Effect of Chloride on Microstructure in Cu Filled Microscale Through Silicon Vias S.-H. Kim<sup>a</sup>, H.-J. Lee<sup>a</sup>, T. M. Braun<sup>b</sup>, T.P. Moffat<sup>b</sup> and D. Josell<sup>b</sup>

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## ABSTRACT

The microstructure of copper filled through silicon vias deposited in a  $CuSO_4 + H_2SO_4$  electrolyte containing micromolar concentrations of deposition rate suppressing poloxamine and chloride additives is explored using electron backscatter diffraction. Regions with distinct microstructures are observed in the vias, including conformal deposition and seam formation localized adjacent to the bottom that can transition to bottom-up filling higher in the features. The presence and extent of each microstructure depends on applied potential as well as additive concentration. Deposition in the presence of higher chloride concentration yields a strong (110) growth texture in regions where bottom-up filling exhibits a horizontal growth front profile while (110) textured or untextured growth is observed for different conditions where upward growth proceeds with a v-notch profile.

# Introduction

Copper, already the dominant electrical conductor at the large length scales of blind vias, through holes and conductor lines on printed circuit board, was introduced for submicrometer onchip interconnects toward the end of the last century<sup>1,2</sup>. It continues to be the material of choice even as divergent needs have pushed copper interconnect technologies both farther down toward nanometer dimensions for on-chip applications as well as farther up toward multi-micrometer

dimensions for through silicon vias (TSV) in wafer stacking applications. Mechanisms for superconformal filling that yield void-free deposits in the highest aspect ratio features are embodied in models that capture interaction of adsorbed accelerating additives and area-change at the nanometer length scales<sup>3-5</sup> and interaction of concentration gradients and critical behavior in breakdown of adsorbed rate suppressing additives at micrometer<sup>6,7</sup> and millimeter<sup>8,9</sup> length scales. These additives remain a focus of research<sup>10-15</sup>. Combined with electrochemical studies of kinetics defining additive interactions and impact, these models can provide accurate prediction of filling observed in nanometer to millimeter sized features. Substantial insight into the interactions of the key chloride, accelerating and suppressing additives that underlie filling at the smallest dimensions has been obtained through standard electroanalytical measurements such as chronoamperometry and cyclic voltammetry<sup>10</sup>, and more refined tools like surface enhanced vibrational spectroscopy have been used to determine the atomic level conformations that motivate these interactions<sup>16,17</sup>. The same can be said regarding microelectrode measurements<sup>18</sup> of the localized suppression breakdown that underlies bottom-up filling as well as continuum level modeling of the resulting evolution of feature filling at the larger dimensions<sup>8,9,18,19</sup>. As a result of these studies, predictive shape change models of superconformal deposition are generally accurate<sup>10,11,20</sup>.

This work studies feature filling from the other side of the interface, which is to say, the microstructure of the deposit. The approach is hardly new; X-ray diffraction investigations of the relationship between deposition rate and deviations from epitaxy go back to the 1950s.<sup>21</sup> The importance of a low stacking fault energy and availability of relevant surface sites to the prevalence of growth twins has been widely discussed.<sup>21-27</sup> Likewise the connection to texture development during growth on single crystalline, polycrystalline or amorphous substrates has also been reported<sup>21-28</sup> while control of the  $\Sigma$  3 twin density has been explored substantially for prospective

enhancement of mechanical properties without compromising the electrical conductivity of Cu.<sup>29-<sup>31</sup> The microstructure of electrodeposited on-chip Cu in particular has been of great interest since its introduction given the recrystallization that occurs in the electrodeposits from superconformally filling multi-additive electrolytes even at room temperature<sup>32-35</sup>. This recrystallization, necessary to obtain the low electrical resistivity material needed for application, comes hand-in-hand with the superconformal filling capability of the electrolyte-additive systems<sup>3-5,36</sup>. Microstructural studies of on-chip interconnects parallel those in thin films, but more often with a focus on understanding how alloying, grain boundaries, surfaces, and twins relate to the degradation of interconnect performance that comes with decreasing device size and extended operation.<sup>37,47</sup> The Cu deposits in these studies are frequently from the multi-additive electrolyte packages that yield superconformal deposition and void-free filling of smaller features.</sup>

While studies of the correlations between additive chemistry and microstructure have been reported, efforts utilizing the powerful tools available for metallurgical analysis, particularly of deposits within patterned features such as interconnects, are more limited.<sup>11</sup> Amongst others, the application of analytical methods such as laser ablation mass spectrometry<sup>48,49</sup> and electron backscatter diffraction (EBSD)<sup>43,44,50</sup> promise to provide new insights into how additive interactions affect not only additive incorporation but also microstructural evolution during feature filling. In one example, a recent EBSD study of Cu deposits in TSV from a CuSO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub> electrolyte containing 1 mmol·L<sup>-1</sup> Cl<sup>-</sup> and micromolar poloxamine shows that the bottom-up fill observed experimentally and predicted by models based on additive transport and adsorption without regard to microstructure exhibits a strong (110) texture along the upward growth direction.<sup>51</sup> The link between bottom-up filling and (110) texture stabilization, and likewise for planar thin film growth in the presence of sub-micromolar additions of Cl<sup>-</sup> or Br<sup>-52-55</sup>, makes clear

the relevance of thin film measurements detailing the influence of halides on surface configuration and growth dynamics even at dilute concentrations.<sup>56-58</sup>

