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Potential oscillation during galvanostatic copper electrodeposition with a leveler-accelerant additive system

Dongpin Liu

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POTENTIAL OSCILLATION DURING GALVANOSTATIC COPPER ELECTRODEPOSITION WITH A LEVELER-ACCELERANT ADDITIVE SYSTEM

BY

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Thesis

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In
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This thesis has been examined and approved.

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8/16/2013
Date
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ABSTRACT

POTENTIAL OSCILLATION DURING GALVANOSTATIC COPPER ELECTRODEPOSITION WITH A LEVELER-ACCELERANT ADDITIVE SYSTEM

By
Dongpin Liu

University of New Hampshire, September 2013

Potential oscillations during copper electrodeposition on a rotating disk electrode (RDE) in acidic-sulfate solution with leveler and an accelerant were investigated. Potential oscillations were observed in the presence of accelerant Bis-(3-sulfopropyl)-disulfide (SPS) and the levelers Enthone L76, a commercial leveler, and Janus green B. In the L76/SPS system, the period and amplitude of oscillation were affected by the concentrations of SPS and leveler, RDE rotation speed and the current density. Within a specific concentration range, higher SPS concentration enhanced the potential oscillation and higher leveler concentration weakened the potential oscillation. Potential oscillation was observed in a certain current density range and the oscillation was enhanced by higher current density. Higher RDE rotation speed promoted the potential oscillation at rotating speeds less than 500 rpm.
In the JGB and SPS system, the potential oscillation was affected by the concentration of SPS and JGB, current density, rotation speed and the presence of oxygen, but no clear trends were determined. A mechanism is proposed which relates potential dependent desorption and adsorption of the additives to the observed oscillation.
CHAPTER ONE

INTRODUCTION

1.1 Objective

As the popularity of smart phones increases, more and more functions have been assembled into them. For this reason High density interconnection (HDI) wiring boards are necessary for smart phones and laptops. Chip stacking is a good choice for HDI packaging. It can be used to build-up multiple interconnection layers in a small space. Copper deposition in microvias has become a good technology for formation of through-chip interconnects. Bottom up filling of the vias requires the use of additives. Additives used in via filling include chloride, suppressor (Poly ethylene glycol, PEG) bis-(3-sulfopropyl)-disulfide (SPS) and Levelers (Janus green B (JGB), the proprietary commercial leveler Enthone L76). In the SPS-leveler-Cl\(^-\) additive system, SPS acts as an accelerant to increase the rate of bottom up via filling and the leveler is mainly adsorbed at the opening of the micro via to suppress copper deposition there. In this study, both JGB and Enthone L76 were used. JGB is an aromatic compound that contains quaternary ammonium. It can be adsorbed on the cathode surface by \(\pi\)-bonding because it is attracted by locally high electron density. Once adsorbed, it suppresses copper electrodeposition. At the electrode, the nitrogen-nitrogen double bond -N=N- is unstable. This function can
be broken to produce another product. The commercial leveler, Enthone L76, 
can be adsorbed on the working electrode, but the mechanism is not clear 
because the molecular structure is proprietary. Adsorption of SPS, the 
commercial leveler and JGB depend on the potential. If SPS and the leveler have 
an adsorption-potential overlap there exists a competition between adsorbed 
SPS and adsorbed leveler. Under this hypothesis, there may be a potential 
oscillation, and this is observed under some conditions. The period of oscillation 
should be affected by the concentration of leveler, SPS, mass transfer rate and 
current density and other factors which produce changes in cathode potential.

1.2 Copper electrodeposition plating bath

The process of copper deposition at the working electrode can be expressed by 
two electron transfers in series with standard potentials was shown below:\(^4\):

\[
\begin{align*}
Cu^{2+} + e^- & \rightleftharpoons Cu^+ E^0 = 0.159 \text{ vs. SHE} \\
Cu^+ + e^- & \rightleftharpoons Cu E^0 = 0.520 \text{ vs. SHE}
\end{align*}
\]

(1.1) 

(1.2)

The intermediate Cu(I) is relatively unstable, and it can be consumed or 
produced by the reaction:\(^5\):

\[
2Cu^+ \rightleftharpoons Cu^{2+} + Cu
\]

(1.3)

It has been reported that reaction (1.1) is slow and reaction (1.2) is fast, so that 
the overall reaction rate is determined by reaction (1.1). In order to modify the 
plating speed and current distribution it is useful to modify the kinetic parameters 
with chemical additives. There are three common types of additives for via filling
processes. Suppressors and accelerants are two normal additives in via filling systems. Polyethylene glycol (PEG) in combination with Cl\(^-\) is used as a suppressor. Bis(3-sulfopropyl) disulfide (SPS) deactivates the adsorbed suppressor and so is termed an accelerator. Janus green B (JGB) is a leveler that is strongly adsorbed and inhibits copper deposition\(^6\).

1.3 Mass Transport

Mass transfer analysis in an electrolytic solution requires a description of the movement of mobile ionic species, material balance, current flow, electroneutrality, and fluid mechanics. The flux of dissolved species can be expressed as\(^7\).

\[
N_i = -z_i u_i F c_i \nabla \phi - D_i \nabla c_i + c_i \nu \quad (1.4)
\]

The first term in equation (1.4) is migration, the second is diffusion and the last term is convection. The flux \(N_i\) of species \(i\) is the number of moles moving per unit time across a plane of 1 cm\(^2\); \(z_i\) is the number of charges carried by the ion; \(u_i\) is the mobility of the ion and expresses the average velocity of species \(i\) in the solution; \(F\) is the Faraday constant; \(\phi\) is the potential; \(c_i\) is the concentration of species; \(D_i\) is the diffusivity of species \(i\); \(\nu\) is the motion of fluid with the bulk velocity.

The relation between current density \(i\) and molar flux can be expressed by equation (1.5), as\(^7\)

\[
i = F \sum_i z_i N_i \quad (1.5)
\]
The overpotential is defined as the difference of between the actual potential $E$ and the open-circuit potential $E_q$.

The first term, the migration term, can be neglected in this system because the potential gradient is small due to the high solution conductivity. The last term is convection, and because there is no bulk flow in the Nernst boundary layer, this term can be neglected also. The only significant term is the diffusion term.

1.4 Rotating disk electrode

The rotating disk electrode (RDE) is used widely in electrochemical studies. As shown in Fig 1.1, the rotating disk consists of an insulated vertical shaft which is connected to a synchronous motor. The disk electrode is embedded at the end of the shaft. The synchronous motor can be used to control the rotation speed.

