

Bottom-up Cu Filling of Annular Through Silicon Vias: Microstructure and Texture

Sang-Hyeok Kim,¹ Hyo-Jong Lee,¹ Daniel Josell² and Thomas P. Moffat²

¹Department of Materials Science and Engineering, Dong-A University, Saha-Gu, Busan 49315 Korea

²Materials Science and Engineering Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899 USA

Keywords: Copper, TSV, EBSD, Microstructure, Crystallographic texture, Bottom-up filling

Abstract (200 words)

Microstructural and morphological evolution during bottom-up Cu filling of Through Silicon Vias in a CuSO₄-H₂SO₄-Cl-poloxamine electrolyte is examined. Deposition proceeds in two distinct stages beginning with a passive-to-active state transition on the via sidewalls whose depth and ultimate thickness depends on the polymer flux. Growth is conformal or tapered with columnar grains whose width and texture differ between the outer and inner sidewalls of the annulus due to area reduction and expansion respectively. The outer sidewall and bottom surface have a preferred texture; <111> // ND (via normal) and <110> // CD (via circumferential). With time the sidewalls passivate and further deposition is localized to the via bottom. The bottom-up growth to fill the TSV is associated with the formation and selective expansion of the <110> // ND textured grains. At higher suppressor concentrations the initial onset and transient period of sidewall deposition is displaced to greater depth and the subsequent transition to bottom-up filling with large <110> // ND texture grains occurs earlier. The dominant <110> // ND texture during bottom-up filling is congruent with Cl⁻ stabilized texture development. The absence of suppression indicates that the polymeric suppressor does not adsorb on the active upward propagating surface.

E-mail: hyojong@dau.ac.kr , thomas.moffat@nist.gov

Introduction

Electrodeposition of Cu is widely used in the fabrication of microelectronic interconnects. Electrolyte additives play a central role in guiding the morphological evolution during deposition on non-planar metallized surfaces. Depending upon the length scale of the recessed features, e.g. trenches, vias, through holes, etc., different additive packages and processing conditions are used for optimal filling. Beyond filling, the additives also impact the as-deposited and post-deposition evolution of the microstructure. Various correlations and models are available that detail the interactions between electrolyte additives and morphological evolution during feature filling. These range from the fabrication of sub-micrometer on-chip interconnects by the Curvature Enhanced Adsorbate Coverage mechanism¹ to the filling of larger scale through silicon vias (TSV)²⁻⁶ and through holes⁷ by the S-shaped Negative Differential Resistance (S-NDR) mechanism. Despite many reports that discuss Cu metallurgy relevant to on-chip Damascene metallization, TSV and other electroplating applications much remains to be understood as to the relationship between additives and microstructural evolution.⁸⁻

13

X-ray based study of the relationships between deposition rate and deviations from epitaxy goes back to the 1950's.¹⁴ The importance of a low stacking fault energy and availability of relevant surface sites to the prevalence of growth twins has been widely explored.¹⁴⁻²⁰ Likewise the connection to texture development during growth on single crystalline, polycrystalline or amorphous substrates has also been described.¹⁴⁻²¹ Controlling the $\Sigma 3$ twin density has proven to be a particularly fruitful development in terms of enhanced mechanical properties without compromising the electrical conductivity of Cu.²²⁻²⁴ Studies of the correlations between additive chemistry and microstructure have been reported but more recent efforts based on the power of modern methods are more limited.²⁵ Amongst others, the application of analytical methods such as laser ablation mass spectrometry^{26,27} and electron backscatter diffraction (EBSD)^{11,12,28} promise to provide new insights to the interplay between additives and microstructural evolution. At the same time interpretation of earlier works is often hampered by limited

specification or knowledge of the purity of the electrolytes used. This is especially true with respect to halides that even at dilute concentrations are known to induce substantial anisotropy into the step and terrace structure and growth dynamics of Cu surfaces.^{29,30,31} Indeed several recent studies of the effect of halide concentration, from the sub-micromolar range upwards, indicate that the <110> texture during galvanostatic deposition in the CuSO₄-H₂SO₄ is actually stabilized by halide Cl⁻ and Br⁻.³²⁻³⁵ Similarly, the role of additive incorporation and its consequence on deposit structure and subsequent microstructural evolution is of continuing interest. In the case of two component halide-suppressor additive chemistry significant negative impacts are evident in forming robust Cu-Sn solder joints that might be addressed with proper consideration of the processing conditions.³⁶⁻³⁸ In the present report results of electron backscatter diffraction (EBSD) examination of the microstructure of Cu TSV filled by extreme bottom-up filling using a prototypical two-component suppressor chemistry are detailed.

The generic binary combination of Cl⁻ and polyethers has been shown to yield robust bottom-up filling in CuSO₄-H₂SO₄ electrolytes.^{2-7,39-42} Suppression arises from co-adsorption of Cl⁻ and the polyether to form a bilayer where the polymer blocks access of the Cu²⁺ to the surface.^{2,43-46} The Cl⁻ layer serves several roles. It displaces the sulfate anion from the surface and acts as a surfactant that guides step faceting during metal deposition.^{29,30,43-45} The halide layer also alters the adjacent water structure to make the interface more hydrophobic, thereby facilitating the co-adsorption of the polymer layer that blocks access of Cu²⁺ to the Cl⁻ covered Cu surface.⁴⁵ Formation of the co-adsorbed suppressor phase can be constrained by the available flux of Cl⁻ or polyether. Its disruption can be sustained by some combination of Cl⁻ incorporation within the growing deposit or preclusion of polymer adsorption on advancing surfaces that is possibly associated with release of the water of hydration following Cu²⁺ reduction.^{2-7,40,43-47}

Electroanalytical and feature filling studies have identified the additive concentration and potential regime where bottom up filling can occur.^{2-7,39-42} When either component of the suppressor is dilute in the electrolyte TSV filling begins with a sharp transition from passive to active deposition at some depth

within the via that is dependent on the concentration and applied potential.³⁹⁻⁴² Active deposition on the lower sidewall and bottom surface can be either conformal or tapered.³⁹⁻⁴² For certain conditions this stage of bifurcation is temporary as the active sidewalls subsequently passivate with a transition to bottom-up filling.^{39,40} As the concentration of the additive increases the extent of transient sidewall deposition decreases with a more rapid shift to bottom-up filling.^{39,40} In larger features and under different conditions filling can require potential waveforms to progressively advance the location of the passive-active sidewall breakdown process.^{40,42} In this report the microstructure of filled annular TSV, such as that shown in Figure 1, and its relationship with the morphological transitions evident during feature filling under fixed applied potential are investigated as a function of the poloxamine concentration.

Experimental

The cross-sectioned TSV samples used in this study were previously examined by scanning electron microscopy (SEM) to follow the morphological evolution during feature filling.³⁹ Electrodeposition was performed at room temperature in 1 mol/L CuSO₄ - 0.5 mol/L H₂SO₄ - 1 mmol/L NaCl with suppression provided by co-adsorption of halide with a poloxamine additive, Tetronic 701 (Aldrich¹). The Tetronic polyether (TET) contains an ethylenediamine core with four propoxylate-blocks capped with ethoxylate giving a molecular mass of 3600 g/mol. Deposition was performed at a fixed applied potential referenced to a Hg/Hg₂SO₄/saturated K₂SO₄ reference electrode (SSE). Working electrodes were rectangular wafer fragments patterned with ≈ 56 μ m deep TSVs of annular cross-section (provided by IBM) with a 1 μ m thick Cu seed in the field and a lesser amount on the sidewalls. Definition of the metal ion and additive transport during deposition was provided by rotating the wafer fragments about one end of a Pt spindle, like a helicopter blade, with the patterned surface facing up. Based on the ≈ 1

¹ Identification of commercial products in this paper was done to specify the experimental procedure. In no case does this imply endorsement or recommendation by National Institute of Standards and Technology.

cm distance between the features and rotational axis for most of the imaged TSVs, the 100 rpm (200π rad/min) rotation rate corresponds to an estimated 10 cm/s flow rate over the surface. Pre-wetting the wafer fragments with ethyl alcohol was used to displace air bubbles that were otherwise trapped in the TSVs during Cu deposition. Following immersion, the specimens were rotated for 2 min to mix the electrolyte with the alcohol in the TSVs and during this period the potential was maintained at $-0.40 V_{SSE}$ (≈ -30 mV relative to the measured open circuit potential of $\approx -0.37 V_{SSE}$) to avoid corrosion of the copper seed layer. It should be noted that for dwell times less than 4 min the delayed arrival of the electrolyte to the most recessed TSV region impacts the initial stages of feature filling. This effect has been seen to persist for at least 4 min.³⁹ In addition, significant Cu^+ can be produced adjacent to the electrode during the dwell period that may also influence subsequent metal deposition. Following this mixing period, the potential was stepped to a specific value for a fixed deposition time followed by removal, rinsing and drying. The applied potential was not corrected for uncompensated cell resistance.

