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# Roles of Additives in Damascene Copper Electropolishing

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This study explores how the dissolution of damascene Cu depends on accelerators of organic acids in alcohol-containing $H_3PO_4$ electropolishing electrolytes. Four two-additive electrolytes that contain different accelerators, acetic, citric, citrazinic, and benzoic acids, are evaluated. At the bottom of damascene features, an esterification reaction between alcohols and organic acids efficiently forms a highly resistive layer and reduces the acidity of the solution. Accordingly, outside the damascene features, the rate of removal of Cu is dominated by the acidity of electrolytes but, inside the features, it is also determined by the resistance of the viscous layer. For a weak acidic additive, acetic acid, an extremely high additive concentration is introduced to sustain the moderate acidity of the solution to initiate intense esterification. Therefore, acetic-acid-based two-additive electrolytes exhibit excellent Cu planarization capability.
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Low-stress planarization techniques, electrochemical mechanical deposition (ECMD),[1] abrasive-free mechanical polishing (AFP),[2] and additive-assisted electropolishing (EP),[3-5] have been demonstrated to be feasible for use in porous dielectric/Cu damascene metallization as an alternative to chemical mechanical polishing (CMP).[6-8] In particular, this latter method involves a pure electrochemical reaction, such as electroplating used in Cu deposition. Hence, the equipment used in both processes is highly compatible.

The electropolishing rate of Cu metals mainly depends on the acidity of the solution,[3] and the resistance of the viscous layer.[9,10] Accordingly, the introduction of additives, whose chemistries can modulate the properties of acidity of electrolyte and surface viscosity, has been demonstrated to enhance a gradient in the Cu dissolution rate within the damascene features.[3] Two additives can be utilized to promote the planarization efficiency (PE) of damascene Cu metallization.[5] One is an organic acid accelerator, which increases the acidity of the solution, and thus the EP rate.[3] Another is an organic alcohol inhibitor, which increases the viscosity of the solution and thus inhibits the dissolution of Cu.[5] Although an increase of electrolyte acidity typically enhances the dissolution of Cu, in some cases it also enlarges the resistance of the passivation layers,[11] which actually inhibits the removal of Cu. This conflict is consistent with the observation that the PE values of various one-additive (organic acids) EP electrolytes almost saturate at a similar level, despite a difference of one order of magnitude among the concentrations of the optimal additives.[3] Of course, the saturation of PE is attributable partially to the limitation of additive hydrolysis in phosphoric acids. Furthermore, for two-additive (alcohol + organic acid) EP electrolytes, an esterification[12] reaction is likely to occur between alcohols and organic acids. This reaction not only changes the concentration of the additives but also generates new constituents within the polished interfaces. Accordingly, the additive-related EP mechanisms that are involved in the electropolishing of damascene features and the optimization of associated recipes are of considerable interest.

In this investigation, the efficiency of planarization of various two-additive EP electrolytes is examined with reference to the chemistry of organic acids. The role of esterification during additive-assisted EP is initially reported. Experimental results indicate that the usage of weak acidic organic acids at dense concentrations facilitates esterification, which efficiently yields strongly resistive layers and reduces local acidity at the bottom of the features. These characteristics promote the planarization of Cu.

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## Experimental

The patterned wafer used in PE measurements consisted 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 thick electroplated Cu as the conduction layer, deposited into trenches with various widths (1–50 μm) and a depth of 1 μm. Experiments on Cu electroplating and electropolishing were performed as described elsewhere.[5] In Cu EP, the EP electrolytes were phosphoric acid (85% $H_3PO_4$) and contained various organic acids and glycerol alcohols; the films were polished under potentiostatic control at room temperature.

The EP characteristics, the chemistry of the electrolytes, esterification during additive-assisted EP, and material analyses of polished Cu metals in the features were determined[5] by a method according to which EP experiments are undertaken on Cu blanket wafers using simulated EP electrolytes that comprise diluted additives with concentrations that are 5, 10, 50, and 100 times less than the optimal additive concentrations. The pH values for each electrolytic system during Cu-EP were measured using a pH meter while the wafer was polished in situ. Electrochemical impedance analyses (Nyquist plots),[11] Raman spectroscopy (type: JASCO Ventuno-21), and electron spectroscopy for chemical analysis (ESCA) (type: VG Microlab) were adopted to conduct these studies. Cross-sectional profiles of Cu films before and after EP were examined using a field emission scanning electron microscope (FESEM).

