Copper electrodeposition in the dual-damascene process for the metallization of semiconductor interconnects has recently become the mainstay for fabricating high-end microprocessors. The key to the successful implementation of this technology is a special mixture of plating additives that inhibits deposition on the more accessible wafer surface and enhances plating at the bottom of the vias (“bottom-up” fill). Without these additives, copper would build up at the via rim and bridge-over, causing unacceptable voids. Although the exact compositions of the commercial additive mixtures are proprietary, all systems incorporate chloride ions, polyethylene glycol (PEG), and bis(3-sulfopropyl) disulfide (SPS). Experiments indicate that the fast PEG adsorption on the wafer is diffusion controlled, while the slow SPS adsorption is controlled by the adsorption kinetics. The results are applied to a transport-kinetics model that provides the additives distribution inside a via. It is noted that the PEG diffusion to the via bottom is extremely slow due to the PEG adsorption on the sidewalls. The role of SPS in the bottom-up fill is characterized by simulating the transport within the via through analogous transport to a flat rotating disk electrode. It is observed that SPS is essential for maintaining fast deposition at the via bottom by preventing PEG adsorption. The critical necessity for a three-additive system comprised of chloride ions, PEG, and SPS is explained, and process parameters essential for bottom-up fill are identified.

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Experimental

The working electrode (WE) consisted of a 0.5 cm² rotating disk made of oxygen-free, high-purity (OFHP) copper. The counter electrode (CE) was a high-surface-area copper sheet placed sufficiently far away (~3 cm) from the WE so that it did not affect the current distribution on the latter. A thin, insulated OFHC copper wire with an exposed tip served as a reference electrode (RE). The RE tip was placed at a distance of about 2 cm from the WE. All electrodes were placed in the plating bath and connected to an EG&G Princeton Applied Research model 283 potentiostat/galvanostat. The system is shown schematically in Fig. 1. The electrodeposition experiments were performed galvanostatically at 5–60 mA/cm² at rotation speeds of 50-200 rpm in an acidified copper. The counter elec-

_**A Time-Dependent Transport-Kinetics Model for Additive Interactions in Copper Interconnect Metallization**_

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In the present work, we report additive injection studies on a rotating disk electrode (RDE) that characterize the transient interactions and provide the time constants for the additive adsorption on copper. PEG transport in a sub-micrometer feature is modeled numerically, identifying the time constant for PEG diffusion to the via bottom. The role of SPS was studied by simulating transport to the via bottom by conducting analogous transport experiments on a flat RDE. It was observed that SPS plays a crucial role in keeping the via bottom essentially PEG-free, thereby maintaining fast deposition kinetics at the bottom.
ties (<5 mV for 30 mA/cm² at 200 rpm). Experiments were also performed with one or two additives already present in the electrolyte and a second and/or a third additive injected. The three additives studied were: HCl (Fisher), PEG [molecular weight (Mw) 3500-4000, Union Carbide], and SPS (Raschig).

**Transient Additives Adsorption on Copper**

The inherent response time of the electrochemical cell was characterized by injecting 2 mL of 0.8 M CuSO₄ into a cell containing 60 mL, distilled water. The potential was recorded (Fig. 2) for galvanostatic deposition from the initial overload condition to a steady-state value corresponding to a current density of 5 mA/cm². The inherent system response exhibits a time constant of 2-3 s. System response time was observed to increase with decreasing rotation speed; however, even for a low rotation speed of 50 rpm, the response time was only 5-6 s. The latter is still short in comparison to the period over which transient additive effects were observed.

In all subsequent additive injection studies, unless stated differently, copper was deposited galvanostatically at 30 mA/cm² from an acidified (pH ~2) 0.5 M CuSO₄. Significant electrode polarization by PEG occurs mainly in the presence of Cl⁻. Cl⁻ ion by itself is a mild accelerator; PEG without chloride is a weak inhibitor. Copper was electrodeposited at 30 mA/cm² on a disk electrode (0.8 cm diam) rotating at 200 rpm.

**PEG adsorption.**—As shown in Fig. 3, injection of 70 ppm Cl⁻ ions into additive-free acidified CuSO₄ electrolyte resulted in a mild (∼20 mV) depolarization. When 100 ppm PEG was injected into an additive-free electrolyte, slight (∼20 mV) polarization was observed. However, injection of 100 ppm PEG into an electrolyte containing 70 ppm Cl⁻ generated considerable (∼160 mV) polarization. This indicates that the Cl⁻ ions strongly enhance the PEG inhibition effects. Injection of different PEG concentrations into a Cl⁻-containing electrolyte, as shown in Fig. 4, indicates fast polarization of the copper electrode, with increased steady-state polarization at higher PEG bulk concentrations. Saturation of this electrode polarization effect was observed at high (>200 ppm) PEG concentrations, probably due to a complete PEG monolayer coverage (θ → 1). An important observation is that the time constant of the PEG adsorption is about 10 s at the experimental conditions (200 rpm). For diffusion-controlled PEG transport to the electrode, i.e., assuming fast adsorption kinetics, an estimate of the time constant \( \tau \sim \delta^2/D_{PEG} \) can be made. Taking \( \delta \), the equivalent Nernst-type boundary layer thickness as 18 \( \mu m \) at 200 rpm rotation and \( D_{PEG} \), the PEG diffusion coefficient, as \( 5 \times 10^{-7} \) cm²/s (estimate based on spherical PEG molecules with 8 nm diam), \( \tau \) is found to be 6 s, of the same order of magnitude as the experimentally observed time constant. This supports the hypothesis of a diffusion-controlled PEG adsorption.

