Electrolyte Composition for Cu Electrochemical Mechanical Planarization

Abhinav Tripathi,a,* Craig Burkhard,b* Ian Ivar Sunia,a,** Yuzhuo Lib,** Francois Doniata, Alex Barajas,c and James McAndrew,c,**

*a Department of Chemical and Biomolecular Engineering and b Department of Chemistry and Biomolecular Science, Center for Advanced Materials Processing (CAMP), Clarkson University, Potsdam, New York 13699, USA

Francois Doniat, Alex Barajas, and James McAndrew, **

American Air Liquide, Delaware Research and Technology Center, Newark, Delaware 19702-2462, USA

Cu electrochemical mechanical planarization (ECMP) is currently being investigated to replace or supplement Cu chemical mechanical planarization (CMP) due to the introduction of porous low-k dielectric materials, which may not withstand the mechanical force applied during conventional CMP. Electrolytes for Cu ECMP at pH 3 containing 5-phenyl-1-H-tetrazole (PTA), hydroxyethylidenediphosphoric acid, and oxalic acid are investigated using electrochemical methods and polishing of Cu-coated blanket and patterned wafers. The Cu removal rate and the planarization efficiency during Cu ECMP can be approximated using electrochemical measurements of the Cu removal rate, with and without surface abrasion. These results predict a 500 mV potential window within which the Cu removal rate is greater than 600 nm/min and the planarization efficiency is greater than 0.90. However, high planarization efficiencies are only obtained when silica abrasives are included within the ECMP electrolyte. In situ electrochemical impedance spectroscopy results indicate that the interfacial impedance is increased by the presence of silica, suggesting that silica is incorporated into the PTA-based passive film and is thus needed for effective planarization. Electrochemical quartz crystal microbalance experiments indicate that PTA may provide better Cu surface passivation at a high anodic potential than benzotriazole, which is widely used during Cu CMP.

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During the last decade, chemical mechanical planarization (CMP) technology has been widely employed during dual damascene processing of Cu interconnects to remove excess Cu and reduce surface topography. The planned introduction of porous low-k dielectric materials has highlighted the need for an alternative technology to replace or augment CMP for Cu planarization.1 CMP is a dynamic process involving the coupled chemical oxidation and mechanical abrasion of Cu in the presence of passive film forming agents. The need for both high downforce and abrasive particles may limit the use of CMP for planarization of devices containing porous low-k dielectric films, which can be damaged by mechanical stress.2,3 Other limitations of CMP include high cost of consumables, frequent replacement of parts, poor end-point detection, and dishing and erosion, which often arise from overpolishing.2,3

The materials integration difficulties described above for Cu CMP with porous low-k dielectrics have led researchers to investigate alternative planarization processes such as electrochemical polishing (ECP) and electrochemical mechanical planarization (ECMP). ECP, which is a purely electrochemical process, has several advantages over CMP, including its noncontact nature, low contamination levels, and easy endpoint detection. However, serious problems such as pattern sensitivity4 and formation of residual Cu islands5 have limited its viability as an interconnect planarization technology.6 ECMP appears to be a more viable approach to bulk Cu removal. High planarization efficiency and high removal rates have been reported using this process at very low applied pressure (<0.5 psi).5,7

During ECMP, an anodic potential supplies the thermodynamic driving force for the oxidation and removal of Cu. In contrast, an oxidizing agent supplies the thermodynamic driving force during Cu CMP.8 Although the precise mechanism of ECMP is unclear, planarization likely occurs due to accelerated electrochemical Cu removal from surface elevations, where the passive film is abraded, coupled with little or no removal at surface recesses, where the passive film remains intact.9,10 Hence, the nature of the passive film formed during ECMP largely determines the planarization efficiency and the Cu surface quality. Benzotriazole (BTA) is the most commonly used inhibitor during CMP and has been studied in great detail.9,10 However, BTA passivation of Cu at higher anodic potentials may be inadequate.10 In addition, BTA is ineffective at low pH, where Cu removal rates are expected to be high. Recently, several alternative triazole derivatives have been tested as low pH inhibitors for Cu CMP,11-16 including 5-phenyl-1-H-tetrazole (PTA), which has been identified as a promising candidate for Cu CMP at lower pH.17

