Experimental and Simulation Investigations of Copper Reduction Mechanism with and without Addition of SPS

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Rotating disk electrode and rotating ring-disk electrode were used to investigate the mechanism of copper reduction and the influence of convection on the effect of Bis-3-sodiumsulfopropyl disulfide (SPS), a widely used accelerator in copper via-filling and copper foil manufacturing. The experimental results show that the commonly accepted single electron transfer for copper reduction is dominating in the low overpotential range, whereas the double electron transfer is also involved in the high overpotential range. SPS was found to exhibit a weak inhibition effect even with \( \text{Cu}^{\text{II}} \) ion in the solution under strong convection, and generate more intermediates in the solution with both \( \text{Cl}^{-} \) and SPS than with \( \text{Cl}^{-} \) alone. Based on the experimental observations, a reaction model for copper reduction considering competition between the single electron transfer and the double electron transfer, as well as desorption and runoff of generated \( \text{Cu}^{1+} \)-containing intermediates, was proposed and used for finite element method modeling. The simulation results enable quantitative description of the proportion of the two charge transfer reactions and the runoff of the intermediates, providing guidelines for selecting the additives and plating conditions in industrial manufacturing.

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Electrodeposition is the most widely used method in the copper industry not only for damascene plating and via-filling to fabricate high quality interconnected wires in ultra large scale integration (ULSI) manufacturing, but also for mass-production of high quality copper foil utilizing relatively high deposition current density. In these processes, the usage of basic additives, including rate-suppressing polyethylene glycol (PEG) and rate-accelerating bis-3-sodiumsulfopropyl disulfide (SPS), is the key technology to obtain defect-free deposits.

As a charge transfer process involving two electrons, copper reduction is commonly believed to occur through two consecutive single-electron reduction steps, without considering the practical conditions. This is because Conway et al. proved that the single electron reduction route is associated with significantly lower activation energy as compared to the double electron reduction route by calculating the potential energy profile diagrams for metal electrodeposition. However, their calculated activation energy could be dependent on the applied potential. In addition, Tindall et al. reported that under certain conditions it is possible to deposit and strip copper without significant \( \text{Cu}^{\text{II}} \) ion formation, and they found that the formation of \( \text{Cu}^{2+} \) ion occurs only in the approximate potential range from +0.05 to −0.15 V vs. saturated calomel reference electrode (SCE) in 0.2 M \( \text{CuSO}_4 \) solution. It seems that the reaction mechanism and the rate-determining step may change in a large enough potential range. Hence, it seems questionable to generally ignore the double electron reaction route for copper reduction in all cases.

To clarify the detailed mechanism of copper reduction is of great importance, because the formation of \( \text{Cu}^{\text{II}} \) ion in the electrodeposition process has been extensively proven to be critical for the acceleration effect of SPS, when used simultaneously with \( \text{Cl}^{-} \) ion. For instance, Vereecken et al. claimed that the concentration of \( \text{Cu}^{\text{II}} \) ion, and of intermediates or complexes near the electrode surface are related to the overpotential and, thus, the kinetics of copper electrodeposition.

The activation effect of SPS is merely attributed to its promotion of the formation of stable cuprous complexes. With the rotating ring-disk electrode (RRDE) measurements, Vereecken et al. also found the runoff of SPS from the disk electrode surface only occurs within the potential range of \( \text{Cu}^{+} \) ion formation. This is indirect evidence that the formation of accelerating intermediates is through interaction between \( \text{Cu}^{+} \) ion and SPS. Moreover, Cho et al. found that SPS weakly inhibits copper reduction on a non-incubated \( \text{Cu} \) electrode. Since the \( \text{Cu}^{+} \) ion initially do not exist in the solution but could be generated from the coproportionation reaction, the transient acceleration effect of SPS with the incubation would be related to the interaction between SPS and \( \text{Cu}^{2+} \) ion. Kondo et al. reported that the current density on the through-mask cathode increases with more narrow opening width of the through-mask. They suggested that the acceleration complex formed between \( \text{Cu}^{+} \) ion and SPS exists free in the solution, is not adsorbed on the electrode surface, and the accumulation of this complex at the bottom of micro via is the reason for a bottom-up via filling.

