Chemical Mechanism of Suppression of Copper Electrodeposition by Poly(ethylene glycol)

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Poly(ethylene glycol) (PEG) is an important additive to electropolating baths used for the deposition of copper interconnects on semiconductor wafers. In an earlier paper, Yokoi et al., Denki Kagaku oyobi Kogyo Butsuri Kagaku, 52, 218 (1984) found a direct relationship between the deposition rate in the presence of PEG and chloride ions with the open-circuit potential measured after plating, suggesting that the rest potential reflects the chemical state of reactive copper ions within a surface polymer film. Here, these measurements were corroborated and then interpreted in terms of a proposed mechanism of copper deposition in the presence of PEG. In this mechanism, aqueous Cu$^{2+}$ ions are reduced to an intermediate complex at the PEG-Cu interface detected earlier by Raman spectroscopy [Z. V. Feng et al., J. Phys. Chem. B, 107, 9415 (2003)], in which Cu$^+$ ions associate with adsorbed Cl$^-$ ions and other oxygen ligands of PEG. The rest potential measurements are quantitatively explained on the basis of competition for these ligands at open circuit with Cu$^{2+}$ ions abstracting from solution. The results indicate that deposition is mediated through ions partially solvated with the polymer, the concentration of which is controlled by the PEG concentration and molecular weight. PEG then behaves as a polymer electrolyte film as opposed to a passive barrier.

Polyethylene glycol [CH$_2$O]$_n$, or PEG, is widely used as an additive to acid sulfate Cu electroplating baths, where it acts to reduce the deposition rate. It is an essential component of damascene baths used for deposition of on-chip interconnects, in which it promotes filling of submicrometer cavities by suppressing deposition on surfaces outside the cavities.1-3 Several studies relevant to the suppression mechanism have been carried out.$^{4,14}$ Suppression is considered to be due to an adsorbed polymer layer, and requires a polymer molecular weight of at least ~1000 g/mol and the presence of Cl$^-$ ions in the bath at a concentration of the order of 1 mM. Yokoi et al. proposed that Cu$^+$ or Cu$^{2+}$ ions coordinate with oxygen atoms of PEG and at the same time with Cl$^-$ ions adsorbed on Cu, in order to bind the polymer to the surface.2 They explained the minimum molecular weight for suppression in terms of the number of monomer units participating in the complex. The molecular structure of the PEG layer has been investigated using surface-enhanced Raman spectroscopy (SERS).$^{6,8,14}$ Recently, Feng et al.$^{14}$ showed that the spectra were consistent with a Cu$^+$-PEG surface complex, as suggested originally by Yokoi et al. Each Cu$^+$ ion in the complex was coordinated with an adsorbed Cl$^-$ ion and two oxygen atoms along the polymer chain. Although this cuprous complex helps explain the binding of the PEG film to copper, there is at present no widely accepted chemical explanation for the suppression of deposition. Different roles for the PEG have been proposed, for example, a blocking layer possibly containing defects,2,6,10 a diffusional barrier,5 or an agent for chemical complexation of reactant ions.14,15

In their paper, Yokoi et al. reported systematic measurements of the rest potential ($E_R$) after deposition. $E_R$ was tens of millivolts negative of the open-circuit potential (OCP) in PEG-free solutions, and it varied with deposition potential as well as with PEG molecular weight and concentration. In solutions containing 2 mM Cl$^-$, $E_R$ increased linearly with deposition potential for potentials more positive than ~150 mV vs. a Cu reference electrode, but it decreased linearly with potential at more negative potentials than this value (Fig. 1). The electrode used as a reference in this figure, and elsewhere in the paper, is that used by Yokoi et al., i.e., a Cu electrode in a PEG-free solution of 0.4 M CuSO$_4$ and 0.5 M H$_2$SO$_4$. A direct relationship was found between $E_R$ and the deposition current density, which held over a wide range of polymer molecular weights and concentrations (Fig. 2). Yokoi et al. suggested that $E_R$ reflects the condition of the adsorbed PEG film during deposition; from their results, the film properties determining $E_R$ apparently control the deposition rate. They did not, however, pursue the mechanistic implications of the slopes of the straight lines in Fig. 1 and 2, which may relate to the stoichiometry of reactions important in the function of the PEG layer. The dependence of $E_R$ on molecular weight was later corroborated by Reid and David,2 who also reported that after deposition, the OCP was initially close to 0 mV on the scale in Fig. 1, but then shifted in the cathodic direction, to values typical of those measured by Yokoi et al.

