Bottom-Up Copper Filling of Millimeter Size Through Silicon Vias

D. Josell, L. A. Menk, A. E. Hollowell, M. Blain, T. P. Moffat

1Materials Science and Engineering Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20878, USA
2Microsystems and Engineering Sciences Applications (MESA) Complex, Sandia National Laboratories, Albuquerque, New Mexico 87123, USA

Abstract

This work demonstrates void-free Cu filling of millimeter size Through Silicon Vias (mm-TSV) in an acid copper sulfate electrolyte using a combination of a poloxamine suppressor and chloride, analogous to previous work filling TSV that were an order of magnitude smaller in size. For high chloride concentration (i.e., 1 mmol/L) bottom-up deposition is demonstrated with the growth front being convex in shape. Instabilities in filling profile arise as the growth front approaches the free-surface due to coupling with electrolyte non-uniform hydrodynamics. The reentrant notches at the bottom of the TSVs caused by intentional over-etching during fabrication negatively impact the filling results. In contrast, deposition from low chloride electrolytes (i.e., 80 μmol/L) proceeds with a passive-active transition on the via sidewalls. For a given applied potential the location of the transition is fixed in time and the growth front is concave in nature reflecting the gradient in chloride surface coverage. Application of a suitable potential wave form enables the location of the sidewall transition to be systematically advanced thereby giving rise to void-free filling of the TSV.

Electrochemical deposition for fabrication of interconnects and devices spans multiple length scales. For fabrication of very large features, through-mask deposition, in which electrical contact is made to a common backplane and the insulating side walls of the template constrain growth to propagation from the bottom of the feature, is often used. Absent subsequent subtractive processing of the common back-plane, the as-built structures are electrically tied, making fabrication of electrically complex multilevel structures difficult if not impossible. In contrast, in Damascene processing the entire templated surface is first metallized for conductivity and then recessed surface features are filled in a void-free manner by either superconformal or bottom-up electrodeposition processes, the growth dynamics determined by additives in the electrolyte. Planarization of the surface yields electrical isolation of the metal filled features while templating and filling repeated ad infinitum can produce intricate multilevel structures of arbitrary connectivity.
The shift toward 3D stacking of computer chips for improved performance has motivated substantial interest in filling of Through Silicon Vias (TSV) that, tens of micrometers in size, dwarf on-chip Damascene features. Concentration gradients in these larger features challenge the ability of conventional superconformal processes that utilize competitive adsorption of deposition-accelerating and suppressing additives to provide void-free filling of submicrometer Damascene features. Alternatively, bottom-up deposition can be obtained in electrolytes containing just suppressing additives (suppressors) that yield S-shaped Negative Differential Resistance (S-NDR) behavior associated with suppression breakdown during voltammetry. Deposition is localized at, or toward, the bottoms of filling features by the nonlinear dependence of suppressor coverage on suppressor concentration as defined by its transport, adsorption and coupling to, and disruption and/or incorporation by, metal deposition. The bottom-up filling evolution is accurately captured by models based on the S-NDR and related suppressor breakdown mechanism.

Among the systems examined are electrolytes containing poloxamine and chloride that co-adsorb to form the suppressor layer that underlies bottom-up Cu filling of 56 μm deep annular TSV. Feature filling based on this additive system has been explored over a broad range of deposition conditions in electrolytes containing 1 mmol/L Cl\(^-\) and 20 μmol/L to 80 μmol/L poloxamine (variable polyether and fixed high Cl\(^-\)) as well as electrolytes containing 20 μmol/L to 80 μmol/L Cl\(^-\) and 40 μmol/L poloxamine (fixed polyether and variable low Cl\(^-\)). A single additive S-NDR model, based on disruption of the passivating polyether by metal deposition with the kinetic parameters obtained from electroanalytical measurements under well-defined hydrodynamics, captures the experimental TSV filling in the high-Cl\(^-\) electrolytes for a range of micromolar polyether concentrations. A two-additive model of Cl\(^-\)-limited polyether adsorption with kinetics obtained from analogous voltammetry predicts experimental TSV filling in the low Cl\(^-\) electrolytes. The two-additive model, where polyether adsorption is required to remain at or below the coverage of Cl\(^-\), differs from prior two-additive models that follow the competitive adsorption between an accelerator and suppressor.