## Results and Discussion

Cross-sectional SEM images in Fig. 1a-e display patterns with widths of 50 μm before and after EP, using four glycerol-containing two-additive electrolytes, which contain different accelerators in the form of acetic, citric, citrazinic, and benzoic acids. For comparison, additive-free electrolytes are also used. The results demonstrate that the acetic acid-containing electrolytes can more efficiently form a gradient in the Cu dissolution rate between the bottom and opening of damascene than can other acid-based electrolytes. A PE value[3,10,11,13,14] index of the planarization capacity of electrolytes is calculated from the changes in the step height of the morphologies. The PE value of those electrolytes for various feature sizes, as presented in Fig. 2, also reveals that acetic acid outperforms other organic acids in the planarization of damascene Cu metals. In the calculation of the PE values of 50 μm wide features, the measured residual Cu thicknesses outside the features and inside the feature at 5, 10, and 25 μm away from the edges of the features yielded the error bars on the PE values; the averages of these values are also shown. For the additive-containing electrolytes, a constant volume glycerol/$H_3PO_4$ ratio of 1/100 is employed, and organic acids are

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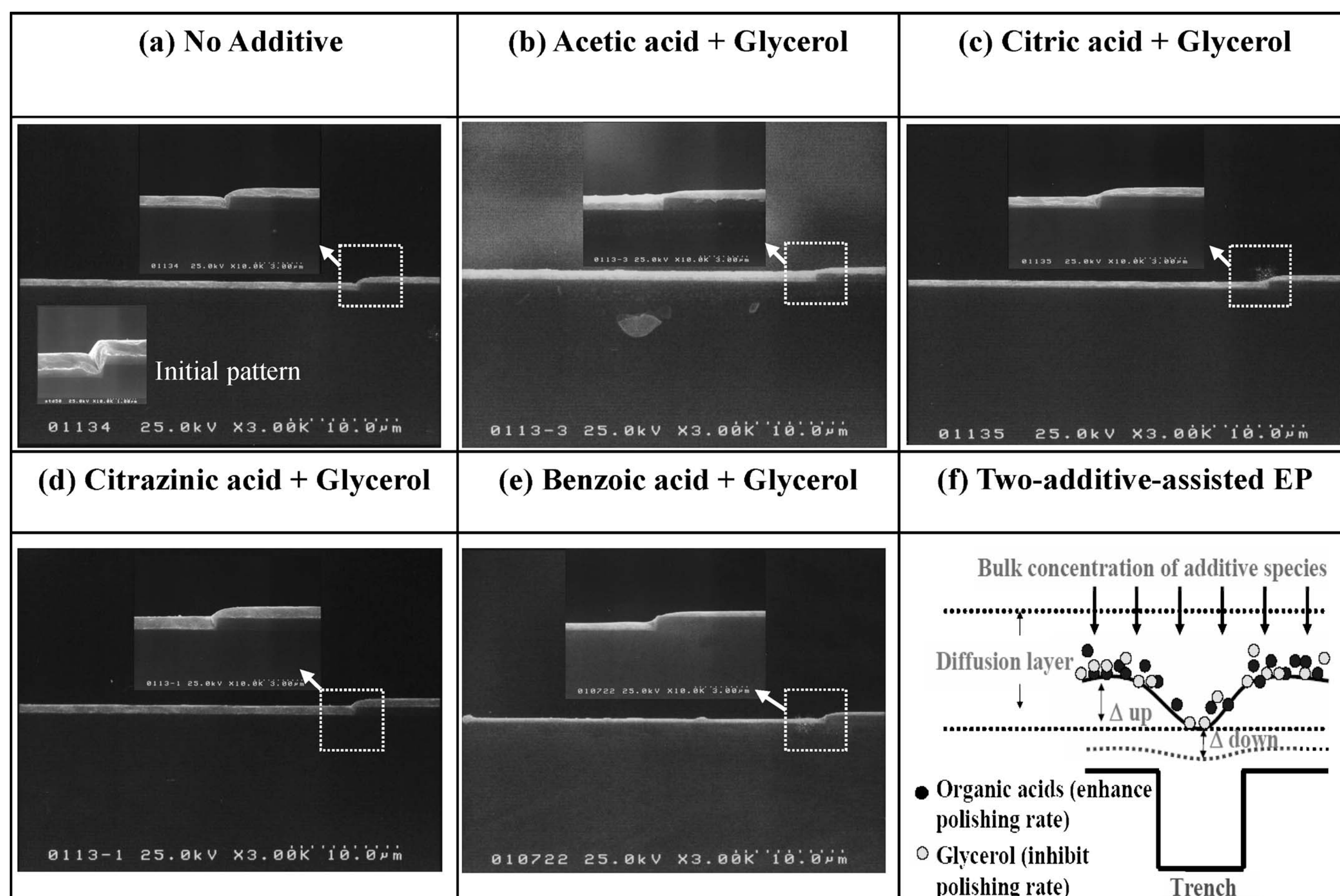