The angular velocity of the rotating disk is $\omega = 2\pi f$, where $f$ is the rotation rate in revolutions per second. The Nernst boundary layer thickness $\delta$ at the disk is given by the Levich equation:

$$\delta = 1.61D^{1/3}v^{1/6}\omega^{-1/2}$$

(1.6)

In equation (1.6), $D$ is the diffusion coefficient and $v$ the kinetic viscosity. The boundary layer thickness can be varied by control of the rotation speed of the disk. When the reaction is under mass transfer limitation, the limiting current is defined by

$$i_L = 0.62nFAD^{2/3}\omega^{1/2}v^{-1/6}C$$

(1.7)
1.5 Accelerant

Sodium-3,3'-disulfanediylbis(propane-1-sulfonate) or sodium bis-(3-sulfopropyl)-
disulfide (SPS), is used as an accelerant in via filling processes. Sodium-3-
mercapto-1-propanesulfonat, MPS, is a derivative of SPS and both are well
studied. The chemical structures are shown in Fig 1.2.

Figure 1. 1 Structure of the rotating disk electrode

Figure 1. 2 Chemical Structure of SPS and MPS
SPS has been widely studied as an accelerant\textsuperscript{9}. Accelerants are understood to be adsorbed on the growing Cu surface and to participate in charge transfer\textsuperscript{4}. SPS reacts with copper ion to form Cu(I)(thiolate)\textsubscript{ads} which acts as the accelerant\textsuperscript{11}. It is reported that the acceleration is affected by the presence of Cl\textsuperscript{-} and is positively correlated with SPS concentration\textsuperscript{12}. Two main mechanisms have been proposed for the action of SPS in acidic plating copper solutions. The first can be described as reduction of SPS to MPS at the cathode. MPS is able to reduce Cu\textsuperscript{2+} to form a Cu (I) thiolate complex. These elementary reactions can be represented by the reactions below:

\begin{align}
SPS + 2H^+ + 2e^- &\rightleftharpoons 2MPS \quad (1.8) \\
2Cu^{2+} + 4MPS &\rightleftharpoons 2Cu(I)\text{thiolate}_{ads} + SPS + 4H^+ \quad (1.9) \\
Cu(I)\text{thiolate}_{ads} + H^+ + e^- &\rightleftharpoons Cu + MPS \quad (1.10) \\
4Cu^+ + SPS &\rightleftharpoons 2Cu(I)\text{thiolate}_{ads} + 2Cu^{2+} \quad (1.11) \\
Cu^+ + SPS &\rightleftharpoons Cu(I) / SPS + H^+ \quad (1.12) \\
2Cu_{s} + SPS &\rightleftharpoons Cu(I) / SPS + H^+ \quad (1.13)
\end{align}

Another mechanism that has been proposed is formation of a film of SPS Cu(I) complex, where intense mass transport to the cathode takes place\textsuperscript{13}. Metallic Cu is a product of electrochemical reduction of this film. T.M.T. Huynh and Hai et al have studied the SPS reaction mechanism on the copper surface by combined DFT (density functional theory) calculation and STM (Scan tunneling microscope) studies as illustrated in Fig 1.3\textsuperscript{14}. 
Bozzini et al has studied the interplay of chloride ions with SPS through in-situ surface enhanced scattering (SERS) measurements during copper electrodeposition\textsuperscript{15,16}. These measurements showed an increased signal when Cl\textsuperscript{-} was present in the plating solution coupled with SPS, while it is hard to distinguish without Cl\textsuperscript{-}. In 1992, Healy and Pletcher found that Cu(II) and MPS generated a Cu(I)-thiolate product. Survila et al reported that Cu(II) and SPS reacted to Cu(I)-thiolate with an equilibrium constant $10^{3.3}$.

$$2\text{Cu(II)} + 4\text{MPS} \rightleftharpoons 2\text{Cu(I)thiolate}_{\text{ads}} + \text{SPS} + H^+ \quad (1.14)$$

Schultz et al. postulated that the attachment of SPS to the surface is accomplished through coordination of the sulfonate end group of SPS with a
CuCl$_{ads}$ (adsorbed species) on the surface$^{17}$, as shown in Figure 1.4. In 2011, Garcia-Cardona and co-workers demonstrated that MPS reacted with CuCl to yield Cu(I)-thiolate and SPS through NMR spectroscopic studies. Walker et al. reported that if the copper electrode was initially exposed to SPS, there was a layer which contained SPS$^{12}$. When Cl$^-$ was added the layer got thicker. Although it was hard to predict the formed complex, the result does indicate significant adsorption of Cl$^-$ on the cathode.

The reactions below have been proposed for the reaction of chloride on the cathode.

\[
Cu^+ + Cl^- \rightleftharpoons CuCl_{ads} \quad (1.15)
\]

\[
Cu(I)(thiolate)_{ads} + Cl^- \rightleftharpoons Cu(thiolate)Cl^- \quad (1.16)
\]

MPS and SPS have different adsorption behaviors. Walker et al have studied the adsorption behavior of MPS and SPS, and shown that MPS adsorption does not depend on potential, but SPS adsorption behavior varies as the potential becomes more negative$^{12}$.

**1.6 Levelers**

Levelers are another type of inhibitor adsorbed in the open via to avoid over-plating or bumps$^{18,19}$. Therefore, levelers were introduced to the via-filling process with the assumption that they cannot be deactivated by MPS$^{14,20}$. It was believed that the leveler produces impurities in the copper film and the morphology of the film$^{21}$. The leveler is a positively charged molecule, which deactivates the accelerator ionic interaction$^{22,23}$. Two levelers were used in this
study. JGB has been used as a leveler in some studied articles\(^4,6\). A commercial leveler, Enthone L76, was also used, but the chemical details of the commercial leveler are unknown.

Janus green B is an aromatic compound that contains quaternary ammonium. The structure is shown in Fig 1.4. It can be adsorbed on the cathode surface by \(\pi\)-bonding. Because it is attracted by locally high electron density, it suppresses copper electrodeposition. In the electrochemical process \(-N=N-\) is an unstable functional group of JGB\(^{12}\).

Janus Green B has been widely used as a leveler in the copper filling system. JGB acts as a leveler in copper filling system because it is adsorbed at the outside of the microvia surface and inhibits the electrodeposition of copper in that area\(^{12}\).
Due to the reaction of JGB on the working electrode we expect that the JGB concentration on the surface should decrease during deposition while the concentration of A, the decomposition product of JGB, should increase. The reaction of JGB on the working electrode is illustrated in Fig 1.6. At more negative potential, product A can be adsorbed on the working electrode more strongly. The potential of the cathode in the actual filling process is more negative than the JGB desorption potential. This process is illustrated in Fig 1.6\textsuperscript{12}. 

![Diagram showing the adsorption behavior of JGB and Product A](image)
Figure 1. JGB reactions on the cathode
Dow et al found a local current peak as the potential is swept from positive to negative during copper plating with PEG-CI–JGB and SPS. The reason given is that the natural increase of current with more negative potential is momentarily interrupted by adsorption of JGB on the cathode.