**SPS adsorption.**—When SPS was injected (along with Cl⁻) into an acidified 0.5 M CuSO₄ (pH ~2) solution, rapid depolarization of the electrode with a time constant of about 3 s was observed (Fig. 5). This indicates that the SPS adsorption kinetics on additive-free electrodes are fast, and the acceleration of copper deposition by adsorbing SPS is initiated almost instantaneously. However, when SPS was injected into an electrolyte already containing PEG + Cl⁻, slow electrode depolarization was observed as noted in Fig. 6. This depolarization had a time constant of ~100 s for SPS concentration of 50 ppm. The time constant was observed to be even...
longer, i.e., corresponding to a slower response, for a lower bulk SPS concentration of 20 ppm. The strong dependence of the adsorption time constant on the SPS concentration and the estimated fast SPS diffusion coefficient ($\sim 10^{-5} \text{ cm}^2/\text{s}$) indicate that the SPS depolarization effect, possibly due to the displacement of PEG from the electrode by adsorbing SPS, is controlled by the displacement kinetics and not by transport. The steady-state polarization ($\sim 120 \text{ mV}$) obtained long after the SPS injection ($>150 \text{ s}$) was close to that of an electrode polarization in an electrolyte containing Cl$^-$ but free of PEG. This is indicative of a slow process in which SPS eventually displaces the adsorbed PEG completely from the electrode.

Competitive adsorption between PEG and SPS.—The competitive adsorption was studied by injecting a mixture of 100 ppm PEG + 50 ppm SPS into an acidified (pH ~2) 0.5 M CuSO$_4$, containing 70 ppm Cl$^-$. The potential response, shown in Fig. 7, consists of two distinct regions. At short times ($t < 10 \text{ s}$) after injection, significant ($\sim 110 \text{ mV}$) electrode polarization was observed, attributable to fast PEG adsorption with a short time constant ($\tau_{\text{PEG}} \sim 10 \text{ s}$). However, at $t > 10 \text{ s}$ after injection, a slow electrode depolarization commenced due to PEG displacement by adsorbing SPS, a process that is controlled by the displacement kinetics with a significantly longer time constant ($\tau_{\text{SPS}} \sim 100 \text{ s}$). The PEG adsorption and its subsequent inhibition of the deposition kinetics is faster than the SPS adsorption and its acceleration effect. This indicates that whenever PEG and SPS species reach the elec-
trode surface simultaneously, PEG adsors first, polarizing the electrode, and only later SPS starts displacing the adsorbed PEG species, thereby slowly depolarizing the electrode. The latter displacement of PEG by SPS is a slow process, requiring over 100 s to approach a steady state. The adsorption characteristics of PEG and SPS are most likely associated with mechanistic details of their interaction with the surface that have not yet been fully established. However, it may be speculated that the faster PEG adsorption is associated with the less specific bonding of the polyether to the copper surface in comparison to the more specific bonding of the sulfur to copper.

**PEG transport and adsorption.** In order to characterize the influence of transient additive interactions on the position-dependent kinetics inside a via, detailed analysis of the additive transport and the associated inhibition/acceleration mechanism is required. While the former is discussed in detail in this paper, we exclude here the latter displacement of PEG by SPS in a slow process, requiring over 100 s to approach a steady state. The adsorption characteristics of PEG and SPS are most likely associated with mechanistic details of their interaction with the surface that have not yet been fully established. However, it may be speculated that the faster PEG adsorption is associated with the less specific bonding of the polyether to the copper surface in comparison to the more specific bonding of the sulfur to copper.

**PEG Transport to the Via Rim**

In order to analyze the transport of PEG to the via top surface, i.e., wafer surface as shown in Fig. 8, we neglect the microscale vias on the patterned wafer and consider the wafer top surface as a flat rotating disk with a diffusion boundary layer thickness \( h \). When the polarized wafer is immersed in the plating bath, copper deposition commences. The deposition is accompanied by the adsorption of PEG with fast adsorption kinetics. Our study of PEG adsorption on a flat RDE indicates that PEG adsorption is diffusion controlled. Therefore the rate constant \( k_{\text{ads}} \) for PEG adsorption is large in comparison to the diffusional mass-transfer coefficient \( k_{\text{int}} \),

\[
k_{\text{ads}} \gg k_{\text{int}} = \frac{D_{\text{PEG}}}{\delta} \approx 10^{-4} \text{ cm/s} \tag{1}
\]

