FUNCTION OF ADDITIVES IN COPPER ELECTRODEPOSITION FOR SEMICONDUCTOR DEVICES METALLIZATION

by

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May, 2008
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(date) 3/28/08

*We also certify that written approval has been obtained for any proprietary material contained therein.
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### List of Abbreviations

**English**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>area, cm$^2$</td>
</tr>
<tr>
<td>BUF</td>
<td>Bottom-up fill</td>
</tr>
<tr>
<td>C</td>
<td>concentration, mol/cm$^3$</td>
</tr>
<tr>
<td>CE</td>
<td>Counter electrode</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>Chloride ions</td>
</tr>
<tr>
<td>D</td>
<td>diffusion coefficient, cm$^2$/s</td>
</tr>
<tr>
<td>F</td>
<td>Faraday’s constant, 96,480 C/equivalent</td>
</tr>
<tr>
<td>JGB</td>
<td>Janus Green B</td>
</tr>
<tr>
<td>i</td>
<td>current density, mA/cm$^2$</td>
</tr>
<tr>
<td>h</td>
<td>height, cm</td>
</tr>
<tr>
<td>k</td>
<td>adsorption or replacement coefficient, cm/s</td>
</tr>
<tr>
<td>K</td>
<td>equilibrium coefficient, mol/cm$^3$</td>
</tr>
<tr>
<td>$M_z$</td>
<td>Matrix used in nonlinear fit</td>
</tr>
<tr>
<td>MW</td>
<td>Molecular weight</td>
</tr>
<tr>
<td>n</td>
<td>number of electrons transferred</td>
</tr>
<tr>
<td>N</td>
<td>Number of experiment data points in nonlinear fit</td>
</tr>
<tr>
<td>P</td>
<td>Number of undetermined factors in nonlinear fit</td>
</tr>
<tr>
<td>PEG</td>
<td>Polyethylene glycol</td>
</tr>
<tr>
<td>PEI</td>
<td>Polyethylenimine</td>
</tr>
<tr>
<td>PVP</td>
<td>Polyvinylpyrrolidone</td>
</tr>
</tbody>
</table>
\( R \) Residual vector in nonlinear fit

\( R \) Ideal gas constant, 8.314 J/mol K

RDE Rotating disk electrode

RE Reference electrode

SPS bis-(3-sulfopropyl) disulfide

t time, s

T Temperature, K

WE Working electrode

Y Dependent variable used in nonlinear fit

\( z \) distance from electrode, cm

**Greek**

\( \alpha \) cathodic current transfer coefficient

\( \varphi \) vector of undetermined parameters in nonlinear fit

\( \alpha \) coefficient used in potential dependent parameters

\( \beta \) Vector of determined parameters in nonlinear fit

\( \Gamma \) maximum surface coverage, mol/cm\(^2\)

\( \delta \) mass transfer boundary layer thickness, cm

\( \eta \) overpotential, V

\( \theta \) fractional surface coverage, dimensionless

\( \Lambda \) weight factor vector, size N

\( \nu \) kinematic viscosity, cm\(^2\)/s

\( \rho \) density, g/cm\(^3\)
\( \sigma \) standard deviation

\( \tau \) time constant

\( \omega \) rotational velocity, rad/s

\( \Omega \) fractional feature coverage on wafer surface

**Subscript**

- ads adsorption
- bottom on the bottom of the feature
- copper copper
- K equilibrium
- PEG polyethylene glycol
- SPS bis(3-sulfopropyl) disulfide
- sidewall on the sidewall of the feature
- top on the to of the wafer surface
Function of Additives in Copper Electrodeposition for Semiconductor Device Metallization

Abstract

by

James David Adolf

The present research is aimed at improving the understanding, developing more accurate modeling tools and extending the capabilities of the bottom-up copper plating process – the current metallization technique of semiconductor interconnects. An analytical technique for extracting accurate transport and competitive adsorption parameters for a multi-component additives system, using relatively simple electrochemical polarization experiments, is presented and specifically applied to polyethylene glycol (PEG), a commonly used plating inhibitor. Further research focused on a second class of inhibitors, based on nitrogen containing additives (‘levelers’). An unusual displacement hierarchy in systems containing PEG, bis-(3-sulfopropyl) disulfide, and the leveler Janus Green B was ascertained experimentally. The underlying principle behind using a very high molecular weight leveler to significantly increase bottom-up fill capabilities is presented and a semi-quantitative model of the process is developed.
Chapter 1: Introduction

Basics of Interconnect Metallization

The basic concept behind microchip design is the construction of a three-dimensional network of integrated interconnects and microelectronic components, primarily transistors. The transistors, or ‘gates’, are connected by very sub-100 nm electrical connections termed ‘vias’. The vias are in turn connected to other vias on the same level by trenches. A schematic diagram of this is shown in Figure 1-1.

![Diagram of connections between the components in the microchip](image)

**Figure 1-1:** Diagram of connections between the components in the microchip.\(^1\) Multiple levels of interconnects are formed on top of one another so that there are multiple layers of metallization.

A diffusion barrier layer, typically either Ta, Ti, TaN, or TiN, is laid down between the dielectric material (SiO\(_2\)) and the metal features to prevent diffusion of the metal into the dielectric material.
Prior to 1998, all metallization for microchip fabrication was done using vapor deposited aluminum. As chip technology progressed, the features became increasingly small in order to improve chip speed. However, resistance is inversely proportional to the cross sectional area of the interconnects, therefore as feature sizes decreased, the resistance of the vias increased. The time-delay, which plays a critical role in determining the chip speed, is a parameter proportional to the resistance of the interconnects. Therefore, as interconnects decreased in sizes, the time-delay began to increase as a consequence of the higher resistance outweighing the increase in speed due to the increased density of interconnects. In order to mitigate this enhanced time delay, copper, which is more conductive than aluminum (by about 50%) was introduced as a replacement to aluminum in the metalized interconnects, causing the time-delay to decrease significantly.

Copper cannot easily be deposited from the vapor phase, therefore electrodeposition of copper was developed as the preferred method. Copper
electrodeposition has two additional advantages over deposition from the vapor phase. First, electrodeposition is significantly faster than deposition from the vapor phase, and second, electrodeposition accommodates the ‘dual-damascene’ process, in which vias and trenches in a given layer can be plated simultaneously, which further reduces the time and cost required to metalize the features.

**Issues Involved in the Electrodeposition of Copper**

Electrodeposition offers a fast, reproducible method for depositing copper into the features present in semiconductor devices. However, in order to achieve full metallization of the features, a ‘bottom-up’ fill process is required. If copper is electroplated with no additives, it will plate preferentially on the corners of the features, leading to pinching, as shown in Figure 1-3.

![Figure 1-3: Image of copper electrodeposition using conventional plating methods. Voids form inside the feature due to preferential plating and pinching at the tops of the trenches.](image)

A bottom-up fill mechanism in which the copper preferentially plates at the bottom of the feature is required to achieve acceptable fill characteristics, as shown in Figure 1-4.
Figure 1-4: Image of copper electrodeposition using plating process in which special additives are used to promote bottom-up fill.\textsuperscript{2} No voids form in the feature.

The plating solutions used to promote the bottom-up fill were empirically determined by IBM in 1998. These were composed of an ether-based suppressor, such as polyethylene glycol (PEG) and a sulfur-based accelerator (‘anti-suppressor’), such as bis-(3-sulfopropyl) disulfide (SPS). Chloride ions were added because PEG-like suppressors do not function without the presence of Cl\textsuperscript{−}. In some cases, an additional ‘leveling agent’ or ‘brightener’ was added to improve the wafer surface characteristics. The levelers are typically nitrogen compounds, \textit{e.g.}, Janus Green B (JGB). The chemical structures of the additives PEG, SPS, and JGB are shown in Figure 1-5.
A copper seed layer is deposited from the vapor phase prior to electroplating.

**Model of the Bottom-Up Fill Process**

The current accepted model for the fill process is a combination of the diffusion-adsorption based model proposed by Akolkar and Landau\(^3\) and the curvature-enhanced geometric model proposed by Moffat *et al.*\(^4\) as well as by West *et al.*\(^5\). The diffusion-adsorption model takes into account the transient interactions associated with the diffusion and competitive adsorption of PEG and SPS. PEG adsorbs very quickly, but diffuses slowly in comparison to SPS, therefore, in the initial few seconds of the fill process, PEG adsorbs onto the wafer top surface and the upper portion of the feature sidewall, locations where mass transport limitations are minimal. SPS adsorbs more
slowly, but diffuses fast, so in the initial seconds, SPS adsorbs on the bottom of the feature, where transport limitations slow down the arrival of PEG. Since SPS is an accelerator and PEG is a suppressor, this distribution promotes enhanced plating at the bottom of the feature and inhibits plating at the top. The adsorption-diffusion mechanism is shown schematically in Figure 1-6.

Figure 1-6: Schematic of adsorption-diffusion model of bottom-up fill. PEG adsorbs preferentially on the upper corners of the feature, and SPS adsorbs preferentially on the bottom.