Recently, the high Cl\(^-\)-polyether additive combination was shown to provide bottom-up Cu deposition in the millimeter scale TSV (mm-TSV) that are also the focus of this study albeit using a sulfonic acid electrolyte that permits a higher Cu\(^{2+}\) concentration. Rapid filling, likely limited by metal ion transport, was obtained at the large overpotentials required to maintain active deposition in the, comparatively speaking, highly suppressed system. Growth instabilities associated with operation in steep gradients were evident during the later stages of filling whereby a subset of the more fully filled TSVs capture a disproportionate share of deposition current, particularly as their growth fronts exit the via mouth. The result was variable deposition heights over and around filled features. In contrast, low Cl\(^-\) electrolytes can yield deposition where the transition from passive to active occurs at a fixed distance down the sidewalls of the features defined by the applied potential. Upon impingement of the sidewall subsequent growth may shift to bottom-up filling or, alternatively, potential ramping or stepping may be implemented to fully fill the features. Analogous behavior has been demonstrated with Ni, Au and Co filling of TSV in suppressor-containing electrolytes and predicted using single additive S-NDR models. While similar behavior may also be obtained in electrolytes containing accelerating and
suppressing additives in combination,\textsuperscript{17–23} concentration gradients make the use of accelerators more problematic for electrodeposition in millimeter sized TSV than for conventional micrometer scale TSV.

This study examines filling of mm-TSV using copper sulfate electrolytes with both the high Cl\textsuperscript{−} + polyether and low Cl\textsuperscript{−} + polyether additive combinations previously detailed for filling of smaller TSV. Filling in the high Cl\textsuperscript{−} electrolyte complements the recent study of mm-TSV filling in sulfonic acid.\textsuperscript{25}

\section*{Experimental}

Depositions were conducted at room temperature in a cell containing 40 mL of 1 mol/L CuSO\textsubscript{4} and 0.5 mol/L H\textsubscript{2}SO\textsubscript{4}. The poloxamine suppressor (Tetronic 701, ethylenediamine tetrakis (propoxylate-\textit{block}-ethoxylate) tetrox, (PEO\textsubscript{4}PPO\textsubscript{12})\textsubscript{2}ED(PPO\textsubscript{12})PEO\textsubscript{4}\textsubscript{2}, average molecular mass \approx 3600, Aldrich, TET) concentrations were obtained through addition of aliquots from a master solution of 1 mmol/L poloxamine dissolved in 18 MΩ water while the chloride concentrations were obtained by addition of aliquots from a master solution of 5 mmol/L NaCl dissolved in 18 MΩ water. Sparging with argon was used between electrochemical measurements to reduce parasitic currents associated with dissolved oxygen. A Hg/Hg\textsubscript{2}SO\textsubscript{4}/saturated K\textsubscript{2}SO\textsubscript{4} reference electrode (SSE) was connected to the working electrode compartment via a fritted bridge filled with a saturated solution of K\textsubscript{2}SO\textsubscript{4}. All experiments were conducted at potentials relative to this reference. A platinum counter electrode was held in a frit-separated cell immersed within the main cell.