The microstructure of the cross-sectioned TSV were examined by EBSD. The EBSD system (EDAX Pegasus with Hikari XP EBSD Camera), was mounted on a Schottky type field emission gun scanning electron microscope (FEI Inspect F50). The orientation imaging maps (OIM) of the cross-sectioned TSV were examined at locations over a two-dimensional array with 70 nm pitch. Each scan took approximately 30 min to acquire, and no correction has been made for beam drift during data acquisition over the nominally rectangular region of each scan. The inverse pole figures were acquired using the software of EDAX-TSL's OIM version 7.3.1 in order to quantitatively analyze the crystallographic texture.

Results

TSV Filling: Dilute Polyether Concentration and Transient Conformal Deposition

The initial stage of Cu deposition after 4 min at $-0.64 V_{SSE}$ in the presence of 6 $\mu\text{mol/L}$ poloxamine

is dominated by passive-active sidewall bifurcation that leads to conformal deposition in the bottom half of the representative annular via shown in Figure 2a. The EBSD analysis was performed on both sides of three annular vias on the specimen. For the purposes of this communication, discussion and analysis is focused on the right side of the annular via highlighted by the yellow arrow. In Figure 1b, the EBSD measurements were analyzed with respect to the normal direction (ND) of the wafer surface i.e., the vertical axis of the via; circumferential direction (CD) is the normal to the cross-sectioned plane, and the radial direction (RD) is normal to the sidewall as indicated by the coordinate axes inset in the lower left corner of Figure 2a. The ND, CD and RD maps are shown in Figure 2b along with colorized stereographic triangle key for the respective grain orientations. The crystallographic microstructure can be largely divided into three regions: the inner sidewall, the outer sidewall, and the trench bottom. The inverse pole figures (IPF) for the respective maps that include both sidewalls and the bottom surface segments are shown in Figure 2c. As will be further detailed below, the respective IPF represents a global report that convolves three different growth surfaces with three different elements of curvature. Nevertheless, significant $\langle 111 \rangle$ texture in the ND direction is evident, the 2.67 factor being the multiplier for the population of grains in the $\langle 111 \rangle$ orientation relative to that of a random powder sample. In the CD direction, a measurable bias toward $\langle 111 \rangle$ and $\langle 110 \rangle$ texture is indicated while, for RD, a maximum near $\langle 321 \rangle$ is evident, consistent with the $\langle 111 \rangle$ and $\langle 110 \rangle$ textures in the orthogonal directions. The grains in the conformal deposits are largely columnar, consistent with epitaxial growth on the Cu seed layer. The distribution of grain size on the far right of Figure 2b reflects binning based on the average grain size of the columnar grains. The average width of the columnar grains appears to be slight larger on the inner (left side) convex wall of the annulus. Relative to the bottom surface, the average width of the columnar grains is larger on the inner sidewall and smaller on the outer sidewall. Assuming the grain size of the seed layer on the two sidewalls and bottom are the same, the area change accompanying deposition on the respective surface segments, i.e. expansion versus shrinkage, will naturally give rise to changes in the average grain width dependent upon the local curvature. Of course, the area change effect will be most evident in the horizontal cross section of the annular via, capturing

the curvature components directly in the regions corresponding conformal columnar growth on the sidewalls. The grain width translates to grain boundary density that can play an important role in the development of growth stresses in the respective deposits.^{49,50}

A more meaningful IPF assessment of the microstructure of the conformal layer is obtained by restricting the ND, CD, RD analysis of the TSV in Fig. 2 to regions with a common growth normal. Accordingly, the IPF for growth exclusively on each opposing sidewall and bottom surface are presented. In Figure 3 the RD maps are aligned with the (growth) normal of the sidewalls, while the ND and CD map show the texture in the orthogonal in-plane directions. The significant difference between the two sidewalls is immediately evident. The outer wall has average texture in the (growth) normal direction (i.e., RD in Fig. 3c) centered close to $\langle 112 \rangle$, the former consistent with the in-plane $\langle 110 \rangle$ texture in the CD direction and $\langle 111 \rangle$ texture in the other in-plane direction ND. In contrast, the inner wall has a broader distribution along the (growth) normal direction (RD) centered near $\langle 134 \rangle$ while the IPF for the in-plane directions reveal a bimodal texture centered around both $\langle 111 \rangle$ and $\langle 014 \rangle$ in the CD direction and $\langle 012 \rangle$ and $\langle 122 \rangle$ in the other in-plane direction (ND). In contrast to the sidewalls, maps of the bottom surface in Figure 4 indicate a strong $\langle 111 \rangle$ texture in the (growth) normal direction (ND) with a band of $\langle 110 \rangle$ to $\langle 112 \rangle$ texture in the in-plane CD direction and an analogous band centered around $\langle 134 \rangle$ in the other in-plane direction RD, both generally consistent with the predominance of $\langle 111 \rangle$ texture in the normal direction. The dominance of columnar growth on the sidewalls and bottom surface are such that the orientation difference reflects either variation in the underlying seed layer or, possibly, the effect of area change and associated variations in growth stress. Quantification of the average grain size of the columnar grains shown in Figure 3d indicates the grains are 20% smaller on the outer sidewall as compared to the inner sidewall, which is attributed to the impact of area change on grain dimensions and selection. For comparison, note that the visible $\approx 1 \mu\text{m}$ thick Cu deposit yields an approximate -15 % reduction of circumference of the $8.5 \mu\text{m}$ outer radius and a 25% increase of the $4 \mu\text{m}$ inner radius. Importantly, despite the significant variation the crystalline

texture between the three surfaces, the conformal nature of the deposit on the feature length scale indicates that anisotropy does not play a major role in the deposition rate nor the morphological evolution at this stage in the filling process. That said, close inspection does reveal variations in the flatness associated with individual grains congruent with the known effect of Cl^- on step faceting on different Cu surfaces.^{14-18,29-31}

Variations in texture between individual vias are seen with a summary of EBSD results in the ND direction for three annular vias presented in Figure S-1 and S-2. Accordingly, the highlight of the preceding analysis and discussion is the distinctive nature of columnar growth on the sidewalls and bottom surface of the annular vias.

TSV Filling: Dilute Polyether Concentration and Bottom-Up Filling

Deposition at $-0.64 V_{\text{SSE}}$ beyond 4 min exhibits a major change in morphological evolution to bottom-up filling that results in the lower third of the via being filled by 8 min as shown in Figure 5. Between 4 min and 8 min the upper sidewalls hardly advance while the shift to bottom-up filling occurs. The EBSD map reveals a small region of extended sidewall growth near the via bottom that collides with the advancing bottom surface, marking the initiation of bottom-up filling. At this junction new grains form that are elongated in the bottom-up growth direction with $\langle 311 \rangle // \text{ND}$ orientation. that subsequently give way to the formation and expansion of large $\langle 110 \rangle // \text{ND}$ grains that quickly expand to fill the available cross-section while propagating upwards in the via before faulting to yield equally wide $\langle 311 \rangle // \text{ND}$ grains. Examination of multiple vias reveal the same general trends in microstructural evolution. The evolution of the ND texture from $\langle 111 \rangle$ to $\langle 311 \rangle, \langle 110 \rangle$ during the propagation of the bottom-up growth front is not unlike that reported in the literature for Cu electroplating in the absence of the polyether suppressor additive.^{14,16,17,18, 21,23} A schematic summary of the microstructural evolution during feature filling at $-0.64 V_{\text{SSE}}$ and 6 mmol/L poloxamine is shown in Figure 6.