**Figure 1.** Cross-sectional SEM images for 50 μm damascene patterns filled with electroplating Cu metals before and after electropolishing at 1.75 V using (a) additive-free and (b)–(e) four two-additive (various organic acids + glycerol) EP electrolytes. (f) A schematic illustration of two-additive-assisted EP within damascene features shown.

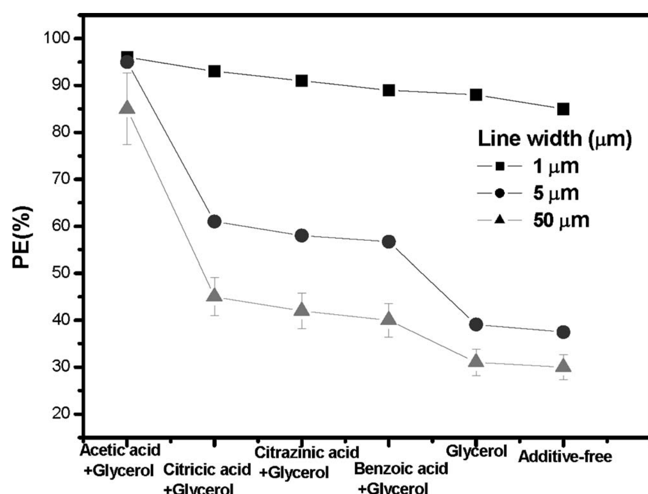


**Figure 2.** PE for additive-free, one-additive (glycerol), and four two-additive (glycerol + various organic acids) EP electrolytes as a function of feature size. EP was conducted at 1.75 V. {PE = [1 − (Δdown/Δup)] × 100%, where Δdown, and Δup are schematically illustrated in Fig. 1 of Ref. 3}.

added to optimize PE; the concentration of the acetic acid was 10,000 ppm, and that of the other acid additives was 1000 ppm.

Comparing the Cu removal rates associated with four two-additive electrolytes at the bottom and opening of the feature for 1 and 50 μm wide patterns, shows that the EP rate at the damascene bottom (in the middle of the feature) depends on the organic acid species and changes by 1.5–5 times the magnitude; at the feature opening, the rate varies by only 20%, as shown in Fig. 3a and b. With reference to the glycerol-containing one-additive electrolyte,[5] all organic acids, except acetic acids, considerably reduced the glycerol-induced inhibition of the removal of Cu at the damascene bottom. Therefore, the difference between the PE of these two-additive electrolytes is closely related to the change in the alcohol-related inhibition of Cu removal rate at the feature bottom in the presence of various organic acids.

Alcohol inhibitors suppress the removal of Cu by increasing surface viscosity,[5,15] whereas organic acids promote the removal of Cu by increasing the acidity of solutions.[3] However, if an elemental esterification reaction occurs between these two additives during EP, then the concentration of the additives changes and the new constituents are formed in solution, and then in the interacting interfaces. Both factors probably influence Cu planarization. The selective Cu dissolution rate, the acidity, the resistance of the passivation layer, and even the interfacial compositions within features cannot be easily determined experimentally, so alternative approaches should be developed. Our previous work stated that electrolytes with additives can be used at various concentrations to electropolish Cu metals, and the associated polishing rates are analyzed to determine the gradient of the Cu removal rate,[5,16] $(R_{up} - R_{down})/R_{up}$. Herein,