Therefore, to investigate the formation kinetics of \( \text{Cu}^{2+} \) ion in the presence of various additives is necessary to understand the mechanism of bottom-up via filling and to get better control of the deposited copper quality. For damascene plating in submicron via with high aspect ratio, the applied deposition current density is relatively low, ca. 2–15 mA/cm², leading to a weak polarization on the electrode surface, which may place the electrode potential within the sensitive potential range for \( \text{Cu}^{+} \) ion. However, for copper plating in through silicon via (TSV), which has a dimension ca. 100 times larger than that of the damascene structure, the applied deposition current density is relatively high, as a result the electrode potential maybe out of the potential range for formation of \( \text{Cu}^{+} \) ion. It is expected that this will limit the acceleration effect of SPS, leading to an insufficient copper deposition rate at the bottom of the via and formation of unexpected defects. However, there are hardly any reported studies on the mechanism of copper reduction under relatively high overpotential range.

Due to the complexity of copper reduction within micro via, especially in the presence of various additives, experimental methods alone are not sufficient to gain a thorough understanding of the kinetic process. As complementary methods, modeling and simulation have in recent decades been increasingly used in the field of copper reduction. So far most of the simulation studies have focused on the filling trend for damascene deposition in micro via based on the curve enhanced adsorption model (CEAM) proposed by Moffat et al. There is very little literature reported about the reaction mechanism of copper reduction over a large potential range and the effect of generated intermediates. Vereecken et al. proposed a physical-chemical adsorption model, taking into account both adsorbed and dissociative intermediates, as well as the inward- and
outward-diffusion of reagents and relevant products. However, the complicated mechanism hindered any quantitative numerical analysis of the kinetic process.

In this work, electrochemical experiments were combined with modelling and numerical simulation to study the kinetic mechanism of copper reduction within a large electrode potential range for the Cu$^{2+}$-SPS-Cl$^-$ system. Rotating disk electrode and rotating ring-disk electrode (RDE/RRDE) were used to mimic different mass transport conditions, providing experimental inputs for the modeling work. The model considers not only the electrochemical reactions and the adsorption/desorption on the electrode surface, but also the inward- and outward-diffusion of reagents and dissociative intermediates (affected by rotating speed of the electrode).

### Experimental

RRDE (PINE co. AFMSRCE) was used to investigate the formation of Cu$^{2+}$-containing intermediates during copper reduction. Linear sweep voltammetry (LSV) scans were performed on the gold disk electrode within a potential range from −0.5 to 0.1 V vs. SCE at a scan rate of 5 mVs$^{-1}$, and the initial potential is −0.5 V, sweeping positively, ended at potential 0.1 V. Meanwhile chronoamperometry (CA) at 0.7 V vs. SCE (high enough to oxidize Cu$^{2+}$-containing intermediates)$^{14}$ were recorded on the platinum ring electrode.

Besides, by using a RDE (PINE co. AFMRSRCE), linear voltammetric stripping (LVS) experiments in the potential range −0.5 V to 0.8 V vs. SCE at a scan rate of 10 mVs$^{-1}$ were conducted to explore the influence of forced convection on the kinetic process of copper reduction in the presence and absence of SPS, respectively. The anodic branches of the LVS curves were used to calculate the deposition amount of copper, while the cathodic branches were used to compare with simulation results, verifying the suitability/reliability of the proposed model in this work.

The compositions of the solutions used are shown in Table I. For better reproducibility and comparability, all the solutions were prepared at the same time. The measurements were carried out in an air-conditioned room so the temperature of the solution was 23 ± 2 °C. Fresh solution was used for each experiment.

A CHI 650D potentiostat was used for the LVS measurements and a CHI 760D Bi-Potentiostat used for the RDE measurements. The RDE with gold disk (Φ 5 mm) and RRDE with gold disk (Φ 4.57 mm) and platinum ring (inner Φ 4.93 mm, outer Φ 5.38 mm) were purchased from PINE co. AFMSRCE. A 30 mm × 30 mm platinum plate and a saturated calomel reference electrode (SCE) were used as the auxiliary electrode and reference electrode, respectively. All potentials quoted hereafter are given with respect to SCE.