We therefore arbitrarily set \( k_{\text{ads}} = 0.1 \text{ cm/s} \), which is three orders of magnitude higher than the lower limit defined by Eq. 1. Because the resistances for PEG diffusional transport and its adsorption are in series, the overall mass-transport coefficient for the complete transport process is

\[
\frac{1}{k_{\text{total}}} = \frac{1}{k_{\text{ads}}} + \frac{1}{k_{\text{int}}} \equiv \frac{1}{k_{\text{int}}} \tag{2}
\]

The approximation on the right side of Eq. 2 is the consequence of Eq. 1. Accordingly, the overall mass-transport coefficient for PEG is controlled by the diffusional mass transport and is relatively independent of the value of the arbitrarily selected adsorption rate constant. Consequently, the time constant of the overall process is expected to have a weak dependence on \( k_{\text{ads}} \).

In the following analysis of PEG transport and adsorption, which occurs on a time scale of a few seconds, we temporarily neglect the role of SPS in displacing the adsorbed PEG molecules, because this displacement occurs slowly, i.e., over a time interval of about 100 s (Fig. 6). In order to characterize the inhibition of the deposition kinetics on the via rim by the fast-adsorbing PEG, we solve the time-dependent diffusion equation for PEG within the diffusion boundary layer

\[
\frac{\partial C_{\text{PEG}}}{\partial t} = D_{\text{PEG}} \frac{\partial^2 C_{\text{PEG}}}{\partial z^2} \tag{3}
\]

We assume a one-dimensional diffusion to the electrode surface, neglecting the local effects introduced by the small vias or trenches. This analysis is valid when the vias or trenches occupy only a small fraction of the wafer surface. PEG adsorption on the copper surface proceeds at a rate given by

\[
\frac{\partial \theta}{\partial t} = \frac{1}{\Gamma_{\text{PEG}}} k_{\text{ads}} C_{\text{PEG}} (1 - \theta) \tag{4}
\]

where \( \theta \) is the PEG surface coverage and \( \Gamma_{\text{PEG}} \) is its saturation surface coverage. At \( z = 0 \), corresponding to the outer edge of the diffusion boundary layer, the PEG concentration is equal to its value in the bulk electrolyte. At \( z = h \) (the wafer surface), a mass balance on PEG gives

\[
-D_{\text{PEG}} \frac{\partial C_{\text{PEG}}}{\partial z} \bigg|_{z=h} = k_{\text{ads}} C_{\text{PEG}} (1 - \theta) \bigg|_{z=h} \tag{5}
\]

To nondimensionalize Eq. 3, we introduce the following parameters

\[
z^* = \frac{z}{h} \tag{6}
\]

\[
C^* = \frac{C_{\text{PEG}}}{C_{\text{PEG}}} \tag{7}
\]

\[
\tau^* = \frac{t D_{\text{PEG}}}{h^2} \tag{8}
\]

Substituting Eq. 6, 7, and 8 into Eq. 3, we get

\[
\frac{\partial C^*}{\partial \tau^*} = \frac{\partial^2 C^*}{\partial z^2} \tag{9}
\]

Initially, i.e., at \( \tau^* = 0 \), the PEG concentration everywhere is uniform and equal to \( C^* = 1 \). In the bulk electrolyte, i.e., at \( z^* = 0 \), \( C^* = 1 \) at all \( \tau^* \). At \( z^* = 1 \) (the wafer surface), the boundary condition given by Eq. 5, takes the dimensionless form
The time-dependent PEG concentration profile inside the diffusion boundary layer on the flat wafer. The PEG concentration near the electrode surface ($z^* = 1$) relaxes to 80% of its bulk value, i.e., $C^* = 0.8$ in about 10 s. This concentration, which approximates the PEG concentration at the via opening, is nearly equal to the bulk PEG concentration (100 ppm) for most of the via-fill duration. Model parameters are: $D_{PEG} = 5 \times 10^{-7}$ cm$^2$/s, $h = 60$ µm, $k_{ads} = 0.1$ cm/s, and $\Gamma_{PEG} = 6 \times 10^{-11}$ mol/cm$^2$.

$$\frac{\partial C^*}{\partial z^*} = -m_1 C^* \exp\left(-m_2 \int_0^w C^* dt^*\right)$$

where $m_1$ and $m_2$ are

$$m_1 = \frac{k_{ads} h}{D_{PEG}}$$
$$m_2 = \frac{k_{ads} C_{PEG} h^2}{\Gamma_{PEG} D_{PEG}}$$