However, the bottom-up fill caused by this mechanism is insufficient to fill features of dimensions commonly encountered in industry. The geometric model provides an explanation for this additional fill capability by incorporating the effect of the changing feature geometry. As the feature fills, the bottom of the feature contracts. SPS
adsorbed on the surface at this location becomes more tightly packed as the surface contracts, leading to an extremely concentrated surface coverage of the accelerator. The change in surface area affects primarily the surface at the bottom of the feature, bringing about increased SPS concentration only at the bottom of the feature. The geometric enhancement is schematically shown in Figure 1-7.

Figure 1-7: Schematic of the geometric model of bottom-up fill. SPS becomes highly concentrated on the copper surface due to the shrinkage of surface area as the feature fills.

The combination of the two models provides a relatively complete explanation of the bottom-up fill process in the PEG-SPS-Cl− system. A number of additional papers have been published expanding on these two models.6-17
Goals of the Current Work

The current work is directed towards three areas in which electrochemical methods and concepts can be applied to the process of bottom-up fill in the plating of high-end semiconductor devices. A combination of experimental and analytical methods was used in the analysis. This work expands upon the analysis of the bottom-up process, provides accurate modeling capabilities and data, and suggests the use of a high molecular weight leveler to enhance the bottom-up fill process capabilities.

Chapter two of this work focuses on unresolved issues regarding the kinetic parameters pertinent to the diffusion adsorption portion of the bottom-up fill model. A general method for determining the parameters is developed, and is demonstrated in analyzing the process parameters associated with PEG.

Chapter three focuses on an unusual displacement hierarchy in a system containing PEG, SPS, and JGB. The model proposed in the literature assumes that JGB displaces all other compounds on the copper surface, but the experimental work reported here does not support this model.

Chapter four focuses on a new class of additives that have the potential capability of significantly improving the bottom-up fill. It has been shown\textsuperscript{18} that leveling compounds of extremely high molecular weight can improve the bottom-up fill, but as of yet, no theoretical basis for this phenomenon has been published. A mechanism for the improvement is proposed in the current work and implemented in a semi-quantitative model.
Chapter 2: A Method for Determining Kinetic Parameters Associated with Plating

Additives

Background

A number of different models have been proposed recently to represent the unique deposition process\textsuperscript{3, 12} that is used for ‘bottom-up’ fill of sub-micron features on semiconductor wafers. These models combine time-dependent adsorption-diffusion behavior of the plating additives that enable the process with geometric effects of the deposit build-up within the features. The applicability of the models to actual production or process design depends on how accurately they reflect the actual process of deposition, which is in turn dependent on the kinetic parameters applied in the analytical work. Unfortunately, quantitative determination of these parameters is not a straight-forward procedure, and there are no commonly accepted values for these parameters. As an example, Akolkar and Landau used an adsorption coefficient for PEG of 0.1 cm/s based on an analysis of the relative importance of kinetic and mass transfer resistances,\textsuperscript{3} but Willey and West used in a later publication a value of 0.006 cm/s based on microfluidic electrochemical experiments\textsuperscript{19}. Ranges for values in the literature are shown in Table 2-1.

<table>
<thead>
<tr>
<th>Property</th>
<th>Minimum</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEG</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_{\text{ads}}$ (cm/s)</td>
<td>0.006</td>
<td>0.1</td>
</tr>
<tr>
<td>D (cm(^2)/s)</td>
<td>5.00E-07</td>
<td>1.00E-06</td>
</tr>
<tr>
<td>$\Gamma$ (mol/cm(^2))</td>
<td>3.30E-11</td>
<td>6.00E-11</td>
</tr>
<tr>
<td>SPS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_{\text{ads, cu}}$ (cm/s)</td>
<td>1.58E-05</td>
<td>0.001</td>
</tr>
<tr>
<td>$k_{\text{ads, peg}}$ (cm/s)</td>
<td>5.00E-06</td>
<td>1.58E-05</td>
</tr>
<tr>
<td>D (cm(^2)/s)</td>
<td>4.00E-06</td>
<td>1.00E-05</td>
</tr>
<tr>
<td>$\Gamma$ (mol/cm(^2))</td>
<td>6.35E-10</td>
<td>8.00E-10</td>
</tr>
</tbody>
</table>

Table 2-1: Range of values for kinetic parameters of PEG and SPS found in the literature.
The major difficulty in accurately determining the values of the constants is that the transport-adsorption-kinetics equations used in modeling the process and in interpretation of the data are coupled to a significant degree, and performing a standard analysis becomes complicated very rapidly. Also, most authors in this area have focused on developing the fundamental models of the process\textsuperscript{3,12}, and for this purpose, even approximate values provide reasonable results. However, if the models are to be used to predict behavior of, and to optimize practical systems, it is important to use constants that give as accurate results as possible. Additionally, previous papers have not devoted any significant analysis of the errors associated with the variables, nor the degree to which error affects the modeled surface coverage of additives.

In this chapter, we provide a method for determining these kinetic parameters, the error associated with them, and the sensitivity of the equations to the different variables. The theoretical analysis is applied to the typical three-component system, and a method is proposed for analyzing general systems with transport and competitive. The complete analysis of determining the kinetic parameters was applied to a system containing a single additive (PEG), for which numerical results are provided. However, the presented method is general and can be extended to a multi-additive system.

**Experimental Methods**

Experimental data were collected using time-dependent injection studies in the manner used extensively by Akolkar and Landau.\textsuperscript{3} The working electrode (WE), counter electrode (CE), and the reference electrode (RE) were fabricated of oxygen-free, high-purity copper. The WE was a rotating disc electrode (RDE) with an area of 0.317 cm\textsuperscript{2}. The CE was a copper sheet with a much greater surface area than the WE, placed
sufficiently far away (~1.5 cm) such that the current distribution on the WE was not affected by its position. The distance required to achieve such a condition was determined using the modeling software Cell Design. The RE consisted of an insulated, thin copper wire with an exposed tip. The wire was placed at the edge of the plating bath (~2 cm from the WE) at the same height as the WE. The electrodes were hooked to a potentiostat/galvanostat (Solartron Mobrey), and the RDE was rotated using an analytical rotator (Pine Instrument Company). The experiments were performed either potentiostatically or galvanostatically, as specified in later sections, at speeds of 200 RPM. The plating bath consisted of a 0.5 M CuSO₄ solution acidified to pH ~2 using concentrated H₂SO₄. 70 ppm of Chloride ions were added in the form of NaCl. A schematic of the experimental system is shown in Fig. 2-1.

![Figure 2-1](image)

**Figure 2-1:** Diagram of experimental setup used to determine kinetic parameters. Additives were injected into the plating bath using a syringe. 100 mL of solution was used in a 200 mL beaker.

A Cu/CuSO₄ reference electrode was used because it does not introduce any new species into the system, and the zero volts versus reference corresponds to no plating or deplating. Another key consideration in using the Cu/CuSO₄ reference was that the addition of any of the additives used (PEG, SPS, JGB, etc) does not cause the reference
electrode thermodynamic potential to shift, meaning that regardless of the chemistry, the reference was at a constant potential.

When steady-state current and potential were reached, a mixture of additives was injected into the system using a syringe, and the response was measured, and corrected for ohmic and mass transport overpotentials. The ohmic overpotential (IR losses) was determined using a simulation software, Cell-Design, and was found to closely agree with Newman’s solution for a rotating disc electrode\textsuperscript{21}. Mass transfer was determined to be insignificant at the currents used in the experiments, as the current density was usually about 30 mA/cm\textsuperscript{2}, whereas the limiting current was over 250 mA/cm\textsuperscript{2}, hence mass transport limitations could be neglected.

Analytical Methodology

The basis of the applied method for extracting the best parameter values from the experimental data is the analytical comparison of experimental data to a mathematical model of the same process, searching for the best-fit parameters.