Besides the inhibitor, the other important ingredients in an ECMP electrolyte are a chelating agent, whose effectiveness varies with pH, and a phosphate-containing species, which is involved in electrochemical passive film formation. Fundamental electrochemical studies of Cu dissolution in hydroxyethylidenediphosphoric acid (HEDP) have identified this as an interesting candidate for applications to both ECP and ECMP.18 Unlike the case for the more commonly used phosphoric acid, the Cu passive film thickness in HEDP can be modulated through control of the applied potential.19 Oxalic acid has been investigated as a chelating agent for application at low pH, where Cu dissolution rates are elevated.19,20

The present article describes electrochemical studies and blanket and patterned wafer polishing results for Cu ECMP electrolytes containing HEDP, PTA, and oxalic acid. Voltammetry measurements with and without abrasion are employed to benchmark this electrolyte formulation. The nature of the passive film formed at different potentials was further investigated by electrochemical impedance spectroscopy (EIS) and electrochemical quartz crystal microbalance (EQCM).

Experimental

Voltammetry measurements were made with and without abrasion using a 99.999% Cu rotating disk electrode (RDE) in a specially designed 400 mL three-electrode Teflon cell shown in Fig. 1. Prior to each experiment, the 1.13 cm diameter Cu working electrode was mechanically polished using 1500 grit sandpaper and then a 5 wt % slurry of 50 nm alumina until a mirror finish was obtained. During the voltammetry experiments with abrasion, the Cu electrode rotation was fixed at 850 rpm, while two cases were studied without abrasion, rotation at 850 rpm, and no rotation. The rotational speed that most closely matched experimental conditions during ECMP was expected to lie between these two extreme values, but is difficult to know given the complexity of ECMP. The downforce of the RDE on the pad was not calibrated, but repeat experiments with abrasion showed variations of only about 10%. Fresh electrolyte was
used for each experiment. All voltammetry measurements were obtained using a Princeton Applied Research 263A potentiostat using a Pt mesh counter electrode and a saturated calomel reference electrode (SCE). EIS was studied by coupling the same potentiostat with a Solartron 1250 frequency response analyzer using an ac probe amplitude of 5 mV.

EQCM measurements were made using a research quartz crystal microbalance from Maxtek Inc. Crystals with a resonant frequency of 5 MHz were used for all the measurements, with an approximate mass resolution of 4 ng/cm². Cu was electrodeposited onto the Au surface from a 0.5 M CuSO₄ solution and 0.5 M H₂SO₄ electrolyte deaerated with Ar. Approximately 2 μm of Cu was electrodeposited on the crystal, with an active working area of 1.37 cm². This corresponds to approximately 2.45 mg of Cu, which is less than 2 wt % of the crystal, as required for accurate measurements.²¹–²³ The freshly deposited Cu surface was rinsed thoroughly in double-distilled deionized water and used immediately for corrosion measurements in the desired electrolyte. Dissolution was assumed to be uniform across the quartz surface and changes in resonance frequency were attributed only to mass changes.

Commercial patterned and blanket Cu-coated wafers were used for testing the ECMP electrolyte. Cu ECMP experiments were performed on 100 mm Cu-coated wafers using a pilot ECMP tool. This tool was donated by Buehler and modified so that an external potential could be applied. The electrical connections were made with the help of stainless steel slip rings and graphite–silver alloy carbon brushes. For all polishing experiments with colloidal silica, Ludox-AM-30 from Sigma Aldrich was used. For all wafer polishing experiments the downforce was 1.5 psi, the platen and wafer rotational speeds were 30 rpm, and the electrolyte flow rate was 380 mL/min. The cathode was a stainless steel disk approximately 0.5 cm thick and 30 cm in diameter. An IC 1570 (Rohm & Haas) pad with XY and K grooves was used for all the experiments. The pad was perforated with holes of 4 and 5 mm diameter at regular intervals, with an overall pad porosity of approximately 20%. To supply the higher currents required, a Kepco power supply was employed to control Cu wafer ECMP. The average Cu thickness was measured with an RS-30 automated four-point probe. Step heights on patterned wafers were measured with an Ambios XP-2 optical profilometer before and after each polishing step. The surface profile was measured using a Burleigh Horizon noncontact optical profilometer.

Results and Discussion

The voltammetry curves shown in Fig. 2, with and without abrasion, have been found to be useful for semiquantitative benchmarking of ECMP electrolytes. The removal rate in the field areas in contact with the pad corresponds to the abrasion curve, while the removal rate within trenches corresponds to the nonabrasion curve. Similar methods have recently been described with a slightly different geometry.⁶ According to recent reports, the current supplied during ECMP can be directly related to the number of electrons transferred during Cu oxidation and dissolution.⁶ Thus, the voltammetry curve with abrasion shown in Fig. 2 can be used to calculate the Cu removal rate, as shown in Fig. 3.