Feature filling was performed using wafer fragments approximately 1 cm × 1 cm in area patterned with vias \approx 625 \textmu m deep and 125 \textmu m in diameter (mm-TSV). The vias have a uniform Pt seed layer deposited by atomic layer deposition, including along the reentrant notch profile at the bottoms of the vias created by intentional over-etch during their fabrication. To give definition to the metal ion and additive transport, the patterned substrates rotated about one end from a Pt spindle during deposition, like a helicopter blade, with the patterned surface facing up. Based on the \approx 1 cm distance between the features and rotational axis for most of the imaged TSVs, a 400 rpm (800\pi rad/min) rotation rate corresponds to an estimated 40 cm/s flow rate over the surface. Vacuum evacuation followed by wetting with ethyl alcohol was used to displace air bubbles that would otherwise be trapped in the TSVs during the Cu deposition. The alcohol pre-wetted specimens were immersed and then rotated at a potential of \approx -0.40 V relative to the reference (an overpotential of \approx 20 mV based on the measured reversible potential of \approx -0.38 V) for two minutes to mix the electrolyte with the alcohol in the TSVs. The deposition potential was applied immediately thereafter. For the conditions used, terminal effects due to seed layer resistance are anticipated to be negligible, and there was no experimental indication to the contrary.

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Deposition on Patterned Substrates

Low chloride concentration

Cross-sectioned mm-TSV following 1 hr of Cu deposition in electrolyte containing 40 μmol/L TET and 80 μmol/L Cl\(^-\) (low Cl\(^-\)) are shown in Figure 1. Based on earlier study of localized deposition in 56 μm deep annular TSV, filling of the mm-TSV was examined at applied potentials between -0.51 V and -0.56 V that lie within the hysteretic voltammetric window previously identified.\(^1\) Deposition is localized in the via bottom, with the position of the passive-active transition moving up the sidewall toward the via mouth at more negative potential. Extended deposition at -0.51 V reveals a shift to upward filling of the via with deposition time that is captured in Figure 2. The upward motion can be accelerated by stepping the potential to more negative values during growth. As shown in Figure 3 the height of the deposit near the sidewall increases when 6 hr at -0.51 V is replaced by three 2 hr steps from -0.51 V to -0.53 V. The position of the sidewall passive-active threshold advances even further when the potential is replaced by six 1 hr steps from -0.51 V to -0.56 V. Despite the additional material required to fill the “foot” along the perimeter of the via bottom (created by the over-etch during fabrication), the growth front develops a v-notch shape, the notch deepening during growth over the wider potential range. This notch in the Cu growth front is analogous to that seen during filling of Cu-seeded TSV using the Cu low Cl\(^-\) electrolyte as well as the Au, Co and Ni S-NDR systems\(^1\)\(^2\)\(^6\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(^\)\(J Electrochem Soc. Author manuscript; available in PMC 2020 October 08.)
electrolyte. The deposit height in the via middle is a maximum, rather than minimum as in Figs. 1 to 4. This suggests difficulty in metal growth proceeding on and up the passivated sidewalls. There is also an asymmetry at the via top that is associated with the direction of fluid flow. Finally, and most significantly for practical application, there is a cusp near the sidewall. These cusps frequently reach the sidewall, particularly as growth approaches the mouth of the mm-TSV (Figure 7). Because the flow direction is generally not parallel to the rows of mm-TSV (the sectioning direction), the full depth of the cusps is generally not reflected in the images.

While deposition proceeds a substantial distance up the mm-TSV at fixed applied potential, comparison of the mm-TSV filled for 7 hr at −0.62 V (Figure 7c) and 12 hr at −0.62 V (Figure 7d) in high Cl\(^{−}\) electrolyte containing 1 mmol/L Cl\(^{−}\) and 50 μmol/L poloxamine makes clear that active deposition stops before the deposit reaches the via mouth. In contrast, the deposition in the low-Cl\(^{−}\) electrolyte in Figure 5 proceeds to just below the via mouth despite a final potential 60 mV positive of that used here. The difference results from the greater suppression obtained with the higher Cl\(^{−}\) concentration even at lower poloxamine concentrations.\(^{11,12}\) Consistent with previously detailed Cu filling of TSV in the low Cl\(^{−}\) electrolyte,\(^{12}\) a change to slightly more negative potential (by −20 mV) moves the passive-active transition higher in the mm-TSV (Figure 7e) giving rise to further filling. It is to be noted that in this instance the potential step program involved an intermediate step to −0.8 V for 2 s to ensure reactivation of the growth front after 4 hours at −0.62 V and prior to finishing at −0.64 V. The bottom of the voided region close to the sidewall marks the position of the growth front and thereby the extent of filling after the first 4 hr at −0.62 V. In an alternative approach, concurrent reduction of the rotation rate with the potential step from −0.62 V to −0.64 V can be used to ensure that the deposit fully exits the mouth of the via (Fig. 7f), despite reduced time at −0.64 V. The above observations are consistent with similar experiments performed with smaller TSV in the low Cl\(^{−}\) electrolyte.\(^{12}\)