Mathematical Model

The mathematical model is based solely on adsorption-diffusion behavior. Since the experimental data were gathered using a flat RDE, geometric effects do not play a role, as the electrode shape (unlike an actual via or trench) does not significantly change throughout the process. The three-component system containing PEG, SPS, and a leveling compound, JGB is used in the analysis. It is assumed here, like elsewhere in the literature\textsuperscript{14} that the JGB displaces all other components on the surface. This assumption is likely incorrect, as described in Chapter 3, however, the analysis presented here can be
changed to accommodate the actual displacement behavior by a relatively simple modification of the equations. The model equations consist of the time-dependent diffusion equations for the three additives in the solution:

\[
\frac{\partial C_{\text{PEG}}}{\partial t} = D_{\text{PEG}} \frac{\partial^2 C_{\text{PEG}}}{\partial z^2}
\]

\[
\frac{\partial C_{\text{SPS}}}{\partial t} = D_{\text{SPS}} \frac{\partial^2 C_{\text{SPS}}}{\partial z^2}
\]

\[
\frac{\partial C_{\text{JGB}}}{\partial t} = D_{\text{JGB}} \frac{\partial^2 C_{\text{JGB}}}{\partial z^2}
\]

The diffusion equations use \( z \) as the only special dimension because the geometry is symmetric in all other directions. The boundary condition at the electrode is a flux condition such that:

\[
\left.\text{Flux}_{\text{elec}}\right| = -D \frac{dC}{dz} \bigg|_{\text{elec}} = -\Gamma \frac{\partial \theta}{\partial t}
\]

\( C \) is the concentration of the additive in the solution, \( D \) is the diffusion coefficient, \( \Gamma \) is the maximum surface coverage on the surface with units mol/cm\(^2\), and \( \theta \) is the fractional surface coverage, which follows the equations below.

\[
\frac{\partial \theta_{\text{PEG}}}{\partial t} = \frac{1}{\Gamma_{\text{PEG}}} \cdot \left[ k_{\text{PEG}} \cdot \left( C_{\text{PEG}} \cdot (1 - \theta_{\text{PEG}} - \theta_{\text{SPS}} - \theta_{\text{JGB}}) - K_{\text{PEG}} \cdot \theta_{\text{PEG}} \right) - 
\right. \\
\left. - k_{\text{SPS,PEG}} \cdot C_{\text{SPS}} \cdot \theta_{\text{PEG}} \right] 
\]

\[
\frac{\partial \theta_{\text{SPS}}}{\partial t} = \frac{1}{\Gamma_{\text{SPS}}} \cdot \left[ k_{\text{SPS}} \cdot \left( C_{\text{SPS}} \cdot (1 - \theta_{\text{PEG}} - \theta_{\text{SPS}} - \theta_{\text{JGB}}) - K_{\text{SPS}} \cdot \theta_{\text{SPS}} \right) + 
\right. \\
\left. + \frac{\Gamma_{\text{SPS}}}{\Gamma_{\text{PEG}}} k_{\text{SPS,PEG}} \cdot C_{\text{SPS}} \cdot \theta_{\text{PEG}} \right] 
\]
\[
\frac{\partial \theta_{JGB}}{\partial t} = \frac{1}{\Gamma_{JGB}} \left[ k_{JGB} \cdot \left( C_{JGB} \cdot (1 - \theta_{PEG} - \theta_{SPS} - \theta_{JGB}) - K_{JGB} \cdot \theta_{JGB} \right) + \frac{\Gamma_{JGB}}{\Gamma_{PEG}} \cdot k_{JGB} \cdot C_{JGB} \cdot \theta_{PEG} + \frac{\Gamma_{JGB}}{\Gamma_{SPS}} \cdot k_{JGB,SPS} \cdot C_{JGB} \cdot \theta_{SPS} \right]
\]

\[\text{[2-7]}\]

\(k_i\) is the adsorption coefficient of additive species \(i\) (\(i.e.; k_{PEG}\) is the adsorption coefficient of PEG on bare copper). The displacement parameter is also written in terms of \(k\), such that \(k_{SPS-PEG}\) is the coefficient of SPS replacing PEG on a PEG covered surface. Upper-case \(K\) is used as an equilibrium constant that takes into account desorption (\(K=k_{des}/k_{ads}\)). Equations 2-5 through 2-7 are based on Langmuir type adsorption, in which one minus the sum of thetas is considered to be available area for adsorption. Chloride ions do play a role in the adsorption of PEG, but it is assumed in this model that Chloride does not limit the process at any stage. Additionally, no steric effects have been incorporated into the current model.

**Least-Squares Algorithm**

The degree of fit of the parameters is formulated using a non-linear least-squares fitting process. The algorithm used\(^2\) is an iterative process in which the parameters become incrementally closer to the ideal values. The iterative process continues until the change in the parameters is smaller than a prescribed amount. The algorithm is a matrix based process, comprised of the following steps:

The starting information given is \(N\) experimental data points of a dependent variable \(Y\), initial guesses for \(P\) parameters contained in vector \(\alpha\) (of size \(P\)), and error estimates for the experimental data points and for \(K\) previously determined scale factors contained in vector \(\beta\) of size \(K\). Such scale factors would include previously determined kinetic parameters, and are used to estimate errors.
The steps taken in any given iteration are:

1. Generate the weight factor \( \Lambda \) of size N such that

\[
\frac{1}{\Lambda_n} = \sigma_n^2 = \sum_i^p \left( \frac{\partial Y}{\partial \alpha_i} \sigma_{\alpha_i} \right)^2 + \sum_k^k \left( \frac{\partial Y}{\partial \beta_k} \sigma_{\beta_k} \right)^2
\]  \[2-8\]

2. Find the square matrix \( M \) of size PxP such that

\[
M_y = \sum_n^N \Lambda_n \frac{\partial Y}{\partial \alpha_i} \frac{\partial Y}{\partial \alpha_j}
\]  \[2-9\]

3. Find the residual vector \( R \) of size P such that

\[
R_i = \sum_n^N \Lambda_n \left( Y_{\text{experimental}} - Y(\alpha, n) \right) \frac{\partial Y}{\partial \alpha_i}
\]  \[2-10\]

Where \( Y_{\text{experimental}} \) is the dependent variable value at the data point, and \( Y(\alpha, n) \) is the dependent variable as predicted by the model using the parameters contained in \( \alpha \).

Steps (4) and (5) are used to define increment step \( \Delta \alpha \) where \( M \cdot \Delta \alpha = R \).  \[2-11\]

4. Find \( M^{-1} \).

5. Determine \( \Delta \alpha \) using \( \Delta \alpha = M^{-1} \cdot R \)  \[2-12\]

6. Determine the new value of \( \alpha \) by adding \( \Delta \alpha \):

\[
\alpha_{\text{new}} = \alpha_{\text{old}} + \Delta \alpha
\]  \[2-13\]

7. Find the \( \chi^2 \) value such that

\[
\chi^2 = \sum_n^N \Lambda_n \left( Y_{\text{experimental}} - Y(\alpha, n) \right)^2
\]  \[2-14\]
8. Find the standard deviation of each parameter where

\[ \sigma_{\alpha_i} = M^{\frac{1}{2}} \frac{X^2}{N - P} \]  

[2-15]

9. Compute the magnitude \( \Delta \alpha \) to determine whether the stop condition has been reached.

In the case of the kinetic parameters for the damascene process, the dependent parameter is the fractional surface coverage, \( \theta \). However, since there is no direct mathematical expression for \( \theta \), issues arise in both calculating the predicted value and in taking the derivative with respect to parameters, determined or undetermined. To solve these problems, a finite element software package (COMSOL Multiphysics)\(^2\) was utilized.

COMSOL Multiphysics allows complex, coupled, time-dependent differential equations to be solved numerically to a high degree of accuracy. Equations 2-1 through 2-7 were modeled in a 2-dimensional system where the x-direction was movement parallel to the electrode, and the y-direction was the direction perpendicular to the electrode. Boundary conditions used were symmetry conditions on the x direction boundaries of the model, flux conditions at the electrode, and a constant concentration condition at the y direction of the model opposite the electrode. This boundary was placed at a distance away from the electrode corresponding to the mass transfer boundary layer for the RDE spinning at an angular velocity \( \omega \) with kinematic viscosity \( \nu \):

\[ \delta = 1.61 \cdot D^{\frac{1}{6}} \nu^{\frac{3}{6}} \omega^{\frac{1}{2}} \]  

[2-16]

The modeled region is shown in Figure 2-2.
In order to determine the derivatives of theta with respect to a parameter, a five-point numerical derivative was used. The equation for a five point derivative is given below.

\[
\frac{\partial \theta}{\partial x} = \frac{-\theta_{|x-2\Delta x} + 8 \cdot \theta_{|x-\Delta x} - 8 \cdot \theta_{|x+\Delta x} + \theta_{|x+2\Delta x}}{12 \cdot \Delta x}
\]  

[2-17]

Data points for the derivative were generated using the Multiphysics program. The data points of theta as a function of time were generated for five different values of each parameter, ±10%, ±5%, and at the predicted value. Since the values generated in this manner are analytical, and accurate to significantly more decimal figures than any of the measured parameters, there is effectively no noise in the data, and thus the 5-point derivatives are smooth, as shown in Figure 2-3.
**Figure 2-3:** Example of numerical derivative of theta. This particular example depicts the derivative of theta with respect to the diffusion coefficient of PEG at the first iteration of a simulation of a single component system.

**Single Component Systems**

In order to simplify the analysis, as many parameters as possible should be fitted using a single component system. A multi-component system should only be used to determine parameters that do not exist in single component systems, such as the displacement coefficient.