The present article offers an interpretation of the rest potential measurements of Yokoi et al. The interpretation is based on the PEG-Cu$^+$-Cl$^-$ complex recently revealed by SERS,14 and it is used to justify values of the straight line slopes appearing in Fig. 1 and 2. It is argued that these measurements are relevant to the structure of the polymer film, as well as to the film properties controlling the suppression of Cu deposition. The analysis given here is subject to experimental corroboration; however, if confirmed, it can serve as a basis for further mechanistic studies of additive effects in copper damascene plating. Although the results of Yokoi and Reid suggest an interpretation of $E_R$ based on the kinetics of copper deposition, before proceeding on this basis, it is important to establish the sensitivity of $E_R$ to stirring of the plating bath and the presence of dissolved oxygen. Hence, experiments are described in which this information was obtained.

Experimental

Electrodes were prepared by electrodeposition copper on a Pt rotating disk electrode (diam 5.0 mm). The electrodes were deposited without rotation, at a constant current density of 10 mA/cm$^2$, from a solution of 0.4 M CuSO$_4$ and 0.5 M H$_2$SO$_4$. Based on the deposition time of 15 min, the copper film thickness was 3.3 µm. Polarization was applied using a potentiostat/galvanostat (Schlumberger 1286) and a Pt wire counter electrode. All solutions were prepared using reagent grade chemicals and deionized water (Barnstead Nanopure). After copper film deposition, PEG (Fluka, 20,000 g/mol Mw) and NaCl were added to the solution, to obtain concentrations of 0.02 g/L PEG and 2 mM Cl$^-$.

The bath composition was the same as that used by Yokoi et al.7 Deposition was continued at an applied potential of −96 mV for 5 min, and then the electrode was switched to open circuit and the potential recorded vs. time. All potentials in this paper are referenced to a copper reference electrode in a solution of 0.4 M CuSO$_4$ and 0.5 M H$_2$SO$_4$ but no PEG, the same reference electrode used by Yokoi et al. The electrode was rotated during the constant potential and open-circuit periods, using a Pine Instruments AFMSRX rotator. When deaerated solutions were desired, nitrogen was bubbled through them for 30 min prior to use in the copper plating cell.
Results and Discussion

OCP measurements.—Figure 3 shows the OCP as a function of time after deposition at a potential of −96 mV vs. the Cu reference electrode. Upon switching to open circuit, the potential increased abruptly to around 30 mV, then within 10 s decreased to a relatively stable negative value, and finally decayed over 10-12 min to −22 mV. In oxygen-containing solutions, the potential prior to the slow decay was −50 to −56 mV. These potentials compare favorably with the E_R values reported by Yokoi et al., and hence corroborate the earlier measurements. In the present paper, E_R denotes the rest potential at the beginning of the slow decay; Yokoi et al. showed that this potential correlates with the deposition potential and rate, and it is therefore of mechanistic significance. Neither E_R nor the potential decay time was sensitive to the rotation speed, indicating that the rest potential is not determined by processes whose rates are influenced by mass transport. Such processes may include diffusion of cuprous ions away from the copper surface, or cathodic reduction of dissolved oxygen.

In the deaerated solution, Fig. 3 shows that the OCP transient was strongly attenuated; the potential at the start of the slow decay was −30 mV, only 8 mV negative of the final steady-state potential. It is argued here that E_R is determined by the concentration of cuprous ions, either in the polymer or in solution near the copper surface. In oxygen-saturated solutions, Cu^+ ions in solution would be rapidly consumed by homogeneous oxidation with dissolved oxygen. Therefore, Fig. 3 suggests that E_R is close to the steady-state potential when Cu^+ ions are present in solution, but when these ions are absent E_R assumes values of at least −50 mV, which are stable for ~10 s. The latter values depend on the polymer molecular weight and concentration (Fig. 2), as well as on the applied potential (Fig. 1). Thus, the analysis that follows proposes a relationship between E_R and the Cu^+ concentration in the polymer during deposition, which applies in aerated solutions. E_R is instead determined by solution-phase Cu^+ ions, when, as in deaerated solutions, their concentration is sufficiently high.