Among the halide-suppression additive systems described for filling of larger interconnects, the generic binary combination of  $Cl^{-}$  and polyether in  $CuSO_4 + H_2SO_4$  electrolyte, which includes the polyether that underlies the (110) texture result just noted, has been shown to yield robust bottomup filling.<sup>6,7,9,10,19,59-64</sup> Suppression arises from co-adsorption of Cl<sup>-</sup> and the polyether to form a bilaver where the polymer blocks access of Cu<sup>2+</sup> to the surface<sup>64-68</sup>; the Cl<sup>-</sup> layer displaces the sulfate anion from the surface and acts as a surfactant that guides step faceting during metal deposition<sup>56,57,65-67</sup> even as it facilitates co-adsorption of the polymer layer that blocks access of Cu<sup>2+</sup> to the Cl<sup>-</sup> covered Cu surface by altering the adjacent water structure to make the interface more hydrophobic.<sup>67</sup> Electroanalytical and feature filling studies have identified additive concentrations and potential regimes where void-free, localized filling occurs in this system<sup>6,7,9,59,60,61-64</sup>. Furthermore, simulations that capture observed transitions from passive to active deposition and filling within 56 µm deep TSV, and to a slightly lesser extent filling in 625 um deep TSV, using stepped potentials to advance the passive-active transition upward in the filling feature indicate reasonably accurate understanding of additive adsorption and incorporation in the system<sup>8,19</sup>.

Because formation of the co-adsorbed suppressor phase can be constrained by the available flux of Cl<sup>-</sup> or polyether, its disruption can be potentially sustained by some combination of Cl<sup>-</sup> incorporation within the growing deposit or preclusion of polymer adsorption on advancing surfaces that is possibly associated with release of the water of hydration from Cu<sup>2+</sup> reduction.<sup>6,7,9,19,59,60,64-69,</sup> The previous EBSD study examined microstructures in TSV filled from this two-component suppressor chemistry as a function of the *poloxamine* concentration; the

4

present report characterizes these microstructures as a function of *chloride* concentration. Grain shapes and crystal orientations obtained by EBSD are examined in light of the morphological evolution observed during feature filling. They are further interpreted using simulations of Cu filling generated by an S-NDR based model of the bottom-up filling process as well as the associated predictions of additive coverage and incorporation to gain further insight.

## **Experimental Methods**

The TSV examined in this work were filled with Cu at room temperature in a cell with 1 mol·L<sup>-</sup> <sup>1</sup> CuSO<sub>4</sub> + 0.5 mol·L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> electrolyte containing 40  $\mu$ mol·L<sup>-1</sup> of a poloxamine suppressor. ethylenediamine tetrakis (propoxylate-block-ethoxylate) tetrol, (PEO<sub>4</sub>PPO<sub>12</sub>)<sub>2</sub>ED(PPO<sub>12</sub>)PEO<sub>4</sub>)<sub>2</sub> (Mass avg  $\approx$  3600, Tetronix 701, Aldrich, TET) and Cl<sup>-</sup> concentrations as indicated while rotating around a central spindle at 100 rpm ( $200\pi$  rad·min<sup>-1</sup>). Additional details can be found in Ref. 19. Although the TSV on these substrates were previously cross-sectioned for imaging by scanning electron microscope, it was found that further processing was required for EBSD analysis. This involved polishing to 1200 grit SiC paper followed by polishing using 1 µm diamond suspension and finally 0.04 µm colloidal silica. Although this process was sufficient to observe electron back scattered diffraction, residual oxide was removed by selective exposure to a focused Ar<sup>+</sup> ion beam (Thermo Scientific Scios 2) at a current of 1 nA for 2 min at an angle of 52° to the specimen normal prior to EBSD mapping. The microstructures of the fully prepared vias were analyzed using a scanning electron microscope (FEI Inspect F50) equipped with an EBSD system (EDAX Pegasus with Hikari XP camera). OIM software was used to acquire the crystal orientations of the exposed grains in the cross-sectioned vias with EBSD maps generated from results obtained across twodimensional arrays of locations having a pitch between 300 nm and 1000 nm. The crystallographic data was analyzed using EDAX-TSL's OIM version 7.3.1 software, with no correction for beam drift during the 2 h to 3 h required to acquire the data over the nominally rectangular area of each scan.

## **Computational Methods**

Finite element method computations are used to simulate copper electrodeposition in the annular through-silicon vias; the full theory and system of equations can be found in Ref. 19. The simulations included herein expand upon those presented in the prior publication. Specifically, the growth front tracking code is replaced by level-set calculations that enable the dynamics of colliding interfaces and subsequent growth beyond the formation of occlusion to be simulated.<sup>5</sup> The main disadvantage of the level set method is the need for more total mesh elements as the mesh is commonly uniform within the entire deforming volume, in this case the entire fillable volume of the feature. Furthermore, for reasonably accurate modeling, the spacing of these mesh elements must be such that the thickness of the "interface" between the deposit and the electrode spans a reasonable quantity of mesh elements (e.g., 4 elements = interface width). In contrast, a front-tracking code typically has spatially refined mesh only near the areas of highest gradient that often exist near the moving interface. For relevant comparison, the front-tracking simulations in Ref. 19 have  $\approx$  2,000 total mesh elements (triangular and 1 µm on each side) and take on the order of tens of minutes to compute; the level-set simulations presented herein have  $\approx 40,000$  total mesh elements (square and 0.125 µm on each side) and take on the order of 12 h to compute. Although simulations with a  $2 \times$  larger mesh (0.25 µm on each side and 10,000 total elements) produced qualitatively identical results and required 3 h to compute the more refined mesh was required to produce the higher resolution maps presented. Detailed equations for modeling Cu feature filling

with the level-set method can be found in Ref. 5, although applied to electrolytes containing accelerator molecules (SPS) and employing the curvature-enhanced-adsorbate-coverage (CEAC) theory. An analogous level-set code was later applied to Cu deposition in an S-NDR system (Ref. 7) in a model considering only the influence of polyether (suppressor) adsorption on the dynamics of feature filling. The simulations presented here employ a level-set implementation of a two-additive S-NDR model of suppressor adsorption limited by chloride coverage whose kinetics capture experimental filling at very low Cl<sup>-</sup> concentrations<sup>19,\*</sup>