**PEG-Equilibrium Term**

The surface coverage equation can be simplified from that shown above (Eq. 2-5) when PEG is the only additive considered:

$$\frac{\partial \theta_{PEG}}{\partial t} = \frac{k_{PEG}}{\Gamma_{PEG}} \left[ C_{PEG} (1 - \theta_{PEG}) - K_{PEG} \theta_{PEG} \right] \quad [2-18]$$

Additionally, the desorption parameter ($K_{PEG}$), taken into account in this equation by using an equilibrium term, can be solved for using a steady state analysis. In this case,
\[
\theta_{\text{PEG}} = \frac{C_{\text{PEG}}}{K_{\text{PEG}} + C_{\text{PEG}}}
\]

[2-19]

As can be seen, the only undetermined parameter in this equation is \( K_{\text{PEG}} \), the PEG equilibrium term, which is defined as the desorption rate constant over the adsorption rate constant, having the units of \( \text{mol/cm}^3 \). In an experiment designed to determine this parameter, different concentrations of PEG were injected into the base plating solution during a galvanostatic polarization at 30 mA/cm\(^2\). The potential response was related to the PEG surface coverage by considering the potential at which no PEG was in the system (prior to its injection) as the zero point, and allowing the potential at which the PEG reached 100% coverage to be a parameter in the fit, knowing that the value should yield a solution that gives a \( \theta \) of almost unity at saturation. This transform is shown in Figure 2-4.

![Figure 2-4: Transform of potential response to fractional surface coverage. Maximum theta value was 0.996, as determined as a parameter of the fit.](image)

The method described previously was applied to the experimental data, yielding an excellent match between experimental and analytical results as shown in Figure 2-5.
**Figure 2-5:** A comparison of the experimental data to the analytical solution. As can be seen, the least-squares analysis provides an excellent fit.

The fit for the equilibrium constant yielded a value of $10.58 \times 10^{-10}$ mol/cm$^3 \pm 1.42\times10^{-10}$ mol/cm$^3$. A sensitivity analysis shows that at the typical PEG concentration of 100 ppm, a 5% increase in the equilibrium constant will cause a 0.20% decrease in theta, and even at a much lower PEG concentrations, around 10 ppm, a 5% increase in the equilibrium constant will cause a 1.24% decrease in $\theta$.

**PEG-Adsorption and Diffusion**

Once the equilibrium coefficient has been determined, the next three parameters to analyze are the PEG adsorption coefficient ($k_{\text{PEG}}$), the maximum surface coverage ($\Gamma_{\text{PEG}}$) and the diffusion coefficient ($D_{\text{PEG}}$). It is not immediately apparent how to distinguish between $k_{\text{PEG}}$ and $\Gamma_{\text{PEG}}$, (as both terms appear as a product) however since the flux boundary condition does not contain $\Gamma_{\text{PEG}}$, separation between the variables is achieved.

The equation that governs the electrode in this system is the same as given previously in equation (2-17).
\[
\frac{\partial \theta_{\text{PEG}}}{\partial t} = \frac{k_{\text{PEG}}}{\Gamma_{\text{PEG}}} \left[ C_{\text{PEG}} (1 - \theta_{\text{PEG}}) - K_{\text{PEG}} \theta_{\text{PEG}} \right]
\]  

In investigating the sensitivity of the coverage to the value of \(k_{\text{PEG}}\), it was determined that the derivative of theta with respect to \(k_{\text{PEG}}\) was over five orders of magnitude smaller than any of the other derivatives. Furthermore, a scaling analysis similar to that presented by Akolkar and Landau\(^3\) shows that mass transfer resistance should dominate the transient behavior. Therefore, the value for the adsorption constant is set to 0.1 cm/s. No error estimate is given, because this value was not precisely calculated, but merely set to a value that is known to be of the correct order of magnitude. This simplification was made because the presence of a parameter with almost no effect causes the fitting algorithm to diverge.

It was found that the fitting method did not function well in determining independently the values of the diffusion coefficient and the maximum surface coverage. To determine the reason for this behavior, a response surface was created for these two parameters. The sum of square errors was plotted on the z-axis with the proposed values for the diffusion coefficient and the maximum surface coverage on the x and y axis. The graph is shown in Figures 2-6 and 2-7. Examples of approximate minima are given in Table 2-2. As can be seen, there is a curve on the response surface with the same minimal sum of square errors. This means that the equations do not have sufficient degrees of freedom to distinguish between the two parameters. No physical dependence is described, as both constants have definite values, but the mathematical analysis cannot distinguish the values independently. There is a definite curve of minimum error, but no precise values can be determined. If either of these parameters can be determined using
alternative experimental or theoretical methods, the other could be found using the non-linear fitting method, and an error estimate could be generated.

**Figure 2-6:** Three-dimensional graph showing the shape of the response surface for the sum of square error between the experimental data and modeled data with respect to the maximum surface coverage and the diffusion coefficient. It can be seen that large plateaus are present at the limits of the diffusion coefficient, but a curve of minima exists in the middle of the range. A side view of this graph is shown in Figure 2-7.
Figure 2-7: Side view of surface described in Figure 2-6. The minimum is clearly visible from this angle. The minimum does not lie at any single value for the diffusion coefficient or the maximum surface coverage, but rather it is represented by a curve across these parameters.

Table 2-2: Table showing selected values for approximate minima in the response surface shown in Figures 2-6 and 2-7.

<table>
<thead>
<tr>
<th>$\Gamma_{\text{PEG}}$ (mol/cm$^2$)</th>
<th>D (cm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2.4 \times 10^{-10}$</td>
<td>$3.84 \times 10^{-6}$</td>
</tr>
<tr>
<td>$3.0 \times 10^{-11}$</td>
<td>$1.94 \times 10^{-6}$</td>
</tr>
<tr>
<td>$7.5 \times 10^{-12}$</td>
<td>$9.64 \times 10^{-7}$</td>
</tr>
<tr>
<td>$1.9 \times 10^{-12}$</td>
<td>$4.84 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

Two Component Systems

Two component systems must be used in order to determine the interaction parameters, e.g., $k_{\text{SPS,PEG}}$. The two-component experiments can be performed by starting with a saturated electrode surface of the additive to be replaced; in the SPS-PEG
example, this can be achieved by first injecting PEG and allowing the surface to come to steady-state. Then, the replacing additive is injected and the response measured. In the SPS-PEG case, SPS would be injected after the steady-state response for PEG was reached and the ensuing potential transient measured. Using the three systems, SPS-PEG, JGB-PEG, and JGB-SPS, the interaction parameters can be determined. In this analysis, it has been assumed that kinetic parameters found using single component systems remain constant in multi-component systems. If this assumption does not hold, the method developed here could also determine how these parameters changed in the presence of other components.

Three Component System

The three component system, containing PEG, SPS, and JGB, does not give any new data to determine any new parameters, but can serve as a check to verify the values determined in earlier analysis. Such work requires significant computational effort and will be carried out in the future.

Conclusions

An analytical method was developed for extracting accurate values of the kinetic parameters necessary for accurate modeling and analysis of the dual damascene bottom-up fill process. The approach is universal and can be applied to general systems involving multi-component additive adsorption. The errors can be determined, and the sensitivity of the surface coverage to the values of the kinetic parameters found. The transport and adsorption kinetics parameters for PEG transport in a copper sulfate plating solution and its adsorption on copper electrodes have been investigated, and values for some critical
parameters determined. The fit for the equilibrium constant yielded a value of $10.58 \times 10^{-10} \text{ mol/cm}^3 \pm 1.42 \times 10^{-10} \text{ mol/cm}^3$. The value of the adsorption coefficient was found to be approximately 0.1 cm/s. No further precision is necessary for the latter because the result is very insensitive to the value of $k_{\text{PEG}}$. It was determined that further experimentation would be required to disentangle the results for the diffusion coefficient and the maximum surface coverage, but if either of these values is given, then the other can easily be found. Such experiments would include further transient polarization experiments, including multi-component systems. If such experiments proved insufficient, other possibilities include use of a quartz crystal micro balance or a high surface area electrode to determine the maximum surface coverage, or the use of NMR to determine the diffusion coefficient.

An additional use of the method presented is as a check for the mathematical model used to generate the parameters. If the parameters can be determined using an alternate method, the values can be compared to each other. If the values were equal, this would be additional evidence in support of the validity of the mathematical model.
Chapter 3: Competitive Adsorption of Janus Green B

Background

In addition to PEG, SPS, and Cl⁻, an additional component, a ‘leveler’ is often added to help reduce the phenomenon of ‘momentum plating’. ‘Momentum plating’ is the occurrence of enhanced copper plating (‘overburden’) above small features, which are particularly noticeable over feature clusters. This ‘momentum plating’ can often be significantly reduced by the addition of a nitrogen-containing suppressor in very low (~5 ppm) concentrations. If the concentration is too large, deterioration of the fill is observed. The effect of levelers can be seen in Figure 3-1.

![Momentum Plating (Overburden) & Deterioration of fill]

**Figure 3-1:** Effect of levelers on electrodeposition of copper. At small concentrations, reduction in momentum plating is observed. At large concentrations, deterioration of the fill occurs.²⁴
Several such levelers have been studied, including Janus Green B (JGB)\textsuperscript{8,25}, dodecyltrimethylammonium chloride (DTAC)\textsuperscript{24}, and polyethylenimine (PEI)\textsuperscript{26}. In general, these studies have focused primarily on the effects of levelers on the bottom-up fill process. The researchers report that any of these levelers, if added in small concentrations, can significantly reduce the formation of bumps over the features. However, if the levelers are added at a higher concentration, the bottom-up fill deteriorates significantly. Such conclusions have been arrived at both experimentally and theoretically\textsuperscript{8,14,24-26}. In the theoretical work, it has been assumed that levelers displace both PEG and SPS on the copper surface and that the levelers have the same or greater inhibitive polarization behavior as PEG\textsuperscript{14}. In this chapter, we demonstrate experimentally that this mechanism does not fully explain the competitive adsorption behavior of JGB, a typical leveling compound and suggest possible alternate mechanisms for the observed behavior.