### Experimental Results and Discussion

**Analysis of intermediates based on the RRDE results.**—It is widely accepted that copper reduction takes place in two consecutive single-electron transfer steps (Reactions 1 and 2):

\[
\text{Cu}^{2+} + e^- \rightarrow \text{Cu}^+ \tag{1}
\]

\[
\text{Cu}^+ + e^- \rightarrow \text{Cu} \ (s) \tag{2}
\]

In the RRDE measurement, the generated intermediate Cu$^+$ ion would be thrown off the disk electrode and some of them could be trapped on the ring electrode hold at a high enough oxidation potential (0.7 V in this work). Thus the measured oxidation current on the ring electrode reflects the amount of Cu$^+$ ion generated on the disk electrode, except for a proportion of loss due to subsequent reactions or submergence in the bulk solution. Combined with specific ligands (e.g., Cl$^-$ ion, thiolate), more stable intermediates may form, increasing the amount of detectable intermediates on the ring electrode.$^{19}$

![Figure 1. Current-potential curves measured on a rotating ring (Pt)-disk (Au) electrode with rotating speed of 2000rpm in the four solutions, x-axis stands for the disk potential, y-axis on the left hand side stands for the disk current density measured during a LSV test from −0.5 V to 0.1 V with scan rate of 5 mVs$^{-1}$, y-axis on the right hand side stands for the ring current density measured from a CA test with the ring electrode held at 700 mV vs. SCE.](image)

**Table I. Composition of the solutions.**

| No. | Electrolyte                                                                 |
|-----|-----------------------------------------------------------------------------|
| A   | CuSO$_4$ 0.2 M, H$_2$SO$_4$ 1.85 M                                           |
| B   | CuSO$_4$ 0.2 M, H$_2$SO$_4$ 1.85 M, HCl 100 ppm                             |
| C   | CuSO$_4$ 0.2 M, H$_2$SO$_4$ 1.85 M, SPS 80 ppm                              |
| D   | CuSO$_4$ 0.2 M, H$_2$SO$_4$ 1.85 M, HCl 100 ppm, SPS 80ppm                  |

The anodic branches of the LVS curves were used to calculate the reduction current densities measured on the disk electrode with rotating speed of 2000rpm. The reduction current densities measured on the disk electrode in the solutions are shown with filled symbols and exhibit negative values in Fig. 1. In general, the reduction current density declines with increasing disk potential from −0.5 V to 0.1 V (decreasing cathodic overpotential). Addition of SPS solely decreases the reduction current density, which is consistent with literature reports.34–36 On the contrary, addition of Cl$^-$ ion increases the reduction current density. When added together, the synergistic effect between Cl$^-$ ion and SPS is potential dependent. Under relatively low overpotential (−0.35 V vs. OCP), SPS and Cl$^-$ ion increase the reduction current density more than adding Cl$^-$ ion alone; on the contrary, under high overpotential (more negative than −0.35 V vs. OCP), SPS and Cl$^-$ ion decrease the reduction current density compared with adding Cl$^-$ ion alone. Additionally, it seems that when the applied potential decreases to −0.5 V, the measured reduction current density on the disk in the solutions reach a limiting current density.

The CA results, i.e., oxidation current densities measured on the ring electrode in the solutions, are shown with open symbols and positive values in Fig. 1. The current peaks appearing in the disk potential range −0.4 V to −0.5 V correspond to oxidation of hydrogen at the ring electrode.$^{15}$ The maximum current density for oxidation of Cu$^{2+}$-containing species appears in the vicinity of the open-circuit potential of the disk electrode. As can be seen from Fig. 1, when the disk potential is more negative than −0.1 V, the oxidation current density measured on the ring electrode is very low (close to zero) for all the solutions. This implies that the amount of Cu$^{2+}$-containing intermediates generated on the disk electrode decreases to an ignorable level in the high overpotential range. This result is consistent with the report of Tindall et al.$^{13}$ showing the sensitive potential range −0.15 V to 0.05 V for generation of Cu$^{2+}$-intermediates. Comparing the CA results measured on the ring electrode in different solutions, it is seen that without additive the amount of intermediates that can be detected is the smallest, owing to the instability of Cu$^{2+}$ ion in the aqueous solution. In the low overpotential region, addition of both SPS and Cl$^-$ ion leads to a relatively higher oxidation
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Figure 2. LVS curves obtained at different rotating speeds with a potential scan rate of 10 mV/s. (a) in the solution with Cl\textsuperscript{−} ion; (b) in the solution with Cl\textsuperscript{−} ion and SPS; (c) the amount of deposited copper calculated from (a) and (b), and corresponding normalized stripping ratio as a function of rotating speed.

Figure 3. Linear fitting for the limiting current density measured as a function of the square root of the rotating speed in the 0.2 M CuSO\textsubscript{4} solution with Cl\textsuperscript{−} ion.