The complete system of equations was solved using the COMSOL Multiphysics version 5.6 software package and the default solver, implementing the following modules: transport of dilute species, secondary current distribution, level set, and separate coefficient form boundary partial differential equations for both chloride and suppressor adsorbates. The system of equations is solved so that the overall charge imbalance (the fractional difference between the total integrated currents at the counter electrode and working electrode) is less than 0.5%. The numerical evaluation error, thus, is acceptably small for much of the present work. All simulations were performed on a Dell Precision 3630 desktop computer with an Intel Xeon E-2186G CPU @ 3.80 GHz and 64 GB RAM using a Windows 10 Enterprise 64-bit operating system.

#### **Results and Discussions**

Cross-sections of the Cu filled TSV that are characterized by EBSD in this study are imaged by scanning electron microscope in **Figure 1**. The specimens in this figure were filled for 30 min at the stated potentials in electrolytes containing 40  $\mu$ mol·L<sup>-1</sup> TET and the indicated micromolar Cl<sup>-</sup>

<sup>\*</sup> The level set code duplicates feature filling and additive incorporation predicted by the earlier finite-element based code<sup>8,19</sup> but can progress past sidewall impingement and/or void formation that necessarily halted the earlier implementation. The model does not account for fluid flow beyond the existence of a diffusional boundary layer. With both codes the kinetics used lead to overestimation of the degree of suppression during bottom-up Cu filling.

concentrations; additional process details have been published previously<sup>19</sup>. The images capture passivation of deposition farther from the via openings that occurs at higher Cl<sup>-</sup> concentration due to a more extended range for effective co-adsorption of the combined Cl<sup>-</sup> and TET suppression layer within the concentration gradients existing down the filling features. More negative potential, increasing the driving force for Cu deposition, on the other hand, is seen to promote breakdown of the suppressing Cl<sup>-</sup>-polymer complex so that deposition approaches closer to, and even beyond, the via openings prior to passivation. That said, use of a potential that is too negative for the given additive concentrations results in voiding at the via bottom; results are not included at potentials negative of that at which such voiding is first observed. Nonetheless, the SEM images make clear that even at the more positive potentials filling exhibits significant variation, with either v-notch profile and seam formation or bottom-up, apparently seam- and void-free filling. These behaviors are well captured in simulations from an S-NDR model using kinetics obtained from a rotating disk electrode (RDE) study of suppression breakdown without consideration of grain orientations or texturing.<sup>19</sup> The next section systematically examines the microstructure associated with deposition at each of the six conditions shown in Figure 1.

## MICROSTRUCTURAL EVALUATION

The crystalline microstructure and voided deposit in a radial cut of the via filled at -0.52 V and 20  $\mu$ mol·L<sup>-1</sup> Cl<sup>-1</sup> (and 40  $\mu$ mol·L<sup>-1</sup> TET common to all the experiments) is detailed in **Figure 2**. The size and shape of the grains varies with their location within the via, as summarized in **Figure 2a**. Three maps in **Figure 2b** obtained using EBSD show the orientations of the face centered cubic Cu crystals that compose the deposit. The maps indicate the crystal planes (hkl) that are oriented normal to the ND, RD and CD directions (i.e., substrate normal and via radial and

circumferential directions, respectively) for each grain. There is no obvious bias toward particular crystal orientations, i.e., texture, manifest in the color distributions across the filled via. Three different regions of distinct microstructure are, however, evident within the filled via. Deposition in the upper region of the feature, extending to several micrometers above the void, exhibits small grains adjacent to the sidewalls and larger, elongated grains toward the midline of the via that are elongated and inclined inward and upward, albeit with some irregularity (Region I). Deposition immediately below exhibits fine grains near the sidewalls with some elongation in the radial (RD) direction nearer the via midline (Region II). The via bottom and majority of the via sidewalls along the void exhibit larger grains, with lateral dimensions that substantially exceed the deposit thickness suggestive of recrystallization (Region III). The distribution of large grains principally in Region III and toward the midline in Region I is evident in the map colored by grain size rather than crystal orientation in **Figure 2c**. Simulation of additive incorporation during TSV filling, obtained from the model of TET adsorption contingent on Cl adsorption<sup>19</sup> for filling at -0.52 V in electrolyte containing 20  $\mu$ mol/L Cl<sup>-</sup> and 40  $\mu$ mol·L<sup>-1</sup> of TET is shown in **Figure 2d**. As noted, the kinetics used in the model overestimate suppression, resulting in prediction of passivation below the level at which it is actually observed. Nonetheless, the simulation generated by the level set code elucidates the microstructure observed in all three regions of the via filling. High Cl<sup>-</sup> incorporation is predicted adjacent to the sidewalls in both Region I and Region II where a finegrained microstructure is observed (the fine grains extending below the top of the void in Region II where additive incorporation is falling off). Where Cl<sup>-</sup> incorporation is predicted to be minimal, nearer the midline in both Regions I and II and below the passive/active transition in Region III, large grains are observed. The possibility of recrystallization in Region III is also consistent with a low level of impurity incorporation. Analogous spatial distributions and anticorrelation between local grain size and additive incorporation has been detailed for Cu filling of TSV from electrolyte containing higher (1 mmol·L<sup>-1</sup>) Cl<sup>-</sup> concentration<sup>51</sup> as well as Ni filling from a sulfate electrolyte containing an S-NDR inducing suppressor that is consistent with predictions of a finite element  $code^{70}$ .