TSV Filling: Increased Polyether Concentration Favors Bottom-Up Filling

Deposition at the same applied potential but with double the poloxamine concentration, 12 $\mu\text{mol/L}$, leads to a much earlier shift to bottom-up filling with minimal transient deposition on the sidewalls as shown in SEM and EBSD time series in Figure 7a-c and accompanying filling schematic in Figure 7d. Dominance of the $\langle 110 \rangle$ texture in the growth direction is obvious, with a single grain occupying $\approx 80\%$ of the filled region after 12 min. Feature filling and texture development still exhibits some variation across the patterned array as shown for a selection of vias after 12 minutes of deposition in Figure S-3. The bottom-up growth dynamic and $\langle 110 \rangle$ growth texture are established by 4 min. Higher magnification maps of the microstructure at 4 min shown in Figure 8 reveal limited columnar sidewall growth that is consistent with an initial period of active deposition on the lower sidewall. Unlike the conformal growth evident in the more dilute poloxamine solution, the sidewall deposits are thinner and tapered, suggesting a more rapid, progressive quenching of the metal deposition reaction due to the higher available flux of poloxamine. Close inspection reveals a slim region of columnar sidewall growth on the upper sidewall of the filled regions in the 8 min and 12 min specimens as well. Its tapered profile reflects the variation of growth time associated with the progressively longer delay in arrival and absorption of the suppressing polymer farther down the feature. Deposition on the bottom surface initially exhibits a $\langle 111 \rangle$ texture along the growth normal, as with the lower concentration (Figure 4), followed by competition between the formation and selection of grains that yields the dominant $\langle 110 \rangle$ motif of the bottom-up growth within the first few minutes and micrometers of deposition. The corresponding CD and RD EBSD maps are shown in Figure 8b. The incorporation of adjacent grains with orientations creating $\Sigma 3$ boundaries, i.e., twinned orientations, during the bottom-up deposition is flagged by similar coloring in the grain size map in Figure 8b. Aside from twinning, once the $\langle 110 \rangle$ texture is established, it is largely sustained during subsequent deposition as seen in Figure 7.

Increasing the poloxamine concentration further to 25 $\mu\text{mol/L}$ leads to an even more limited transient sidewall deposition and an earlier shift to bottom-up filling as shown in Figure 9. Likewise, the transition from $\langle 111 \rangle$ to the dominant $\langle 110 \rangle$ texture is also more rapid, being evident within the first

few grains (i.e., micrometers of deposit). The original study of Cu deposition in these TSV included results that yielded partially bottom-up filled features adjacent to the fully filled was noted for this deposition condition. The partial filling demonstrates that the behavior observed is not due to poor wetting by the electrolyte but rather is a phenomenon associated with critical systems.³⁹ Fortunately, the uniformity of filling can be improved by appropriate process control, such as a more negative applied potential or, alternatively, galvanostatic conditions.^{5,7,40-42}

Discussion

EBS analysis of Cu TSV filled using a simple two component polyether-halide suppressor in a sulfate-based electrolyte reveals important insight into the deposition process. The filling experiments described were all performed at a fixed applied potential with the poloxamine concentration varied from 6 $\mu\text{mol/L}$ to 25 $\mu\text{mol/L}$. However, the iR losses in the electrolyte are such that the actual deposition overpotential depends on the current flowing through the system. Two regimes of behavior are observed dependent on the polyether concentration. With dilute concentrations, the initial stage of deposition is dominated by a passive-to-active transition on the sidewalls with conformal growth of columnar grains in the lower portion of the via. Columnar grain growth reflects the epitaxial constraint associated with $\langle 111 \rangle$ surface normal textured vapor deposited Cu seed layer. Nevertheless, microstructural development on the opposing curved sidewalls is measurably different. Other things being equal, area change results in the columnar grains becoming wider on the inner sidewall and narrower on the outer sidewall. The evolving grain boundary density and grain orientation may impact the residual stress, but, in the absence of related measurements, further discussion lies beyond the present work.^{48,49} The deposit on the outer sidewall has preferred orientations in the in-plane direction of $\langle 111 \rangle // \text{ND}$ and $\langle 110 \rangle // \text{CD}$ while the deposit on the inner sidewall has a bimodal in-plane texture. This sidewall growth occurs only during the first few minutes before shutting down, with subsequent deposition restricted to the bottom of the feature. Coincident with the transition is a decrease in the

electroactive area; the associated decrease in total deposition current decreases resistive losses, increasing the overpotential that drives deposition.^{2-4,7,39,40} This accounts for the acceleration in growth velocity associated with bottom-up deposition between 4 min, Figure 2, and 8 min, Figure 5. Coincident with the accelerated upward motion is development of a dominant <110> texture. At this juncture the sidewalls are passivated and it is not unreasonable to expect the adsorbed suppressor bilayer (comprised of carbon, oxygen, nitrogen and chloride) to be trapped and buried at the interface between the columnar sidewall grains and advancing bottom up growth front. Indeed, Auger electron spectroscopy observation of C-rich material distributed along the TSV sidewalls was recently reported although the chemistry of the bath and filling conditions were not disclosed.²⁵ In contrast, the faster growth and large elongated grains that accompany bottom-up filling suggest weakened interactions between the polymer suppressor and the bottom surface during the upward propagation of the growth front. Importantly, in polymer-free systems, Cl⁻ is known to stabilize the <110> growth texture during Cu electrodeposition over the range of current density that span, at least, 7 mA/cm² to 45 mA/cm².³²⁻³⁵ Accordingly, the inability of the polymer to suppress metal deposition on the advancing bottom surface is consistent with prior suggestions that the metal deposition itself alters the ability of the polymer to assemble on the surface.^{2,6,45,46} This is likely related to metal deposition induced changes in the hydrophilicity of the interface.^{2,45,46} The polymer is subject to localized equilibrium attachment and detachment dynamics; the low current on the passive surface can be viewed as a reflection of the lifetime of such openings where Cu²⁺(H₂O)₅ can access the surface. As the overpotential increases the release of water of hydration with acceleration of the deposition rate would be expected to hinder polymer reattachment to the surface, thereby providing positive feedback for the deposition process. The possible role of lateral surface forces in conveying the polymer to the passive sidewalls is also worthy of consideration.⁵⁰

Higher poloxamine concentration decreases the initial stage of transient sidewall deposition as the increased flux of the polymer leads to more rapid formation of the polyether-halide suppressor bilayer. There is a correspondingly more rapid shift to bottom-up filling and development of the <110> growth habit. As indicated in Figure 7, Figure 9 and Figure S-3 the <110> // ND elongated grains can span the

full width and majority of the length of the via. The transition from the $\langle 111 \rangle$ // ND texture of the bottom surface to $\langle 110 \rangle$ // ND occurs rapidly, often with no more than one or two intermediary grains.

The observation of $\langle 110 \rangle$ as a dominant texture during deposition in uninhibited $\text{CuSO}_4\text{-H}_2\text{SO}_4$ electrolytes has a long history.¹⁴⁻²¹ Electrodeposits initially grow under the influence of the substrate, with subsequent deviations from substrate orientation mediated largely by twinning. More recent work indicates that the transition to $\langle 110 \rangle$ texturing, as well as and the rate of its expression, is reinforced by the presence of Cl^- .³²⁻³⁵ In the case of polycrystalline substrates the transition from isotropic deposition to $\langle 110 \rangle$ texture has been noted for Cl^- concentration as low 10^{-6} mol/L. It is not unreasonable to speculate that many older reports of $\langle 110 \rangle$ growth texture were based on electrolytes with (unspecified or unknown) Cl^- levels above this value. The impact of adsorbed halide adlayers on texture development and sustained growth of Cu(110) oriented surfaces is related to the Cl^- adlayer structure. Specifically, it influences step faceting, terrace reconstruction and the associated surface phase transitions that, in combination, greatly reduce the presence and lifetime, i.e. probability, of Cu (111) microfacets that provide the necessary pathway for twinning to occur.

The uninhibited nature of bottom-up growth combined with sustained growth of $\langle 110 \rangle$ oriented grains is consistent with the absence of suppressor on the growth surface. Suppressor co-adsorption has been related to the hydrophobic character of the interface induced by adsorbed Cl^- . Its absence can be attributed to a change in the hydrophilicity of the moving interface due to the combination of disruption of the adsorbed Cl^- layer and the release of water of hydration at the site of $\text{Cu}^{2+}/\text{Cu}^+/\text{Cu}$ reduction.

Conclusions

Microstructural and morphological evolution during bottom-up Cu filling of TSV in a $\text{CuSO}_4\text{-H}_2\text{SO}_4\text{-Cl-poloxamine}$ electrolyte is examined. In dilute polyether electrolyte the morphology and microstructure develop in two well defined stages. The first begins with a passive to active transition on the via sidewalls. At depths below this transition a conformal layer with columnar grain that arise from epitaxy with the Cu seed layer is formed. The grain width and texture between the inner and outer

sidewalls of the annular vias differ, with the former linked to area change accompanying growth on the curved surfaces. The deposit on the outer wall has the same texture as that on the bottom surface with respect to the ND and CD directions. Subsequently, passivation propagates down the sidewall, ultimately leaving deposition localized to the bottom surface. The transition to bottom-up filling is accompanied by the development of a strong $\langle 110 \rangle$ texture and elongated grains in the growth direction.