The time-dependent PEG surface coverage is given by

$$\theta = 1 - \exp\left(-m_2 \int_0^w C^*|_{z=1} dt^*\right)$$

Equation 9, coupled with Eq. 13, was solved using a finite element algorithm to obtain the time-dependent PEG concentration profile inside the boundary layer as shown in Fig. 9. The concentration near the electrode drops rapidly, at short times, due to the adsorption of PEG. However, as the surface coverage of PEG on the electrode builds up, opposing further adsorption, the concentration gradient near the electrode drops to zero. This is accompanied by the slow relaxation of the concentration profile in the boundary layer, which asymptotically progresses to $C^* = 1$, i.e., no further concentration gradient throughout the entire diffusion boundary layer. Figure 9 also shows that the PEG concentration near the wafer flat surface, which can be approximated to the PEG concentration near the opening of a submicrometer scale via, relaxes to 80% of its bulk value in about 10 s. Therefore, for practical purposes, the concentration of PEG near the opening of the via during the majority of the via-fill duration (∼30-60 s) can be approximated as its value in the bulk. Equation 13 can be used to determine the time-dependent PEG surface coverage from the concentration profile. Figure 10 indicates that the PEG surface coverage on the flat wafer surface builds up to about 90% of its full saturation value in just 4-5 s, producing extremely fast inhibition. This low time constant for inhibition is the result of the large volume/area ratio at the wafer top surface. The availability of sufficient PEG near the electrode surface, the adsorption of which is fast, gives rise to the rapid inhibition. We re-emphasize that SPS activity during this time period has not been considered here because of the relatively longer time scale (>100 s) over which it affects the PEG-covered surface.

**PEG Transport inside the Via Accounting for Adsorption on the Sidewalls**

In order to extend the understanding of competitive adsorption on a flat electrode to submicrometer features and elucidate the role of additives in the bottom-up fill, we now consider the transport of additives inside the via. It was shown earlier that the rate of the electrode inhibition by PEG is controlled by its diffusional transport due to its low diffusion coefficient (∼$5 \times 10^{-7}$ cm$^2$/s). However, SPS diffuses rapidly (∼$10^{-5}$ cm$^2$/s) and therefore we can assume that SPS adsorption is not transport limited, i.e., the via geometry does not present diffusion resistance for SPS and its concentration inside the via is always maintained at its bulk value. Consequently, we must focus on analyzing the transport limitations on PEG inside the via and determine its transient surface coverage.

When a patterned wafer is immersed into a plating bath, the electrolyte penetrates the via instantaneously due to capillary forces. This electrolyte carries with it the full bulk additive composition. Due to the short radial diffusion length and the fast adsorption kinetics, PEG present in the electrolyte within the via begins to adsorb rapidly on the sidewalls and on the bottom of the vias and trenches. If the bulk PEG concentration is 100 ppm ($2.5 \times 10^{-2}$ mol/cm$^2$), the PEG available within a 0.1 µm diam, 1 µm deep via ($10^{-22}$ mol) is three orders of magnitude smaller than the PEG required to completely cover the via sidewalls and bottom ($10^{-19}$ mol). Therefore, fast adsorption of this small amount of PEG, which is insufficient to cause any significant effect on the electrode kinetics, results in its rapid depletion within the electrolyte inside the via, thereby giving rise to a PEG concentration gradient between the via exterior and the via interior. This also implies that the initial PEG surface coverage can be approximated to zero and any additional PEG must first diffuse from the exterior into the via before it can adsorb. The low PEG diffusion coefficient imposes significant limitations on this PEG transport.

Figure 11 represents a one-dimensional (axisymmetric) model for PEG transport inside a via. For high-aspect-ratio vias, the time constant for radial diffusion ($R^2 / D_{PEG}$) can be neglected in compari-
It was shown\textsuperscript{12} that a high-aspect-ratio cylindrical via with conducting sidewalls and a conducting bottom can be approximated by a similar via with an insulated bottom (Fig. 11b), i.e., at \( z = L \)
\[
\frac{dC_{\text{PEG}}}{dz} = 0 \quad \text{and} \quad \frac{\partial \theta}{\partial z} = 0
\]  \[19\]

As discussed earlier, assuming fast adsorption of the insignificant quantity of PEG present initially inside the via, the initial PEG concentration inside the via and its surface coverage can be set to zero. At \( t = 0 \)
\[
C_{\text{PEG}}(z) = 0 \quad \text{and} \quad \theta(z) = 0
\]  \[20\]

We nondimensionalize the transport equations by introducing the dimensionless parameters
\[
z^* = \frac{z}{L}
\]  \[21\]
\[
C^* = \frac{C_{\text{PEG}}}{C_{\text{PEG}}^b}
\]  \[7\]
\[
t^* = \left( \frac{1}{R_{\text{PEG}} k_{\text{ads}} C_{\text{PEG}}^b} \right)
\]  \[22\]

Substituting these dimensionless groups in Eq. 4 and 17, we obtain the following set of transport equations
\[
C_1 \frac{\partial C^*}{\partial t^*} - C_2 \frac{\partial^2 C^*}{\partial z^*^2} = -C^*(1 - \theta)
\]  \[23\]
\[
\frac{\partial \theta}{\partial t^*} = C^*(1 - \theta)
\]  \[24\]

where the constants \( C_1 \) and \( C_2 \) are given by
\[
C_1 = \frac{C_{\text{PEG}} R}{2 L_{\text{PEG}}}
\]  \[25\]
\[
C_2 = \frac{D_{\text{PEG}} R}{2 k_{\text{ads}} L_{\text{PEG}}^2}
\]  \[26\]