The angled orientation of many of the elongated grains in Region III can also been understood from the simulation, in particular, that electrodeposition is locally normal to the growth surface, whether the surface is flat or curved, horizontal or angled. The experimental surface profile is seen in sequential filling experiments at 5 min, 10 min, 20 min and 30 min in Figure 3a. The predicted filling evolution is summarized by contours of the surface profile at 5 min intervals in Figure 3b. Although overestimating the suppression, so that it passivates somewhat farther below the via opening than is observed, the simulation anticipates the voided geometry and subsequent upward filling. At 5 min of deposition both experiment and simulation manifest a transition from passive to active deposition on the sidewalls approximately one-third of the way down the via. Deposition remains localized below this passive-active transition through impingement of the sidewall deposits that occurs prior to 10 min and defines the top of the void in the lower half of the via. Active deposition is subsequently localized to the upper profile of the impinged deposits, the vnotch in the profile at 10 min resulting from the impingement. The angled orientations of the elongated grains in several locations in Region I are understood to be the consequence of the vnotch deposit growth front, where the relevant grains extend orthogonally to the profile. The dispersion in the angular grains over the height of the deposit reflects weakening of the notched growth front profile that is evident in the images of filling at 20 min and 30 min. The passiveactive transition that defines the earliest stage of deposition in this S-NDR system thus plays a long-lasting role in defining microstructural evolution throughout filling.

Filling of TSV with the intermediate concentration of 40 µmol·L<sup>-1</sup> Cl<sup>-</sup> (and 40 µmol·L<sup>-1</sup> TET) in the same Cu sulfate electrolyte is examined in Figure 4. EBSD maps capture the crystal orientation in the substrate- and via-defined normal direction ND, in this case at both -0.52 V and -0.54 V in Figure 4a and b, respectively. Microstructures analogous to those detailed in Regions I, II and III for the lower Cl<sup>-</sup> concentration are observed, although, consistent with increased suppression at the higher additive concentration, the respective regions do not extend as far up the vias. Deposition at each potential yields a voided region of large grains along the bottom and adjacent sidewall that, as with the lower Cl<sup>-</sup> concentration, is labeled Region III. Reduced metal ion depletion due to the shorter active region yields a comparatively narrower void than that in Figure 2 even at the more negative -0.54 V while that at -0.52 V is little more than a seam. The region of very small grains observed immediately above the large grains at both potentials is again labeled Region II. For deposition at -0.52 V the seam along the midline in Region III persists along the midline of Region II and no grain enlargement is observed either inward toward the midline or higher up before deposition passivates. At -0.54 V, on the other hand, a region of larger elongated grains angled upward toward the midline of the via is observed above the fine-grained Region II and is correspondingly labeled Region I. Although the simulation at -0.54 V does not fully encompass the observed Cu filling, comparison of the grain size maps and simulations of Cl<sup>-</sup> incorporation that are also included for both potentials in **Figure 4** reinforces the previously observed inverse correlation between grain size and additive incorporation.

Regarding the texture, in this case the EBSD maps do appear to suggest a bias in Region III filled at -0.52 V toward (211) texture in ND. However, no such bias is evident in a second radial cut while several large grains with (211) texture are also observed in RD and CD (not shown). There is suggestion of texture close to (211) in Region III at -0.54 V as well but in CD (not shown).

In both cases, the small number of grains negatively impacts the statistical significance of these observations. The microstructure immediately over Region I at -0.54 V reflects the change to a hemispherical growth geometry as the growth emerges from the via.

The evolution of filling, observed as well as simulated, is examined in Figure 5. In contrast to the behavior with 20  $\mu$ mol·L<sup>-1</sup> Cl<sup>-</sup>, the sequential filling at -0.52 V and 40  $\mu$ mol·L<sup>-1</sup> Cl<sup>-</sup> shows deposition passivating upon impingement of the deposits below the passive-active transition; identical deposits at both 10 min and 20 min match the position of the passive-active transition at 5 min, preserving the v-notch formed upon impingement; the slightly higher fill and shallower vnotch at 30 min suggests additional passive deposition or unintended process variation. The simulation captures the observed evolution. The absence of active upward deposition after the impingement underlies the absence of a Region I containing larger grains manifesting upward filling and decreased additive incorporation. In contrast, both experiment and simulation at -0.54 V exhibit upward filling after the sidewall impingement (albeit the kinetics used in the simulation once again result in overestimation of the level of suppression). The v-notch observed at 10 min is predicted to remain until passivation that, perhaps serendipitously, is located where a second, smaller central void is observed near the top of the filled feature. As noted with the lower Cl<sup>-</sup> concentration, the early v-notch profile is recorded in the angled grains toward the bottom of Region III in **Figure 4**. Angled growth is not, however, obvious higher in the filled feature.

