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Role of Chloride Ions in Suppression of Copper Electrodeposition by Polyethylene Glycol

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Chloride ions and polyethylene glycol (PEG) are used together as additives to copper damascene electroplating baths, in which they suppress deposition. When the Cl− concentration is lower than the order of 1 mM, suppression abruptly breaks down below a critical potential, around which hysteresis between active and inhibited deposition is observed. A mathematical model is presented which successfully predicts the observed Cl− concentration-dependent breakdown of PEG suppression and current-potential hysteresis. The model assumes that adsorbed Cl− ions are involved in binding of PEG to the Cu surface, and that these ions are incorporated in the deposited film. The expressions for Cl− incorporation and adsorption are consistent with experimental measurements of Cl in deposits. Hysteresis was found to depend on the high sensitivity of polymer surface coverage to the concentration of adsorbed Cl− ions, possibly because each PEG molecule has a small number of binding sites to the surface.

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The copper damascene process is currently used in the semiconductor industry to electrodeposit on-chip metallization. The critical ability to produce seam- and void-free deposits in submicrometer-scale cavities, or features, relies on the presence of additives in the electroplating bath.1 The additives in damascene baths include a polymer serving as a suppressor, e.g., polyethylene glycol (PEG), an accelerator, e.g., sulfopropyl sulfonate (SPS), and Cl− ions.2 Cl− is apparently necessary for effective inhibition by PEG, as current-potential curves measured with PEG but no Cl− are similar to those with no PEG.3 During plating, PEG inhibits deposition on the surface outside the feature, while activation by SPS occurs preferentially near the feature bottom.4.5 Thus, effective inhibition by PEG is required to obtain the necessary differential deposition rate between surfaces inside and outside the cavity. While significant quantitative understanding of feature filling has been achieved in the past several years, there is much yet to be learned about the chemical interactions involving the additives, as well as the relationship between their chemistry and the microstructure, electronic, and mechanical properties of the deposited Cu film.

The present work focuses on the synergistic role of PEG and Cl− additives in suppression. It is found that inhibited deposition is achieved over a range of Cl− concentration around 1 mM. Higher Cl− concentrations lead to precipitation of CuCl salt.6 Voltammetric experiments in PEG solutions with Cl− concentrations significantly lower than 1 mM were reported by Jovic and Jovic, and are displayed in Fig. 1.7 There was no inhibition at any potential when the Cl− concentration was 10−3 M; at 0.01 and 0.1 M, deposition was inhibited only at potentials positive of a critical value which decreased with increasing concentration. During the cathodic scans, the abrupt increase of deposition rate at the critical potential was followed by a current peak, which was likely due to transient depletion of Cu2+ ions from the diffusion layer. Hysteresis between active and inhibited states was found over a potential range near the critical potential. Hysteresis was observed in steady-state potentiostatic measurements as well as the potentiodynamic scans in Fig. 1, indicating that it is not associated with slow transitional kinetics between active and inhibited states. This latter type of hysteresis is found in potentiodynamic scans in baths containing both accelerator and suppressor; in these experiments, current increases accompanying activation are much more gradual than those in Fig. 1.4.8

Additional recent investigations have provided important information relevant to the activation of Cu deposition in PEG−Cl− solutions. During Cu deposition at constant applied current, Hayase et al. observed transient activation from an initially inhibited state, when the order of magnitude of the Cl− concentration was less than 1 mM (18 ppm).9, a value typical of industrial plating baths.2.5 For the same experiments, secondary ion mass spectrometry (SIMS) revealed incorporated Cl in the deposit. These results suggest that consumption of Cl− ions initiated activation, implying that they are needed for PEG inhibition. Feng et al. used surface enhanced Ramanscopicry (SERS) to probe the chemical interaction of Cl− and PEG when the Cu surface was covered by a PEG film.10 They showed that adsorbed Cl− ions are coordinated with Cu+ ions, which in turn bond to oxygen atoms of PEG. Similar adsorbed Cl−−Cu+−PEG complexes had been suggested earlier on the basis of other spectroscopic and electrochemical investigations.11-13