Higher polyether concentrations shorten the transient period of sidewall deposition, leaving a thinner, tapered profile that thickens toward the bottom of the via. The more rapid transition to bottom-up filling is associated with more rapid evolution of the texture from the epitaxially defined $\langle 111 \rangle // \text{ND}$ to the Cl^- mediated $\langle 110 \rangle // \text{ND}$ within just one to two grains for the highest poloxamine concentration examined. It has been known for many years that $\langle 110 \rangle$ is the dominant texture developed during deposition in uninhibited $\text{CuSO}_4\text{-H}_2\text{SO}_4$ electrolyte. More recent work indicates that this is related to the presence of Cl^- in the electrolyte. The dominance and durability of the $\langle 110 \rangle$ texture reflects the lowered probability of developing growth twins due to faceting induced by Cl^- adsorption that limits the probability and size of $\langle 111 \rangle$ microfacets required for twin formation. The uninhibited nature of the bottom-up growth and the extended grains in the growth direction are consistent with the absence of the polymer suppressor on the growth surface. Suppressor co-adsorption has been related to the hydrophobic character induced by adsorbed Cl^- . Its absence on the rapidly moving bottom interface is attributed to a change in the hydrophilicity of the interface related to the combination of disruption of the adsorbed Cl^- layer and perturbations related to released water of hydration at the site of $\text{Cu}^{2+}/\text{Cu}^+/\text{Cu}$ reduction.

Acknowledgement

The copper seeded, annular TSV were kindly provided by D. Edelstein of IBM. Research by S.-H. Kim and H.-J. Lee was supported by the National Research Foundation of Korea (NRF) funded by the Ministry of Education (NRF-2019M3A7B9072142).

References

1. T. P. Moffat, D. Wheeler, M.D. Edelstein and D. Josell, *IBM J. Res. Dev.*, **49**, 19-36 (2005).
2. T. P. Moffat and D. Josell, *J. Electrochem. Soc.*, **159**, D208-D216 (2012).
3. D. Josell and T. P. Moffat, *J. Electrochem. Soc.*, **160**, D570-D576 (2013).
4. D. Wheeler, T.P. Moffat and D. Josell, *J. Electrochem. Soc.*, **160**, D3260 (2013).
5. L. Yang, A. Radisic, J. Deconinck, P.M. Vereecken, *J. Electrochem. Soc.* **160**, D3051–D3056 (2013).
6. L. Yang, A Radisic, J. Deconinck, P.M. Vereecken, *J. Electrochem. Soc.*, **161**, D269–D276 (2014).
7. T. M. Braun, D. Josell, J. John and T. P. Moffat, *J. Electrochem. Soc.*, **in press** (2020).
8. C. Link and M.E. Gross, *J. Appl. Phys.* **84**, 5547 (1998).
9. J.M.E. Harper, C. Cabral, P.C. Andricacos, L. Gignac, I.C. Noyan, K.P. Rodbell and C.K. Hu, *J. Appl. Phys.*, **86**, 2516-2525 (1999).
10. M. Stangl, M. Liptak, A. Fischer, J. Acker, J. Thomas, H. Wendrock, S. Oswald and K. Wetzig, *Microelectronic Engineering*, **85**, 534-541 (2008).
11. H.-J. Lee, D. I. Kim, J. H. Ahn, D. N. Lee, *Thin Solid Films* **474**, 250 (2005).
12. H.-J. Lee, H. N. Han, D. H. Kim, U.-H. Lee, K. H. Oh, and P.-R. Cha, *Appl. Phys. Lett.*, **89**, 161924 (2006).
13. Q. Huang, A. Avekians, S. Ahmed, C. Parks, B. Baker-O’Neal, S. Kitayaporn, A. Sahin, Y. Sun and T. Cheng, *J. Electrochem. Soc.*, **161**, D388-D394 (2014).
14. T.H. Orem, *J. Res. Natl. Bur. Std.*, **60**, 597-608 (1958).
15. S.C. Barnes, *Electrochimica Acta*, **5**, 79-86 (1961).
16. F. Ogburn and C. Newton, *J. Electrochem. Soc.*, **110**, 1148-1150 (1963).
17. J. Bebczuk de Cusminsky, *Electrochimica Acta* **17**, 237-246 (1972).
18. W.A. Schultze, *J. Cryst. Growth*, **13/14**, 421-426 (1972).
19. J.G. Wang, M.L. Tian, T.E. Mallouk, M.H.W. Chan, *J. Phys. Chem B*, **108**, 841-845 (2004).
20. D. A. Brown, S. Morgan, V. Peldzinski, R. Brüning, *J. Cryst. Growth*, **478**, 220-228 (2017).
21. H.D. Merchant, *Mater. Charact.*, **53**, 335 (2004).
22. L.Lu, Y. Shen, X. Chen, L. Qian, K. Lu, *Science*, **304**, 422-426 (2004).
23. T-C Liu, C-M Liu, H-Y Hsiao, J-L. Lu, Y-S Huang, C. Chen, *Cryst. Growth. Des.*, **12**, 5012-5016 (2012).
24. M. Hasegawa, M. Mieszala, Y. Zhang, R. Erni, J. Michler, L. Philippe, *Electrochimica Acta*, **178**, 458-467 (2015); and references therein.
25. T.P. Moffat, D. Wheeler and D. Josell, *Advances in Electrochemical Science and Engineering*, eds. R.C. Alkire, D.M. Kolb, J. Lipkowski and P.N. Ross, **10**, 107-189 (2008); and references therein.
26. P. Moreno-García, I. V. Grimaudo, I. A. Riedo, M. Tulej, M. B. Neuland, P. Wurz, Peter Broekmann, *Electrochimica Acta*, **199**, 394–402 (2016).

27. V Grimaudo, P Moreno-García, A Riedo, AC López, *J. Electrochem. Soc.* **166** (1), D3190-D3199 (2019).
28. K. Pantleon, A. Gholinia, M.A.J. Somers, *phys.stat.sol.*, (a) **205**, 275-281 (2008); and reference therein.
29. T.P. Moffat, Electrochemical Processing in ULSI Fabrication and Semiconductor/metal Deposition II. *The Electrochemical Society Proceedings*, **99-9**, 41-51, (1999).
30. O.M. Magnussen, *Chem. Rev.* **102**, 679-725 (2002).
31. K. Wandelt, Encyclopedia of Electrochemistry, Surface Science and Electrochemistry, 166-181 (2018).
32. V.I. Lakshmanan, D.J. MacKinnon and J.D. Brannen, *J. Appl. Electrochem.*, **7**, 81-90 (1977).
33. H.D. Merchant and O.B. Grin, *Mat. Res. Soc. Symp.*, **451**, 433-444 (1997); and references therein.
34. N. Vasiljevic, M. Wood, P.J. Heard and W. Schwarzacher, *J. Electrochem. Soc.*, **157**, D193-D198 (2010).
35. T-C Chan, Y-L Chueh and C-N Liao, *Cryst. Growth. Des.*, **11**, 4970-4974 (2011).
36. F. Wafula, Y. Liu, L. Yin, S. Bliznakov, P. Borgesen, E. Cotts, N. Dimitrov, *J. Electrochem. Soc.*, **157**, D111-D118 (2010).
37. H. Lee, T.-Y. Yu, H.-K. Chneg, K.-C. Liu, P.F. Chna, W.P. Dow, C.-M. Chen, *J. Electrochem. Soc.*, **164**, D457-D462 (2017).
38. H. Lee, Y-A Wang, C-M Chen, *J. Alloys and Compounds*, **765**, 335-342 (2018); and references therein.
39. D. Josell and T.P. Moffat, *J. Electrochem. Soc.*, **165**, D23-D30 (2018).
40. T. M. Braun, D. Josell, M. Silva, J. Kildon, and T. P. Moffat, *J. Electrochem. Soc.*, **166**, D3259 (2019).
41. L.A. Menk, D. Josell, T.P. Moffat, E. Baca, M.G. Blain, A. Smith, J. Dominguez, J. McClain, P.D. Yeh and A.E. Hollowell, *J. Electrochem. Soc.*, **166**, D3066-D3071 (2019).
42. D. Josell, L.A. Menk, A.E. Hollowell, M. Blain and T.P. Moffat, *J. Electrochem. Soc.*, **166**, D3254-D3258 (2019).
43. Z.V. Feng, X. Li and A.A. Gewirth, *J. Phys. Chem B*, **107**, 9415 (2003).
44. M.L. Walker, L. Richter and T.P. Moffat, *J. Electrochem. Soc.*, **152**, 403-407 (2005).
45. G.-K. Liu, S. Zou, D. Josell, L. J. Richter, and T. P. Moffat, *J. Phys. Chem. C*, **122**, 21933 (2018).
46. Yang, H.; Dianat, A.; Bobeth, M.; Cuniberti, G. Copper, *J. Electrochem. Soc.*, **164**, D196-D203 (2017).
47. K. R. Hebert, *J. Electrochem. Soc.*, **152**, C283 (2005).
48. A. Saedi and M. Rost, *Nature Comm.*, **7**, 107733 (2016).