The boundary and the initial conditions take the dimensionless form
at \( z^* = 0 \), \( C^* = 1 \) and \( \theta = 1 \)
\[27\]
at \( z^* = 1 \), \( \frac{\partial C^*}{\partial z^*} = 0 \) and \( \frac{\partial \theta}{\partial z^*} = 0 \)
\[28\]
at \( t^* = 0 \), \( C^* = 0 \) and \( \theta = 0 \)
\[29\]

Equations 23 and 24, with Eq. 27 and 28 as the boundary conditions, and Eq. 29 as the initial condition, were solved numerically to obtain the time-dependent PEG surface coverage at different positions along the via sidewalls. A nonlinear increase with time of the portion of the sidewalls that are saturated with PEG (\( \theta = 1 \)) is noted (Fig. 12). At short times (<1 s), almost 40% of the via sidewall (0 \( \leq z^* \leq 0.4 \)) is occupied by PEG, as indicated by the PEG surface coverage exceeding 0.2 in this region. Our steady-state polarization measurements indicate significant inhibition when the bulk concentration of PEG exceeded 3 ppm. This corresponds to a fractional surface coverage of 0.2 and therefore, we assume that this surface coverage is sufficient to cause significant inhibition. By contrast, the time required for PEG to reach the via bottom (as shown in Fig. 12) is about 10 s, which is two orders of magnitude larger than the time constant calculated from \( L_{\text{PEG}}^2 / D_{\text{PEG}} = 0.02 \) s. The larger time constant for PEG diffusional transport inside the via is the consequence of its adsorptive consumption on the sidewalls. The 1 \( \mu \)m deep via therefore behaves, with respect to PEG diffusional...
transport to its bottom, as if it were equivalent to a 22 μm deep via, i.e., $L_{eq} \approx (aD_{PEG})^{1/2}$ where $\tau = 10$ s (from the solution of the transport equations) and $D_{PEG} = 5 \times 10^{-7}$ cm$^2$/s. If PEG alone was used as an additive (in addition to Cl$^-$), it would promote bottom-up growth during the initial 10 s due to the transport delay of the inhibiting PEG, but after about 10 s, diffusing PEG reaches the via bottom and nullifies the differential kinetics between the via top and its bottom. Therefore, if PEG alone is used, the current density (or the deposit growth rate) at the via bottom and at the via top equalize after about 10 s, forcing the deposition to a conformal growth. Because the normal duration of the via fill is 30-60 s and accelerated bottom-up growth in the presence of PEG alone cannot be sustained for more than 10 s, it is clear that PEG by itself cannot generate bottom-up fill.

**Effect of PEG Transport Delay on the Electrode Kinetics:**

**RDE Simulation**

Because the RDE allows precise control of the diffusion boundary layer thickness and presents a well-defined and easily accessible electrode area, we apply this device as a model system for simulating additive transport, instead of the less accessible via.

The analysis presented indicates that PEG by itself cannot produce a bottom-up fill. The essential presence of SPS in order to obtain superconformal growth is well recognized. The transient electrode polarization measurements performed on a flat electrode indicate that SPS counteracts the inhibition provided by PEG and depolarizes the electrode. In order to analyze the role of SPS in via plating, we simulate the via rim and the via bottom on a RDE. The via rim is characterized by a thin diffusion boundary layer and a lower current density. The via bottom is characterized by a much larger diffusion boundary layer (~20 μm larger than at the via top) and a higher current density. We consider the wafer immersion and plating process as one in which the wafer is placed in the plating bath and the additives are instantaneously introduced. We simulate the via top as an RDE rotating at 200 rpm (equivalent to $\delta \sim 40$ μm) and plating at a current density of 15 mA/cm$^2$. The via bottom was simulated as an RDE rotating at 90 rpm (equivalent to $\delta \sim 60$ μm; 20 μm larger than at the top) and plating at $i = 30$ mA/cm$^2$. Additives were injected at a known time interval and the potential response (corrected for the ohmic and mass-transfer overpotentials) was recorded. The ohmic overpotential was about 50 mV at $i = 15$ mA/cm$^2$ and about 100 mV at $i = 30$ mA/cm$^2$; the mass-transport overpotential (<5 mV) was negligible. The kinetic resistance was calculated as