1.7 Potential oscillation

JGB can absorb on the electrode surface at more positive potentials. As a result, the inhibiting effect of JGB on copper is stronger, and the inhibition effect at constant current forces the potential to shift in the negative direction, toward a higher driving force. But at more negative potentials, the adsorption of JGB is weakened. JGB desorbs from the working electrode gradually when it reaches the desorption potential of JGB. JGB will be desorbed totally from the working electrode when the deposition potential is higher than its desorption potential. At this moment, the SPS concentration on the working electrode increases. Because SPS is an accelerant, at constant current the potential now shifts in the positive direction toward a lower driving force. This mechanism may account for the appearance of potential oscillation at constant current.

According to Nguyen et al, the combination of the leveler (PEI) with MPS and Cu(I) forms an inner salt. For other types of leveler the inner layering leveler action model and the interaction with the other co additives is still not clear.

Bohannan et al has reported oscillation behavior in copper electrodeposition with formation of a nanoscale laminate of Cu2O and mixture of Cu/Cu2O in an alkaline Cu (II) lactate solution. They related the oscillation with the periodic film formation.
composition and morphology along the growth direction. Similar potential oscillation was observed by Nakanishi et al. in acidic o-phenanthro-line-containing Cu (II) solution. The grown film also showed a periodic composition of the film by cross-section SEM inspection.

Nguyen et al reported a potential oscillation in the Imep (Polymerizates of imidazole and epichlorohydrin)-SPS/MPS-CI system in acidic environment. They reported a bidentate Imep-Cu (I)-MPS precipitate ensemble at the copper/electrolyte interface. The potential oscillation observed in this system was related to alternating precipitation and dissolution of Imep-Cu (I)-MPS. The oscillation was affected by the SPS, MPS and Cl concentration. An N-shaped negative differential resistance, in which the middle portion of the curve exhibits a negative differential resistance, produces the instability under galvanostatic conditions. Cross-section FIB analysis also demonstrated a periodic or laminated deposit structure produced by the potential oscillation. The mechanism of SPS reaction with Imep is illustrated in Fig 1.7.

Huang et al reported a potential oscillation with two commercial levelers, the oscillation was related to the potential and impurity of the copper film. They also found alternating layers of large Cu grains and fine Cu grains in the Cu films under oscillation conditions.
Figure 1. Reaction scheme demonstrating SPS surface electrochemistry coupled with the Imep precipitation reaction.
CHAPTER TWO

EXPERIMENTAL

2.1 Apparatus and setup

The three electrode equipment set up is shown in Fig 2.1. A potentiostat provides power to this system and the electrons are transferred through the working electrode and the counter electrode. Potential differences between the working and reference electrodes are measured by the potentiostat. Copper metal was deposited on the working electrode which is a cathode in this system. The counter electrode is the anode in this system. The cell is a three neck flask with a jacket for circulation of heat transfer fluid. The MRSX speed controller was connected to the working electrode.

The potential difference and current were measured by the potentiostat and reported to the computer.
2.1.1 Electrolysis cell

In this experiment, the electrolytic solution sits in a three neck flask with three electrodes coupled in three necks. A Rotating Disk Electrode (RDE), works as a working electrode. The reference electrode is Ag/AgCl. The counter electrode was platinum wire. There is a water jacket outside of this 125ml three neck flask as shown in Fig2.2. The water jacket is used to keep the solution temperature constant during plating. The set up is shown in Fig 2.1
2.2 Instrument

2.2.1 Rotating Disk Electrode (RDE)

The hydrodynamic conditions of RDE are fully defined by the angular velocity of the disk. The angular velocity forces the fluid away from the disk center, which brings fresh reactants to the surface and establishes a mass transfer boundary layer that is independent of position on the disk.

The RDE used in this system consists of a platinum disk embedded in an inert non-conductive Teflon cylinder, as shown in Fig 2.3. The platinum was embedded at the end of the Teflon cylinder which attached to a rotating motor. The flat Platinum surface is the working electrode. The diameter of the Platinum disk is 5mm.
2.2.2 Reference electrode

The reference electrode used in this study was the silver/silver chloride (4M KOH) electrode. It is made up of a silver wire immersed in 4M KCl-sat'd-AgCl solution. A bridge tube was used to separate the KCl-AgCl solution from experimental solution. The potential of this reference electrode is 200mV versus the Normal Hydrogen Electrode (NHE).

The reference electrode provides a standard potential to the system for measuring the potential of the working electrode.

2.2.3 Counter electrode

A platinum wire was used as counter electrode. It is laced in a fritted tube with a membrane at the end of the tube. This arrangement prevents mixing of the anolyte with the solution in contact with the working electrode.
2.2.4 Potentiostat/Galvanostat

A VersStat™II potentiostat-galvanostat was used in these experiments to control and measure current or potential. It is controlled with a PC via an interface port GPIB (IEEE-488) and use of EG&G Electrochemical Command Set software. In this work, the current was controlled by the potentiostat and the working electrode potential was measured with respect to the reference electrode. Fig 2.4 and Figure 2.5 show typical experimental result and the experimental apparatus.
2.2.5 Electrode Rotator

A PINE MRS Rotator electrode rotator was used to control the RDE rotating speed, as shown in Fig 2.6. The type of electrode rotator is AFMSRX #1808. It is a solid-state-controlled servo-system and is capable of speeds of 5-10000 rpm.

2.3 Reagents, Ultrapure water and Solution Preparation

2.3.1 Chemical Reagents

Seven reagents were used in this experiment see table 2.1.
<table>
<thead>
<tr>
<th>Number</th>
<th>Reagents</th>
<th>Lot#</th>
<th>Company</th>
<th>Purity</th>
<th>Chemical formula</th>
<th>Molecule weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>1#</td>
<td>copper (II) Sulfate pentahydrate</td>
<td>115560</td>
<td>Fisher Scientific</td>
<td>100.1%</td>
<td>CuSO₄·5H₂O</td>
<td>249.68</td>
</tr>
<tr>
<td>2#</td>
<td>Janus Green B</td>
<td>101643</td>
<td>Alfa Aesar</td>
<td>---</td>
<td>C₃₀H₃₁ClN₆</td>
<td>511.07</td>
</tr>
<tr>
<td>3#</td>
<td>Bis-(sodium-sulfopropyl)-disulfide</td>
<td>022003</td>
<td>RASCHIG GmbH</td>
<td>---</td>
<td>C₆H₁₄NaO₆S₄</td>
<td>354.54</td>
</tr>
<tr>
<td>4#</td>
<td>Sodium Chloride</td>
<td>L19609</td>
<td>J.T.Baker</td>
<td>99.5%</td>
<td>NaCl</td>
<td>58.44</td>
</tr>
<tr>
<td>5#</td>
<td>Enthone Leveler ×76</td>
<td>------</td>
<td>Enthone</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>6#</td>
<td>Sulfuric Acid</td>
<td>K03054</td>
<td>J.T.Baker</td>
<td>96.4%</td>
<td>H₂SO₄</td>
<td>98.08</td>
</tr>
<tr>
<td>7#</td>
<td>Sodium-3-mercaptopropanesulfonate</td>
<td>S35831</td>
<td>ALDRICH</td>
<td>---</td>
<td>C₃H₇NaO₃S₂</td>
<td>178.2</td>
</tr>
</tbody>
</table>

2.3.2 Ultrapure Water

A Millipore Milli-Q ultrafiltration system was used to prepare water with a resistivity of the 18 MΩ cm. All the electrolysis containers were rinsed with this water. Chemical solutions were also prepared with ultrapure water.