\textit{Experimental Results}

The experimental setup used in this chapter is similar to that described in Chapter 2. The additives are injected using a syringe into the cell where the WE is a copper RDE, the CE is a large flat copper plate placed far away from the WE, and the RE is an insulated wire with an exposed copper tip. Here, the focus is on the direction of displacement and the magnitude of the polarization observed. The specific experiments and results thereof are detailed below; however, in general, one additive is injected into a solution already containing a mixture of additives. In addition to the additives specified in the individual experiment, the base solution contained 0.5 M CuSO$_4$, 70 ppm Cl$^{-}$, and
were acidified to approximately pH =2. All experiments were run at 30 mA/cm² and 200 RPM, and the reference electrode was Cu/CuSO₄.

**SPS Injection into a Solution Containing PEG**

It has been shown by Akolkar and Landau that SPS displaces PEG on the copper surface.³ This result is widely accepted. We repeated this experiment as a baseline for comparison. SPS (50 ppm) was injected into the base solution containing an additional 150 ppm PEG. The ensuing polarization curve is shown in Fig. 3-2.

![Figure 3-2](image)

**Figure 3-2:** Polarization response to injection of SPS into a solution containing PEG. Voltage transient at a constant current density of 30 mA/cm² is shown. PEG was introduced at 120 s, followed by SPS injection at 165 s.

As can be seen, PEG causes approximately a 150 mV increase in polarization as compared to the base solution. Upon addition of the SPS, a slow recovery is seen, indicating replacement of PEG by SPS on the surface. This result is in good agreement with previous work³.
**Injection of JGB by Itself**

The individual effect of JGB in solution is also pertinent; therefore, JGB was injected into the base solution. The concentration dependence of JGB was investigated by injecting 4 ppm of JGB sequentially five times up to a total of 20 ppm JGB. In this way the appropriate JGB concentration for use in plating applications and the saturation concentration for JGB on the surface could be determined. The voltage transient is shown in Fig. 3-3.

![Potential transient following Injection of JGB into base solution. Five injections of 4 ppm JGB were performed sequentially.](image)

**Figure 3-3:** Potential transient following Injection of JGB into base solution. Five injections of 4 ppm JGB were performed sequentially.

The JGB additions cause increased polarization (more negative), with the subsequent increases becoming smaller as the JGB surface concentration reaches near saturation at about 20 ppm (bulk solution concentration). However, even at saturation, this polarization increase is moderate, corresponding to approximately 80 mV. This polarization is significantly less than the 150 mV observed when PEG was present alone.
in the system, a discrepancy with previously published data\textsuperscript{14}, since the eventual polarization seen here near JGB saturation is not identical to that of PEG.

**JGB Injection into a Solution Containing PEG and SPS**

As a next step, we investigated the effect of JGB on a solution containing PEG and SPS. The concentration dependence was again investigated, as shown in Fig. 3-4.

![Graph showing the effect of JGB injection into a solution containing PEG and SPS.](image)

**Figure 3-4:** Injection of JGB into a solution containing PEG and SPS. Transient voltage indicates initial passivation due to PEG injection at 150 s, followed by depolarization due to SPS injection at 180 s. Subsequent 5 injections of 4 ppm JGB (each) results in repolarization, which is, however, somewhat lesser than the initial polarization due to the PEG alone and significantly lower than that due to JGB alone (Fig. 3-2).

The resulting polarization, after five injections of 4 ppm JGB (for a total of 20 ppm JGB) is approximately 150 mV negative with respect to the base solution. This polarization is close to that of PEG alone, and is significantly less than that of JGB alone (Fig. 3-3). This suggests that either PEG is adsorbed (possibly readsorbs) on the surface...
or that JGB is a stronger polarizer when acting in competition than when it is present just by itself. This observation is consistent with the belief that levelers replace all other additives on the electrode surface, resulting in a polarization about identical to that of PEG. The results presented in Figs. 3-2 and 3-4 support this hypothesis, but is, however, in conflict with the subsequent experiments described later in this chapter.

**JGB Injection into a Solution Containing SPS**

As a further test, JGB was injected into a solution initially containing only SPS. Small additions of JGB were made at first, in order to determine the initial reaction to small concentrations of JGB, and then sufficient JGB was added to drive the surface to saturation.

![Graph](image)

**Figure 3-5**: Potential transient following injection of JGB into a solution containing SPS
As can be seen in Fig. 3-5, upon the addition of JGB, a polarization of approximately 80 mV below that of bare copper is seen (i.e., the electrode is more polarized than copper in the base solution by about 80 mV). This suggests that JGB displaces SPS on the surface, and since the final polarization is nearly the same as that seen for JGB alone, this is indicative that replacement is complete. This result is expected, because a major function of the leveler is to inhibit growth on a surface covered in highly concentrated SPS (e.g., on copper rapidly growing over via clusters).

**Injection of JGB into a Solution Containing PEG**

In order to better characterize the order of displacement of PEG and JGB, the latter was injected into a solution containing PEG. If the JGB displaces PEG pre-adsorbed on a copper surface, a depolarization of about 70 mV would be expected (based on Figure 3-3), because JGB is a weaker suppressor than PEG by about 70 mV at the applied current density (30 mA/cm²).
Figure 3-6: Injection of JGB into a solution containing PEG. Three additions of 4 ppm JGB (each) were made as indicated.

No polarization or depolarization is noted in Fig. 3-6 upon the addition of JGB. Small bumps in the potential transient are observed at about the point of addition; however, these are minor, and likely due to the physical addition of solution to the system. This behavior supports the statement that JGB does not replace PEG on the copper surface.

Injection of PEG into a Solution Containing JGB

As a companion test to the injection of JGB into PEG, an injection study where PEG was injected into JGB was performed. The published model suggests that no response should be seen; however, the experimental results described in this chapter (Figure 3-5) suggest that we should observe polarization of around 70 mV.
As noted in Fig. 3-7, we do see a polarization of about 80 mV. This is strong evidence that PEG displaces JGB on the surface.

**Injection of PEG into a Solution Containing Both JGB and SPS**

The potential transient following injection of JGB into a solution containing both PEG and SPS indicates significant polarization, back to nearly the polarization value in the presence of PEG alone. This result is anomalous, because JGB is a weaker polarizing agent than PEG. Subsequent experiments indicate that PEG displaces JGB, and therefore the final polarization in the previously described experiment (Figure 3-4) is likely due to the presence of adsorbed PEG on the copper surface. To test this, PEG was injected into a solution containing JGB and SPS so that it could be determined whether PEG would still displace JGB on the surface even in the presence of SPS. It was expected that a
polarization of about 70 mV should be seen upon the addition of PEG, if PEG displaces JGB completely.

**Figure 3-8:** Potential transient following the injection of PEG into a solution containing SPS and JGB

A polarization of about 65 mV was seen (Fig. 3-8), which is slightly lower than the expected 70 mV, suggesting that PEG does not completely displace JGB in the presence of SPS.

**Proposed Mechanisms**

**Summary of Observed Action**

We have seen that JGB displaces SPS on the surface, PEG displaces JGB, and SPS displaces PEG. This seemingly cyclical displacement pattern is illustrated schematically in Figure 3-9. However, when all three additives are present, the observed polarization is very close to that of PEG. Three possible mechanisms for this unexpected
behavior are suggested, but since there is no definitive model for the surface bonding of either JGB or PEG on copper, little fundamental justification can be given for any of the models.

**Figure 3-9:** Diagram depicting observed displacement hierarchy of PEG, SPS, and JGB

**Mechanism 1: Protective Coverage of PEG by JGB**

In this proposed mechanism, PEG can displace JGB, but the JGB forms a protective layer (monolayer or multi-layer) on top of the PEG, as illustrated schematically in Fig. 3-10. This protective layer prevents the SPS from displacing the PEG. This model could potentially be tested by surface spectroscopy, capable of detecting the concentration of each of the three species on the surface. If this model were correct, large signals of both PEG and JGB would be expected near the surface. This would not be the case in either of the other proposed mechanisms.
Figure 3-10: Diagram of proposed mechanism in which JGB prevents PEG from being displaced by forming a protective layer

**Mechanism 2: Rate Determined Coverage**

An alternate mechanism is based on the observation that the displacement rate of PEG by SPS is much slower than the rates for either of the other displacements (i.e., JGB by PEG and SPS by JGB). It takes SPS over 200 s (Figure 3-4) to displace PEG on the surface at the current density used (30 mA/cm²), whereas it takes JGB about 50 s to displace SPS (Figure 3-5) and PEG less than 10 s to displace JGB (Figure 3-8). We note that this mechanism appears to violate thermodynamic restrictions on the driving force for adsorption. It may be that one or more of the replacement interactions occur directly on the surface, and others may take place in the solution close to the surface. Nonetheless, in validating this model, significant attention must be given to the thermodynamic driving force for the adsorption.