49. E. Chason and A.F. Bower, *J. Appl. Phys.*, **125**, 115304 (2019).
50. D. Ihara, T. Nagai, R. Yamada and S. Nakanishi, *Electrochimica Acta*, **55**, 358-362 (2009).

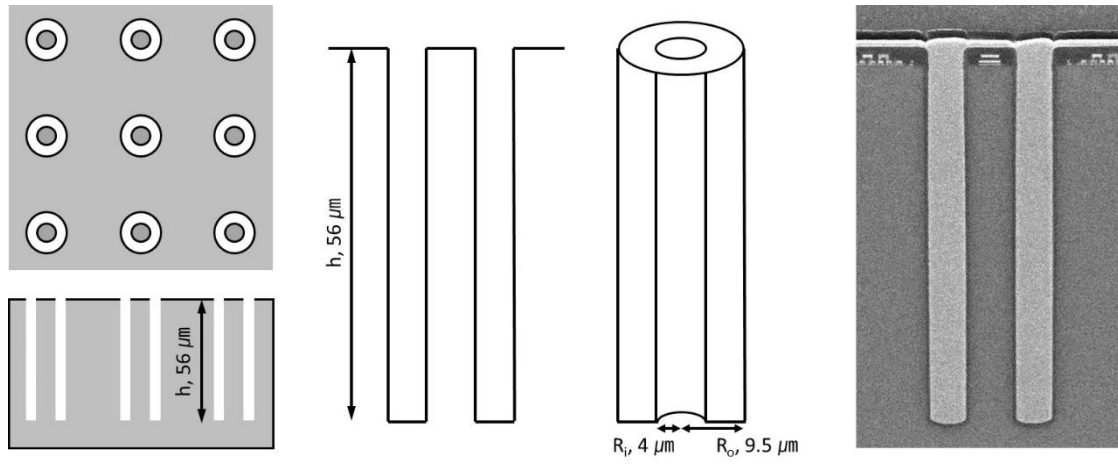


Figure 1. Schematic diagrams of annular TSVs pattern and its cross-sectioned SEM images after filling.

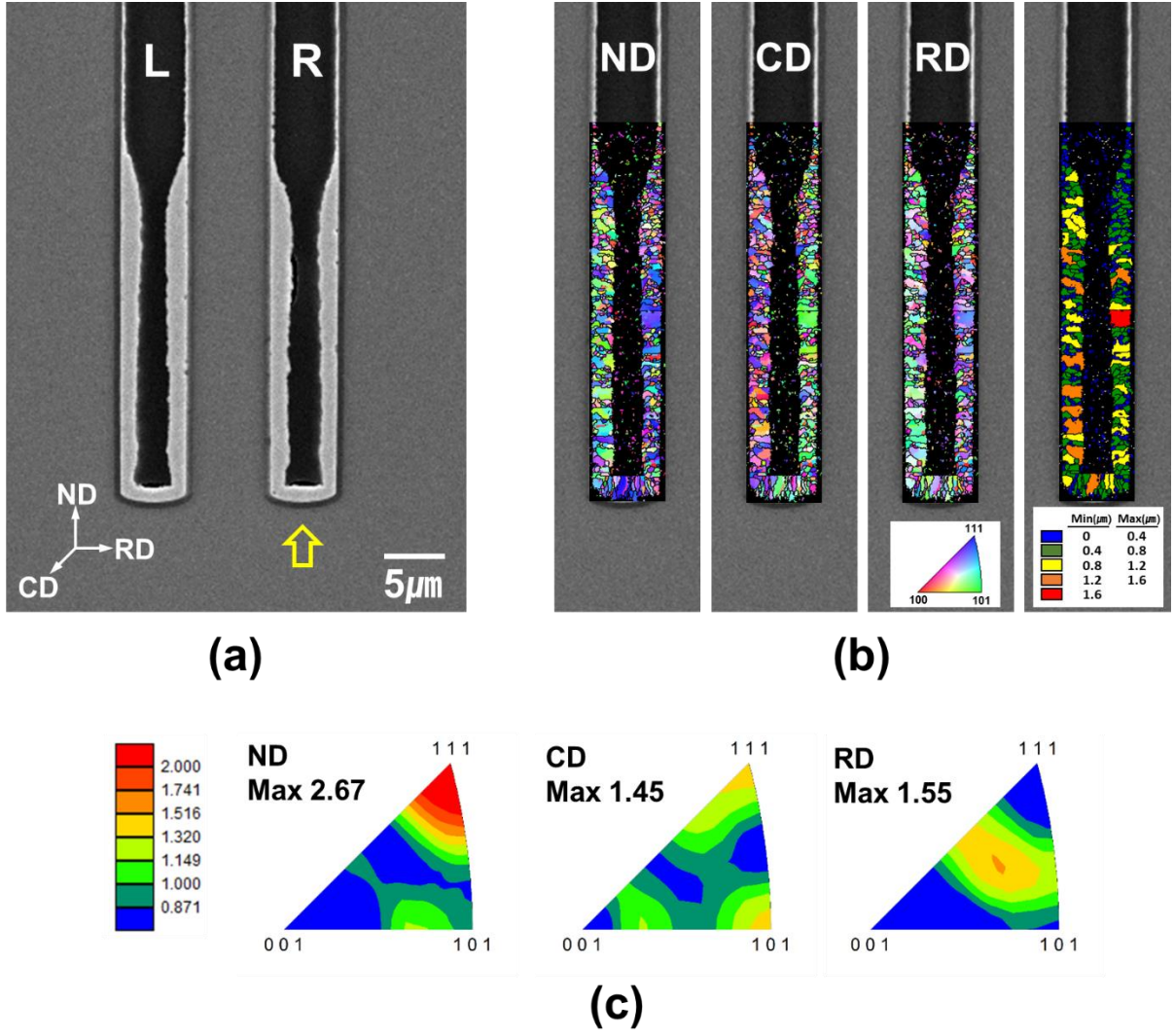


Figure 2. Cross-sectioned annular TSVs after Cu deposition in electrolyte containing 6 $\mu\text{mol/L}$ TET at $-0.64 V_{\text{SSE}}$ for 4 min. (a) SEM image, (b) EBSD measurement data and grain size colored mapping with scale ranges in micrometers and (c) IPF images for ND, CD and RD. Three directions of ND, CD and RD are shown in the lower left of figure 2a.