2.3.3 Solution preparation

Both a primary plating solution and additive solutions were used in these experiments. The primary solution was made of 0.8M sulfuric acid solution and 0.78MCuSO₄·5H₂O. Chloride solution was made of 13.2g/L sodium chloride and 0.8M sulfuric acid solution. The accelerant solution is made of 1.28g/L SPS and 0.8M sulfuric acid solution. The JGB solution is made of 1.6g/L Janus Green B and 0.8M sulfuric acid solution. Leveler Enthone L76 solution is made of 1ml/l
L76 original solution and 14ml/L 0.8M sulfuric acid solution. The concentrations of these additives added to the plating solution were varied.

### 2.4 Cleaning Procedure

**Glass ware**

Clean the glass ware with soap;

Rinse the glass ware with tap water 3 times;

Rinse glass ware with Ultra pure water 3 times.

**Working electrode**

Clean RDE by immersion in 75%(V/V) nitric acid;

Rinse with ultrapure water 3 times.

**Reference and counter electrode**

Rinse with ultrapure 3 times

### 2.5 Experimental Procedure

#### 2.5.1 Experiment Conditions:

All the experiments were carried out at 25°C and ambient atmosphere pressure. The temperature was controlled by a circulating temperature controller bath with water. Saturated oxygen solutions were created by purging oxygen through the solution for 2 hours. To exclude oxygen from the solution, it was purged nitrogen (99.99% pure) for 1 hour.
2.5.2 Chronopotentiometry

The experiment was carried out by application of constant current to the working electrode with the potentiostat-galvanostat and measurement of the potential difference between the working electrode and reference electrode as a function of time.

Different currents were used to test different adsorption and desorption behavior of additives (see the experimental matrix). These potential oscillations only exist under certain conditions of current density, RDE speed and concentrations of suppressor and leveler.

2.5.3 Commercial leveler with SPS

Procedures for these experiments

Prepare additive solutions. Dissolve all the additives in 0.8M sulfuric acid
Dissolve the Cu_2SO_4 in 0.8M sulfuric acid
Transfer all the solutions into the three neck flask;
Set the circulating temperature control bath to 25 °C;
Add the additives (Cl, SPS, x76) solution into the primary plating solution;
Connect all the electrodes to the potentiostat (Green for working electrode, Yellow for reference electrode and red for counter electrode.);
Open power suit soft ware >> experiment>> new>> power set>> chronopotentiometry>> set current and time, and then run the experiment.
<table>
<thead>
<tr>
<th>Item</th>
<th>Cu²⁺ (g/mL)</th>
<th>Cl⁻ (ppm)</th>
<th>Rotating speed (rpm)</th>
<th>Current density (mA/CM²)</th>
<th>SPS Concentration (ppm)</th>
<th>×76 Concentration (ml/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Different leveler concentration</td>
<td>50</td>
<td>100</td>
<td>500</td>
<td>10</td>
<td>8.0</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
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2.5.4 Janus Green B with SPS

Procedures for these experiments

Prepare additives solutions. Dissolve all the additives in 0.8M sulfuric acid;

Dissolve the Cu₂SO₄ in 0.8M sulfuric acid;
Transfer all the solutions into the three neck flask;

Set the circulating temperature bath to 25 °C;

Add the additives (Cl\(^-\), JGB) solutions in the copper primary solution;

Connect all the electrodes to the potentiostat;

Open power suit soft ware >> experiment>> new>> power set>> chronopotentiometry>> set current and time and then run the experiment.

At 500s inject the exact amount of SPS.

Table 2.3 Experiment matrix for JGB with SPS at constant current

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<tr>
<th>Item</th>
<th>Cu(^{2+}) (g/mL)</th>
<th>Cl(^-) (ppm)</th>
<th>Rotating speed (rpm)</th>
<th>Current density (mA/CM(^2))</th>
<th>SPS (ppm)</th>
<th>JGB (PPm)</th>
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2.5.5 Recurrent galvanic pulses
In these experiments, a short galvanic pulse was applied part way through the chronoamperometric experiment.
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<th>Cl⁻ (ppm)</th>
<th>Rotating speed (rpm)</th>
<th>Current density (mA/cm²)</th>
<th>SPS (ppm)</th>
<th>x76 (ml/L)</th>
<th>Pulse current (mA/cm²)</th>
<th>Pulse time (s)</th>
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CHAPTER THREE

RESULTS AND DISCUSSION

3.1 Commercial leveler (L76) and SPS with a pulse current

In these measurements, the concentration of Cu²⁺ and Cl⁻ were held at 50g/L and 100ppm, respectively. The concentration of commercial leveler (L76) was varied from 0.5ml/L to 10.0ml/L. These represent volumes of aqueous solution of leveler as provided by the manufacturer. The real concentration of the leveler itself is not known. The concentration of Bis-(sodium sulfopropyl)-disulfide (SPS) was varied from 4ppm to 24ppm. The current density was varied from 4 to 12mA/cm² and the rotation speed from 125 rpm to 1000 rpm. In some experiments, a current pulse was applied to disrupt the oscillation and observe its return to a quasi-steady oscillation. The parameters for the current pulse were pulse time and current density. In some experiments, MPS was also added to the solution. Most of the experiments were performed under air, but in some cases either oxygen or nitrogen were sparged through the solution.

In these experiments, the plating solution and additives were added to the cell to a total volume of 80mL. After the experiment, the oscillation period and amplitude of the oscillation were extracted from the potential versus time data. The other important measured parameters are the slopes of waves, as shown in Fig 3.2. Pulse currents are a high current imposed during the deposition process for a short time as shown in Fig 3.1. The pulse current can disturb the balance...
between leveler and accelerator on the working electrode. The pulse time and current density were 10 seconds and 20mA/cm², respectively. Also, we tested the effect of pulse current and pulse time on the time period and the amplitude of the oscillation.

Potential was measured with respect to time, as shown in Fig 3.2. The time period, amplitude and the slopes of the waves of oscillation were measured after the pulse.

![Diagram](image)

**Figure 3.1 Current and pulse current**
3.1.1 Effect of SPS concentration on the potential oscillation

In these experiments, the SPS concentration was varied while the other parameters were held constant at the following values: Leveler L76 concentration 1ml/L, constant current density 10mA/cm², rotation speed 500 rpm and pulse current of 20mA/cm² for 10s. The concentration of SPS has a substantial effect on the oscillation period (the time between consecutive
potential peaks, Tw). At SPS concentrations greater than 20ppm, no potential oscillations were observed.