Filling of TSV at -0.52 V, -0.54 V and -0.56 V in electrolyte having the highest concentration of 80  $\mu$ mol·L<sup>-1</sup> Cl<sup>-</sup> (and 40  $\mu$ mol·L<sup>-1</sup> TET) in the Cu sulfate electrolyte is examined in **Figure 6**. EBSD maps capture the spatial distribution of crystal orientations in ND as well as grain size for each potential in **Figure 6a**, **b**, and **c**, respectively. Microstructures analogous to those labeled Regions I and II with the lower Cl<sup>-</sup> concentrations are observed in the maps of grain size, even further recessed from the via opening than with the lower additive concentrations as a result of further increased suppression. The regions immediately adjacent to the via bottoms at all three potentials exhibit fine grains along the sidewall and strictly radial growth, including clear central seams at -0.54 V and -0.56 V, indicative of conformal filling that resembles the transition zone microstructure at the lower Cl<sup>-</sup> concentrations; they are correspondingly labeled Region II. This region extends only a few micrometers, its height increasing modestly at more negative potential. The deposit above Region II contains larger, elongated grains with orientations that depend on the potential. The EBSD map for deposition at -0.52 V shows grains that are elongated along ND. The grains are so strongly (110) textured in the upper half of the via that the ND map is almost entirely green. This result is in accord with elongated grains with (110) texture in ND characteristic of bottom-up filled Cu deposits from electrolytes containing micromolar concentrations of TET and chloride concentrations more than an order of magnitude higher at 1 mmol·L<sup>-1</sup>.<sup>51</sup>

The deposits at both -0.54 V and -0.56 V exhibit elongated grains that are angled inward and upward but with only a modest texture in any of the substrate and via defined directions. At -0.54 V, these grains are particularly large and discontinuously grouped; at -0.56 V they are not as large but more regularly distributed for approximately 10  $\mu$ m immediately above Region II. Given the enlarged grains indicative of bottom-up filling, the regions containing them are accordingly labeled Region I at all three potentials. Highly elongated, vertically oriented grains over Region I where the deposit exits the via opening are observed again, now at -0.56 V.

The simulation of additive incorporation at -0.52 V that is also included in **Figure 6** does not anticipate the final profile reflected in the EBSD maps. Rather than a flat profile from truly vertical grain growth that finishes approximately one-third of the way up the TSV it predicts a v-shaped

13

profile from passivation at a passive-active transition near the bottom of the via. The simulations at -0.54 V and -0.56 V do exhibit additive incorporation distributions and final v-notch profiles similar to those seen in **Figure 2** at -0.52 V and **Figure 4** at -0.54 V but suggesting passive-active transitions originally much nearer the via bottoms. While the simulations again over-estimate the suppression, and thus underestimate the height at which passivation occurs, both simulations are generally consistent with the microstructure seen in Region I of the EBSD maps. As at the lower concentrations, the presence of larger grains toward the midline, particularly large at -0.52 V and -0.54 V, is consistent with prediction of lower additive incorporation. Especially strong (110) texture in ND at -0.52 V and enlarged grains at -0.52 V and, in localized regions, at -0.54 V in the same locations stand out. On the other hand, other than the inclined orientation, elongation with minimal widening at -0.56 V looks little different than might be expected in any thin film growth process.

Sequential filling experiments and the growth contours in the simulations in **Figure 7** indicate that the microstructures located just above the via bottoms in **Figure 6** at all three potentials derive from passive-active transitions evident at 5 min; they are accordingly all labeled Region II. The modest increase in length of the region arises from a small upward shift of the passive-active transition at a more positive potential. The growth contours show that the inclined grains above this region at -0.54 V and -0.56 V in **Figure 6** derive once again from upward filling over the v-notch profile formed upon sidewall impingement; the region is correspondingly labeled Region I in the figure. The inhomogeneous distribution of large grains in Region I at -0.54 V in **Figure 6**, in particular, is reflected in the sequential filling results in **Figure 7** at later times; the v-notch profile is visible at 10 min, disappears at 20 min and then reappears at 30 min. The temporal fluctuation is likely related to the asymmetric filling of the left and right sides of the

annular via, neither variation being predicted by the radially symmetric simulations of filling under quiescent conditions. The more uniform distribution of angled grains in the lower half of Region I at -0.56 V, in contrast, is consistent with the simulation as well as the via-notch seen in the sectioned vias at 5 min, 10 min and even 20 min.

## TEXTURE ASSESSMENT

It is interesting that the bottom-up filling Cu with a horizontal (planar) growth front observed with the TET and 80  $\mu$ mol·L<sup>-1</sup> Cl<sup>-</sup> electrolyte at -0.52 V assumes a (110) growth direction in analogy to that observed with TET and 1 mmol·L<sup>-1</sup> Cl<sup>-</sup> under various conditions<sup>51</sup> and Cu deposition more broadly in the presence of Cl<sup>-</sup>.

It is logical to ask whether the chloride adsorbate induced (110) texture is unique to the flat profile, bottom-up morphology or whether there should be texture formation in the other experimental results exhibiting localized bottom-up filling. In this respect, the EBSD maps presented to this point detail crystallographic texture only in ND defined by the substrate and via geometry. With bottom-up filling exhibiting a flat profile at -0.52 V with 80  $\mu$ mol·L<sup>-1</sup> Cl<sup>-</sup> in **Figure 6** and **7**, as observed with 1 mmol·L<sup>-1</sup> Cl<sup>-,51</sup> the growth direction coincides with ND, and it is along this direction that the growth texture is thus observed. In the remainder of the experimental results the enlarged and/or elongated grains associated with upward filling in Region I are angled due to their growth on the v-notch profile formed by sidewall impingement. Meaningful analysis of texture requires evaluation of crystalline orientation along the direction of growth in each grain, which changes across the midline and, as seen in the sequential fill images, can vary along the via height as well.