$$R_k = \frac{\Delta V - \eta_0 - \eta_i}{iA} = \frac{\eta_i}{iA}$$

The results (Fig. 13) show that the kinetic resistance at the via top remains high in comparison to the via bottom. This implies that under potentiostatic conditions, the current density at the via bottom is larger than that near the via top for approximately the first 100 s, a longer duration than the 30-60 s typically required for via fill. The rationale for this is that the thinner diffusion boundary layer accommodates a faster diffusional transport of PEG to the via rim, which inhibits plating within the first 10 s, i.e., almost instantaneously. However, as time passes, deposition at the via rim is accelerated due to slower PEG displacement by the adsorbing SPS. The transport of PEG to the via bottom is relatively slow due to the significant adsorption of PEG on the via sidewalls. This provides the SPS, which is not transport limited and reaches the bottom readily, with sufficient time to adsorb preferentially on the via bottom. Transient polarization measurements on the flat electrode (Fig. 5) indicate that the SPS adsorption on an additive-free surface (like the via bottom where PEG arrival is delayed due to the diffusional transport resistance) is relatively fast with a time constant of <5 s. The outcome is that the polarization of the via bottom is small and copper deposition proceeds at rates closer to those of the SPS-accelerated kinetics. The delayed arrival of PEG at the via bottom again reduces the significant inhibition. Relatively long time (~10 s) is required for PEG coverage to reach 0.2 at the via bottom. The horizontal dotted line at $t = 0.2$ indicates that after 8 s, the lowest 5% ($z^* = 0.95$) of the sidewalls is approaching 20% PEG coverage. By this time (8 s) the via bottom ($z^* = 1$) has reached a PEG coverage of only 0.1. Model parameters are $k_{a,w} = 0.1$ cm/s, $D_{PEG} = 5 \times 10^{-7}$ cm$^2$/s, and $\Gamma_{PEG} = 6 \times 10^{-11}$ mol/cm$^2$.

**Figure 12.** Time-dependent PEG surface coverage inside a 0.1 μm diam, 1 μm deep via. Within a short time (~1 s) the PEG occupies 38% of the via sidewalls at a surface coverage of at least 0.2, which is sufficient to impart significant inhibition. Relatively long time (~10 s) is required for PEG coverage to reach 0.2 at the via bottom. The horizontal dotted line at $t = 0.2$ indicates that after 8 s, the lowest 5% ($z^* = 0.95$) of the sidewalls is approaching 20% PEG coverage. By this time (8 s) the via bottom ($z^* = 1$) has reached a PEG coverage of only 0.1. Model parameters are $k_{a,w} = 0.1$ cm/s, $D_{PEG} = 5 \times 10^{-7}$ cm$^2$/s, and $\Gamma_{PEG} = 6 \times 10^{-11}$ mol/cm$^2$.

**Figure 13.** Kinetics resistances at the via top and bottom, simulated by RDE experiments. The kinetic resistance is defined as the ratio of the activation overpotential to the deposition current. The resistance at the via bottom always remains smaller than that on the via top. Deposition was carried out from an acidified 0.5 M CuSO$_4$ (pH ~7) on a disk electrode rotating at 90 and 200 rpm. 50 ppm SPS + 100 ppm PEG were injected at $t = 10$ s.
The Via Fill Process

Transient additives interactions, as shown previously, play a crucial role in the bottom-up fill process. The key aspects of these transient interactions are:

1. PEG strongly inhibits the copper deposition kinetics. The rate of inhibition is controlled by the diffusional transport of the relatively large PEG molecules to the electrode surface.

2. SPS de polarizes the PEG-covered electrode, most likely by displacing PEG. However, SPS adsorption on a copper surface that is already saturated by PEG occurs slowly with a time constant of about 100 s. By contrast, SPS adsorption on an additive-free surface is a relatively fast process with a time constant of less than 5 s. SPS diffusional transport is extremely fast, and consequently, SPS adsorption on a PEG-free surface is controlled by the adsorption kinetics and not by transport.

3. During competitive adsorption of SPS and PEG, when both species are simultaneously present in the electrolyte next to the electrode, PEG preferentially adsorbs on the electrode, due to its faster adsorption kinetics (as compared to SPS), and inhibits the kinetics of the deposition reaction. As time passes, SPS gradually displaces the adsorbed PEG, thereby depolarizing the electrode.

Coupling this quantitative understanding of the time-dependent additive interactions during copper deposition on a flat electrode with the characteristics of the transport process within the via as analyzed previously, we now propose a model for the transient additive interactions during the bottom-up fill process (Fig. 14):

1. Flat wafer surface (short times): When the wafer is immersed into the plating electrolyte, PEG present near the wafer surface adsorbs instantaneously and inhibits the deposition on the via top surface. SPS present near the flat surface starts displacing the adsorbed PEG; however, the rate of this displacement is extremely slow. For the normal duration of the via fill (30-60 s), the flat wafer surface remains significantly inhibited.

2. Via sidewalls (short times): When a patterned wafer is immersed into the plating solution, capillary forces carry the electrolyte with its full bulk composition into the via. Due to the high area/volume ratio inside the via, the small radial diffusion length, and the fast PEG adsorption kinetics, PEG present initially inside the via (corresponding to ~100 ppm bulk PEG concentration) rapidly adsorbs on the side walls and on its bottom. This results, however, in only an extremely low PEG surface coverage and therefore causes hardly any inhibition. The PEG depletion within the via gives rise to a PEG concentration gradient between the via interior and its exterior, causing PEG diffusional transport into the via. The characteristics of this PEG transport and inhibition were discussed previously (Fig. 12): rapid (~1 s) inhibition of the top 40% of the via sidewalls and slow (~10 s) transport of PEG to the via bottom. The major portion of the via sidewalls, therefore, is rapidly inhibited by PEG. SPS, which is not diffusion limited, starts displacing the adsorbed PEG; however, this process is slow and for the normal duration of via fill (~30-60 s), the upper portion of the via sidewalls remains highly inhibited.