As shown in Fig 3.3 the amplitude of the oscillations varied with SPS concentration. From 4-8ppm SPS, the amplitude of oscillation decreased by a small amount. At a SPS concentration of 12ppm, the amplitude of oscillation increased with time, while at 16ppm the amplitude of oscillation decreased with time.

In this range the oscillation period varied with SPS concentration, as shown in Fig 3.3. With increasing SPS concentration, the oscillation period increased in the range from 6-16ppm. No oscillation was observed for SPS concentrations lower than 4ppm and higher than 16ppm.
As shown in Fig 3.4, the slope $K_1$ decreased with increasing SPS concentration from 4ppm SPS to 8ppm SPS. From 8-14ppm, the slopes, $K_1$, didn’t change. The slopes, $K_{+1}$, increase with the SPS concentration increasing. $K_1$ represents the process of deactivation of SPS by L76 and $K_{+1}$ represents the process of deactivation of L76 by SPS.
3.1.2 Effect of concentration of Enthone leveler L76

In these experiments, the oscillation was analyzed at different leveler concentrations which varied from 0.5ml/L to 10ml/L, with the other factors held constant: 8ppm SPS, rotation speed 500 rpm and current density 10mA/cm².

Fig3.5 shows, the effect of increasing leveler concentration to prolong the oscillation period. The oscillation period increased proportionally with respect to
the leveler concentration from 0.5ml/L to 4ml/L. There was no oscillation at 0.5ml/L. Above 4ml/L L76 the oscillation period changed by only a few seconds. The amplitude of oscillation increased with increasing L76 concentration from 1-2ml/l, as shown in Fig 3.5. There was no oscillation when the L76 concentration with 0.5ml/L L76. The amplitude of oscillation didn’t change with leveler concentration, after L76 concentration higher than 2ml/L.

Figure 3.5 Effects of L76 Concentration on Potential Oscillation
Fig 3.6 shows the effect of L76 concentration on the slopes of the oscillations. $K_{+1}$ decreases with increasing L76 concentration and $K_{-1}$ decreases with increasing L76 concentration.

3.1.3 Effect of average current density

Current density is an important factor that affects potential oscillations. In these experiments, current densities were varied from $4\text{mA/cm}^2$ to $12\text{mA/cm}^2$ with
1.0ml/L leveler, 8ppm SPS and 500 rpm rotation speed. The current density determines the reaction rate of copper deposition on the working electrode.

Potential represents the driving force. A more negative potential corresponds to a higher driving force. Therefore, a lower current density would be expected with more positive potential in otherwise equivalent conditions.

The oscillation period was shortened at higher current density, as shown in Fig3.7. At the lowest current density of 4-6mA/cm² there was no oscillation. In the 8-12mA/cm² current density range, there were oscillations, and the time period of oscillations decreased with increasing current density. When the current density was higher than 16mA/cm² the potential signal became noisy, and it was difficult to determine the period and amplitude of the oscillation.

In the 8-12mA/cm² current density range, the amplitude of the oscillation decreased with increasing current density as shown in Fig3.6.
The dependence of slope on current density is shown in Fig 3.8. The slope $k_{-1}$ decreases and $k_{+1}$ increased with increasing current density. The deactivation of SPS by L76 and the deactivation of L76 by SPS were more rapid at higher current density.
3.1.4 Effect of rotation speed

In these experiments, the rotation speed was varied from 125 rpm to 1500 rpm. The other parameters were held constant at 8ppmSPS, 1.0ml/L L76 and 10mA/cm².

As shown in Fig 3.9, as rotation speed increases, the time period of the oscillation decreases until the rotation speed reaches 500 rpm. At rotation
speeds higher than 500 rpm, the reaction was kinetically controlled. The oscillation period did not change further with increasing rotation speed beyond 500 rpm as shown in Fig 3.9. The amplitude of the oscillation decreased as the rotation speed increased up to 800 rpm. At rotation speeds higher than 800 rpm, the amplitude of oscillation did not change.

Figure 3.9 Effect of rotation speed on potential oscillations
The dependence of slopes on rotation speed is shown in Fig 3.10. Slope $K_{-1}$ increased a small amount from 125 rpm to 500 rpm, and then it leveled off. Slope $K_{+1}$ increased with rotation speed up to 800 rpm. Hence, the rotation speed increased the rate of deactivation of L76 by SPS up to 800 rpm.

![Figure 3.10 Effect of rotation speed on the potential-time slopes](image)

**Figure 3.10** Effect of rotation speed on the potential-time slopes
3.1.5 Effect of oxygen

In these experiments, the dissolved oxygen concentration was the independent variable. The other parameters were held constant at 8ppmSPS, 1.0ml/L L76, 500 rpm and 10mA/cm². One solution was purged with pure oxygen for 2 hours and one was purged with pure nitrogen for one hour in order to eliminate dissolved oxygen. The first solution we took to be oxygen saturated solution and the second we took to contain no oxygen. Oxygen can react with additives and thus affect the oscillation of the potential.

As shown in Fig 3.11, time period of potential oscillation was prolonged 7s in saturated oxygen solution.
3.1.6 Effect of pulse current and pulse time

The effects of pulse current wave forms were tested in these experiments. During the galvanostatic experiments, a short pulse higher current density was applied. This pulse is used to disturb the quasi-steady state of the interactions between SPS and leveler L76. At higher current density, the potential is more negative so...
that some additives or the product of the additives will be desorbed from the working electrode. Therefore, the steady state interaction between these additives can be disturbed. If the system spontaneously returns to the steady state, it represents a stable operating condition. Various current pulses were applied in these experiments and the other parameters were held constant at 8ppm SPS, 1.0mL/L leveler, 500 rpm rotation speed, 10mA/cm² current density.

The pulse current density did not affect in the oscillations as shown in Fig3.12, because the concentrations of additives in bulk solution stayed constant and the ratio of these concentrations did not change. Pulse time did not affect the oscillation period or the amplitude of the oscillation very much either, as shown in Fig3.13.
Figure 3.12 Effect of pulse current on potential oscillations
3.1.7 Effect of MPS on the potential oscillation

Mercaptopropane sulfonic acid, MPS, is a decomposition product of SPS. SPS is a dimer composed of two MPS molecules. In this experiment, the concentration of MPS was 16ppm. The other parameters were 10mA/cm², 1ml/L L76 and rotation speed 500 rpm.
As shown in fig 3.14. The potential oscillation was inhibited by MPS. With the same concentration of MPS there was no oscillation was found.

**Effect of MPS on potential oscillation**

Solid line: 8ppm SPS with L76
Dash line: 8ppm MPS with L76

*Figure 3.14 Effect of MPS on potential oscillations*
3.2 Enthone Leveler L76 and SPS system with constant current

3.2.1 Effect of L76

These experiments were carried out with Enthone leveler L76 at concentrations varying from 0.5ml/L to 10ml/L, with 8ppm SPS and 100ppm chloride. The plating solution was kept the same as the primary plating solution. The current density was kept at 10mA/cm² and the rotation speed was held at 500 rpm.