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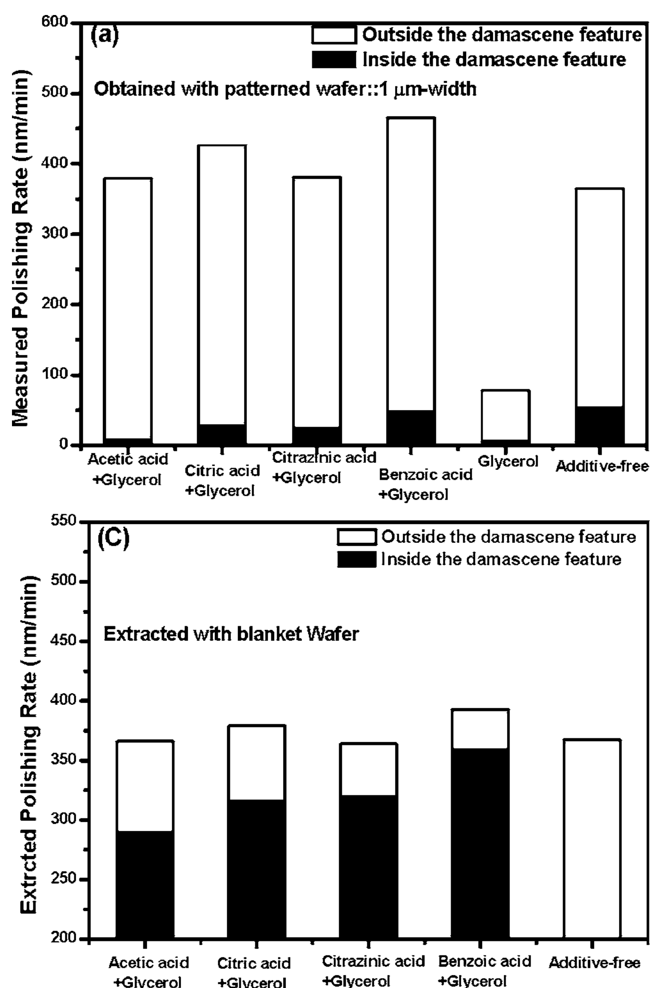


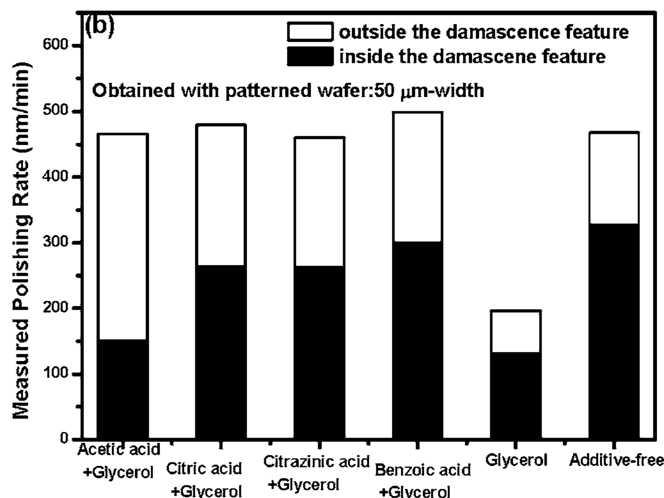


**Figure 3.** Polishing rates outside and inside the features for four two-additive, glycerol-containing one-additive and additive-free EP electrolytes: (a) obtained with 1 μm width patterned substrates; (b) obtained with 50 μm width patterned substrates; and (c) extracted with blanket substrates. EP was conducted at 1.75 V.

$R_{up}$ represents the Cu removal rate at the damascene opening and is obtained using two-additive EP electrolytes with additives at optimal concentrations. $R_{down}$ represents the Cu removal rate at the damascene bottom and is obtained using electrolytes with diluted additives. This method predicts Cu removal rates within the features and $(R_{up} - R_{down})/R_{up}$ for four organic acid-containing two-additive electrolytes, as shown in Fig. 3c and 4. The trend concluded from these extracted values agrees closely with those in Fig. 1, 2, 3a, and b. Notably, the error bars displayed in Fig. 4 and later figures represent the data concerning electrolytes with variously diluted additives. Hence, within the damascene features, the chemistry of the electrolytes, the EP properties, and the compositions of polished Cu surfaces could be evaluated.

In maximizing the PE of the two-additive electrolytes, the measured solution acidities around the damascene opening, as shown in Fig. 5a, appear to fluctuate around pH −0.62. Basically, an insufficiency of additives results in the small modulation of the Cu removal rate within the features, whereas an excessive additive concentration[3] fails to form a mass-transport-controlled distribution of additives. Both conditions degrade the organic acid-enhanced PE, which explains the small observed change in optimal pH values in response to organic acid, as presented in Fig. 5a.