Copper deposition kinetics in additive-free solutions.—Using the kinetic model for the copper electrode, the potential dependence of E_R in Fig. 1 can be related to that of the Cu^+ concentration at the metal surface during deposition. In this section, a review of the kinetics of copper deposition in polymer-free solutions is presented, which serves as a basis for the model for open-circuit behavior in the presence of PEG. Copper plating occurs in two steps in additive-free acid baths

\[
\text{Cu}^{2+} (\text{aq}) + e^{-} \rightleftharpoons \text{Cu}^{+} (\text{aq})
\]

[1]

\[
\text{Cu}^{+} (\text{aq}) + e^{-} \rightleftharpoons \text{Cu}
\]

[2]

with the first step kinetically slow compared to the second. The corresponding kinetic expressions for the molar rates of steps 1 and 2 are

\[
r_1 = k_{C1}[\text{Cu}^{2+}]\exp\left(-\frac{\beta_1FE}{RT}\right) - k_{A1}[\text{Cu}^{+}]\exp\left(\frac{(1 - \beta_1)FE}{RT}\right)
\]

[3]
at the Cu\(^+\) concentration during deposition. In this context, it is worthwhile to consider measurements of the potential dependence of the Cu\(^+\) concentration during deposition from additive-free solutions, which were carried out by Yokoi et al.\(^{14}\) and open-circuit conditions following dissolution, as illustrated by the schematic of Fig. 4. After deposition, the Cu\(^+\) concentration at the electrode surface builds up, and the potential drifts in the anodic direction, until a steady state is reached where formation of Cu\(^+\) balances its removal by the combination of reaction with dissolved oxygen and diffusion to the bulk. Because of the fast kinetics of the Cu\(^+\)/Cu reaction, the OCP is close to the equilibrium potential of Reaction 2, corresponding to the steady-state Cu\(^+\) concentration

\[
E = E^0_2 + \frac{RT}{F} \ln[\text{Cu}^+] \tag{6}
\]

i.e., 0 mV on the scale used in Fig. 1-3.

Relationship of Eq\(_R\) to Cu\(^+\) concentration during deposition.—Because the potential at steady state in Eq\(_6\) is independent of the deposition potential, it is inconsistent with the behavior of Eq\(_R\) in PEG solutions (Fig. 1). Thus, the polymer film may inhibit the increase of the Cu\(^+\) concentration by Reaction 5 on open circuit, such that the rest potential is determined by E\(_2\) at the Cu\(^+\) concentration during deposition. In this context, it is worthwhile to consider measurements of the potential dependence of the Cu\(^+\) concentration during deposition from additive-free solutions, which were carried out by Yokoi et al.\(^{14}\) using rotating ring-disk electrode voltammetry.\(^{19}\) Similar experiments using indicator electrodes to sense the Cu\(^+\) concentration had been reported by Molodov et al.\(^{19}\) At potentials within about 160 mV of the OCP, Yokoi et al. found that the Cu\(^+\) concentration decreased with more negative potentials, according to the Nernst equation of Reaction 2

\[
[Cu'] = \exp\left(F(E - E^0_2)/RT\right) \tag{7}
\]

This relationship was followed because, over this potential range, Cu\(^+\) formed much more rapidly by the anodic partial reaction of 2 than by Reaction 1. However, at potentials more than 160 mV cathodic to open circuit, the Cu\(^+\) concentration increased exponentially with more negative potentials. In this range, the overpotential was negative enough to overcome the slow kinetics of Reaction 1, and so Cu\(^+\) ions were formed much faster by the cathodic component of Reaction 1 than by the anodic component of 2. Because both Reactions 1 and 2 were then effectively irreversible, the Cu\(^+\) concentration obeyed

\[
[Cu'] = \frac{k_C [Cu^{2+}]}{k_{C2}} \exp\left(\frac{(\beta_2 - \beta_1)FE}{RT}\right) \tag{8}
\]