3. Via bottom (short times): PEG transport to the via bottom occurs slowly (~10 s). This provides sufficient time for SPS to adsorb, given that SPS adsorption kinetics on an additive-free surface is relatively fast. Therefore, SPS accelerates the kinetics at the via bottom before PEG ever reaches this region. Figure 13 indicates that if SPS is allowed time to adsorb on the electrode before PEG reaches it, only marginal polarization occurs. This implies that once SPS has adsorbed on the surface, the inhibiting PEG can no longer displace it, and the bottom keeps propagating rapidly.

4. Flat wafer surface and the propagating via fill (long times): The kinetics at the via top region are essentially inhibited during the via-fill period; however, as the via fill approaches completion, i.e., after about 60 s, the inhibition provided by PEG is eventually counteracted by SPS, which gradually displaces the PEG, depolarizing the via top. Because the complete recovery of the SPS accelerated kinetics requires more than 100 s, the recovery during the first 30-60 s is marginal as compared to the noninhibited, high current density at the via bottom (50-100 mA/cm²). It should be noted, however, that if the via bottom does not propagate at sufficiently high current densities (e.g., due to the application of too low current or voltage), longer time is available for the recovery of the accelerated kinetics on the via sidewalls and the top surface, leading to the possible formation of a seam or a void.

Simulation of via fill.—In order to simulate the bottom-up fill process, the additive-modified kinetics of copper deposition, which are position-dependent, must be known. The exact simulation of the
bottom-up fill process requires the local current density, which is determined by solving the Nernst-Planck transport equations, in conjunction with the position-dependent copper deposition kinetics. The moving boundaries, due to the fill process, introduce further complications and necessitate the use of robust numerical simulation. The positioning, due to the fill process, introduce future complications and necessitate the use of robust numerical simulation algorithms. Such simulations are discussed elsewhere and are not employed here. Instead, we demonstrate semiquantitatively the deposit growth in high-aspect-ratio vias by assigning position- and time-dependent kinetics for the copper deposition that are determined from transient polarization measurements.

To measure the time-dependent kinetics on the via top surface, via sidewalls, and the via bottom, we injected 100 ppm PEG + 50 ppm SPS into acidified 0.5 M CuSO$_4$ (pH ~2) containing 70 ppm Cl$^-$ during copper deposition at various current densities (5-60 mA/cm$^2$) on a RDE rotating at 50 rpm. The electrode potential response was measured and corrected for the ohmic and mass-transport overpotentials, thus providing the activation overpotential as a function of the current density and time after injection:

$$\eta_{a}(i,t) = V(i,t) - \eta_{0}(i) - \eta_{a}(i)$$  \[31\]

Assuming Tafel kinetics, the activation overpotential is related to the current density by

$$\eta_{a}(i,t) = \frac{RT}{\alpha_F} \ln \left( \frac{i}{i_0} \right)$$  \[32\]

where $\alpha_a$ and $i_0$ are the cathodic charge-transfer coefficient and the cathodic exchange current density, respectively. Thus, at any time $t$, after the additives injection, we obtain $\eta_a$ from electrode potential measurements under galvanostatic conditions and estimate the time dependence of the kinetic parameters $\alpha_a$ and $i_0$. Figure 15 shows the variation of the activation overpotential with the applied current density and time. For these RDE experiments, which correspond to the via rim and via sidewalls, fast polarization (inhibited kinetics) with a short time period (<10 s), followed by slow depolarization (due to the slow displacement of adsorbed PEG by SPS), is observed. The parameters of these inhibited kinetics, which were applied to the via top and the via sidewalls during the fill simulations, are listed in Table I. The via bottom was simulated using accelerated kinetics corresponding to SPS + Cl$^-$ alone (Fig. 15) as per our previous analysis. The kinetic parameters for this location (bottom) were $\alpha_a = 0.83$ and $i_0 = 1.12$ mA/cm$^2$.