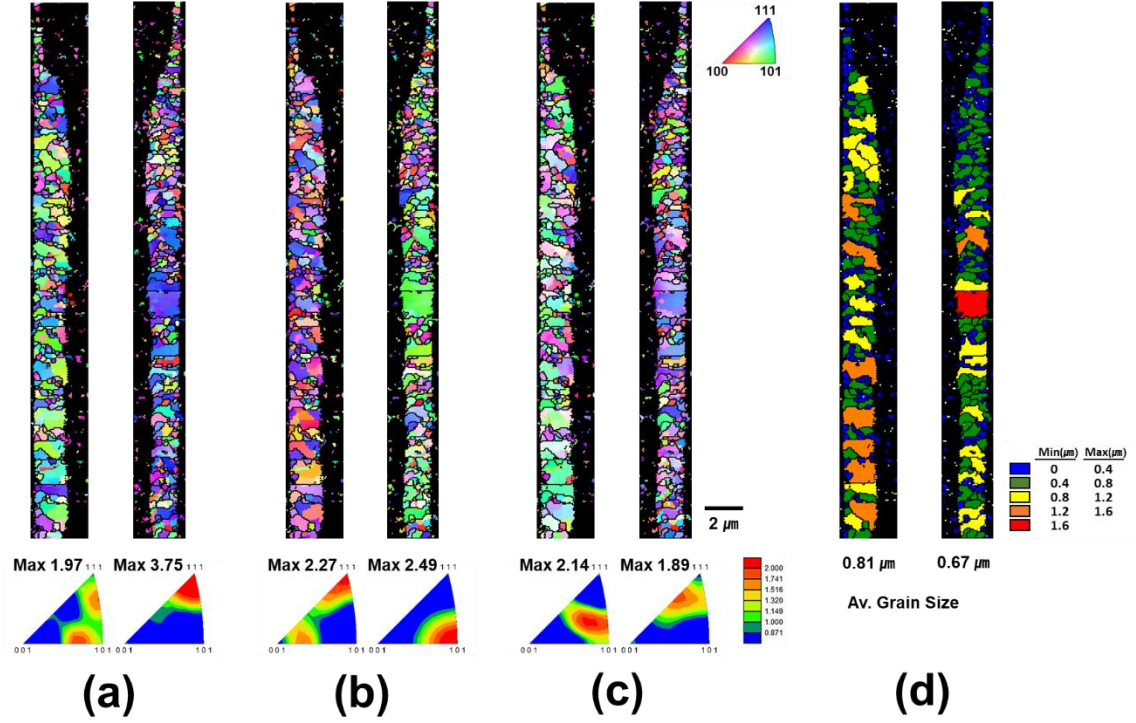


Figure 3. EBSD results of left (inner) and right (outer) sidewalls for cross-sectioned annular TSV after Cu deposition in the electrolyte containing 6 $\mu\text{mol/L}$ TET at $-0.64 \text{ V}_{\text{SSE}}$ for 4 min. EBSD mapping and IPF results for (a) ND, (b) CD and (c) RD. (d) Colored grain distribution binned by grain size, with the average grain size values indicated beneath the maps.

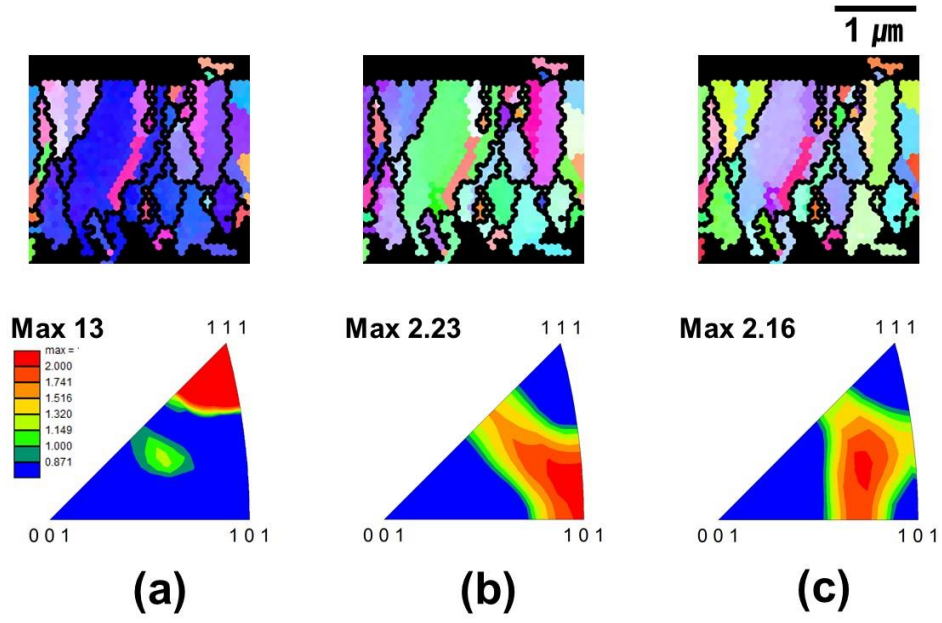


Figure 4. EBSD results of the central bottom region for cross-sectioned annular TSV after Cu deposition in the electrolyte containing 6 $\mu\text{mol/L}$ TET at $-0.64 V_{\text{SSE}}$ for 4 min. EBSD mapping and IPF results for (a) ND, (b) CD and (c) RD.

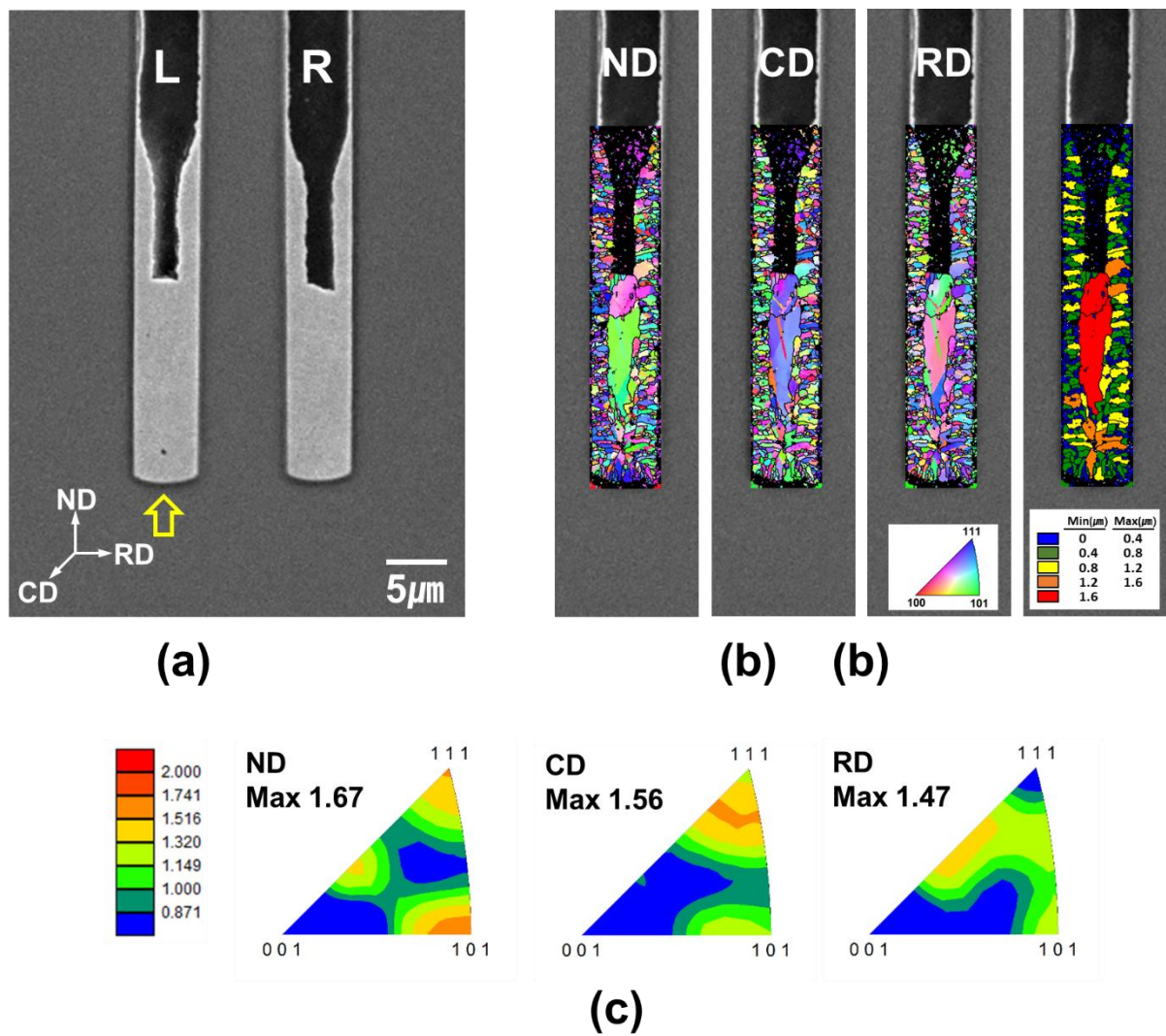


Figure 5. Cross-sectioned annular TSVs after Cu deposition in electrolyte containing 6 μmol/L TET at -0.64 V_{SSE} for 8 min. (a) SEM image, (b) EBSD measurement data and grain size colored mapping result and (c) IPF images for ND, CD and RD.