Another important EP parameter of these electrolytes, the resistance of the passivation layer within the reacting interfaces, is also measured by Nyquist plots, as displayed in Fig. 6 and summarized in Fig. 5b. An additive-free electrolyte with a higher acidity has a larger viscous resistance; just adding sulfuric acid to $H_3PO_4$ electrolytes increases the viscous resistance.[11] Accordingly, on the feature opening, even though the acidity-related EP rate for the additive-free

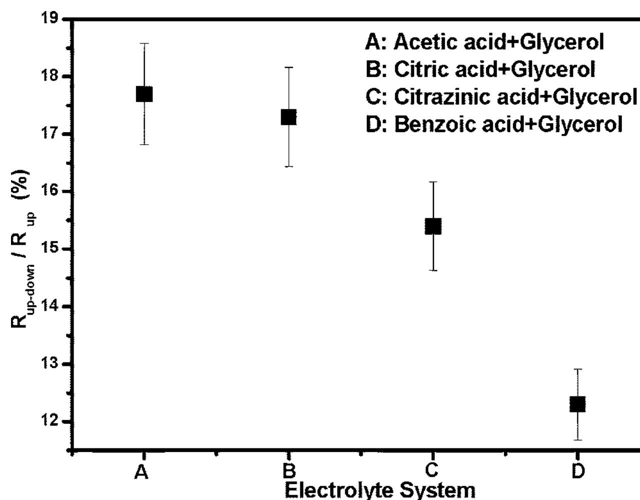


**Figure 4.** The extracted Cu removal rate gradient for four two-additive EP electrolytes. EP was conducted at 1.75 V.

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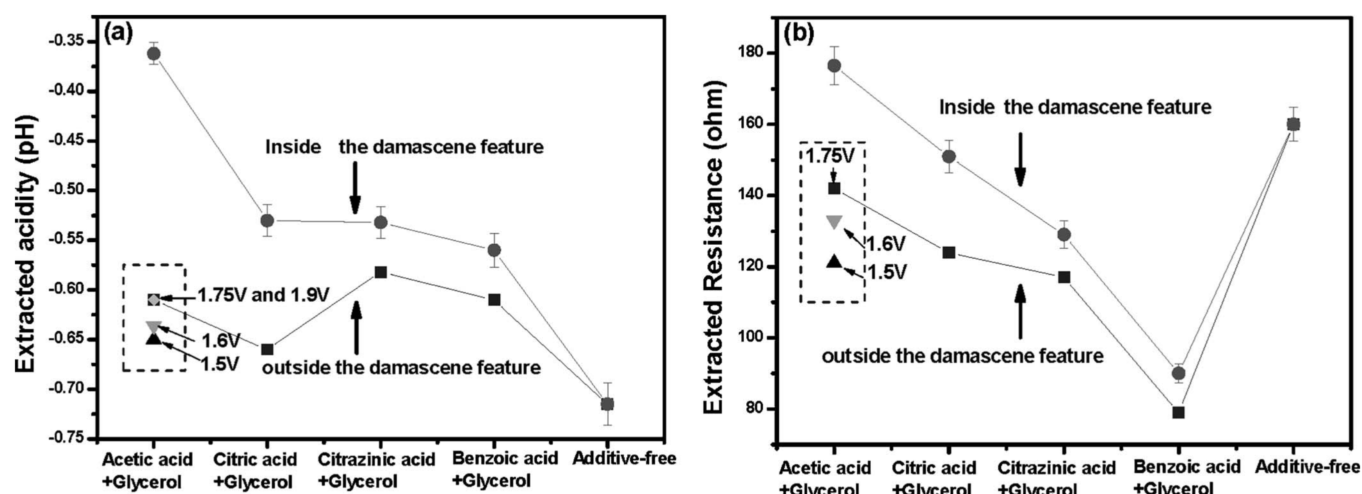


**Figure 5.** (a): Extracted acidity, and (b) extracted viscous layer resistance (calculated from Nyquist plots shown in Fig. 6) outside and inside the features for four two-additive, and additive-free EP electrolytes. EP was conducted at 1.75 V. For evaluating the impact of applied voltage on esterification, EP using acetic acid-containing two-additive electrolytes was also conduced at 1.5, 1.6, and 1.9 V, respectively.

electrolyte is expected to exceed that for the two-additive electrolytes, the fact that the real polishing rate of the former electrolyte is lower is reasonably attributed to the inhibition of the removal of Cu by viscous layers. The situation is different when four two-additive solutions are involved. The extracted viscous resistances around the feature opening, as shown in Fig. 5b, monotonically increase from 80 to 140 Ω, even though the two-additive solutions exhibit similar bulk acidities. The data displayed in Fig. 3 and 5 indicate that, at the opening of the feature, the solution acidity is determined to dominate the removal of Cu, but the acidity of the solution and the removal rate of Cu differ slightly because of the modulation of viscous layers.