where \(\beta_1 = 0.60\) from the Tafel slope and \(\beta_2 = 0.26\). On the basis of Eq\(_6\) and 7, the rest potential would increase with applied potential at potentials more positive than about −160 mV, with a slope of \(dE_R/dE = 1\). At potentials more negative than −160 mV, E\(_R\) would decrease with E according to Eq\(_6\) and 8, \(dE_R/dE = \beta_2 - \beta_1 = -0.34\). Although the sign change of the slope at −160 mV is qualitatively consistent with Fig. 1, the expected slopes in the two regions are each about a factor of two larger than the experimental slopes of approximately 0.5 and −0.2. The same concepts can be applied to the dependence of E\(_R\) on the deposition current density, in Fig. 2. At molecular weights higher than 1000 g/mol, the figure indicates a logarithmic relationship according to \(dE_R/d \log i \approx 30\) mV. According to Fig. 1, this overpotential is in the region where Reaction 2 is irreversible. Combination of the cathodic term of Eq\(_3\) with Eq\(_6\) then leads to the expected slope \(dE_R/d \log i = 2.303RT/F\), or 60 mV, twice the experimental value. Therefore, the simple concept, that the rest potential is close to the equilibrium potential of the Cu/Cu\(^+\) reaction (Eq\(_6\)), leads to dependences of E\(_R\) on both E and \(\log i\), which are qualitatively similar to those obtained experimentally. However, in quantitative terms, the expected slopes are a factor of two large in both cases. Such a discrepancy may be attributable to a different stoichiometry of reactions on the polymer-copper interface compared to Reaction 2, which applies to copper-aqueous solution interfaces.

Proposed kinetic model in PEG-containing solutions.—A reaction mechanism for the PEG-filmed copper electrode is now presented which is consistent with experimental rest potential measurements. The proposed reaction scheme is based on Reactions 1 and 2, but assumes that the cuprous intermediate is the complex at the polymer-copper interface which was identified by Feng et al.\(^{14}\) In this complex, a Cu\(^+\) ion is coordinated with a C\(^{\text{I}}\) ion adsorbed on the copper metal and two ether oxygen atoms belonging to PEG

\[
\text{Cu}^{\text{II}}\text{(aq)} + \text{Cl}^{-}\text{(ad)} + 2\text{(-EtO-) + }e^- \rightleftharpoons \text{Cu}^{+\text{-}(-\text{EtO-})\text{Cl}^{-}\text{(ad)}} \tag{9}
\]

\[
\text{Cu}^{+\text{-}(-\text{EtO-})\text{Cl}^{-}\text{(ad)}} + \text{Cu} + 2\text{(-EtO-)} + \text{Cl}^{-}\text{(ad)} \tag{10}
\]

where −EtO− represents an ether oxygen ligand on the polymer chain. The corresponding kinetic equations during deposition are
\[ r_1 = k_1 [\text{Cu}^{2+}(\text{aq})] \Gamma_S (1 - \theta_{\text{Cu}^+}) \exp\left( -\frac{\beta_1 FE}{RT} \right) \]
\[ -k_{d1} \Gamma_S \theta_{\text{Cu}^+} \exp\left( -\frac{\beta_1 FE}{RT} \right) \]
\[ r_2 = k_2 \Gamma_S \theta_{\text{Cu}^+} \exp\left( -\frac{\beta_1 FE}{RT} \right) - k_{d2} \Gamma_S (1 - \theta_{\text{Cu}^+}) \exp\left( -\frac{\beta_1 FE}{RT} \right) \]

[11]

[12]

\[ \Gamma_S \] is the concentration per unit area of sites at the polymer/metal interface, where an adsorbed CT' ion and two –EtO− ligands are close enough so a bridging Cu^+ ion can form a Cu^+[–EtO−]_2CT' complex. Such sites should be numerous, as Cl− is adsorbed at the interface, where an adsorbed Cl− ion and two –EtO− ligands are present. It is assumed that Cu^2+ absorption reaches equilibrium on open circuit after deposition. At this point, a quasi-steady-state condition would be obtained in which formation of new Cu^+[–EtO−]_2CT' complexes is blocked by the low concentration of free –EtO− ligands.

The concentration of –EtO− ligands in the polymer is determined in the following manner. Because the adsorbed Cu^+[–EtO−]_2CT' complexes bind polymer molecules to the copper surface, the quantity of these complexes present during deposition determines the number of polymer molecules attached to the surface. The adsorbed polymer molecules all have a characteristic number of –EtO− ligands, dependent on molecular weight and possibly conformation, which on open circuit are available for binding of Cu^2+ ions. Hence, the concentration of –EtO− ligands is proportional to the surface concentration of Cu^+[–EtO−]_2CT' complexes during deposition.