In the present work, a mathematical model of Cu electrodeposition in the presence of PEG and Cl− additives is reported. The model formulates a proposed relationship between adsorbed PEG and Cl−, in which the PEG surface coverage is determined by that of Cl−, which in turn is dictated by the rates of adsorption and incorporation. After parameter fitting using the experiments of Hayase et al.,9 the model is applied to predict steady-state current-potential curves, for comparison with those in Fig. 1. The results help illuminate the synergism between PEG and Cl− additives, and the reasons for the optimum Cl− concentration in damascene baths.

Mathematical Model

The model is based on the finding from SERS that polymer molecules link to the surface through Cu+ ions coordinated with adsorbed Cl− ions.6.11 Hence, adsorption of the polymer is considered to be restricted by the underlying Cl− adlayer. The proposed model of the Cu surface with adsorbed PEG and Cl− ions is depicted in Fig. 2. The polymer molecules are represented by roughly spherical shapes, consistent with the findings of a quartz crystal microbalance study of PEG adsorption on Cu.3 The Cu+ ions associated with Cl− and PEG are not shown. The figure identifies a critical Cl−-fractional coverage (θ*) at which the polymer completely covers the Cu surface. θ* is the ratio of the contact area of a PEG molecule with the surface through its Cl− binding sites, to the surface area shielded by the PEG molecule. This ratio depends on the polymer conformation and the number of binding sites per molecule, neither of which are known in detail. θ* would likely decrease with increasing polymer molecular weight. The lower limit of θ* is about 0.1, based on the ratio of the saturation coverages of PEG (10−10 mol/cm2) and Cl− (10−7 mol/cm2) and PEG on Cu. For simplicity, when θCl is smaller than θ*, all adsorbed Cl− ions are assumed to participate in polymer adsorption (Fig. 2). At larger Cl− coverage, the excess Cl− ions above the critical coverage do not coordinate with PEG.

Since the PEG coverage depends on that of adsorbed Cl−, a surface mole balance on Cl− is necessary to predict inhibition. This balance assumes that the Cl− adsorption and incorporation rates are independent of the presence of polymer. That is, Cl− ions adsorb onto all open Cu surface sites at the same rate, whether or not the

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sites are shielded by polymer. Also, all adsorbed Cl\(^{-}\) ions are taken to desorb and incorporate at the same rate, regardless of their coordination with PEG. While these assumptions would clearly be subject to refinement in more detailed treatments, they effectively uncouple the Cl\(^{-}\) balance from the PEG coverage, and thus simplify the model considerably. Including polymer-dependent Cl\(^{-}\) adsorption and incorporation would require knowledge of polymer adsorption kinetic parameters, which is not presently available. The Cl\(^{-}\) balance is

\[
\Gamma_{\text{Cl}} \frac{d\theta_{\text{Cl}}}{dt} = k_a \theta_{\text{Cl}}(1 - \theta_{\text{Cl}}) - k_d \theta_{\text{Cl}} - \frac{i_d \Omega_{\text{Cl}} \Gamma_{\text{Cl}}}{2F \xi} \theta_{\text{Cl}} \tag{1}
\]

The terms on the right represent adsorption, desorption, and incorporation of Cl\(^{-}\) ions. The rate of Cl\(^{-}\) adsorption is controlled by kinetics rather than by diffusion, despite evidence for diffusion-controlled adsorption of halides on Ag.\(^{1,7}\) A version of Eq. 1 based on diffusion-controlled adsorption was also considered, in which the net adsorption rate was given by \(\frac{D_{\text{Cl}}}{\delta} \left( C_{\text{Cl}}^0 - C_{\text{Cl}} \right)\). As discussed below in the Results section, the hypothesis of diffusion-controlled adsorption was rejected because of inconsistency with experimental measurements of Cl\(^{-}\) incorporation.