The EP properties at the feature bottom are investigated by diluting the additive. The extracted acidity for all two-additive electrolytes decreases from pH $\sim -0.62$ at the feature opening to pH $\sim -0.5$ at the feature bottom, as presented in Fig. 5a. Moreover, different organic acid species correspond to a wide distribution of local acidities (pH of $-0.5$ to $-0.35$) at the feature bottom, rather than an almost constant value at the feature opening. A less acidic electrolyte results in greater viscous resistance for a passivation film, as determined in relation to four local two-additive electrolytes at the feature bottom. A similar observation is also made by comparing local electrolyte systems at the opening and bottom of the feature. This pH-dependent viscous resistance obviously differs from the increase in the viscous resistance due to acidity, exhibited by sulfuric acid-diluted electrolytes that contain no organic additives.[11] Both pH variance and such a pH-dependent viscous resistance within the features cannot be simply attributed to the additive distributions, based on the transport-limited law.[3,4,15]

Before the real causes of the interesting organic additive-assisted EP properties can be examined, an attempt is made to correlate the acidity with the viscous resistance to the removal of Cu or the planarization efficiency. Outside the damascene feature, the measured acidity and the related EP rate are almost the same for all electrolytes. Inside the damascene feature, two additives in one electrolyte not only reduce the acidity of the solution but also increase the resistance of the interacting surfaces, both of which enhance the inhibition of Cu removal. At the bottom of the feature, the acetic acid-containing two-additive electrolyte has the lowest acidity but

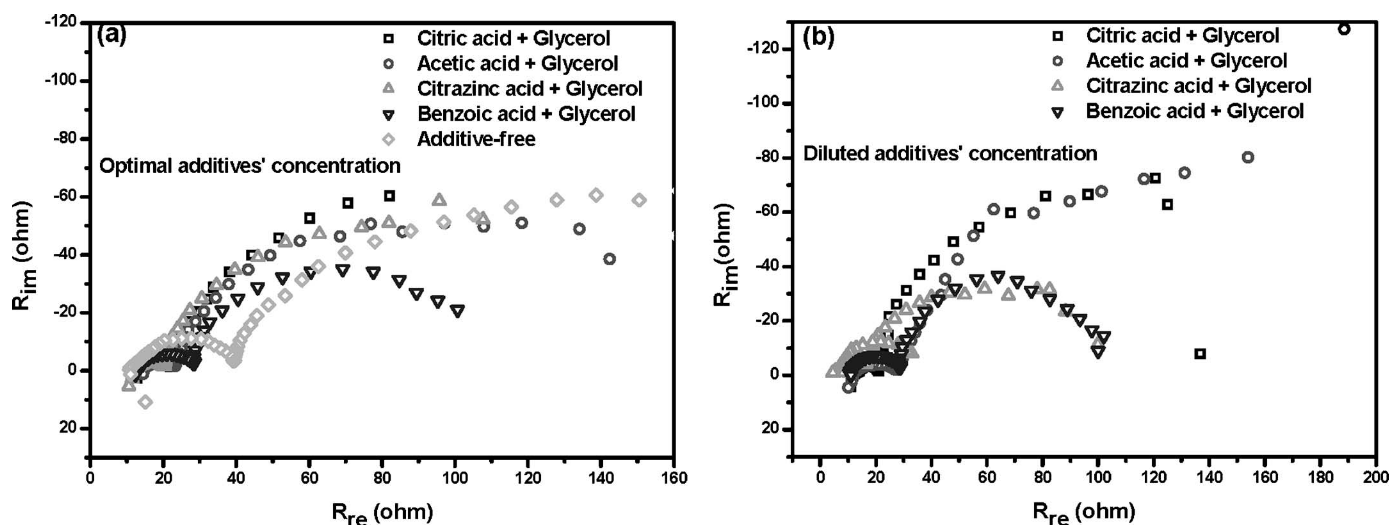


**Figure 6.** Nyquist plots for four two-additive EP electrolytes using (a) optimal, and (b) diluted additive concentrations. For comparison, the plot for additive-free electrolytes was also shown. EP was conducted at 1.75 V.