Interestingly there is only a very modest enhancement of deposition at the bottom of the mm-TSV if a lower rotation rate such as 100 rpm or even 200 rpm is used from the start of deposition; bottom-up filling does not initiate at the same potentials and additive concentrations used with Fig. 7 (not shown). The same is true at −0.66 V. Reduced transport of suppressor would be expected to produce the opposite behavior; this indicates the impact of reduced transport of metal ion, i.e., an insufficient deposition rate to maintain an actively growing surface.

**Discussion**

As previously detailed with micrometer scale TSV, the filling of millimeter TSV with Cu based on polyether-Cl suppressor chemistry can be controlled using two different strategies that depend on the Cl\(^{−}\) concentration. For low Cl\(^{−}\) concentration, suppression breakdown is determined by flux limitation on the Cl\(^{−}\) whose co-adsorption is required to form the blocking polyether-Cl\(^{−}\) suppressor phase.\(^{13}\) The transition from passivated surface to active deposition is localized at fixed depth in the TSV that reflects the balance point between the concentration- and transport-dependent rate of halide adsorption onto the surface and the potential-dependent rate of its removal by consumption.\(^{12}\) This is congruent with previous
S-NDR bifurcation models of feature filling that capture discontinuous deposition within features due to gradients in additive and metal ion concentration that translate to potential-dependent depth of suppression breakdown. Accordingly, the use of monotonically increasing applied overpotential enables well-controlled feature filling. In contrast, at higher Cl\(^{-}\) concentration bottom-up filling is associated with disruption of polyether adsorption on the advancing surface and is associated with convex growth front analogous to previous results observed in micron scale TSV.

**Conclusions**

The void-free filling of millimeter scale TSV with Cu is demonstrated using a CuSO\(_4\)-H\(_2\)SO\(_4\) electrolyte containing micromolar poloxamine concentration with either a low (80 \(\mu\)mol/L) or high (1 mmol/L) Cl\(^{-}\) concentration. The low and high chloride electrolytes give rise to distinctly different growth morphologies during feature filling. For electrolytes with 1 mmol/L Cl\(^{-}\) + 40 \(\mu\)mol/L poloxamine, bottom-up filling occurs with a growth front exhibiting a convex shape that is amplified initially by the over-etched regions at the bottom of the via. As the growth front approaches the free surface, via to via variations in fill height due to variations in the hydrodynamics are evident. In contrast, deposition from the electrolytes with a lower chloride concentration occurs by suppression breakdown on the sidewall due to the limited flux of Cl\(^{-}\) required to form the passivating layer. For a given applied potential the location of the passive-active transition is fixed and the growth front has a concave shape whose dimension and shape reflect the gradients in Cl\(^{-}\) coverage. Importantly, with an appropriate potential waveform the position of the passive-active transition can be advanced upwards to enable feature filling.