As in previous models of adsorbate incorporation during electrodeposition,\(^{8,18}\) the incorporation rate in Eq. 1 is proportional to the adsorbate coverage and the deposition current density. The particular form of the incorporation rate expression is based on the proposal that incorporation is due to lateral growth of surface asperities.\(^{8}\) It is postulated that when the side surfaces of two growing asperities come into contact, adsorbates on these surfaces are trapped in the deposit. Other possible incorporation models, based on growth steps enveloping immobile adsorbates on terraces,\(^{9,20}\) are considered less likely in view of the high surface coverage of Cl\(^{-}\) ions.\(^{15,16}\) In Eq. 1, the incorporation rate is the volumetric deposition rate, \(\frac{i_d \Omega_{\text{Cl}}}{2F \xi}\), multiplied by the asperity surface area per deposit volume, \(\xi\), and the adsorbed Cl\(^{-}\) surface concentration, \(\Gamma_{\text{Cl}} \theta_{\text{Cl}}\), can be viewed as a type of surface roughness, \(\xi\), and a characteristic length scale of the surface asperities contributing to incorporation. While \(\xi\) is treated as a fitting parameter in the present model, the proposed incorporation mechanism suggests a range of possible values. If incorporation results from collisions of subgrain nanometer-scale features such as growth steps, \(\xi\) may be on the order of the step dimension, or somewhat larger if the steps are not closely spaced. On the other hand, \(\xi\) would be on the order of the grain size, if incorporation occurs primarily at grain boundaries.\(^{8}\)

As suggested by kinetic studies of inhibition of copper deposition by PEG, the potential dependence of the kinetically limited deposition rate in the model follows Butler-Volmer kinetics on either PEG-covered or PEG-free surfaces.\(^{7,11}\) These results imply that the charge-transfer coefficients on both surfaces are approximately the same, but the exchange current density on the polymer-covered Cu surface is a small fraction (here denoted \(r_p\)) of that on a clean surface. The kinetically controlled deposition current density is then

\[
i_k = i_d \rho f(\eta) \left[ \left( 1 - \frac{\theta_{\text{Cl}}}{\Theta^*} \right) + \frac{\theta_{\text{Cl}}}{\Theta^*} \right] \tag{2}
\]

when \(\theta_{\text{Cl}} < \Theta^*\), and

\[
i_k = i_d \rho f(\eta) \tag{3}
\]

when \(\theta_{\text{Cl}} > \Theta^*\). The potential dependence of deposition follows the typical Butler-Volmer form,

\[
f(\eta) = \exp \left( \frac{\beta F}{RT} \eta \right) \exp \left( \frac{1}{2} \frac{\beta F}{RT} \eta \right)
\]

where \(\beta\) is the charge-transfer coefficient. The deposition current density \(i_k\) is determined by \(i_k\) and the mass-transfer limiting current density \(i_h\), according to \(\frac{i_k}{i_h} = \frac{\xi^*}{\xi} + \frac{\xi^*}{\xi}\).

The model equations were converted to dimensionless form. With dimensionless time defined as \(\tau = \frac{i_d \Omega_{\text{Cl}}}{2F \xi I}\), the Cl\(^{-}\) balance is...
Table I. Parameter values used for model calculations.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_{Cu})</td>
<td>0 V</td>
<td>Ref. 7</td>
</tr>
<tr>
<td>(i_0)</td>
<td>0.77 mA/cm²</td>
<td>Ref. 7</td>
</tr>
<tr>
<td>(\beta)</td>
<td>0.46</td>
<td>Ref. 7</td>
</tr>
<tr>
<td>(r_p)</td>
<td>0.0357</td>
<td>Ref. 7</td>
</tr>
<tr>
<td>(i_l)</td>
<td>17 mA/cm²</td>
<td>Ref. 7</td>
</tr>
<tr>
<td>(k_{Cl} )</td>
<td>2.0 (\times) 10^{-9} cm²/mol</td>
<td>Ref. 21</td>
</tr>
<tr>
<td>(\Gamma_{Cl})</td>
<td>1.3 (\times) 10^{-3} cm²</td>
<td>Ref. 15</td>
</tr>
<tr>
<td>(\xi)</td>
<td>13 nm</td>
<td>Fitting (Fig. 3)</td>
</tr>
<tr>
<td>(\theta^*)</td>
<td>0.2</td>
<td>Fitting (Fig. 4)</td>
</tr>
<tr>
<td>(k_A)</td>
<td>1.8 (\times) 10^{-4}</td>
<td>Fitting (Fig. 3)</td>
</tr>
</tbody>
</table>