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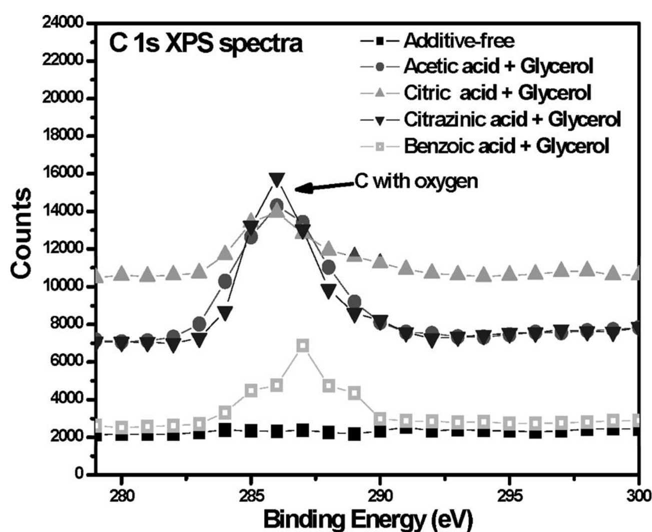


**Figure 7.** XPS spectra for Cu metals polished using four two-additive, and additive-free EP electrolytes.

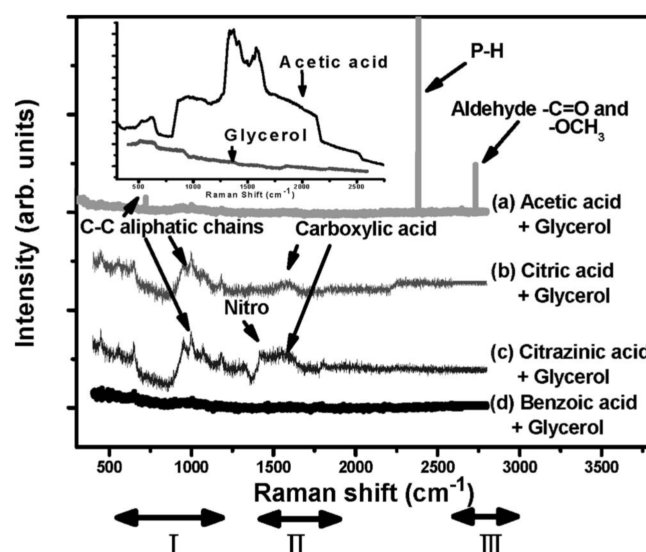


**Figure 8.** Raman spectra for Cu metals polished using four two-additive EP electrolytes that comprise diluted additives with concentrations that are 10 times less than the optimal additive concentrations. The inset shows the spectra associated with glycerol-containing, and acetic acid-containing one-additive EP electrolytes.

the highest viscous resistance of all the electrolytes, so the corresponding EP rate is lowest. It therefore has the best PE.

The esterification between alcohols and organic acids is an essential organic chemical reaction.[12] This reaction probably occurs in the two-additive-assisted EP experiments performed herein. It generates new species in solutions, interacting interfaces, and even polished Cu surfaces, so surface material analyses are conducted to elucidate the mechanisms. Figure 7 displays XPS spectra of carbon (1s) for Cu surfaces polished using these two-additive and additive-free electrolytes. Comparing all spectra reveals that the C–O peak is present only in spectra obtained using two-additive electrolytes, rather than using the additive-free electrolyte. Furthermore, a shift in the binding energy for the benzoic acid-containing two-additive electrolyte is observed. Such results suggest the adsorption of organic constituents (including ester-related by-products) on Cu metals polished with organic additive-containing solutions. High-resolution chemical composition analyses using Raman spectroscopy were performed to characterize the adsorbed species in polished Cu, as shown in Fig. 8. Later, EP electrolytes with diluted additives are adopted to explore esterification at the bottom of damascene.