The oscillation period increased with increasing concentration of Enthone leveler 76 from 1ml/L to 5ml/L, as shown in fig 3.15. At concentrations of L76 was higher than 5ml/L, the oscillation period did not vary.

We found that the higher the concentration of L76 on the working electrode, the greater the oscillation period was, as shown in Fig 3.15. The amplitude of potential oscillation increased with increasing L76 concentration from 0.5-5ml/L as shown in Fig 3.15. The amplitude of oscillation stayed the same when the L76 concentration was higher than 5ml/L.
As shown in Fig 3.16, the slopes, \( k_1 \) and \( k_{-1} \), decrease with increasing L76 concentration from 1ml/L76 to 10ml/L L76.
3.2.2 Effect of SPS

In these experiments, the SPS concentration was varied from 4ppm to 16ppm and the leveler concentration was held at 1ml/L. The current density was held at 10mA/cm\(^2\) and rotation speed at 500 rpm. The oscillation period decreased with increasing SPS concentration, as shown in Fig 3.17. Oscillation was observed at
SPS concentrations between 4ppm to 16ppm. Outside of this range no oscillation was observed. In the 4-12ppm SPS concentration range, the oscillation period decreased with increasing SPS concentration. Above this range the oscillation period did not change.

The amplitude of potential oscillation decreased with increasing SPS concentration as shown in Fig 3.17. The amplitude of oscillation increased with time in 12ppm SPS and the amplitude of oscillation decreased with time at 16ppm SPS.
Figure 3.17: SPS concentration effect on potential oscillations at constant current.
The slope $k_{+1}$ increased with increasing SPS concentration and $k_{-1}$ decreased a small amount with increasing SPS concentration. As the SPS concentration increasing, the surface coverage of SPS should increase, promoting the deactivation of SPS by L76.

**Figure 3.18 Effect of SPS concentration on potential-time slopes**

Effect of SPS concentration on $k_{+1}$ and $k_{-1}$.
3.2.3 Effect of rotation speed

Rotation speed was varied in these experiments from 125 rpm to 1500 rpm, with the other parameters held at 8ppm SPS, 1ml/L leveler L76, and 10mA/cm² current density. As shown in Fig 3.19, the oscillation period decreased with increasing rotation speed up to 500 rpm. At rotation speeds higher than 1000 rpm, the oscillation period did not change.

Figure 3.19 Effect of rotation speed on potential oscillations at constant current
As shown in Fig 3.20, the slope of $K_{-1}$ increased with increasing rotation speed.

The slope of $K_{+1}$ was not affected.

![Graph showing the effect of rotation speed on potential-time slopes.](image)

**Figure 3.20 Effect of rotation speed on the potential-time slopes**

3.2.4 Effect of current density

The experiment was carried out with 8ppm SPS, 1ml/L leveler, 500 rpm at various current densities. Oscillation was observed in the range of 8-12mA/cm², and there was no oscillation at current densities lowers than 8mA/cm². At current
densities higher than 12mA/cm², the potential became noisy with respect to time. In the 8-12mA/cm² range, the oscillation period decreased with increasing current density.

Figure 3.21 Current density effect on potential oscillations at constant current
As shown in Fig 3.22, the slope $k_{\cdot1}$ did not change with increasing current density. However $k_{\cdot1}$ decreased with increasing current density.

**Figure 3.22 Effect of current density on the potential-time slopes**

3.3 Janus green B (JGB) and SPS with constant current

JGB, a heterocyclic aromatic compound with quaternary ammonium, can be adsorbed on the working electrode through $\pi$-bonding due to the electrostatic attraction caused by the locally high electron density. JGB can suppress the
copper electrodeposition on the working electrode. The nitrogen-nitrogen double bond, \(-\text{N}=\text{N}-\) is another functional group of JGB and this bond can be broken on the working electrode surface during the copper plating process. It has been reported that JGB can be decomposed to another product A on the working electrode surface. JGB and Product A have different potential-dependent adsorption behavior. JGB tends to be adsorbed on the working electrode at more positive potential and A tends to be adsorbed on the surface at more negative potential.

The primary plating solution contained copper 50g/L, Cl\(^-\) 100ppm and H\(_2\)SO\(_4\) 0.8M. There are several factors that affect the oscillations: concentration of SPS and JGB, current density, rotation speed, MPS and oxygen in the solution. A controlled current (chronopotentiometric) technique was used in these experiments. JGB was added to the plating solution at the start of the experiment, SPS was added after the potential was stable around 500s to 700s. The oscillation was observed after SPS was added. The potential oscillation is different than with commercial leveler. The oscillation period with JGB is much longer than with the commercial leveler.

3.3.1 Effect of SPS

The JGB concentration was held at 12ppm, the current density at 5mA/cm\(^2\) and the rotation speed at 1000 rpm. SPS concentration was the independent variable in these experiments, and it was varied from 28ppm to 40ppm. These
experiments were carried out at 25 °C. The dependence of the oscillation period on SPS concentration is shown in Fig 3.23.

The oscillation period decreased with increasing SPS concentration up to 36ppm. Above 36ppm, the oscillation period increased with increasing SPS concentration. There was no oscillation at SPS concentrations higher than 48ppm or lower than 28ppm.

Figure 3.23 SPS concentration of effect on potential oscillations
As the SPS concentration was increased from 28ppm to 36ppm, the oscillation period decreased. At SPS concentrations higher than 40ppm, the JGB domain was decreased compared to lower SPS concentration. The oscillation period was increased by increasing the SPS concentration.

3.3.2 Effect of JGB

The effect of JGB on the copper deposition potential oscillation period was studied. 50ppm of chloride ions was added to the electrolyte. Sodium chloride was the source of chloride ions. Current density was 5mA/cm². JGB concentration was measured at 8ppm, 12ppm, 16ppm, 20ppm and for 32ppm SPS.

Figure 3.24 shows the plot of JGB concentration vs. oscillation period and amplitude. The shortest time period of oscillation is at 12ppm JGB. There was no oscillation if the JGB concentration was less than 8ppm or higher than 28ppm. With increasing JGB concentration the oscillation period was shortened from 8ppm to 12ppm JGB. With JGB concentration increasing from 12-28ppm, the oscillation period increased. As the JGB concentration higher than 28ppm, working electrode was dominated by JGB and there is no oscillation observed in these experiments.
3.3.3 Effect of Current Density

With the optimized JGB and SPS concentration, the current density effect on the oscillation period was studied in the same copper plating solution. The primary plating solution contained 12ppm JGB, 32ppm SPS 100ppm Cl\(^-\) and 50g/L Cu\(^{2+}\) in 0.8M H\(_2\)SO\(_4\). Potential was recorded at current densities of at 4mA/cm\(^2\), 4.5mA/cm\(^2\) and 5mA/cm\(^2\). Oscillation was observed at current densities from...
4mA/cm$^2$ to 5mA/cm$^2$. Beyond this region there was no oscillation. At lower current density the potential was stable within 5000s. At higher current density the potential was noisy, and it was hard to recognize the oscillation.