Effect of convection on copper electrodeposition.—LVS tests were conducted in Cl\textsuperscript{−} containing solutions with and without SPS under different electrode rotating speeds (0, 100, 500 and 2000 rpm) of the RDE. The current density-potential curves and the normalized stripping ratio, defined as the amount of deposited copper in solution with SPS divided by same amount without SPS, are shown in Fig. 2. The amount of deposited copper in the solution with SPS is slightly larger than that without SPS at low rotating speeds, but the amount becomes smaller with SPS at relatively higher rotating speeds (e.g. 500 rpm ∼ 2000 rpm), see Fig. 2c. This suggests that SPS acts as an accelerator at low rotating speed, but as a weak inhibitor under strong convection in the solution. This abnormal inhibition effect of SPS under strong convection in the solution cannot be explained by any existing hypothesis, and has never been simulated by modeling. In the following sections, a more thorough discussion on this scenario will be given based on our modeling and simulation.

Reaction mechanism of copper reduction under high overpotential.—Fig. 2 shows that, under high overpotential, the mass transport of Cu\textsuperscript{2+} ion become dominant for the whole kinetic process, the current density reach a limiting value, i.e., 50, 110, 150, 230 mA/cm\textsuperscript{2} for 100, 500, 1000, 2000 rpm, respectively. For the RDE, as shown in Equations 3 and 4, the limiting current density \( I_d \) should be proportional to the square root of rotating speed of the electrode \( \omega \). Here \( n \) is the number of electrons transferred in the reduction reaction, \( F \) the Faraday constant, \( \nu_i \) the stoichiometric coefficient, \( C_i^0 \) the concentration in the bulk solution, \( D_i \) the diffusion coefficient of species \( i \), and \( \nu \) the dynamic viscosity coefficient.

\[
I_d = \frac{nF}{\nu_i} \gamma_i \omega^{1/2} C_i^0 \tag{3}
\]

\[
\gamma_i = 0.62D_i^{2/3} \nu^{-1/6} \tag{4}
\]

By plotting and linear fitting between the limiting current densities vs. the square root of electrode rotating speeds, Fig. 3, \( n \) can be calculated from the measured data. This turns out to be approximately 2.11, indicating transfer of two electrons in the copper reduction. This result and the analysis of the intermediates from the RRDE results (§ 3.1) suggest that copper reduction is more likely taking place through double electron transfer (Reaction 5) under high overpotential, instead of two consecutive single electron transfer steps. This reaction mechanism will be used to build a competitive reaction model.
Cu(I)Cl(thiolate)\(^{-}\) (ads) ⇔ Cu(I)Cl(thiolate)\(^{-}\) (aq) \[10\]

2Cu(I)Cl(thiolate)\(^{-}\) (ads) + 2H\(^{+}\) + 2e\(^{-}\) ⇔ 2Cu (s) + SPS + 2Cl\(^{-}\) \[11\]

**Table II. Parameters used in the simulation.**

| Reaction Kinetic Parameters | Reaction 5 | Reaction 6 | Reaction 9 |
|----------------------------|------------|------------|------------|
| Equilibrium Potential/V(SCE) | 0.13(38)   | 0.05       | 0.05       |
| Exchange Current Density/mA - cm\(^{-2}\) | 0.02\(^{37}\) | 6          | 10         |
| Transfer Coefficient       | 0.32       | 0.35       | 0.35       |
| Mass Transport             | Value      |            |            |
| Diffusion Coefficient of Cu\(^{2+}\)/10\(^{-5}\)cm\(^{2}\) s\(^{-1}\) | 0.52\(^{37}\) |            |            |
| Diffusion Coefficient of CuCl/10\(^{-5}\)cm\(^{2}\) s\(^{-1}\) | 0.2\(^{37}\)   |            |            |
| Diffusion Coefficient of CuCl/10\(^{-5}\)cm\(^{2}\) s\(^{-1}\) | 0.3\(^{37}\)   |            |            |
| Dynamic Viscosity Coefficient/10\(^{-2}\)cm\(^{2}\) s\(^{-1}\) | 3\(^{37}\)    |            |            |
| Ad/desorption Kinetic      |            |            |            |
| Parameters                | Value      |            |            |
| K\(_{ads}\), Cu(I)Cl      | 0.03       |            |            |
| K\(_{ads}\), Cu(I)thiolateCl | Function of Potential (Equation 14) | | |
| B\(_{1}\)                   | 3000       |            |            |
| B\(_{2}\)                   | 9          |            |            |
| U_{peak}/V                 | 0.1        |            |            |

taking into account both single electron transfer and double electron transfer.

\[Cu^{2+} + 2e^{-} \rightarrow Cu(s)\] \[5\]

**Model Description**

Considering the above-mentioned experimental results and to get a detailed and quantitative understanding of copper reduction over a wide potential range with or without SPS, a comprehensive kinetic model is proposed next, which includes the mass transport in the solution, surface adsorption/desorption of reactive ions and generated intermediates, electrochemical reactions on the electrode surface, as well as their coupling. The simulation was realized by Matlab programming. Model discrimination, assumption verification and parameter estimation of kinetic models were carried out, by fitting the experimental curves obtained under different electrode rotating speeds and different potential scan rates.