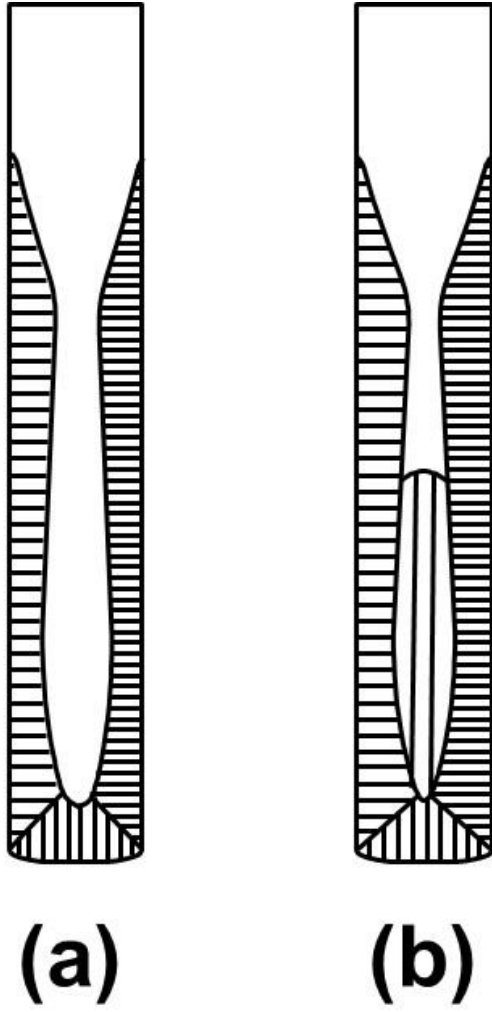


Figure 6. Schematic diagrams of cross-sectioned annular TSVs after Cu deposition in the electrolyte containing 6 $\mu\text{mol/L}$ TET at $-0.64 V_{\text{SSE}}$ for (a) 4 min and (b) 8 min. Growth direction and evolution is reflected in grain boundaries sketched within the regions of sidewall deposit, initial bottom surface deposit and bottom-up growth region.

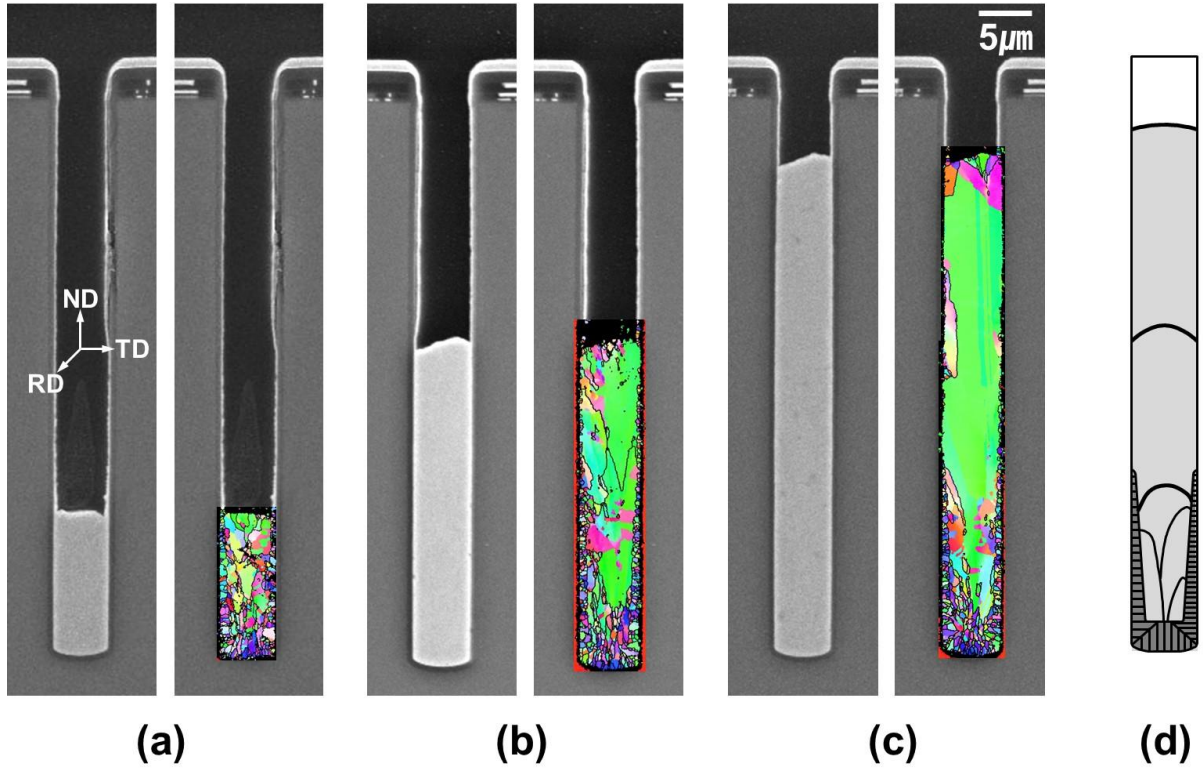


Figure 7. Cross-sectioned annular TSVs after Cu deposition in the electrolyte containing 12 $\mu\text{mol/L}$ TET at $-0.64 V_{\text{SSE}}$ for (a) 4 min, (b) 8 min and (c) 12 min. (d) Schematic diagram of Fig. 7c. EBSD maps are of ND texture.

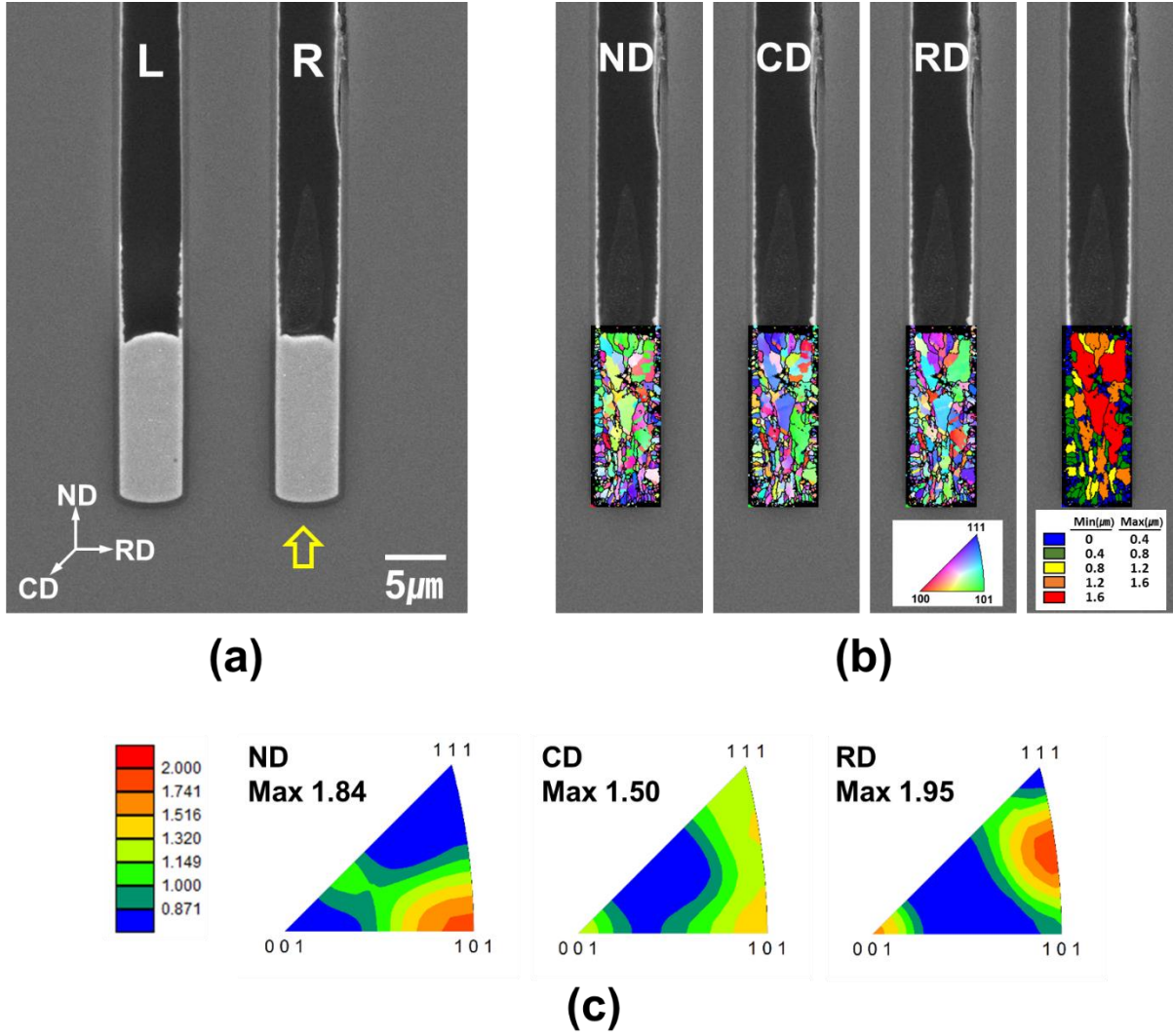


Figure 8. Cross-sectioned annular TSVs after Cu deposition in the electrolyte containing 12 μmol/L TET at -0.64 V_{SSE} for 4 min. (a) SEM image, (b) EBSD OIM mapping results and colored grain size distribution and (c) IPF images for ND, CD and RD. The grain size color map on the far right considers adjacent grains with Σ 3 orientations (i.e., twins) as single entities with colors representing the maximum dimension of the grains.