Figure 3-11: Diagram of proposed mechanism based on differing rate constants of additive adsorption.
To more clearly illustrate the concept behind this mechanism, it is useful to investigate the following reaction equations. The equations represent the reaction model of the displacement reaction. A species with a * as a superscript is adsorbed on the surface. The reverse reactions are insignificant, therefore the equations have been written without the reverse reaction.

\[
\begin{align*}
SPS^* + JGB & \rightarrow SPS + JGB^* \\
JGB^* + PEG & \rightarrow JGB + PEG^* \\
PEG^* + SPS & \rightarrow PEG + SPS^*
\end{align*}
\]

These equations sum to zero, meaning at steady state the rates of reaction have to be zero for all species. Therefore, the rates can be simplified to equations 3-4 through 3-6:

\[
\begin{align*}
k_{JGB,SPS} C_{SPS} C_{JGB} &= k_{SPS,PEG} C_{PEG} C_{SPS} \\
k_{PEG,JGB} C_{JGB} C_{PEG} &= k_{JGB,SPS} C_{SPS} C_{JGB} \\
k_{SPS,PEG} C_{PEG} C_{SPS} &= k_{PEG,JGB} C_{JGB} C_{PEG}
\end{align*}
\]

The concentrations in solution are all roughly the same, therefore the non-adsorbed species concentration will be canceled for a first approximation. Solving for one and using this approximation, equations 3-4 through 3-6 can be written:

\[
\frac{k_{JGB,SPS} C_{SPS}^*}{k_{SPS,PEG} C_{PEG}^*} \approx 1
\]
\[
\frac{k_{\text{PEG,JGB}} C_{\text{JGB}^*}}{k_{\text{JGB,SPS}} C_{\text{SPS}^*}} \approx 1
\]  
[3-8]

\[
\frac{k_{\text{SPS,PEG}} C_{\text{PEG}^*}}{k_{\text{PEG,JGB}} C_{\text{JGB}^*}} \approx 1
\]  
[3-9]

The rate at which PEG replaces JGB is approximately the same as the rate at which JGB replaces SPS, therefore equation 3-8 simplifies to:

\[
C_{\text{JGB}^*} \approx C_{\text{SPS}^*}
\]  
[3-10]

Likewise, the rate at which PEG displaces JGB is much faster than the rate at which SPS displaces PEG, therefore equation 3-9 simplifies to:

\[
C_{\text{JGB}^*} \ll C_{\text{PEG}^*}
\]  
[3-11]

Equations 3-10 and 3-11 can be written together to show the crux of this mechanism, specifically that the surface concentrations of JGB and SPS are much less than the surface concentration of PEG:

\[
C_{\text{JGB}^*} \approx C_{\text{SPS}^*} \ll C_{\text{PEG}^*}
\]  
[3-12]

It has been suggested that the SPS adsorption rate is potential dependent\textsuperscript{12}. It might be possible to exploit this property to test the hypothesis. If this hypothesis is correct, the steady-state current should be an average of the currents expected at that potential for each individual additive weighted by its fractional surface coverage, which at steady-state would be dependent on the displacement rates. If the adsorption rates for PEG, SPS, and JGB were determined using the method described in Chapter 2, the weighting factors, which would be potential dependent for SPS, could be calculated for a range of potentials. The projected current could then be calculated, and if it matched the
experimental polarization curve, this would be indicative that this mechanism is prevailing.

A simpler, but less conclusive test would be to calculate projected surface coverages of SPS and combined PEG and JGB by analyzing the polarization curves of SPS alone, PEG and JGB together, and a system of all three components. If the surface coverage would be found to be potential independent, this would suggest that this mechanism was incorrect.

**Mechanism 3: Decomposition Products Interaction**

A third possible mechanism is based on interaction of decomposition products with the other additives, leading to the seemingly cyclical action of displacement. This could be tested by investigating the displacement behavior of the additives in the presence of additive mixtures of varying ages. It is expected that there will be more decomposition by-products in aged solutions, and thus there should be changes in the action depending on the concentrations of these components.

**Conclusions**

For an initial qualitative analysis of levelers, or for a study of the process of ‘momentum’ plating, the cyclical nature of the displacement mechanism described herein is not as important, because the combined action of the three additives system is similar to that of a highly polarizing leveler that displaces both PEG and SPS. However, for an in-depth study of levelers in momentum plating, especially any investigation that includes precise quantitative results, this behavior has to be taken into account, and furthermore, elucidating the actual mechanism by which it occurs is important. The surface
concentrations of each of the species will change depending on which model is correct. Additionally, the concentrations in the solution close to the surface will be affected. This becomes more complicated in the study of momentum plating, because it has been shown\textsuperscript{14} that significant geometric effects play a major role in this process. This is especially true for the first suggested mechanism, because the action would depend on whether or not the JGB would preferentially stay adsorbed on top of PEG or transfer to an adjacent bare copper surface.
Chapter 4: High Molecular Weight Levelers for Improved Gap Fill in Copper

Interconnect Metallization

Background

As discussed in Chapter 3, levelers have historically been used to reduce ‘momentum plating’, the excessive plating encountered particularly over via clusters, once the gap-fill is completed and the plated copper emerges out of the trenches. Levelers are small, nitrogen containing compounds such as JGB, which adsorb strongly on copper, producing very high polarization, thus slowing down the plating rate. Once levelers enter the plated features to any significant extent, they interfere with the bottom-up fill; hence they are added in very small amounts (few ppms) in order to assure that their effects are limited to the plated copper as it emerges out of the vias. Recently, Zhou and Reid have shown that the addition of an extremely high molecular weight leveler, polyvinylpyrrolidone (PVP) can improve the bottom-up fill in addition to reducing the overburden. We provide here an explanation to this observed phenomena and a rationale for the benefit of using such levelers, model the effect quantitatively, and suggest more effective leveling compounds.

As feature sizes get increasingly smaller, gap-fill becomes more challenging and any improvement in the bottom-up fill can extend the process to smaller sizes. Even a small improvement in the capability of plating smaller feature sizes can yield another generation of semiconductor devices. Previously, bottom-up fill has mainly been achieved through the combination of two plating additives: an accelerator and a suppressor, typically PEG and SPS. The possibility of introducing a new class of fill-enhancing additives is exciting. Although Zhou and Reid indicate the possibility for
such improvement, their work includes only tentative data and no rationale or recommendation is provided. In this chapter, we provide a theoretical basis for this improvement and show initial validation for the model. Furthermore, we give a plan for further validation of the approach.

Proposed Model

Effect of Activation Overpotential on Fill Rates Inside the Feature

The process of bottom-up fill is based on slowing down the plating of the via rim and sidewalls while enhancing the plating rate at its bottom. If sufficient inhibition and acceleration are provided at the rim and the bottom, respectively, the plated bottom reaches the top surface before the sidewalls merge, which would form a void. A key interaction that provides this mechanism is the preferential distribution of SPS on the bottom of the feature, and PEG on the side walls and particularly near the via top. The SPS accelerates the plating of copper, whereas the PEG is a plating inhibitor. Therefore, a key parameter of interest is the ratio of current density on a surface covered with SPS as opposed to a surface covered with PEG. We define the bottom-up fill (BUF) ratio:

\[
\text{BUF ratio} = \frac{i_{\text{SPS}}}{i_{\text{PEG}}}
\]

[4-1]

Since the copper surfaces on which the PEG and SPS are absorbed are electrically connected (i.e., are at the same potential, V), and since the ohmic drop in solution across the nano-scale features is negligible, we may assume that the solution electrostatic potential (Φ) is also constant. Accordingly, the overpotential along the surface (η = V - Φ) must be constant. It is desirable to model the currents mathematically; however, the polarization curve for SPS does not follow the Butler-Volmer equation over extended
ranges of potentials. Nonetheless, the SPS polarization can still be approximately modeled by the Butler-Volmer equation if it is restricted to the narrow range of activation overpotentials pertinent to the copper plating process used in the gap-fill metallization process. Therefore, when a simplified cathodic Butler-Volmer expression is substituted for the current density, the BUF ratio can be represented as:

\[
BUF \text{ ratio} = \frac{i_{o, \text{SPS}} \cdot e^{-\frac{\alpha_{\text{SPS}} F \eta}{RT}}}{i_{o, \text{PEG}} \cdot e^{-\frac{\alpha_{\text{PEG}} F \eta}{RT}}} = \frac{i_{o, \text{SPS}} e^{\frac{(\alpha_{\text{SPS}} - \alpha_{\text{PEG}}) F \eta}{RT}}}{i_{o, \text{PEG}}} \quad [4-2]
\]

Note that the polarization here is given as a magnitude of polarization, not the actual voltage observed. It is desirable to have as large a BUF ratio as possible, and this is possible in either of two ways. First, alternative additives with better suppression or acceleration behavior could be sought and used instead of either PEG or SPS. Second, and more importantly for this investigation, the ratio has a dependence on the activation overpotential, \( \eta \). In order to better understand this relationship, the derivative is examined:

\[
\frac{\partial BUF \text{ ratio}}{\partial \eta} = \frac{(\alpha_{\text{SPS}} - \alpha_{\text{PEG}}) F}{RT} \frac{i_{o, \text{SPS}}}{i_{o, \text{PEG}}} e^{\frac{(\alpha_{\text{SPS}} - \alpha_{\text{PEG}}) F \eta}{RT}} = \frac{(\alpha_{\text{SPS}} - \alpha_{\text{PEG}}) F}{RT} \left( BUF \text{ ratio} \right) \quad [4-3]
\]

It is clear that the BUF ratio is always positive; therefore the sign of the derivative is dependent on the relative magnitudes of the cathodic transfer coefficients of PEG and SPS. It has been shown that SPS has a greater cathodic transfer coefficient, \( \alpha_c \) than PEG\(^{28} \), therefore the BUF ratio increases with increasing overpotential. Alternatively, this ratio could be represented through empirical data if it becomes desirable or necessary to exceed the range of validity for the BUF ratio and the Butler-Volmer equation can no longer be applied.
Furthermore, if more current is directed towards the features, the resultant rise in current density will cause the overpotential to rise, and therefore further improvement in the bottom-up fill rate will be observed.