In order to simulate the fill process, the deposit growth rate at the via rim, via sidewalls, and the via bottom was calculated using Faraday’s law

$$y(z,t) = \frac{Mt}{Fpn}(z,t)$$  \[33\]

where $M$ is the molecular weight of copper, $F$ is Faraday’s constant, $p$ is the density of copper, and $n$ is the number of electrons transferred. The current density $i(z,t)$ was calculated using the time and position-dependent kinetic parameters listed in Table I for copper deposition at an overpotential of 120 mV. The electrode boundaries were translated, step-wise, depending on the calculated growth rate from Eq. 33, generating the progression of the growth profiles shown in Fig. 16. The growth profiles indicate an accelerated bottom-up growth at the via bottom. During the initial stages of the via-fill, insignificant growth occurs on the via sidewalls and the via top surface due to their inhibited kinetics. However, the current density on these faces gradually increases with time. Figure 16 indicates

![Figure 15. Polarization curves for steady-state SPS + Cl$^-$ kinetics (the left-most curve, representing the via bottom) and unsteady-state SPS + PEG + Cl$^-$ kinetics (the progression of curves on the right), corresponding to the via rim and sidewalls, indicating slow depolarization. The kinetics were measured for copper deposition from an acidified 0.5 M CuSO$_4$ (pH ~2), with the indicated additives, on an RDE rotating at 50 rpm.](image)

![Figure 16. Simulations of bottom-up fill in a via with $R = 0.05$ μm and $L = 1$ μm at an overpotential of 120 mV. Note the sustained accelerated growth of the bottom due to the adsorbed SPS (in the absence of the diffusion-hindered PEG). The growth rate on the sidewalls and the via rim (which is covered by the slower diffusing but faster adsorbing PEG) is slowly accelerated by the gradual displacement of the adsorbed PEG by SPS. The kinetics parameters are listed in Table I. All dimensions are in micrometers.](image)

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>$\alpha_a$</th>
<th>$i_0$ (mA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-10</td>
<td>0.9</td>
<td>0.0031</td>
</tr>
<tr>
<td>10-20</td>
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<tr>
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</tr>
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</tr>
<tr>
<td>50-60</td>
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<td>0.0472</td>
</tr>
</tbody>
</table>

*These kinetics parameters, which correspond to the via rim and its sidewalls, were applied in the fill simulations.
that the via fill is completed, under the simulated conditions, within about 50 s, corresponding to an average current density of 54 mA/cm² on the via bottom. As stated earlier, the details of the exact shape evolution during the bottom-up fill are not considered here but are analyzed in a subsequent publication.14

Conclusions

Transient electrode potential measurements provide valuable information about PEG and SPS adsorption time constants. Because the adsorption kinetics of the inhibiting PEG are fast, its surface adsorption is controlled by transport (τ_{PEG} ≈ 10 s at the via bottom). The depolarizer, SPS, which diffuses rapidly but adsorbs slowly, displaces PEG gradually (τ_{SPS} ≈ 100 s), enhancing the copper deposition kinetics. An important outcome of modeling the PEG transport and adsorption inside a via is that PEG requires about 10 s to diffuse down the via length because of its adsorption on the sidewalls. This slow diffusion coupled with the fast adsorption of SPS on the initially additives-free via bottom leads to faster deposition kinetics at the bottom as compared to the via top. The via-top surface remains inhibited due to the large PEG diffusional flux and the slow displacement of adsorbed PEG by SPS. Based on transient electrode polarization measurements and analysis of additive interactions, a model for bottom-up fill of high-aspect-ratio vias is presented. The time-dependent additive interactions and the additive-modified kinetics were used to semiquantitatively model the bottom-up fill process. The analysis indicates that a defect-free bottom-up fill requires an additive mixture with special characteristics: an inhibiting additive (PEG) that is transport limited but adsorbs fast, and an accelerator (SPS) that diffuses rapidly but adsorbs slowly, yet, probably due to its stronger binding to copper, displaces the PEG and gradually counteracts the inhibition provided by PEG.

Acknowledgments

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List of Symbols

\[A\] electrode area, cm²
\[C_1, C_2\] constants in PEG transport equations, dimensionless
\[D\] diffusion coefficient, cm²/s
\[F\] Faraday’s constant, 96,480 C/equiv
\[h\] diffusion layer thickness on the flat wafer surface, \(60 \times 10^{-4}\) cm
\[i_c\] exchange current density, A/cm²
\[k\] rate constant, cm/s
\[L\] via depth, cm
\[m_1, m_2\] constants in PEG transport equations, dimensionless
\[M\] molecular weight of copper, 63.55 g/mol
\[n\] number of electrons transferred during copper deposition, 2
\[N\] adsorption flux, mol/cm² s
\[N^t\] diffusional transport flux, mol/cm² s
\[R\] via radius, cm
\[R_a\] activation resistance, \(\eta_i / A\) Ω
\[R_g\] universal gas constant, 8.314 J mol⁻¹ K⁻¹
\[t\] time, s
\[T\] temperature, K
\[V\] measured voltage at the cathode, V
\[y\] deposit thickness, cm
\[z\] position coordinate, cm

Greek

\[\alpha_c\] cathodic transfer coefficient, equiv/mol
\[\delta\] diffusion boundary layer thickness, cm
\[\eta\] overpotential, V
\[\theta\] surface coverage, dimensionless
\[\rho\] density of copper, 8.92 g/cm³
\[\tau\] time constant, s
\[\Gamma\] surface concentration at saturation, mol/cm²

Subscripts

a activation
ads adsorption
c concentration
mt mass transport
PEG polyethylene glycol
SPS bis(3-sulfopropyl) disulfide

Superscript

* dimensionless quantity

References