An example of growth texture evaluation in deposits with angled grains is shown in Figure 8 for a TSV that was also filled in the 80  $\mu$ mol·L<sup>-1</sup> Cl<sup>-</sup> electrolyte at -0.54 V but for only 20 min. A map for the substrate defined ND is shown on the left. A large grained Region I is evident in the upper portion. The microstructure has been used to guide separation of the deposit into growths originating from the two sides. EBSD orientation maps are shown where the direction in which the crystal planes are assessed is systematically rotated as indicated within the plane containing ND and RD. The deposit on the left side is analyzed in the upper sequence of orientation maps for directions whose range allows alignment with the elongated grains in it. The deposit on the right side is analyzed in the lower sequence of orientation maps for directions whose range allows alignment with its elongated grains. The elongated grains growing from the left side show (110) texture (i.e., green) in the map for  $60^{\circ}$  and adjacent angles that align the direction in which the texture is being evaluated with their elongated structure (their major axis). The elongated grains growing from the right side exhibit a weaker (110) texture in the map for 120°, the comparative weakness possibly indicating the impact of the differing concave and convex curvatures of the inner and outer surfaces of the annular TSV. The distribution of orientations in each side of Region I is summarized in the inverse pole figure (IPF) shown beneath each map that displays the normalized fraction of the area having a given orientation. Values greater than unity indicate a bias toward the particular (hkl) orientations, with larger value indicating greater bias (stronger texture). There is a clear (110) peak in the IPF of the left side at 60° inclination, with a maximum value indicating average texture that is nearly twice the random distribution. The value reflects the strong (110) growth texture evident in the elongated, angled grains that is tempered by the absence of such texture in the smaller grains adjacent to the sidewalls and farther down, adjacent to Region II.

Texture along the crystal growth directions is similarly evaluated for the specimens filled for 30 min in the 80  $\mu$ mol·L<sup>-1</sup> Cl<sup>-</sup> electrolyte at -0.52 V, -0.54 V and -0.56 V. The full sequence of EBSD orientation maps along analogously varied orientations is shown for a TSV filled in the 80  $\mu$ mol·L<sup>-1</sup> Cl<sup>-</sup> electrolyte at -0.52 V, the specimen already understood from **Figure 6** to exhibit a strong (110) growth texture along ND, in **Figure 9**. When the arrow indicating the direction of the texture evaluation aligns with the major axes of the elongated grains in the map for 90°, which is along the substrate normal (ND), an extremely strong bias toward (110) texture (green) is obvious. At other angles (110) textured grains are comparatively few and randomly distributed.

The sequence for a TSV filled in the 80  $\mu$ mol·L<sup>-1</sup> Cl<sup>-</sup> electrolyte at -0.54 V is shown in **Figure 10**. This specimen was not observed to exhibit any clear texture in **Figure 6** in ND (or in RD or CD, which were not shown). However, examination of the maps for the different rotation angles makes clear that there is, in fact, a significant (110) growth texture in this case as well. In particular, when the arrow indicating the direction in which the texture is being evaluated aligns with the major axes of most of the largest grains the texture is (110), i.e., the grains are green. This is seen with the large grains growing from the left side near the top of the via in the maps for 30° and 45° and the large grains growing from the right side farther down in the via in the maps for 105° and 120°. The elongated grains therefore tend to have a (110) growth texture close to their major axes, the upward and inward angled orientations of which are consistent with growth normal to the general v-notch of both experimental and simulated growth front profiles.

The sequence shown in **Figure 11** is for a TSV filled in the 80  $\mu$ mol·L<sup>-1</sup> Cl<sup>-</sup> electrolyte at - 0.56 V, which also exhibited no clear texture in **Figure 6** in ND, RD or CD. In this case the absence of a clear texture remains true for all the orientations examined. Even when the arrow indicating the direction in which the texture is evaluated aligns with the axes of most of the

elongated grains coming from the left side or the right side in the upper Region III deposit, at approximately 45° and 135°, respectively, there is no clear bias toward a particular texture (i.e., color) in those grains. There is thus no growth texture. The average grain size and characteristics of each region are summarized according to the concentration of Cl<sup>-</sup> and applied potential in Table I and the crystallographic microstructure and growth characteristics for each region in Table II.

#### DISCUSSION AND CONCLUSIONS

These results in low Cl<sup>-</sup> electrolytes reinforce previous observation of (110) growth texture during bottom-up Cu filling of TSV from copper-sulfate electrolyte containing substantially higher 1 mmol·L<sup>-1</sup> Cl<sup>-</sup> and somewhat lower micromolar TET concentrations. That the different observed geometries of bottom-up filling have been previously predicted by S-NDR models that are independent of microstructure makes clear that the texture is not causal for the observed filling. That the model used here fails to predict the flat profile where it is observed at -0.52 V with 80  $\mu$ mol·L<sup>-1</sup> Cl<sup>-</sup> suggests kinetics or simplifying assumptions in the model are not sufficiently accurate, as previously noted.<sup>19</sup>

A more detailed analysis of EBSD measurements was required for evaluation of grain growth texture when upward filling manifested a v-shaped surface profile. For the particular case of 80  $\mu$ mol·L<sup>-1</sup> Cl<sup>-</sup> an evolution from strongly textured (110) growth to untextured growth is observed as overpotential increases from -0.52 V to -0.56 V. The geometry changed from a flat bottom-up profile with (110) growth texture along the via ND at -0.52 V to (110) growth at orientations defined by the surface normal of the v-notch profile at -0.54 V to growth without obvious texture, although the angled growth from the v-notch remained, at -0.56 V. The occurrence of v-shaped

profiles both with and without (110) growth texture is in keeping with prediction of the geometry in the microstructure-free S-NDR model; the v-shaped profile during upward filling is simply a residual of the notch that is formed when sidewall impingement occurs.

