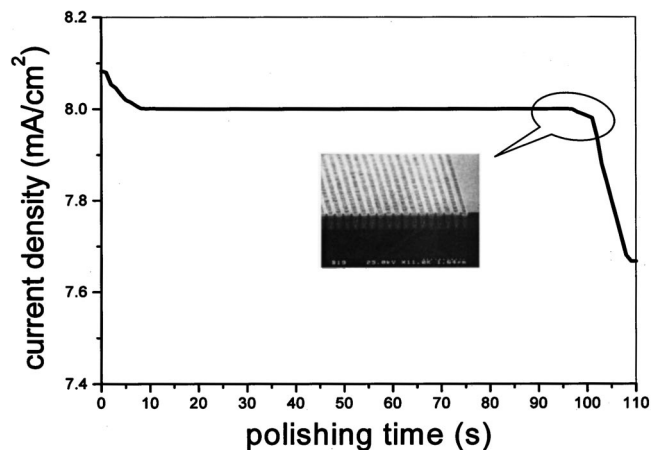


FIG. 7. *In situ* current-time curve for Cu electropolishing in 85%  $\text{H}_3\text{PO}_4$  electrolyte.

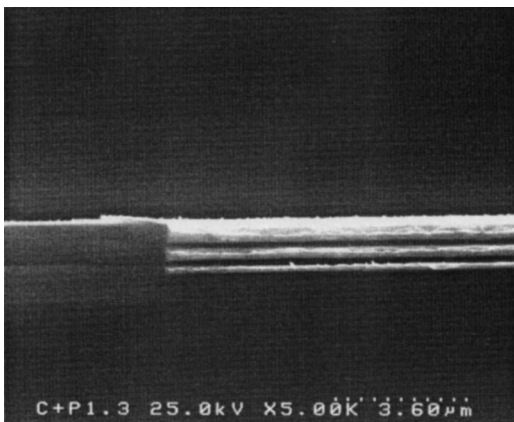


FIG. 8. SEM cross section of a 50  $\mu\text{m}$ , 1.4- $\mu\text{m}$ -deep trench after electropolishing at an applied voltage of 1.3 V (with respect to the Ag/AgCl reference electrode) in 85%  $\text{H}_3\text{PO}_4$  electrolyte.

face was 1.1 nm, as compared to 15.2 nm before electropolishing.

Notably, another angle of view for the “plateau region” is that a nearly constant current maintains electropolishing regularly. The PS curves in Figs. 3 and 6 show that the passivation film on polished surfaces gradually forms, and after about 30 s this layer completely forms, thus causing the bias current to saturate at a limited value. Therefore, this characteristic of the formation of the passivation layer during Cu electropolishing contributed to not only a uniform removal rate of polished metals but also a stable current flow (the limiting current). For electropolishing damascene Cu, the current flow changes when the interface between the polished Cu and the barrier metal is reached: this useful property can be used to determine the end point of Cu electropolishing.

Figure 7 displays an *in situ* current-time curve for Cu electropolishing in 85%  $\text{H}_3\text{PO}_4$  solution. The end point was reached when the saturation current began to fall, due to a change in the film’s resistance, at which time the barrier layer was exposed. To be limited to the simple apparatus for Cu electropolishing, Cu dishing with 20–100 nm into the trench/line area occurred in 0.35  $\mu\text{m}$  trench when the end point of Cu electropolishing was measured. However, Cu dishing could be reduced by precisely controllable equipment or by employing small signal modulation/demodulation in this *in situ* current time measurement. In Cu-CMP studies, copper dishing becomes seriously as an increase in linewidth.<sup>16</sup> The SEM image in Fig. 8 shows a 50  $\mu\text{m}$  trench

with dishing of  $\sim 50$  nm was obtained at the end point of Cu electropolishing. In the author’s opinion, Cu electropolishing is able to integrate into the global planarization processes due to its low mechanical damage on polished surfaces and excellent planarization capability.

#### IV. CONCLUSION

Excellent Cu electropolishing occurred in the mass-transfer-limited plateau and in concentrated phosphoric acid. The existence of the passivation film, verified by x-ray photoelectron spectroscopy and electrochemical impedance data, contributed to the microleveling effect of Cu electropolishing and maintained the smoothness of polished surfaces. A smoothly polished surface with  $R_a$  of 1.1 nm was achieved after electropolishing. By applying the end-point technique and the optimal electropolishing process, planarized trenches with dishing below 50 nm were obtained even with a linewidth of 50  $\mu\text{m}$  considered.

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