\[
\frac{d\theta_{Cl}}{dt} = \sigma - \left(\frac{\alpha}{K} + I\right)\theta_{Cl}
\]  
where the parameters are \(\sigma = \frac{2F\theta_{Cl}}{n_{Cl}\Gamma_{Cl}}\), \(K = \frac{\theta_{Cl}}{i_0}\), and \(I = \frac{r_p}{\sigma}\). \(\sigma\) is the ratio of rate constants for adsorption and incorporation, and \(K\) and \(I\) are the dimensionless adsorption equilibrium constant and deposition rate. The deposition rate \(I\) for \(\theta_{Cl} < \theta^*\) is

\[
I = \frac{\chi(\theta_{Cl})}{\chi + f(\theta_{Cl})}
\]

and when \(\theta_{Cl} > \theta^*\), \(I\) is

\[
I = \frac{\chi(\theta_{Cl})}{\chi + f(\theta_{Cl})}
\]

where \(\chi\) is a dimensionless limiting current density, \(i_l/i_0\).

The surface mole balance Eq. 4 may be integrated directly to model the transient galvanostatic experiments carried out by Hayase et al.\(^7\) Adsorbed \(\text{Cl}^-\) is assumed to be initially at equilibrium coverage, \(\theta_{Cl}(0) = \frac{K}{\kappa t_s}\). The time-dependent chloride coverage is then

\[
\theta_{Cl}(\tau) = \frac{\sigma}{\sigma + \frac{\alpha}{K} + I} + \frac{K}{K + 1} \left(1 - \frac{\sigma}{\sigma + \frac{\alpha}{K} + I}\right) \exp \left[- \left(\frac{\sigma}{\sigma + \frac{\alpha}{K} + I}\right) \tau\right]
\]  

The mole fraction of Cl in the deposit is the ratio of the \(\text{Cl}^-\) incorporation rate to the Cu deposition rate, or \(\gamma_{Cl} = \frac{\theta_{Cl}}{\theta_{Cu}}\). Since \(\gamma_{Cl}\) is proportional to \(\theta_{Cl}\), Eq. 7 may be used to model the dependence of the incorporated \(\text{Cl}^-\) on deposition thickness for comparison with the experimental measurements of Hayase et al. For the case of steady-state potentiostatic experiments, the model was expressed as two algebraic equations relating \(I\) and \(\theta_{Cl}\), a kinetic expression (Eq. 5 and 6), and a surface mole balance. The latter is obtained from Eq. 4

\[
I = \frac{\sigma}{\theta_{Cl}} - \sigma \left(1 + \frac{1}{K}\right)
\]

The steady-state deposition rate at a given potential is determined by the simultaneous solution of Eq. 8 with Eq. 5 and 6. As shown below, the steady-state behavior is conveniently illustrated by plotting \(I\) vs. \(\theta_{Cl}\) according to both equations. The steady-state model is applied to the potentiodynamic scans of Jovic and Jovic,\(^1\) which, as mentioned above, showed similar hysteresis behavior as potentiostatic experiments.