**Competitive reaction model for copper reduction.**—Considering the experimental results in § 3.1 and § 3.3, a competitive reaction model is proposed, including both double electron transfer (Reaction 5) and single electron transfer. The two different reduction routes share the Cu\(^{2+}\) ion in the solution close to the electrode surface, and the rate of electrochemical reactions occurring on the electrode surface is used to calculate the current density.

For the single electron transfer route, in the solution with Cl\(^{-}\)ion, copper electrode-deposition involves Reactions 6–8.\(^{14}\) In the solution with both Cl\(^{-}\)ion and SPS, additional Reactions 9–11 are also possible.\(^{38}\) The relevant kinetic parameters of these reactions are shown in Table II.\(^{37,38}\)

\[Cu^{2+} + e^{-} + Cl^{-} \rightarrow CuCl(ads)\] \[6\]

\[CuCl(ads) \leftrightarrow CuCl(aq)\] \[7\]

\[CuCl(ads) + e^{-} \rightarrow Cu(s) + Cl^{-}\] \[8\]

\[2Cu^{2+}(aq) + SPS + 2Cl^{-} + 2e^{-} \rightarrow 2Cu(I)Cl(thiolate)(ads) + 2H^{+}\] \[9\]

**Mass transport in the solution.**—The electrochemical reactions taking place on the electrode surface lead to generation of Cu\(^{+}\)-containing intermediates and consumption of Cu\(^{2+}\) ion in the solution close to the electrode. The concentration gradient of the species provides driving force for the diffusion in the solution. In the present model, Nernst–Planck equations for conservation of relevant species (e.g., Cu\(^{2+}\) ion, Cu\(^{+}\)-containing intermediates, etc.) in the solution are the governing equations (Equation 12), which include diffusion, convection and migration terms.

\[
\partial c_{i}/\partial t = -\nabla \cdot (D_{i} \nabla c_{i} + c_{i} u - Z_{i} m_{i} F c_{i} \nabla \phi_{i}) \tag{12}
\]

where \(t\) is the time, \(c_{i}\), \(D_{i}\), \(Z_{i}\), \(m_{i}\) are the concentration, diffusion coefficient, charge number and mobility of species \(i\), respectively. \(u\) is the flow velocity of the solution. Since the calculation area of this model is within the diffusion layer where the flow velocity equals to zero, the second term on the right side of Equation 12 can be ignored, whereas the different convection conditions are reflected by different thicknesses of the diffusion layer under different rotating speeds of RDE. For RDE, the thickness of the diffusion layer is uniform for the whole electrode surface, so the concentration field can be simplified to one-dimensional in the calculation. In this case, the boundary condition refers to only two points, one is on the electrode surface and the other is on the outside boundary of the diffusion layer. At the point on the electrode surface, a Neumann boundary condition is defined to describe the flux density of reactive species caused by the reactions occurring on the electrode surface. At the point on the outside boundary of the diffusion layer, a Dirichlet boundary condition is defined to describe the concentration of all the species equal to the bulk concentration. Moreover, the effective thickness of the diffusion layer \(\delta_{i}\) can be different under different rotating speeds \((\omega)\) of RDE, which can be calculated according to the following equation:

\[
\delta_{i} = 1.61 D_{i}^{1/2} \omega^{-1/2} \nu^{1/6}
\]

in which, \(D_{i}\) is the diffusion coefficient of specie \(i\), and \(\nu\) is the dynamic viscosity coefficient.

Moreover, owing to the concentrated supporting electrolyte, the electric migration can also be ignored in this model. This mass transport model is adaptable not only for reactive ions but also for dissociative intermediates desorbed from the electrode surface (Reactions 7 and 10).