Similarly, the Cu removal rate within trenches can be determined from the voltammetry results without abrasion, where the surface inhibitor is intact. This allows calculation of the planarization efficiency (PE) for the electrolyte studied in Fig. 2 according to

\[
\text{PE} = \frac{j_{\text{no abrasion}} - j_{\text{no abrasion}}}{j_{\text{abrasion}}} \tag{1}
\]

Figure 3 also illustrates the PE obtained from applying Eq. 1 to the voltammetry results shown in Fig. 2, using the results without rotation for \(j_{\text{no abrasion}}\). Thus, the voltammetry measurements with and without abrasion can be employed to predict the removal rate and the PE, which are two critical benchmarks for ECMP. Figure 3 nicely illustrates the trade-off between the removal rate and PE. At modest anodic potentials, the passive film is quite protective at surface recesses, but the Cu removal rate is low. If the anodic potential is too high, then the removal rate will be substantial, but the passive film will be compromised at surface recesses. Because ECMP is not widely used, these benchmarks are not yet rigidly defined, but removal rates of 600 nm/min are desired with PE > 0.7. By inspection of Fig. 3, a wide potential window of approximately 500 mV...
Cu removal rate and PE predicted from voltammetry experiments at 0.29 M HEDP, 1 mM PTA, and varying concentrations of oxalic acid at pH 3. PE (○) and Cu removal rate (●) for 0.0325 M oxalic acid, PE (●) and Cu removal rate (●) for 0.065 M oxalic acid, and PE (△) and Cu removal rate (△) for 0.13 M oxalic acid.

These results suggest that the added silica is actually incorporated by the addition of 3 wt % silica to the ECMP electrolyte. Without silica, no planarization occurs. This is surprising, given that the introduction of silica into the electrolyte has a negligible effect on the Cu removal rate. The PE has therefore been measured on Cu patterned wafers. Some of the Cu overburden was removed in one 45 s polish. The profile of a 100 × 100 µm feature before and after polishing at a current density of 20 mA/cm² is illustrated in Fig. 6 for an electrolyte containing 0.29 M HEDP, 0.065 M oxalic acid, 1.0 mM PTA, and 3 wt % silica. To obtain an absolute comparison, the surface profile after polishing has been normalized using the average Cu removal rate. The measured PE was between 0.9 and 1.0 for both 100 × 100 and 50 × 50 µm features measured on different dyes on the patterned wafer. This compares well with the predicted value from Fig. 3.

However, the excellent PE shown in Fig. 6 can only be obtained by the addition of 3 wt % silica to the ECMP electrolyte. Without silica, no planarization occurs. This is surprising, given that the introduction of silica into the electrolyte has a negligible effect on the electrochemistry results, both with or without abrasion, shown in Fig. 2. Even though passivation appears to be effective in the results of Fig. 2 without abrasion, this passivation is inadequate for ECMP. These results suggest that the added silica is actually incorporated into the PTA film, providing either static or dynamic Cu corrosion inhibition. Static inhibition means that silica fills defects in the PTA film, whereas dynamic inhibition means that silica stabilizes the PTA film and prevents its removal by convective mixing during ECMP.

Incorporation of silica into the passive film is supported by the electrochemical impedance studies shown in Fig. 7, which are taken in a quiescent electrolyte. These impedance results are not fit here, because their shape is somewhat unusual, with a straight line at high frequency, a highly depressed semicircle at intermediate frequency, and a nearly vertical line at low frequency. However, the magnitude
of the real impedance, which corresponds to the resistive impedance component, increases dramatically upon the addition of silica to the ECMP electrolyte. This is consistent with increasing blockage of the Cu surface due to an increase in either the surface coverage or thickness of the passive film. Silica incorporation into the passive film is also supported by energy-dispersive X-ray analysis experiments on Cu foil, because silicon peaks are observed only for erosion from ECMP electrolytes that contain silica.

In addition, effective passivation can only be obtained if the Cu-coated wafer is immersed into the ECMP electrolyte at a cathodic potential to form a passive film prior to application of the anodic potential that initiates Cu removal. This indicates that the formation of passive film is restricted once Cu removal is initiated. In BTA-based ECMP electrolytes, unlike PTA-based ECMP electrolytes, Cu passivation can be initiated at anodic potentials. However, this comparison may be misleading, because the concentration of BTA in those experiments is much higher (50 mM) than the PTA concentration in the current experiments (1 mM).