The Cl<sup>-</sup> additive plays a key role in inhibiting deposition by facilitating co-adsorption of the suppressing polymer. Its incorporation within the growing deposit creates a gradient within the TSV that underlies geometrical evolution during feature filling more generally and bottom-up filling more particularly. Comparison of model prediction and microstructural assessment by EBSD makes clear that Cl<sup>-</sup> incorporation plays a substantial role in defining grain size and that its adsorption plays a no less significant role in defining crystal texture within the deposits. The results suggest that faster deposition at more negative potentials, given that deposition at these potentials is not limited by Cu<sup>2+</sup> transport, is associated with faster consumption and thus lower adsorbate coverage. The observed decrease of <110> texture is consistent with a decreased impact of Cl<sup>-</sup>. However, the role of potential in defining microstructure, whether through its impact on kinetically defined deposition rate, or adsorption and incorporation of additives, requires further study.

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#### FIGURES



**Figure 1**: Cross-section TSV after Cu deposition at the indicated potential in 1 mol·L<sup>-1</sup> CuSO<sub>4</sub> +  $0.5 \text{ mol}\cdot\text{L}^{-1}$  H<sub>2</sub>SO<sub>4</sub> electrolyte containing 40 µmol·L<sup>-1</sup> of the poloxamine suppressor TET and the indicated Cl<sup>-</sup> concentration. The annular TSV are 56 µm deep with inner and outer radii of 4 µm and 9.5 µm, respectively. In all cases deposition was for 30 min while the substrate rotated at 100 rpm around a central spindle with flow parallel to the surface of the substrate.



**Figure 2:** Radial cut through annular TSV after 30 min deposition at -0.52 V in 1 mol·L<sup>-1</sup> CuSO<sub>4</sub> + 0.5 mol·L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> electrolyte containing 20  $\mu$ mol·L<sup>-1</sup> Cl<sup>-</sup> and 40  $\mu$ mol·L<sup>-1</sup> TET. a) Schematic diagrams of cross-sectioned annular TSVs. b) Three EBSD texture maps show the local orientation of the crystals over the area of the sectioned Cu deposit. On the maps, the color indicates the family of (hkl) planes orthogonal to the direction of the substrate normal (ND), the via radius (RD) or the via circumference (CD). c) Map colored by grain size, with legend defining the color scale as well as color triangle for part c). d) Map of Cl incorporation in the Cu deposit predicted by level set simulation; the kinetics, identical to those used in front tracking code<sup>19</sup>, overestimate suppression.



**Figure 3:** a) Vias cross-sectioned after 5 min, 10 min, 20 min and 30 min capture the evolution of filling at -0.52 V in 1 mol·L<sup>-1</sup> CuSO<sub>4</sub> + 0.5 mol·L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> electrolyte containing 20  $\mu$ mol·L<sup>-1</sup> Cl<sup>-</sup> and 40  $\mu$ mol·L<sup>-1</sup> TET. b) Growth contours predicted by level set simulation are shown at 5 min intervals. The kinetics, identical to those used in front tracking code<sup>19</sup>, overestimate suppression.



**Figure 4:** Annular TSV sectioned after 30 min deposition at a) -0.52 V and b) -0.54 V in 1 mol·L<sup>-1</sup>  $^{1}$  CuSO<sub>4</sub> + 0.5 mol·L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> electrolyte containing 40 µmol·L<sup>-1</sup> Cl<sup>-</sup> and 40 µmol·L<sup>-1</sup> TET. In each case, an EBSD orientation map shows the local orientation of the crystals across the sectioned Cu deposit along ND. A map of grain size and simulation of Cl<sup>-</sup> incorporation is also shown in each case. The color triangle for the orientation maps and legend for the color scale of the grain size maps are shown in the upper left corner.



**Figure 5:** Annular TSV sectioned after 30 min deposition at (top) -0.52 V and (bottom) -0.54 V in 1 mol·L<sup>-1</sup> CuSO<sub>4</sub> + 0.5 mol·L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> electrolyte containing 40  $\mu$ mol·L<sup>-1</sup> Cl<sup>-</sup> and 40  $\mu$ mol·L<sup>-1</sup> TET. Vias cross-sectioned after the indicated deposition times show the evolution of filling. Simulations of filling show growth contours at 5 min intervals predicted for each potential.



**Figure 6:** Annular TSV sectioned after 30 min deposition at a) -0.52 V and b) -0.54 V and c) - 0.56 V in 1 mol·L<sup>-1</sup> CuSO<sub>4</sub> + 0.5 mol·L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> electrolyte containing 80  $\mu$ mol·L<sup>-1</sup> Cl<sup>-</sup> and 40  $\mu$ mol·L<sup>-1</sup> TET. In each case, an EBSD orientation map shows the local orientation of the crystals across the sectioned Cu deposit along ND. A map of grain size and simulation of Cl<sup>-</sup> incorporation is also shown in each case. The color triangle for the orientation maps and legend for the color scale of the grain size maps are shown in the upper left corner.



**Figure 7:** Annular TSV sectioned after 30 min deposition at top) -0.52 V and middle) -0.54 V and bottom) -0.56 V in 1 mol·L<sup>-1</sup> CuSO<sub>4</sub> + 0.5 mol·L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> electrolyte containing 80  $\mu$ mol·L<sup>-1</sup> Cl<sup>-</sup> and 40  $\mu$ mol·L<sup>-1</sup> TET. vias cross-sectioned after 5 min, 10 min, 20 min and 30 min showing the evolution of filling; simulation of filling in the annular TSV at the given conditions with growth contours at 5 min intervals.