[–EtO−] \, \, + \, \, 4[\text{Cu}^{2+}][–EtO−]_2] \, = \, \sigma[\text{Cu}^{+}[–EtO−]_2CT'\text{(ad)}] \quad [16]

where \, \, \sigma \, \, \text{is the characteristic number of –EtO− ligands per complex.}

It is assumed that Cu^2+ absorption reaches equilibrium on open circuit, and that the number of ligands complexed with Cu^2+ greatly exceeds the number of free ligands. The open-circuit concentration of –EtO− is then given by

\[ [–\text{EtO−}] = \left( \frac{\sigma}{4K_A} \right)^{1/4} \left[ \text{Cu}^{2+}(\text{aq}) \right] \quad [17] \]

where \, \, K_A \, \, is the equilibrium constant of Reaction 15.

The OCP \, \, E_{R1} \, \, after deposition is found by inserting Eq. 17 into Eq. 14 to obtain

\[ E_2 = E_1^\circ + \frac{RT}{2F} \ln \left( \frac{\sigma}{4K_A} \right) + \frac{RT}{2F} \ln \left[ \frac{\text{Cu}^{+}[–EtO−]_2CT'\text{(ad)}}{\text{[CT']^2}} \right] \quad [18] \]

In a plating bath with given concentrations of Cu^2+ and CT', all factors in Eq. 18 are fixed except for the concentration of Cu^2+ complexes, which is determined by the conditions of deposition. Thus, as in Eq. 6, \, \, E_{R1} \, \, varies linearly with the logarithm of the concentration of Cu^2+ intermediate, but with a proportionality factor of RT/2F as opposed to RT/F in the case of Eq. 6. As shown below, this difference accounts correctly for the experimental slopes in Fig. 1 and 2. The abrupt increase and decrease of the OCP upon switching to open circuit (Fig. 3) may be due to consumption of oxygen absorbed in the polymer film, after which the potential is determined by Eq. 18. The slow decay over 10-12 min is tentatively attributed to slow adsorption of additional polymer molecules, which would increase the concentration of Cu^+[–EtO−]_2CT' complexes compared to that present during deposition.

The kinetic model of the PEG-covered copper electrode can also be applied to predict the rest potential after anodic polarization, for which experimental data are shown in Fig. 1. During copper dissolution, the concentration of Cu^+[–EtO−]_2CT' would be high, so that the equilibrium potential of the kinetically facile Cu/Cu2+ reaction (Eq. 10) is positive to that of the relatively sluggish Cu^2+/Cu+ reaction (Eq. 9). On open circuit following dissolution, the direction of Reaction 10 would change from anodic to cathodic, and that of the Cu^2+/Cu+ reaction would be blocked, as the complexed Cu^2+ ions can simply be reduced to copper metal. Therefore, both Reactions 9 and 10 would reach equilibrium, resulting in a condition satisfying the disproportionation equilibrium.

\[ \text{Cu}^2+ + 4[–\text{EtO−}] \, \, + \, \, \text{Cu}^{2+}(\text{aq}) \, \, + \, \, 2\text{Cu}^{2+}(\text{ad}) \quad [15] \]

This mechanism is further supported by paramagnetic resonance measurements which detected aqueous Cu^2+ ions in molecular-scale cavities in the polymer.27 On open circuit, Cu^2+ ions should accumulate in the polymer to higher concentrations than those found during deposition, because they are consumed by cathodic reduction at a lower rate than that the deposition potential. The high Cu^2+ concentration in solution suggests that the rate of Cu^2+ absorption may be much more rapid than Reaction 13. If this is the case, nearly all the available –EtO− ligands react with Cu^2+ ions before the Cu^+[–EtO−]_2CT' concentration has appreciably increased from its value during deposition.

\[ r_1 = k_1 [\text{Cu}^{2+}(\text{aq})] \Gamma_S (1 - \theta_{\text{Cu}^+}) \exp\left( -\frac{\beta_1 FE}{RT} \right) \]
\[ -k_{d1} \Gamma_S \theta_{\text{Cu}^+} \exp\left( -\frac{\beta_1 FE}{RT} \right) \]
\[ r_2 = k_2 \Gamma_S \theta_{\text{Cu}^+} \exp\left( -\frac{\beta_1 FE}{RT} \right) - k_{d2} \Gamma_S (1 - \theta_{\text{Cu}^+}) \exp\left( -\frac{\beta_1 FE}{RT} \right) \]
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