**Desorption and runoff of Cu\(^{+}\)-containing intermediates.**—The Reactions 6 and 9 are commonly considered being the rate limiting steps in copper deposition.\(^{12,14}\) The desorption Reactions 7 and 10 can be ignored since they are very slow relative to the reduction Reactions 8 and 11. Thus, the amount of Cu\(^{+}\)-containing species produced in Reactions 6 and 9 equals the amount consumed in Reactions 8 and 11, respectively. However, when strong convection exists in the solution, e.g., for RDE with high rotating speeds, desorption (Reactions 7 and 10) and runoff of the Cu\(^{+}\)-containing intermediates from the surface cannot be ignored. For a better description, the schematics of electrode/electrolyte interface including the intermediate runoff is depicted in Fig. 4. Here, both inward diffusion of reactants and additives and outward diffusion of Cu\(^{+}\)-containing intermediates were considered in this model.

Assuming that the adsorption/desorption of intermediates is quick enough (i.e., in equilibrium), for solution containing Cl\(^{-}\)ion, the adsorption/desorption of generated Cu(I)Cl was simplified to be non-potential dependent, with a fixed equilibrium constant \(K_{ads}Cu(I)Cl(ads)\) for the whole potential range. The amount of adsorbed intermediates can be determined according to Langmuir equation (Equation 13).
However, it has been reported that adsorption/desorption of SPS or its relevant intermediates is highly potential dependent. Thus, for the solution with SPS, a potential-dependent adsorption/desorption relationship was used in this model, with the equilibrium constant of generated intermediates calculated from Equation 14, which is similar to the one proposed by Moffat et al.

\[
\theta_{ads,Cu(I)Cl} = K_{ads,Cu(I)Cl} \times c_{Cu(I)Cl}
\]

The constants, B_1, B_2, U_{peak}, can be obtained by fitting the experimental data, and are listed in Table II. Considering that the detected amount of Cu^{+}\text{-containing intermediates on the ring electrode in the solution with Cl}^{-}\text{ion and SPS is much more than that in the solution with Cl}^{-}\text{ion only (Fig. 1), runoff of the intermediates provides a possible explanation for the measured weak inhibition of SPS under high rotating speed (§ 3.2). Detailed quantitative evidence will be presented in the following sections.

### Simulation Results and Discussion

**Single electron and competitive reactions in the solution with Cl\text{-}ion.**—For comparison, simulated current densities under different rotating speeds calculated by using single electron transfer model are shown in Fig. 5, where (a) and (b) display the simulation results excluding and including the desorption and runoff of the intermediates, respectively. Fig. 5a shows that, excluding the runoff of intermediates, the simulated current density (hollow line) agrees quite well with the experiment result (solid line) under a low rotating speed of 100 rpm, whereas the simulated ones are larger than the measured ones under higher rotating speeds (1000, 2000 rpm) in the entire potential region. This indicates that the runoff of intermediates becomes non-negligible with the increase of rotating speed. As shown in Fig. 5b, when the desorption and runoff of the intermediates are considered, the simulated current densities agree well with experiment results for the low overpotential range. This is consistent with the experiment results in § 3.1 and § 3.3, indicating that single electron transfer reaction is dominant in copper reduction under low overpotential. On the other hand, the experimental results suggest that the double electron reduction reaction is dominant under high overpotential. The discrepancy between the experimental and simulation results in the high overpotential range (Fig. 5b) implies that the competitive reaction model including the double electron transfer should be used for the simulation at high overpotential.

Fig. 6 displays the simulated current densities calculated by using the competitive reaction model (described in § 4.2) and taking into account the runoff of intermediates.

![Figure 4. Schematics of the electrode/electrolyte interface in copper plating solution with additives, showing the reaction and adsorption/desorption of reactive species on the electrode surface, the inward diffusion of reactants and outward diffusion of dissociative intermediates within the diffusion layer, and convection outside the diffusion layer.](image)

![Figure 5. Experimental and simulation results of voltammograms obtained at 10 mV/s under different rotating speeds in the solution with Cl\text{-}ion. Simulation results were calculated by using single electron reaction model for copper reduction.](image)

![Figure 6. Experimental and simulation results of voltammograms obtained at 10 mV/s under different rotating speeds in the solution with Cl\text{-}ion. Simulation results were calculated by using competitive reaction model (considering both single electron and double electron transfer reactions) for copper reduction.](image)
account the runoff of generated Cu$^{+}$-containing intermediates, which agree well with the experiment results for the whole potential range and under different rotating speeds. Clearly the competitive reaction model provides a better description of the kinetics of copper reduction over a wide potential range. Moreover, by using the competitive reaction model, the proportion of each reaction route can be calculated, and an example is shown in Fig. 7 for the rotating speed of 2000 rpm. Fig. 7a illustrates the contributions of single electron transfer and double electron transfer as a function of electrode potential, and Fig. 7b shows the corresponding proportions of each reduction reaction. It can be seen that the single electron transfer reaction dominates in the low overpotential range, with a proportion exceeding 90% when the electrode potential is more positive than $-0.2$ V. And the runoff of intermediate is around 40% of the amount of the first single electron transfer reaction. On the contrary, under a high overpotential (electrode potential more negative than $-0.2$ V), the double electron transfer reaction plays an important role.