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Figure 1.
Cross-sectioned mm-TSV after 1 hr Cu deposition at the indicated applied potentials in low Cl$^-$ electrolyte containing 80 μmol/L Cl$^-$ + 40 μmol/L TET. All were preceded by 2 min at −0.40 V to mix electrolyte into the alcohol-prewetted features. The patterned substrates were rotating at 400 rpm during deposition. Insets are at 2 × relative magnification.
Figure 2.
Cross-sectioned mm-TSV showing Cu filling after the indicated deposition times at $-0.51$ V in low Cl$^-$ electrolyte containing $80$ μmol/L Cl$^-$ + $40$ μmol/L TET. All were preceded by 2 min at $-0.40$ V to mix electrolyte into the alcohol-prewetted features. The patterned substrates were rotating at 400 rpm during deposition. Insets are at $2 \times$ relative magnification.
Figure 3.
Cross-sectioned mm-TSV showing Cu filling after 6 hours of deposition: a) 6 hr at −0.51 V, b) 2 hrs at −0.51 V, −0.52 V, −0.53 V and c) 1 hr at −0.51 V, −0.52 V . . . −0.56 V. All were preceded by 2 min at −0.40 V to mix electrolyte into the alcohol-prewetted features. The low Cl\(^-\) electrolyte contained 80 μmol/L Cl\(^-\) + 40 μmol/L TET. The patterned substrates were rotating at 400 rpm during deposition.
Figure 4.
Cross-sectioned mm-TSVs showing the evolution of Cu filling during deposition at a sequence of potentials stepped from −0.51 V (top) to −0.56 (bottom) in 10 mV increments. Deposition times were (left) 1 hr or (right) 1.5 hr at each potential from −0.51 V to −0.55 V, finishing with 5 hr at −0.56 V in each case, for total deposition times of 10 hr and 12.5 hr, respectively. All were preceded by 2 min at −0.40 V to mix electrolyte into the alcohol-prewetted features. The low Cl\(^-\) electrolyte contained 80 μmol/L Cl\(^-\) + 40 μmol/L TET. The patterned substrates were rotating at 400 rpm during deposition.
Figure 5.
Cross-sectioned mm-TSVs showing Cu filling obtained by stepping in 10 mV increments from −0.51 V to −0.56 V. Deposition times were (a) 3 hr at each potential from −0.51 V to −0.55 V followed by 0.75 hr at −0.56 V, (b) 1 hr at each potential from −0.51 V to −0.55 V followed by 5 hr at −0.56 V and (c) 1.5 hr at each potential from −0.51 V to −0.55 V followed by 5 hr at −0.56 V. Total deposition times are thus a) 15.75 hr, b) 10 hr and c) 12.5 hr. All were preceded by 2 min at −0.40 V to mix electrolyte into the alcohol-prewetted features. The low Cl\(^-\) electrolyte contained 80 μmol/L Cl\(^-\) + 40 μmol/L TET. The patterned substrates were rotating at 400 rpm during deposition.
Figure 6.
Cross-sectioned mm-TSVs showing Cu filling after the indicated deposition times at −0.60 V in high Cl$^-$ electrolyte containing 1 mmol/L Cl$^-$ and 25 μmol/L TET. All were preceded by 2 min at −0.40 V to mix electrolyte into the alcohol-rewetted features. The patterned substrates were rotating at 400 rpm during deposition.
Figure 7.
Cross-sectioned mm-TSVs showing Cu deposition after a) 3 hr and b) 5.75 hr at −0.61 V in high Cl\(^{-}\) electrolyte containing 1 mmol/L Cl\(^{-}\) and 35 μmol/L TET and c) 7 hr and d) 12 hr at −0.62 V in high Cl\(^{-}\) electrolyte containing 1 mmol/L Cl\(^{-}\) and 50 μmol/L TET. In all four cases the patterned substrates were rotated at 400 rpm during deposition. e) 4 hr at −0.62 V followed by 2 s at −0.8 V then 2 hr at −0.64 V, all at 400 rpm and f) 4 hr at −0.62 V at 400 rpm followed by 1.5 hr at −0.64 V at 200 rpm, both in high Cl\(^{-}\) electrolyte containing 1 mmol/L Cl\(^{-}\) and 50 μmol/L TET. Wafers with slightly different via layouts are responsible for the different spacings. All were preceded by 2 min at −0.40 V to mix electrolyte into the alcohol-prewetted features.