For completeness, Cu removal rates have also been measured on blanket Cu wafers in an electrolyte containing 0.29 M HEDP, 0.065 M oxalic acid, and 1.0 mM PTA, with and without silica. For an applied voltage of 3.5 V, the current density during Cu ECMP was 28 and 29 mA/cm², respectively, with and without silica. This again illustrates that the presence of silica does not increase the Cu removal rate. The average Cu removal rates were measured as 680 and 710 nm/cm², respectively, with and without silica. These measured Cu removal rates on blanket wafers are about 10% higher than predicted by Faraday’s law.

While the removal rate and PE are quite comparable to or superior to conventional CMP, the surface quality is not. Noncontact optical profilometry results for blanket Cu-coated wafers after ECMP in a PTA-based electrolyte are shown in Fig. 8. Blanket Cu-coated wafers looked slightly dull after polishing, and root-mean-square (rms) surface roughness values were as high as 7–10 nm in some spots. The higher surface roughness might be due to the corrosive nature of oxalic acid, or to the absence of a Cu oxide film at lower pH. The extent to which low surface quality impacts the first step of Cu removal, where ECMP was first introduced, is unclear. In other words, if the first step of Cu removal by ECMP, which prepares a planar surface, is followed with a second step of Cu removal by CMP to clear the remaining Cu, then the surface quality following the first Cu removal step may not be critical.

In addition to the Cu removal rate, PE, and surface quality, another benchmark for Cu ECMP is the within-wafer nonuniformity, which is expected to be less than 10%. Figure 9 illustrates the within-wafer nonuniformity for a blanket Cu-coated wafer polished at a current density of 20 mA/cm², where the within-wafer nonuniformity is approximately 10%.

EQCM studies were also conducted to compare the effectiveness of BTA and PTA for Cu passive film formation at anodic potentials. The results are shown in Fig. 10 and were obtained with a potential scan rate of 5 mV/s. The quartz crystal microbalance studies demonstrate that the Cu surface passivation breaks down for an ECMP electrolyte containing 1.0 mM PTA at an anodic potential of approximately +900 mV vs SCE. Comparison studies of BTA-containing electrolytes were planned carefully, because BTA-based passive films are well known to break down at low pH when they become protonated. 24,25 EQCM studies of BTA-based ECMP electrolytes were conducted at pH 5.8 using the same HEDP concentration, and the same concentration (0.065 M) of tribasic ammonium citrate, which is a more appropriate complexing agent in this pH range than oxalic acid or glycine. The results shown in Fig. 10 illustrate the much poorer passivation obtained at anodic potentials for ECMP electrolytes containing BTA, with passive film breakdown at approximately +350 mV vs SCE, even with a much higher BTA concentration of 10 mM. However, as discussed above, the Cu passivation observed in Fig. 10 is inadequate without the addition of silica to the ECMP electrolyte.
Electrolytes for Cu ECMP at pH 3 containing PTA, HEDP, and oxalic acid are investigated using electrochemical methods and polishing of Cu-coated blanket and patterned wafers. The performance of such electrolytes was evaluated using the four main ECMP benchmarks: the Cu removal rate, PE, surface quality, and within-wafer nonuniformity. The Cu removal rate and the PE during Cu ECMP can be approximated using electrochemical measurements of Cu removal rate, with and without surface abrasion. These results predict a 500 mV potential window within which the Cu removal rate is greater than 600 nm/min and the PE is greater than 0.90. However, experiments on patterned wafers indicate that this PE can only be achieved with the inclusion of silica in the ECMP electrolyte. This appears to reflect incorporation of silica within the PTA-based passive film, as supported by in situ measurements by EIS. The rms surface roughness after polishing of Cu-coated blanket wafers was 7–10 nm. The within-wafer nonuniformity during polishing of blanket Cu-coated wafers was approximately 10%.

In addition, EQCM experiments were employed to compare the passivation provided at high anodic potential by PTA with that provided by BTA, which is widely used during Cu CMP. At the pH (5.8) where BTA works well, and using a complexing agent appropriate for that pH, passive film breakdown occurs at +350 mV vs SCE for BTA, whereas it does not occur until +900 mV for PTA.

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