Competitive reduction reactions in the solution with Cl$^{-}$ ion and SPS.—The competitive reaction model (Reactions 9–11) was also used to simulate the copper reduction kinetics in the solution with both Cl$^{-}$ ion and SPS. Fig. 8 shows the simulated current densities with and without runoff of intermediates under different rotating speeds, using the same kinetic parameters for Reactions 5 and 6 determined from the above-mentioned fitting for the solution with Cl$^{-}$ ion (Fig. 6).

The kinetic parameters for Reaction 9 determined by the experiment and our simulation are also given in Table II. For the higher rotating speeds, the simulation including the runoff of intermediates (Fig. 8b) gives a better agreement with the experimental results as compared to the simulation excluding runoff of intermediates (Fig. 8a).

For the lower rotating speed (100 rpm), the simulation (Fig. 8b) is less satisfactory in the low overpotential range. In the presence of SPS, the variety of possible intermediates implies a complicated mechanism of copper reduction, and an accurate description of SPS adsorption/desorption is still absent. The adsorption/desorption model of SPS used in this work is likely too simplified. Nevertheless, the competitive reactions model for copper reduction process provides a better description for the kinetics in a wide potential range, by taking into account the double electron transfer reaction, which has always been ignored in related studies. For a precise description of this complicated process, more detailed information is needed, such as kinetics of each sub-processes, e.g., generation of the intermediates and quantification of the adsorption/desorption of the additives.

Effect of strong convection on the action of SPS.—The experimental results show an abnormal inhibition effect of SPS on the copper reduction under high rotating speeds (§ 3.2). The fact that a higher oxidation current on the ring electrode was observed in the presence of SPS (Fig. 1) suggests a larger amount of desorption and runoff
of Cu(I)Cl(thiolate)– intermediate than that of Cu(I)Cl intermediate, especially under strong force convection.

Taking the example of electrode rotation speed of 2000 rpm, Fig. 9 displays the experimental and simulation results for the contribution of different reactions as a function of electrode potential and corresponding proportions of each reaction. It can be seen in Fig. 9b that the single electron transfer is dominant (higher than 90%) in the low overpotential range, i.e., at electrode potential more positive than $-0.2 \, \text{V}$, whereas the double electron transfer has a relatively large contribution in the high overpotential range (electrode potential more negative than $-0.2 \, \text{V}$). Moreover, the ratio of intermediate runoff, with the same electrodes potential more positive than $-0.2 \, \text{V}$, is higher than 0.8 for the solution without SPS (Fig. 7b), is higher than 0.8 for the solution without SPS (Fig. 7b). This implies that the runoff of the intermediates is more severe in the presence of SPS even in the presence of Cl$^-$ ion, confirming the assumption made in the competitive reaction model for copper electrodeposition. This provides a possible explanation for the potential-dependent behavior of SPS in the copper electrodeposition process.

**Implications on Industrial Copper Electrodeposition**

In order to establish a universal model that can describe the kinetics of the copper reduction in a wide overpotential range, this work has demonstrated that both single and double electron transfer reactions have to be included in the model. The simulation results suggest that the single electron transfer is the predominant reaction for copper reduction in damascene plating process, which is done by applying a small current density, resulting in a low overpotential of the electrode ($\text{c.a.} -0.2 \, \text{V vs. OCP}$). Even though the adsorbed layer of PEG inhibitor on the upper sidewall is found to be critical for a bottom up via filling process recently, under damascene plating condition, the generated amount of Cu$^{2+}$ ions according to our work is sufficient, and SPS can effectively accelerate the copper deposition at the bottom of the micro via, favorable for obtaining a bottom-up filling process.