A plot of potential oscillation period vs. current density was shown in Figure 3.25. At higher current density, the oscillation period was shorter. As Fig 3.25 shown, the shortest oscillation period occurred at 5mA/cm$^2$. There was no oscillation observed at current densities of 3.4mA/cm$^2$ and 6mA/cm$^2$. 
3.3.4 Effect of Rotation speed

The effect of rotation speed on the potential oscillation was studied. The copper plating solution was identical to the solution described above. Potential was measured with the current density fixed at 5mA/cm² at various rotation speeds. A plot of potential oscillation period vs. rotation speed was shown in Fig3. 26. The oscillation period decreased with increasing rotation speed. The amplitude of
oscillation passed through a maximum at 1000 rpm and then dropped down as the rotation speed was increased further. This result is related to the diffusion of additives to the working electrode.

3.3.5 Effect of Oxygen

The effect of oxygen and nitrogen on the potential oscillation was studied in these experiments. The potential was measured at a fixed current density of 5mA/cm² and rotation speed of 500 rpm. The plating solution contained 12ppm...
JGB, 32ppm SPS, 50g/L Cu$^{2+}$ and 100ppm chloride. One solution was sparged with pure (99.99%) O$_2$ for one hour, the other with pure (99.99%) N$_2$ for one hour. A plot of potential vs. time is shown in Fig 3.27. There was potential oscillation with the oxygen sparged solution, but there was no oscillation occurred without oxygen in the plating solution. It can be concluded that the presence of oxygen is an important condition for potential oscillations.
3.3.6 Effect of MPS

The effect of MPS on potential oscillation was studied in these experiments. The potential was measured in copper plating solution at a current density of 5mA/cm² and rotation speed of 500 rpm. The copper plating solution contained 12ppm JGB, 50g/L, 100ppm and varying amounts of SPS and MPS. These experiments measured the potential for 32ppm SPS, 16ppm MPS and 16ppm
SPS, 32ppm MPS with JGB copper plating solution. A plot of potential vs. time is shown in Fig 3.28.

As shown in Fig 3.28, there was no oscillation in the presence of MPS. As Fig 3.28 shows, the potential in solution containing both MPS and SPS was not as stable as that with only MPS.

Figure 3.28 Effect of MPS on potential oscillations
3.4 Cyclic Voltammetric Scan

3.4.1 Enthone leveler and SPS Cyclic Voltammetric Scan

Cyclic Voltammetric scans were carried out in 8ppm SPS and 1ml/L Enthone leveler, with a rotation speed of 500 rpm from 0.0V to -0.3V. Corresponding to the oscillation potential and current density, there was no obvious N-shape in the oscillation current area.

![Cyclic Voltammetric Scan Graph](image)

**Figure 3.29 CV scan for L76 and SPS solution**
(Scan rate: 5mv/s, from 0v to -0.3v.)
3.4.2 Janus green B and SPS cyclic Volta metric scan.

Cyclic Voltammetric scan was carried out in 32ppm SPS and 12ppm JGB, with a rotation speed of 100 rpm. No N-shaped curves were found. Instead, the polarization behaviors were linear. This result rules out any oscillation mechanism based on a locally negative polarization slope.

Figure 3. 30 CV scan for JGB and SPS solution  
(Note: scan rate: 5mv/s, from 0.0V to -0.3V)
CHAPTER FOUR

DISCUSSION AND CONCLUSIONS

4.1 Mechanism of the potential oscillation

Oscillations in potential appear at constant current in the presence of both leveler and accelerant. The occurrence of oscillation and their frequency depend on current density, mass transfer rates and additives concentration. Both additives adsorb on the metal surface and can be transformed in potential dependent reactions. If the surface is largely covered by leveler, the potential will be more negative. If it is largely covered by accelerant, the potential will be more positive. Hence, we expected that there is competition for surface coverage between the two additives under oscillating-potential conditions.

It has been found that SPS can be decomposed to MPS on the working electrode\(^2\) and that SPS is more readily adsorbed on the working electrode at more negative potentials. MPS is the true accelerant which promotes copper deposition and drives the potential to more positive values during galvanostatic deposition. Hence, adsorption of SPS and its transformation to accelerant promotes a condition that inhibits further adsorption of SPS\(^3\).

The levelers L76 and JGB, inhibit copper deposition. At the same time they may be decomposed on the working electrode. Some investigators have reported that levelers can be adsorbed on the working electrode more readily at more positive
potential⁴. When a leveler is adsorbed on the working electrode during galvanostatic deposition, the potential of working electrode is driven to more negative values. But as the potential becomes more negative, the leveler is desorbed from the working electrode or decomposes¹⁹.

Bases on these observations, the following mechanism is proposed (see Figure 4.1). At more positive potential, the leveler adsorbs onto the working electrode to a greater extent than does SPS. As the leveler adsorbs on the working electrode, the potential is driven to a more negative values. As a result, the leveler is displaced by SPS at a diffusion controlled rate. When SPS is adsorbed and transformed to MPS, the potential returns to a more positive value and the cycle repeats.
Figure 4.1 Schematic of the mechanism of potential oscillations

At different potentials, there are different surface coverages of leveler \((\theta_l)\) and accelerant \((\theta_a)\). The current densities on surfaces covered by accelerant and leveler are respectively \(i_a\) and \(i_l\). The total current is the sum of the currents on the two domains. \(\bar{I}\) is the average current density in the working electrode.

\[
A_l \times i_l + A_a \times i_a = \bar{I} = \bar{I} \times A
\]  \hspace{1cm} (4.1)

\[
\theta_l \times i_l + \theta_a i_a = \bar{I}
\]  \hspace{1cm} (4.2)

\[
\theta_a = \frac{A_a}{A} \quad \text{and} \quad \theta_l = \frac{A_l}{A}
\]  \hspace{1cm} (4.3)
4.1.2 The effect of SPS concentration on the oscillations

In the 4-16ppm SPS range, the oscillation period decreased with increasing SPS concentration, as shown in Fig 3.3. Fig 3.17 showed the oscillation period was constant at SPS concentrations higher than 12ppm. At higher SPS concentration, more SPS is adsorbed on the working electrode surface and probably it is a mass transfer controlled process. Hence, MPS can be generated more rapidly and the recovery to the more positive values is more rapid. With a higher concentration of SPS, the reaction rate is higher and more MPS is produced. As shown in Fig 3.4 and Fig 3.18, as the SPS concentration increases, the slope of \( K+1 \) increases. As a result, the rate of displacement of L76 increases, \( \theta_a \) is larger and the oscillation period is shorter at higher SPS concentration. At SPS concentrations higher than 20ppm SPS, the oscillation was inhibited as shown in Fig 3.3. This may be due to the fact that SPS dominated the working electrode and there was no competition between SPS and L76.