Table I lists values of model parameters used in calculations. A nonlinear model numerical fitting procedure (Igor Pro, WaveMetrics) was used to estimate values of the parameters \(E_{Cu}\), \(\beta\), and \(i_0\) using the region of the current-potential curves in Ref. 7 well below the limiting current density. \(r_p\) was taken as the ratio of the exchange current densities for polymer-covered and polymer-free surfaces. The maximum adsorbed \(\text{Cl}^-\) surface concentration \(\Gamma_{Cl}\) was taken from scanning tunneling microscopy observations of Cu (100),\(^5\) and the adsorption equilibrium constant \((k_{Cl}/i_0)\) was obtained from results of radiotracer measurements of \(\text{Cl}^-\) adsorption.\(^21\) The three remaining parameters \(\xi\), \(\theta^*\), and \(k_A\) were found by fitting, as described below.

Results and Discussion

Figure 3 shows the potential transients measured by Hayase et al.\(^6\) during constant current deposition, along with the depth profiles of incorporated \(\text{Cl}^-\) obtained with SIMS. For direct comparison of the two measurements, the potential is shown vs. deposit thickness and SIMS signal vs. distance from substrate/Cu interface. Dashed line is surface coverage of \(\text{Cl}^-\) calculated with model. In legend, the first identifying number is current density in mA/cm² and second is bulk NaCl concentration in mM. PEG molecular weight was 3000 g/mol.

Figure 3. Overpotential (\(E\)) and normalized SIMS signal from incorporated Cl, for constant current deposition from Ref. 9. \(E\) is plotted vs. deposit thickness and SIMS signal vs. distance from substrate/Cu interface. Dashed line is surface coverage of Cl calculated with model. In legend, the first identifying number is current density in mA/cm² and second is bulk NaCl concentration in mM. PEG molecular weight was 3000 g/mol.
experiments $K$ and $l$ are both significantly larger than one, so a small ratio is obtained only when $\sigma \ll 1$, in which case the ratio can be approximated by $\sigma/l$. Therefore Eq. 7 is approximately

$$\theta_{\text{Cl}}(\tau) = \frac{\sigma}{l} - \left( \frac{\sigma}{l} - \frac{K + 1}{K} \right) \exp(-\tau)$$  \hspace{1cm} [9]$$

From the definitions of $l$ and $\tau = z/l$, where $z$ is the distance from the Cu/substrate interface. The expected attenuation length of the exponential decays in Fig. 3 is therefore simply $\zeta$, the length parameter associated with incorporation. The decay length depends explicitly neither on chlorine concentration nor current density. This is consistent with Fig. 3, in which potential transients from experiments using two different current densities and chloride concentrations have approximately the same decay length. This equation was used to calculate the dashed line in Fig. 3, using $z = 13$ nm from the potential decays. $\sigma/l = 0.3$ was estimated as 0.1 from SIMS profile at 10 mA/cm$^2$, along with $K = 40$ from the Cl$^-$ concentration of 0.2 mM for this experiment. The fit value of $\sigma$ led to an adsorption rate constant $k_\text{s}$ of $1.8 \times 10^8$ cm/s. As mentioned earlier, a model based on diffusion-controlled Cl$^-$ adsorption was also considered. With reasonable values of the chloride diffusivity and diffusion layer thickness, adsorption was so rapid that values of $\zeta$ smaller than atomic dimensions were required to fit the profiles. In view of the physical interpretation of $\zeta$ as an asperity length scale, this was taken to be evidence for kinetics as opposed to diffusion control. The $\zeta$ value of 13 nm suggests that Cl$^-$ incorporation occurs on a subgrain scale, by collisions of nanometer-scale growth features such as step edges. Incorporation by this mechanism is possible, since STM images of Cu in 1 mM Cl$^-$ solutions show that step edges are decorated by a high Cl$^-$ coverage.$^{15}$