However, in the case of through silicon via (TSV) filling, the size of the micro via is much larger than the one used in damascene plating. To improve the via filling rate, usually a much higher deposition current density is applied and the plating time is also much longer. As a result, even with the same additives used in damascene plating, formation of defects, such as crevice and voids, were frequently observed, which is commonly explained by depletion of Cu$^{2+}$ ion within the micro via. However, the experimental and simulation results in the present work demonstrate that under high overpotential (associated with a large applied deposition current), the generation of Cu$^{2+}$ ion is limited, leading to a weakened acceleration effect of SPS and insufficient bottom-up via filling. To guarantee a relative high via filling rate (relative high overpotential), simultaneously avoid formation of defects, for TSV filling, $-0.2 \, \text{V} \sim -0.25 \, \text{V}$ seems to be a suitable applied potential range, which enables bottom-up filling.

Kondo et al. reported that reverse pulse current waveform could help to achieve perfect via filling in TSV. The reverse current level of the periodic pulse current has a strong influence on the filling behavior. Through RRDE measurements, they found that the generated Cu$^{2+}$ concentration was markedly increased with increasing periodic reverse pulse current. With a higher reverse pulse current, the generated Cu$^{2+}$ concentration during copper dissolution is high. As a result, the Cu$^{2+}$ ion would concentrate within the micro via and leading to preferential copper deposition at via bottom, achieving the V-shape bottom-up filling. This could be regarded as an experimental support to the competitive reaction model for copper reduction, which emphasizes the importance of considering the applied condition in the electrochemical process. Specifically, for copper reduction, the applied potential may influence the action of SPS used in copper manufacturing.

The results from this work confirm that the generation of Cu$^{2+}$-containing intermediate is of critical importance for the acceleration effect of SPS in copper reduction process. However, a unified description about the detailed reaction mechanism is still absent, although there are different hypotheses about the state of the intermediates. Kondo et al. claimed that the intermediate was dissociative in the solution, and its accumulation inside the micro via caused the bottom-up filling. Vereecken et al. suggested that SPS can react with Cu$^{2+}$ ion generated from synproportionation and then adsorb on the electrode surface as Cu(I)(thiolate)$_2$. They believed that the increase in Cu$^{2+}$ concentration rather than surface accumulation of catalyst is the major factor determining the acceleration effect of SPS. Based on the experimental observations, Vereecken et al. proposed a physical-chemical model taking into account the catalytic effect of SPS for Cu$^{2+}$ complex formation, and the concentration change due to in-and out-diffusion of reagents and products. However, because of the complicated reaction mechanism, a better model is needed to enable quantitative description of the kinetics.

In this study, adsorption of SPS was assumed to occur through an electrochemical reaction with Cu$^{2+}$ ion forming Cu(I)Cl(thiolate)–(ads), and the desorption and outward diffusion of this intermediate was considered instead of SPS itself. The competitive reaction model proposed includes both single electron and double electron transfer reactions in copper reduction, able to describe the...
reaction kinetics over a wide overpotential range. One of the most important features of our model is that the runoff of the dissociative intermediates gives a reasonable explanation of the abnormal inhibition effect of SPS observed under strong convection.

Conclusions

Combined experimental measurements, using rotating disk electrode and rotating ring-disk electrode, and theoretical simulations were carried out to investigate the reaction mechanism of copper electrodeposition with and without bis-3-sodiumsulfopropyl disulfide (SPS) additive. Based on the results and discussion, the following conclusions have been drawn:

Dissociative Cu\(^{2+}\)-containing intermediates are formed in the solutions with Cl\(^{-}\) as well as with both Cl\(^{-}\) and SPS. The amount of the intermediates reaches the highest level in the low overpotential range (c.a. OCP to ~0.2 V vs. OCP).

The limiting current density measurements under different rotating speeds suggest the occurrence of double electron transfer in the copper reduction process in the high overpotential range (more negative than around ~0.4 V vs. OCP). A competitive reaction model is proposed, taking into account the proportion of single and double electron transfer reactions, as well as desorption and runoff of the intermediates. The simulation results are consistent with experimental observations for the solutions with or without SPS.

The simulation shows that the single electron transfer reaction is dominant in the low overpotential range, whereas the double electron transfer reaction plays an important role in the high overpotential range.

Considering the proportion of single and double electron transfer and the net generation rate of Cu\(^{+}\) ion (first single electron transfer), ~0.2 V ~ ~0.25 V is a suitable potential range for SPS to be effectual, which enables bottom-up filling in TSV plating. The runoff of the intermediates provides a reasonable explanation for the abnormal inhibition effect of SPS on copper reduction under strong convection.

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