These Raman spectra are divided into three bands associated with the chemical compositions of carbon aliphatic chains $(500\text{–}1200\ \text{cm}^{-1})$, carboxylic acids $(1500\text{–}1650\ \text{cm}^{-1})$, aldehyde $-\text{C}=\text{O}$ and $-\text{OCH}_3$ bonds $(2700\text{–}2850\ \text{cm}^{-1})$.[17] In the inset of Fig. 8, the Raman spectrum of glycerol-containing one-additive electrolytes includes only the signal associated with the bonds of carbon aliphatic chains $(500\text{–}1200\ \text{cm}^{-1})$, whereas that for acetic acid-containing one-additive electrolytes includes only the Raman signal associated with the bonds of the carboxylate salt and the carboxylic acids $(1300\text{–}1700\ \text{cm}^{-1})$. Both cases indicate no aldehyde-related bonds. However, the Raman spectra for two-additive electrolytes reveal an aldehyde-related bond. Esterification[12] between alcohols and organic acids is described by the following formula: $R\text{COOH} + R'\text{OH} \rightarrow R\text{COO}R' + \text{H}_2\text{O}$. The symbol "$R$" represents the group of alkanes such as $-\text{CH}_3$.

Ester contains aldehyde-related bonds, so esterification occurs during two-additive-assisted EP. The Raman signal strengths, related to aldehyde-related bonds, exhibit a trend associated with viscous resistances.[17,18] Of four two-additive electrolytes, the acetic acid-containing two-additive electrolytes exhibit the greatest viscous resistance and strongest Raman intensity associated with aldehyde-related bonds. Therefore, the viscous resistance increases with the degree of esterification. The signal from the P–H bond $(2400\ \text{cm}^{-1})$ in the spectrum from the acetic acid-containing two-additive electrolytes further shows that the strong ester-containing passivation film efficiently traps phosphoric acids, reducing electropolishing at the damascene bottom. Notably, for benzoic acid-containing two-additive electrolytes, the absence of an observable signal throughout the spectrum reveals negligible adsorption, indicating fast Cu removal throughout the features, as confirmed by the data presented in Fig. 3a and b.

During esterification, accompanying consumption of organic acids may reduce local acidity, the effect of which becomes evident when intense esterification occurs or when a few additives are present at the feature bottom. The most intense esterification and highest viscous resistance are observed when acetic acid is used as the additives, markedly reducing the related acidity at the damascene bottom. For the citrazinic acid-based solution, the Raman spectra show a nitrogen-related composition, presumably because of the chemistry of this organic acid. The nitrogen-related species slightly retards the dissolution of Cu throughout the feature, increasing the PE value close to that obtained using the citric acid-based solution. The latter solution exhibits higher bulk acidity and a more intense esterification reaction than the former solution.

The proposed esterification successfully explains the two-additive-related EP characteristics. However, what causes the difference between the degree of esterification among the electrolytes that contain various organic acids? Among four two-additive electrolytes, the concentration of the weak acidic acetic acids is the highest, 10,000 ppm, being one order of magnitude greater than that of other accelerators. Essentially, the number of acetic acid additives allows them to react more easily than other accelerators with alcohols. It thus fairly predicts the difference in PE values in response to organic acid species. Efforts must be made to evaluate more additive species to study the additive-assisted EP mechanisms and optimize multi-additive-containing EP electrolytes.

Cu electropolishing is normally carried out at an applied voltage of 1.3–2.0 V in the plateau region, [9-11] so the impact of the applied voltage on the determined acidity and viscous layer resistance was evaluated by EP at 1.5, 1.6, 1.75, and 1.9 V (Fig. 5a and b). As the applied voltage increases, for acetic acid-containing two-additive electrolytes the acidity decreases moderately but the viscous resistance rises. Hence, esterification increases with the applied voltage in the plateau region. Additionally, increasing the applied voltage

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can overcome the heightened electropolishing barrier associated with esterification-induced viscous resistance. However, further increasing the applied voltage to ~1.9 V initiates oxygen evolution,[11] detrimentally affecting the passivation of the viscous layer with quite low resistance. Therefore, an applied voltage of 1.75 V is favorable in additive-assisted electropolishing.

## Conclusion

Electropolishing mechanisms for two-additive electrolytes that contain alcohol and organic acid additives were investigated. Experimental results demonstrate that an esterification reaction modulates the acidity of solutions and the viscous resistance of passivation layers at the reacting interfaces. This reaction becomes dominant at the feature bottom, where a few additives are present. The use of weak acidic organic acids at high concentration, such as acetic acids used as accelerators, enables numerous accelerators to participate in esterification, resulting in not only the formation of highly resistive layers but also a significant decrease in local acidity. Therefore, the acetic acid-containing two-additive EP electrolyte outperforms other electrolytes that contain accelerators at low concentration.

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