**Effect of Targeted Polarization of the Wafer Surface**

It is common in semiconductor plating applications to control the total current directed to the wafer. This current can be thought of as consisting of two parts, the portion of current directed into features, and the portion directed to the exposed wafer surface. The total current can be expressed mathematically in terms of the average current density directed to each of these surfaces multiplied by the respective areas:

\[
I_{\text{total}} = i_{\text{feature}} \cdot A_{\text{feature}} + i_{\text{top}} \cdot A_{\text{top}} \quad [4-4]
\]

Under constant current control, the sum does not vary with time or chemistry changes. Therefore, a change in polarization behavior of the wafer surface would change the local current densities, but the total current would have to remain constant. If a method was developed to significantly suppress copper deposition on the wafer surface without interfering with the deposition process within the features, then the current density would drop on the wafer surface. In order to maintain a constant total current, the wafer would have to become more polarized, and since the kinetics within the features is assumed to remain constant, more current would be preferentially distributed to the features. This is shown schematically in Figures 4-1 and 4-2.
Figure 4-1: Simplified diagram of the current distribution on a wafer in which the top surface has not been significantly suppressed. Note that the current is distributed to both the wafer surface and the features.

Figure 4-2: Simplified diagram of the current distribution on a wafer in which the top surface has been totally suppressed. The entire current in this case is preferentially distributed towards the features.

It has already been demonstrated that an increase in current distributed to the features will cause an increase in the bottom-up fill ratio. Therefore, it can be concluded that if the wafer surface can be significantly inhibited without significantly affecting the feature, the bottom-up fill rate will increase, and thus extend the process to smaller feature sizes.
Effect of Very High Molecular Weight Levelers

A promising method for inhibiting the surface of the wafer is the addition of a high molecular weight leveler. This terminology refers to a leveler that is simply a suppressor which cannot be displaced by SPS on a copper surface. A leveler with a large suppression capability could suppress the surface sufficiently to redirect the current towards the features in a significant way. However, the leveler must be prevented from entering the vias, because it has been demonstrated that if a leveling compounds enter the features, the bottom-up fill is significantly degraded\textsuperscript{24}. In the case of small features, diffusion control can significantly limit compounds from entering the feature. Additional inhibition on the feature rim, close to the wafer surface, is also beneficial as it prevents pinching, as long as the leveler does not penetrate significantly into the feature. For a sufficiently diffusion limited molecule, it is possible to prevent any significant entry to the feature in the time frame that is pertinent to the gap-fill process (approximately 10 s). Therefore, it is proposed that the driving force for improvement in bottom-up fill rate seen when high molecular weight levelers are added is this preferential current distribution to the features caused by the strong passivation of the wafer surface.

Effect of Process Conditions on Improving the Bottom-up Fill Using Levelers

It was assumed earlier that the total current at which the process was run remains constant irrespective of the chemistry. However, the choice of maintaining the total current as a constant may not be the proper choice for device fabrication. The current at which the devices are plated is determined mostly empirically in order to obtain the best results. The value at which the optimized results are obtained almost certainly varies with different device designs, thus the constant current condition may be misleading.
It is clear that one method for improving the bottom-up fill would be to simply increase the total current applied to the wafer. This would raise the current directed towards the features and the surface alike, and therefore improve the bottom-up fill. However, there are other considerations besides the bottom-up fill that must be taken into account, including electromigration effects on the surface. Due to these considerations, industry sets limits on the maximum current density directed to the surface. Since SPS does replace PEG on the surface to a significant extent over the course of the plating process, this limits the maximum current that can be applied to the wafer. However, if a leveler is used to passivate the flat wafer surface, a significantly higher overpotential will be reached before the maximum current density condition is reached. Therefore a much higher current can be directed towards the features, thus improving bottom-up fill.

Effect of Feature Coverage on Bottom-up Fill Improvement

The improvement in the bottom-up fill seen due to the passivation of the wafer surface is based on the redirection of current away from the relatively flat wafer surface towards the features. The magnitude of the redirected current towards the features is proportional to the amount of current directed away from the wafer surface, which is in turn related to the amount of area taken up by the wafer surface. Assuming that we define the fractional coverage of features on the surface as $\Omega$, then the improvement in bottom up fill due to the addition of a high molecular weight leveler is shown in Figure 4-3. Here, the leveler was assumed to completely passivate the surface, and a 50 mA/cm$^2$ nominal current density was applied in the analysis.
Figure 4-3: The effect of the fraction coverage of features on the wafer. The leveler was assumed to completely passivate the exposed wafer surface. A nominal current density of 50 mA/cm² was assumed.

As can be seen, there is a significant improvement due to the high molecular weight leveler. This improvement is particularly noted at low feature coverages, because under those conditions a larger fraction of the total current is directed towards the fewer features. It should be noted that the plating conditions in the presence of the leveler are identical to assumed conditions without the leveler; therefore this analysis does not incorporate any improvement due to changes in process conditions.

**Possible Choice for a High Molecular Weight Leveler**

A leveler for this application requires three properties. First, it must strongly passivate the surface. The stronger the leveler suppresses the surface, the greater it will improve the bottom-up fill. Second, the leveler must quickly and strongly adsorb onto the copper surface. It must reach near saturation on the wafer surface at the very
beginning of the process, and it cannot be replaced by SPS during the course of the plating process. Third, the leveler molecule must be sufficiently large that it does not diffuse appreciably into the features. Only polymeric levelers have the prospect for being effective as high molecular weight levelers in this context, because it has been shown that levelers of 3500 g/mol are far too small to fulfill the third requirement, and only once the leveler has a molecular weight exceeding about 60000 g/mol improvement is seen\textsuperscript{18}. A leveler with an even larger molecular weight is preferable, because it does not bring about deleterious effect on the process inside the feature even at high concentration. This has been shown to hold true at a molecular weight of 1.3 million g/mol\textsuperscript{18}.

Reid and Zhou used polyvinylpyrrolidone (PVP) as a possible leveler for this application\textsuperscript{18}, but only minor improvements were seen when it was added. It is desirable to find a leveler offering a greater suppression. One such compound is polyethylenimine (PEI). PEI in its branched form is very soluble in water, and it can be synthesized at a sufficiently high molecular weight. A graph of polarization curves for a number of representative additive chemistries is shown in Figure 4-3. The polarization is plotted versus the corrected kinetic current, which isolates the activation overpotential from the concentration overpotential by reducing the current density:

$$\frac{1}{i_k} = \frac{1}{i} + \frac{1}{i_L}$$

[4-5]
Figure 4-4: Polarization curves for four different additive chemistries, showing the corrected kinetic current density as a function of the activation overpotential. Each solution contained 0.5 M CuSO$_4$ and was acidified to pH=2. All species were present in effectively saturated concentrations. The experiments were performed under the experimental setup described in Chapter 2 using a rotation speed of 200 rpm.

PEI yields a significantly larger polarization than the other additive mixtures, especially at low current densities, corresponding to the range in which the plating process would occur.