The specification of adsorption and incorporation rate parameters allows calculation of the steady-state current-potential-curves. Figure 4 shows $i-E$ curves for bulk Cl$^-$ concentrations of $10^{-2}, 10^{-3}, 0.1$, and 1 mM. The parameter $\theta^*$ was set at 0.2; the reason for this choice is discussed below. At 10$^{-3}$ mM Cl$^-$, the polymer did not affect deposition because its coverage was very small at all potentials, and accordingly active kinetics were found. On the other hand, at 1 mM the polymer coverage remained high at all potentials, leading to fully inhibited kinetics. For the two intermediate Cl$^-$ concentrations, deposition was inhibited at potentials near $E_{\text{CuCl}}$, but became activated at more negative potentials. Between regions of inhibited and active deposition, there were ranges of potential yielding two solutions to the steady-state model equations, corresponding to low and high Cl$^-$ coverage. These regions correspond to the hysteresis loops in Fig. 1 for the same bulk Cl$^-$ concentrations. Not only the Cl$^-$ concentrations producing hysteresis, but also the potential range of hysteresis when it occurred, are in reasonable agreement between Fig. 1 and 4. For example, at 0.1 mM Cl$^-$, steady-state hysteresis was found experimentally at potentials positive of $-0.7$ V, compared to $-0.65$ V in Fig. 3. In both Fig. 1 and 4, the hysteresis loop was displaced toward the equilibrium potential at $10^{-2}$ mM Cl$^-$, relative to its location in 0.1 mM Cl$^-$.

Figure 5 demonstrates that a necessary condition for multiple kinetic curves, which are independent of bulk Cl$^-$ concentration, are plotted at various potentials, while the potential-independent mole balance curves are displayed for the bulk Cl$^-$ concentrations in Fig. 4. In each of the kinetic curves, deposition is active at $\theta_{\text{Cl}} = 0$, then decreases with $\theta_{\text{Cl}}$ due to increasing polymer coverage, and eventually reaches a constant value at $\theta_{\text{Cl}} = \theta^*$ corresponding to fully inhibited kinetics on the polymer-covered surface. The deposition current density at a given potential and Cl$^-$ concentration is determined by the intersection of the dashed and solid lines. At 1 mM, these intersections at various potentials lie only on the inhibited plateau at $\theta_{\text{Cl}} > \theta^*$. For the concentration of $10^{-3}$ mM, there was also only one intersection near $\theta_{\text{Cl}} = 0$, corresponding to active kinetics. On the other hand, at the two intermediate concentrations of $10^{-2}$ and 0.1 mM, the curves have two intersections at potentials where hysteresis is found in Fig. 4. Figure 5 demonstrates that a necessary condition for multiple steady states and hysteresis is the steep decline of the deposition kinetic curve at low Cl$^-$ concentration. Such a steep decay occurs for $\theta^* = 0.2$, as in the figure. Somewhat larger $\theta^* = 0.3$ produced hysteresis at 1 mM Cl$^-$, which was not seen experimentally; for $\theta^* < 0.2$, the deposition rate decreased gradually with $\theta_{\text{Cl}}$ and there was only one steady state. The small $\theta^*$ is due to the small area of chemical contact between a polymer molecule and the Cu surface, compared to the Cu area effectively inhibited by the molecule. This characteristic is reasonable in view of the QCM mea-

![Figure 4](image1.png)  
**Figure 4.** Predicted steady-state deposition current density vs. potential, for different indicated bulk Cl$^-$ concentrations. Potential regions of hysteresis between high and low branches of polarization curves are delimited by vertical lines.

![Figure 5](image2.png)  
**Figure 5.** Deposition current density vs. Cl$^-$ surface coverage, according to kinetic equation (solid lines) and Cl$^-$ surface mole balance (dashed lines).
measurements of PEG adsorption, which suggest that the molecules have diffuse roughly spherical shapes, as opposed to lying flat on the surface.