**Figure 8:** Annular TSV sectioned after 20 min deposition at -0.54 V in 1 mol·L<sup>-1</sup> CuSO<sub>4</sub> + 0.5 mol·L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> electrolyte containing 80  $\mu$ mol·L<sup>-1</sup> Cl<sup>-</sup> and 40  $\mu$ mol·L<sup>-1</sup> TET. EBSD texture maps show the crystalline planes in each grain that are normal to the direction indicated by the arrow above the map; the family of planes is indicated by the color triangle on the right. A map for texture across the full TSV in the vertical direction is seen on the left. The seam created by the grains growing from the left and right sides is used to separate the Cu fill into the respective

halves for analysis of the deposits originating from each. The upper sequence of maps is for the deposit on the left side and includes directions aligned with the elongated grains within it. The lower sequence of EBSD maps is for the deposit on the right side and includes directions aligned with the elongated grains within it. The distribution of orientations in each map is summarized by the inverse pole figure (IPF) below it. The IPF shows the fraction of area having a given hkl orientation normalized by the fraction of a random distribution that would have the same hkl and plotted on the orientation triangle. The scale bar for the IPFs is on the right and the maximum value in each is indicated.



**Figure 9:** Annular TSV sectioned after 30 min deposition at -0.52 V in 1 mol·L<sup>-1</sup> CuSO<sub>4</sub> + 0.5 mol·L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> electrolyte containing 80  $\mu$ mol·L<sup>-1</sup> Cl<sup>-</sup> and 40  $\mu$ mol·L<sup>-1</sup> TET. The EBSD texture maps refer to crystalline texture in the direction indicated by the arrow above the map. The family

of planes oriented along the indicated direction is indicated by the color using the color triangle. As texture is the same rotated by an additional 180°, the twelve angles covering 180° convey the full texture information for rotation in the plane.



**Figure 10:** Annular TSV sectioned after 30 min deposition at -0.54 V in 1 mol·L<sup>-1</sup> CuSO<sub>4</sub> + 0.5 mol·L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> electrolyte containing 80  $\mu$ mol·L<sup>-1</sup> Cl<sup>-</sup> and 40  $\mu$ mol·L<sup>-1</sup> TET. The EBSD texture maps refer to crystalline texture in the direction indicated by the arrow above the map. The family of planes oriented along the indicated direction is indicated by the color using the color triangle.



**Figure 11:** Annular TSV sectioned after 30 min deposition at -0.56 V in 1 mol·L<sup>-1</sup> CuSO<sub>4</sub> + 0.5 mol·L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> electrolyte containing 80  $\mu$ mol·L<sup>-1</sup> Cl<sup>-</sup> and 40  $\mu$ mol·L<sup>-1</sup> TET. The EBSD texture

maps refer to crystalline texture in the direction indicated by the arrow above the map. The family of planes oriented along the indicated direction is indicated by the color using the color triangle.

Table I. Summary of average grain size and characteristics of each region according to the bu	ılk
Cl <sup>-</sup> concentration and applied potential	

Concentration of Cl <sup>-</sup>	Potential	Average grain size for each Regions	Characteristics
20 µmol∙L <sup>-1</sup>	-0.52 V	$\begin{split} I &= 0.99 \ \mu m^2 \\ II &= 0.30 \ \mu m^2 \\ III &= 5.8 \ \mu m^2 \end{split}$	<ul> <li>Passive-active transition above midheight in the via</li> <li>Active deposition in Region I exhibiting angled growth with moderate (110) preferred growth orientation (not shown)</li> <li>Coarse grains in Region III</li> </ul>
40 μmol·L <sup>-1</sup>	-0.52 V	$\begin{split} II &= 0.53 \ \mu m^2 \\ III &= 6.2 \ \mu m^2 \end{split}$	<ul> <li>Passive-active transition below midheight in the via</li> <li>Filling stopped without significant activation above Region II</li> </ul>
	-0.54 V	$\begin{split} &I - 1.2 \ \mu m^2 \\ &II - 0.46 \ \mu m^2 \\ &III - 14 \ \mu m^2 \end{split}$	<ul> <li>Passive-active transition shifted upward relative to that at -0.52 V</li> <li>Active deposition in Region I exhibiting angled growth without obvious preferred growth orientation (not shown)</li> </ul>
80 µmol∙L <sup>-1</sup>	-0.52 V	$\begin{array}{c} I-2.43 \ \mu m^2 \\ II-0.68 \ \mu m^2 \end{array}$	• Bottom-up growth with strong (110) preferred growth orientation in Region I
	-0.54 V	$I - 1.6 \ \mu m^2$ II - 0.52 $\ \mu m^2$	• Active deposition in Region I exhibiting angled growth with (110) preferred growth orientation in Region I
	-0.56 V	$\frac{I - 0.69 \ \mu m^2}{II - 0.40 \ \mu m^2}$	• Active deposition in Region I exhibiting angled growth with no clear preferred growth orientation

Region	Characteristics
Ι	<ul> <li>Elongated grains are inclined except at -0.52 V with 80 μmol·L Cl<sup>-</sup> where they are vertically oriented. Cl<sup>-</sup> templated (110) growth increases at more positive potentials and higher Cl<sup>-</sup> concentrations</li> </ul>
Π	<ul> <li>Localized transition from passive to active deposition, with associated change in grain size, at overpotential-defined location where Cl<sup>-</sup> concentration transitions from near bulk to near zero value</li> </ul>
III	<ul> <li>Active deposition in Cl<sup>-</sup> deficient solution with coarse grains observed post deposition</li> </ul>

Table II. Summary of growth characteristics for each region