Validation of Proposed Model

Validation of Diffusion Based Effects

The diffusion process for a high molecular weight leveler was modeled using Comsol Multiphysics in order to prove analytically that there is no significant diffusion into the feature. It was determined that the concentration inside the features was on the order of three orders of magnitude smaller than the concentration in the bulk solution.
after the pertinent time frame (15s). This should be compared to PEG, in which the concentration inside the features can reach almost the full bulk concentration after only a short (10-15s) period of time. The diffusion coefficient for the leveler was calculated using the Stokes-Einstein equation (Equation 4-6) for a spherical polymeric molecule of molecular weight 750,000, was found to be on the order of $2.5 \times 10^{-7}$ cm$^2$/s. The density was assumed to be 1.2 g/cm$^2$, leading to a radius of 1.10 nm.

$$D = \frac{k_B T}{6\pi \mu r}$$

[4-6]

**Simplified Model Showing Improvement Due to Surface Passivation**

In order to validate the theory of improvement due to surface passivation, a semi-analytical model was developed to test the concept. The basic equation upon which the model hinges is that $I_{\text{total}}$ remains constant throughout the entire process, but the current densities are allowed to vary. For the initial modeling of the problem, the following assumptions were made:

1. $i_{\text{bottom}}$ is considered to follow the kinetics of copper with only SPS and Cl$^-$ adsorbed (as assumed to be close to pure copper kinetics)
2. The “High Molecular Weight Leveler” diffuses sufficiently slowly that it can considered not to diffuse into the feature during the timescale of the fill process
3. The sidewalls are considered to be uniform, with no difference with respect to how deep in the feature a given point is.
4. The various current densities are dependent only on time and overpotential.

Functions were developed semi-empirically that match theoretical functions to experimental results. The basic form was an exponential interpolation function
between the initial value and the final value. This form has no theoretical basis, but it fits the data well. For example, the function for a surface with competitive PEG and SPS adsorption was:

\[ i = \left(1 - e^{-t/\tau_{PEG}}\right) \cdot (i_{SPS} - i_{PEG}) + i_{PEG} \]  \[4-7\]

Where the time constant \( \tau_{PEG} \) was determined using injection studies.

5. \( i_{\text{sidewall}} \) is considered to follow the kinetics of copper with PEG, SPS, and Cl\(^{-}\) in competitive adsorption with each other. Here, we assume that the sidewalls are covered by PEG which is replaced.

6. \( i_{\text{top}} \) is considered to follow the copper kinetics with PEG, SPS, and Cl\(^{-}\) in competitive adsorption with each other (as the sidewalls) if a high molecular weight leveler is not present. If such a leveler is present, \( i_{\text{top}} \) is considered to follow the kinetics of copper with adsorbed leveler.

7. The activation overpotential is assumed to be the only significant overpotential

Obviously, the overpotential at any given point on the wafer has to be the same at any given time, thus equation 4-4 can be written:

\[ I_{\text{total}} = i_{\text{bottom}}(\eta, t) \cdot A_{\text{bottom}} + i_{\text{sidewall}}(\eta, t) \cdot A_{\text{sidewall}} + i_{\text{top}}(\eta, t) \cdot A_{\text{top}} \]  \[4-8\]

However, the corresponding areas also change with time, according to the following equations:

The bottom area is:

\[ A_{\text{bottom}}(t) = A_{\text{bottom}}(t_0) \cdot \frac{\text{Trench Width}(t)}{\text{Trench Width}(t_0)} \]  \[4-9\]

The sidewall area is:
\[ A_{\text{sidewall}}(t) = \frac{2 \cdot \text{Trench} \_ \text{Depth}(t)}{\text{Trench} \_ \text{Width}(t)} A_{\text{bottom}}(t) \]  \[4-10\]

Essentially, the bottom area decreases directly proportionally to the amount the sidewall has grown, and the sidewall is defined by the current aspect ratio and bottom area.

The top area is merely whatever nominal wafer area not taken up by the bottom:

\[ A_{\text{top}}(t) = A_{\text{wafer}} - A_{\text{bottom}}(t) \]  \[4-11\]

The trench height and width are functions of how much current has been plated at those surfaces. Using Faraday’s Law to relate the current to the plated height:

\[ h_{\text{wall}} = \int_0^t i_{\text{wall}} \cdot \frac{M_{\text{copper}}}{n \cdot F \cdot \rho_{\text{copper}}} dt \]  \[4-12\]

Equation 4-12 is merely a function of current density and time, and since it has already been determined that current density is only a function of time and overpotential, equation 4-4 can be rewritten:

\[ I_{\text{total}} = i_{\text{bottom}}(\eta,t) \cdot A_{\text{bottom}}(\eta,t) + i_{\text{sidewall}}(\eta,t) \cdot A_{\text{sidewall}}(\eta,t) + i_{\text{top}}(\eta,t) \cdot A_{\text{top}}(\eta,t) \]  \[4-13\]

\( I_{\text{total}} \) is a specified condition, therefore if a time-stepping approach is used, so that each equation is solved for a specific time, and integrals are performed by summing differential elements, equation 4-13 has only one variable, \( \eta \), at each time step.

The result of this model is shown below, in Figure 4-5, and shows significant improvement with the addition of PEI.
Figure 4-5: Simplified model results showing the expected improvement of the bottom-up fill in a solution containing high molecular weight PEI compared to a solution without PEI. The process was modeled as using a nominal current density of 5 mA/cm² for 10 s with a fractional feature coverage of 1%. An improvement of 34% in the bottom-up fill is seen in the solution containing PEI.

Suggested Further Validation

It is desirable to perform an experimental test of the bottom-up fill using a solution containing high molecular weight PEI. A commercially available PEI with a nominal molecular weight of 750,000 g/mol was obtained, however it was found that this PEI has a extremely wide molecular weight distribution, and contains significant amounts of very low molecular weight PEI. A fractionation of the PEI in order to separate the high molecular fraction is in progress.
It is also planned to model the bottom-up fill process using Comsol Multiphysics, in order to compare exact analytical results with the experimental data, however currently geometric effects have not fully been taken into account in the commercial software, and the use of Comsol’s moving boundaries to model the growth of the sidewalls has not been successfully implemented due to the software limitations.

**Conclusions**

In summary, improvement in gap-fill is expected through the introduction of high molecular weight levelers due to the increased polarization on the top wafer surface. This improvement is expected to be amplified in wafers with low pattern densities and high aspect ratio features. The improvement due to this type of leveler could help extend the copper electroplating process to smaller feature sizes. The incorporation of a new type of plating additive opens a new area of research into this technology, namely, to find the best additives for this application, as it is unlikely that PEI will be the final choice. The theoretical basis for the improvement has been given, and has been validated using simplified models.
Chapter 5: Summary, Conclusions, and Future Work

Summary and Conclusions

The focus of this work was the investigation of three areas in which electrochemical methods and concepts can be applied to the process of bottom-up fill in the plating of high end semiconductor devices. A combination of experimental and analytical methods was used in the analysis. The results have application in and of themselves. Additionally, these results can be directly extended to provide additional insight, modeling capabilities, and improve the processes.

A method was presented that has broad application to the determination of kinetic parameters of diffusion and adsorption of additives that change the electrochemical polarization behavior of plated species. A method based on comparing experimental transient polarization behavior with analytical models of the same processes was developed. A combination of non-linear least squares fitting and examination of response surfaces was used to match experimental data to analytical data generated using a finite element analysis algorithm. The equilibrium coefficient and the adsorption rate constant for PEG were determined using this method. The method does not allow for the independent determination of the diffusion coefficient and the maximum surface coverage, however an apparent relationship between the two was determined, which facilitates their use in analytical and numerical studies.

The competitive adsorption behavior of the commonly used leveling compound JGB in the presence of PEG and SPS was carefully studied. Previously published work had assumed that JGB displaces both PEG and SPS on the copper electrode surface. Experimental results presented herein show that this model does not fully describe the
observed action of JGB. A seemingly cyclical displacement order is observed that is more complicated than a simple rank order hierarchy. A number of possible mechanisms for the observed behavior are given, and tests that would determine which of the models is correct are proposed.

Analysis was performed to further the theoretical understanding of the improved bottom-up fill observed in the presence of a high molecular weight leveler. This analysis demonstrates that the addition of a highly passivating leveler with a sufficiently large molecular weight would preferentially direct the current to the features, leading to much improved bottom-up fill. The increased surface passivation should allow for plating to occur at higher total currents without the degradation of the wafer surface, further improving bottom-up fill. The improved bottom-up fill would allow the electrodeposition process to be extended to smaller feature sizes. The magnitude of improvement associated with the high molecular weight leveler is a function of the fraction feature coverage of the wafer surface, with larger improvement on wafers with low feature coverage. PEI was proposed as a possible additive for this application. A simplified analytical model was used to show proof-of-concept, demonstrating the improvement associated with the addition of PEI to the plating solution. Further experimental and theoretical validation steps were proposed.

**Future Work**

All three major topics may be extended through additional work. The method developed for the determination of kinetic parameters can be used to determine the kinetic parameters associated with SPS. This determination is more complicated than
that of PEG due to the fact that the rate of SPS adsorption is believed to be potential dependent.

The competitive adsorption in the PEG-SPS-JGB system requires further analysis in order to determine which of the proposed mechanisms is correct. The tests proposed are detailed in Chapter 3, and include in situ spectroscopic measurements. Also, a further theoretical investigation into the effect of JGB on the chemical mechanism of PEG and SPS adsorption will be performed, including the effects of the Cl⁻ ions and steric effects associated with the PEG.

The model proposed in Chapter 4 for the action of a high molecular weight leveler should be experimentally validated. Experimental evidence of the improvement seen due to the addition of a very high molecular weight PEI could be gathered from fill experiments. A comprehensive theoretical model of the process can also be constructed, and the results compared to experimental evidence.
Bibliography