The model can also be used to predict the potential transients at constant current (Fig. 2). However, unlike the experimental transients, the predicted curves displayed constant potentials at small times, when \( \theta_{Cl} > 0 \); the potential began to increase only when \( \theta_{Cl} \) fell below \( 0^+ \). Apparantly, Eq. 6 and 7 adequately model the steady-state but not the transient response of the deposition rate to chloride coverage. However, it may be possible to correct this problem by using a more detailed treatment of desorption. For example, during transient activation, \( Cl^- \) ions may desorb from random positions on the surface, so as not to permit arrangements of the \( Cl^- \) adlayer at low \( \theta_{Cl} \) which would be necessary to maintain high polymer coverage. For this reason, during transient activation open surface may begin to appear when \( \theta_{Cl} \) is still larger than \( 0^+ \).

Conclusions

A mathematical model has been described for \( Cu \) deposition in the presence of \( Cl^- \) and PEG additives. The model includes the suppression of deposition kinetics by an adsorbed PEG film, which binds to the surface through a complex involving adsorbed \( Cl^- \) ions. In the model, the adsorbed \( Cl^- \) coverage is determined by a surface balance accounting for kinetically limited adsorption and incorporation into the \( Cu \) deposit. This balance was shown to be consistent with experimentally obtained depth profiles of incorporated \( Cl \) in deposited films. The model was used to predict steady-state current-potential curves during deposition, for \( Bath Cl \) concentrations from \( 10^{-3} \) to 1 mM. The following aspects of model voltammetric behavior agreed with experiment: (i) deposition was suppressed through the entire potential range at 1 mM \( Cl^- \), but there was no suppression at any potential at 10 mM \( Cl^- \). (ii) At \( 10^3 \) and 0.1 mM \( Cl^- \), deposition abruptly activated at potentials cathodic to a critical value, in the neighborhood of which hysteresis between activated and suppressed deposition was found. (iii) Critical potential was more negative at higher \( Cl^- \) concentrations. Adsorption in the model was not potential-dependent; the critical potential was instead a consequence of faster incorporation as the potential was made more cathodic. Hysteresis in the model predictions resulted from the high sensitivity of the PEG coverage to the adsorbed \( Cl^- \) concentration, owing possibly to a limited number of binding sites for each polymer molecule. The present results reveal the reason for the minimum \( Cl^- \) concentration of about 1 mM in copper damascene plating baths.

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List of Symbols

- \( C_{Cl} \) chloride concentration in bulk solution, mol/cm³
- \( D_{Cl} \) chloride diffusivity, cm²/s
- \( F \) Faraday's constant, 96,487 C/equiv
- \( f(n) \) potential-dependent factor in kinetic rate expression, dimensionless
- \( I \) dimensionless deposition rate
- \( j_0 \) exchange current density of \( Cu \) deposition, A/cm²
- \( j_0^\prime \) Cu deposition current density, A/cm²
- \( j_{Cl} \) mass-transfer limiting current density for \( Cu \) deposition, A/cm²
- \( K \) dimensionless equilibrium constant for chloride adsorption
- \( k_{p} \) rate constant for chloride adsorption, mol/(cm²s)
- \( k_{p}^\prime \) rate constant for chloride desorption, mol/(cm²s)
- \( r_p \) ratio of deposition current density on polymer-free to polymer-covered surface
- \( s \) distance from the deposit-substrate interface, cm
- \( y_{Cl} \) mole fraction of chloride incorporated in the deposit

Greek

- \( \alpha \) charge-transfer coefficient for \( Cu \) electrodeposition, dimensionless
- \( \beta \) surface concentration of adsorbed chloride, mol/cm²
- \( \gamma_{Cl} \) maximum surface concentration of adsorbed chloride, mol/cm²
- \( \delta \) diffusion layer thickness, cm
- \( \xi \) effective length scale associated with chloride incorporation, cm
- \( \eta \) overpotential for \( Cu \) electrodeposition, V
- \( \theta_{Cl} \) fractional surface area coverage of chloride ion and polymer
- \( \sigma \) dimensionless parameter expressing the ratio of adsorption to incorporation rates
- \( \tau \) dimensionless time
- \( \chi \) dimensionless exchange current density
- \( \Omega_{Cl} \) molar volume \( Cu \), 7.12 cm³/mol

References