The amplitude of the oscillation is related to the desorption and adsorption potentials of the additives. As the SPS concentration was increased from 4ppm to 6ppm, the amplitude of oscillation increased a small amount probably because a more positive potential is required to drive SPS off the surface when it is present in higher concentration. At SPS concentrations between 8-12ppm, as the SPS concentration increased the amplitude of oscillation decreased. The possible reason is the MPS concentration is higher in working electrode with
higher SPS concentration, and then, the SPS is sensitive to the potential and can be desorbed from working electrode at more negative potential.

In the SPS concentration range from 12ppm to 16ppm, the process is kinetically controlled. The transformation of SPS to MPS is controlled by kinetics, and as SPS concentration increases, the MPS concentration and desorption rate remain constant. As a result, the oscillation period doesn’t change much with SPS concentration.

4.1.2 Effect of L76 in the oscillation

As the leveler concentration increases, there is more available leveler in the bulk solution. The surface coverage of $\theta_L$ is higher, as shown in Figs3.6 and 3.16. With increasing L76 concentration $K^{+1}$ increased and $K^{-1}$ decreased. The ratio of SPS to L76 on the surface was smaller as the L76 concentration increases. As a result, SPS is less readily absorbed.

There is competition between the reaction of leveler and the reaction of SPS on the working electrode. At higher leveler concentration, the concentration of SPS on the working electrode is low. At higher concentrations of leveler (more than 5ml/L), it can be assumed that the working electrode is dominated by the leveler. As a result, the oscillation is slower. This can be seen from Figure 4.2.

The amplitude of potential oscillation is related to the desorption and adsorption potentials of the additives on the working electrode. With higher L76 concentration, less SPS is adsorbed on the working electrode. When the L76 concentration is higher the potential can be pushed to more negative potential.
than at lower L76 concentration. Therefore, the amplitude of potential oscillation is longer in higher L76 concentration.

4.1.3 Effect of Current density on potential oscillation

The current density fixes the reaction rate of copper deposition on the working electrode. Potential affects the driving force. A more positive potential indicates that a relatively lower driving force is required to maintain the current.

The oscillation period was decreased linearly with higher current density as shown in Fig3.7. In the lower current density range of 4-6mA/cm² no oscillation was found. In the more positive potential region SPS doesn’t adsorb on the working electrode at all. Therefore, there is no competition between accelerant and leveler. In 8-12mA/cm² current density range there were oscillations, and the oscillations period decreased with higher current density. This may be related to the fact that at more negative potential SPS can be activated more easily and the process of deactivation of L76 by SPS and deactivation of SPS by L76 both are faster. As shown in Fig 3. 3.8 and Fig 3.22 K-1 decreases and K+1 increases with increasing current density. In this potential range both accelerant and leveler adsorbed on the working electrode and there is a competition between them. At higher current densities the potential is more negative and SPS is more easily adsorbed on the working electrode.
4.1.4 Effect of rotation speed on oscillations

The RDE rotation speed was used to control the boundary layer thickness in these experiments. As shown in Figures 3.10 and Fig 3.20, with increasing rotation speed from 125 rpm to 500 rpm, the oscillation period increased and the amplitude of oscillation increased. Evidently, from 125 rpm to 500 rpm the process is diffusion controlled\textsuperscript{23}.

At higher rotation speed the boundary layer is thinner and the process is kinetically controlled above 500 rpm.

4.1.5 Effect of JGB

Figure 3.13 shows the time period of oscillation vs. JGB concentration. At 12ppm JGB, the time period of oscillation was the shortest. There was no oscillation at JGB concentrations less than 8ppm or higher than 28ppm. With increasing JGB concentration the time period of oscillation shortened from 8ppm to 12ppm JGB. The working electrode was dominated by SPS when the JGB concentration was lower than 8ppm, and there wasn't obvious competitive between them. When the concentration of JGB was between 8ppm to 12ppm, JGB adsorption on the working electrode was controlled by diffusion. As the JGB concentration was increased above 12ppm the time period of oscillation was controlled by the diffusion of SPS into the working electrode (The diffusion coefficients of SPS and JGB are $2.9 \times 10^{-6} \text{cm}^2/\text{s}$ and $4.0 \times 10^{-6}$ to $10 \times 10^{-5} \text{cm}^2/\text{s}$.) therefore, as the increasing of JGB concentration the oscillation period increased.
4.2 Conclusions

Potential oscillation was found during copper plating on the rotating disk in a solution containing the accelerant SPS and the levelers JGB or Enthone L76. Conditions which affect the potential oscillation and oscillation period were studied. These conditions included concentration of leveler and SPS or MPS, rotation speed, current density and the presence of dissolved oxygen. In a specific SPS concentration range, higher concentration of SPS tended to shorten the time period of the oscillations and decrease the amplitude of oscillation. In a specific leveler concentration range, higher concentration of leveler tended to increase the time period of the oscillations and increase the amplitude of oscillation. This result is probably related to the adsorption and desorption behavior of SPS and leveler. SPS and levelers have different potential-dependent adsorption behaviors. SPS is adsorbed at more negative potential and promotes the copper deposited on cathode. This promotion results in a lower driving force or more positive potential. At more positive potential leveler can be adsorbed on the cathode. Leveler tends to inhibit copper deposition on cathode, which forces the potential to the negative direction at constant current. Following this sequence the potential oscillation can be understood. The oscillation behavior was produced by desorption and adsorption of SPS and leveler and the ratio of the two specie concentrations.

In a certain current density range, higher current density can decrease the time period of oscillation. This may be related to the more negative potential imposed
at higher current. Different levelers have different desorption and adsorption potentials. That maybe was the reason that JGB and L76 have oscillations in different current density ranges and the oscillations has different time periods. Increased RDE rotation speed can promote oscillation. JGB and L76 produced oscillation at different rotation speeds. These levelers have different diffusivities. A higher rotation speed decreased the boundary layer thickness and promoted diffusion of additives to the cathode, thereby enhancing the oscillation. Oxygen has an important effect on the oscillation behavior in JGB solution but not in commercial leveler solution. A possible reason for that is the true accelerator Cu(I)/MPS was inhibited by the presence of oxygen, because oxygen reacts with Cu(I). When the decomposition reaction of SPS slows down, the oscillation period is prolonged.

MPS can be adsorbed on the cathode and inhibit the oscillation. MPS and SPS have different desorption and adsorption behaviors.

4.3 Recommendations

More studies are expected on desorption and adsorption potential for SPS and commercial leveler L76, JGB. These results can help us well understand the oscillation behavior and the mechanism of this oscillation behavior. Fill the microvia with the oscillation conditions to find the filling result. With the real filling performance can help us understanding the effect of oscillation in the
filling result and bottom up filling behavior. Test the oxygen concentration effect on the oscillation behavior.
Reference