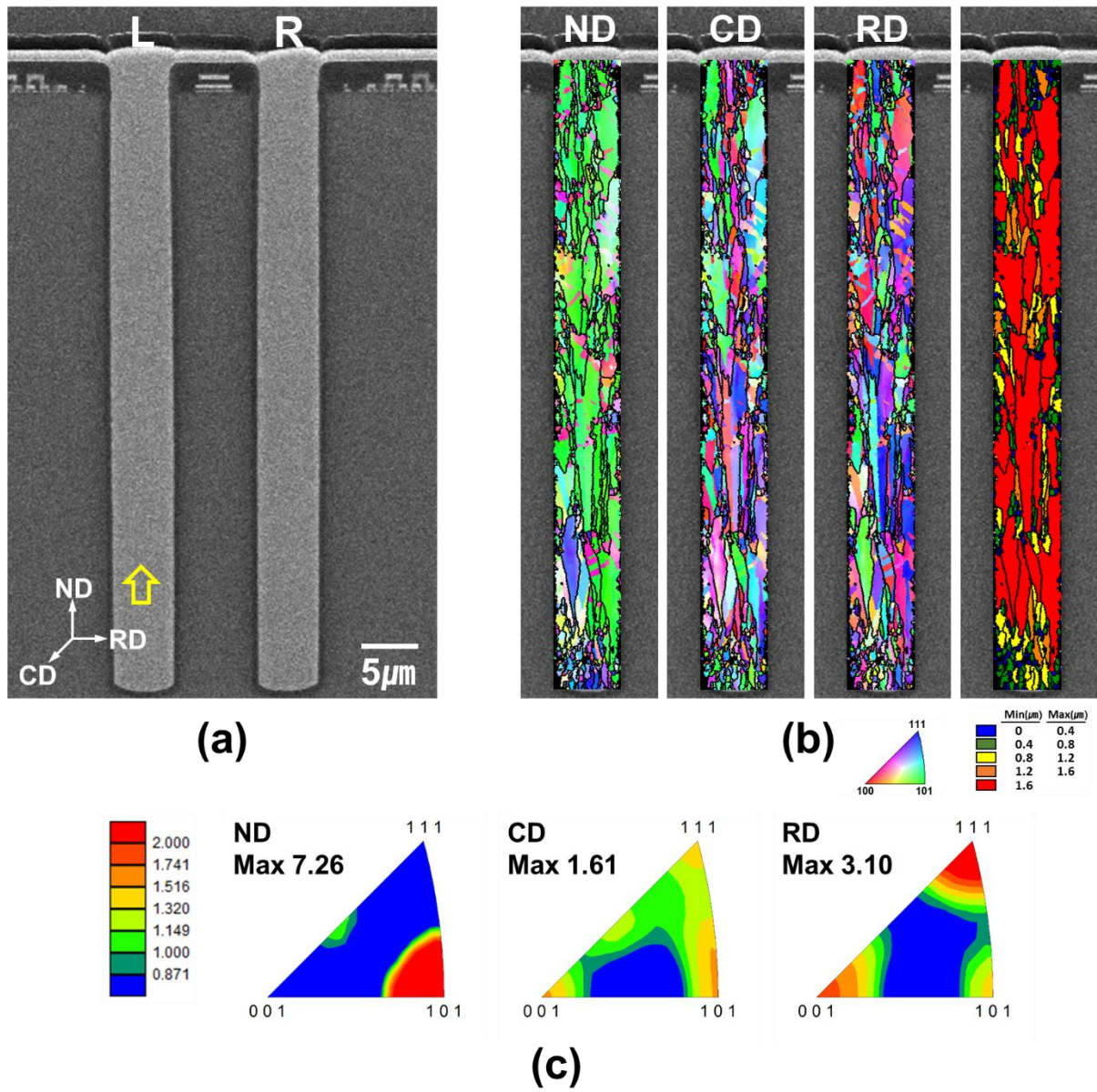


Figure 9. Cross-sectioned annular TSVs after Cu deposition in electrolyte containing 25 μmol/L TET at -0.64 V_{SSE} for 15 min. (a) SEM image, (b) EBSD measurement data and grain size colored mapping result and (c) IPF images for ND, CD and RD.

Supplemental Information

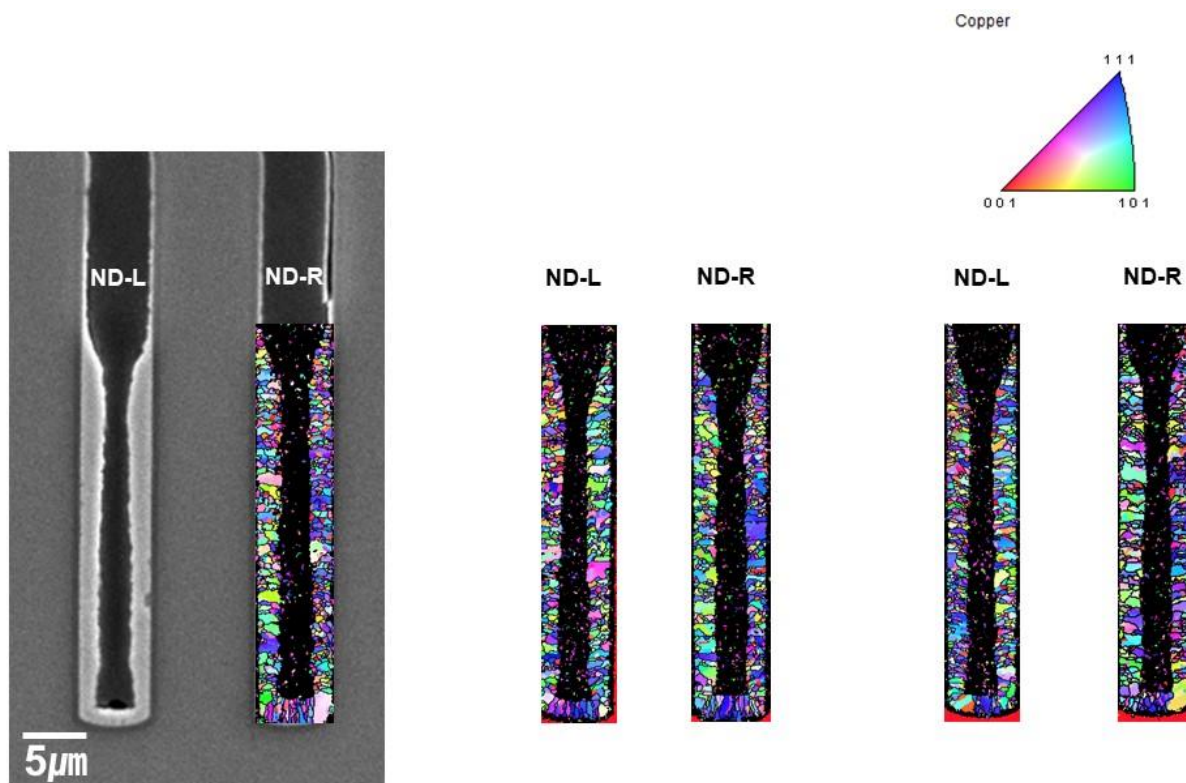


Figure S-1. Five EBSD maps of texture in the ND direction for three different annular vias from one specimen after Cu deposition in electrolyte containing 6 μmol/L TET at -0.64 V_{SSE} for 4 min.

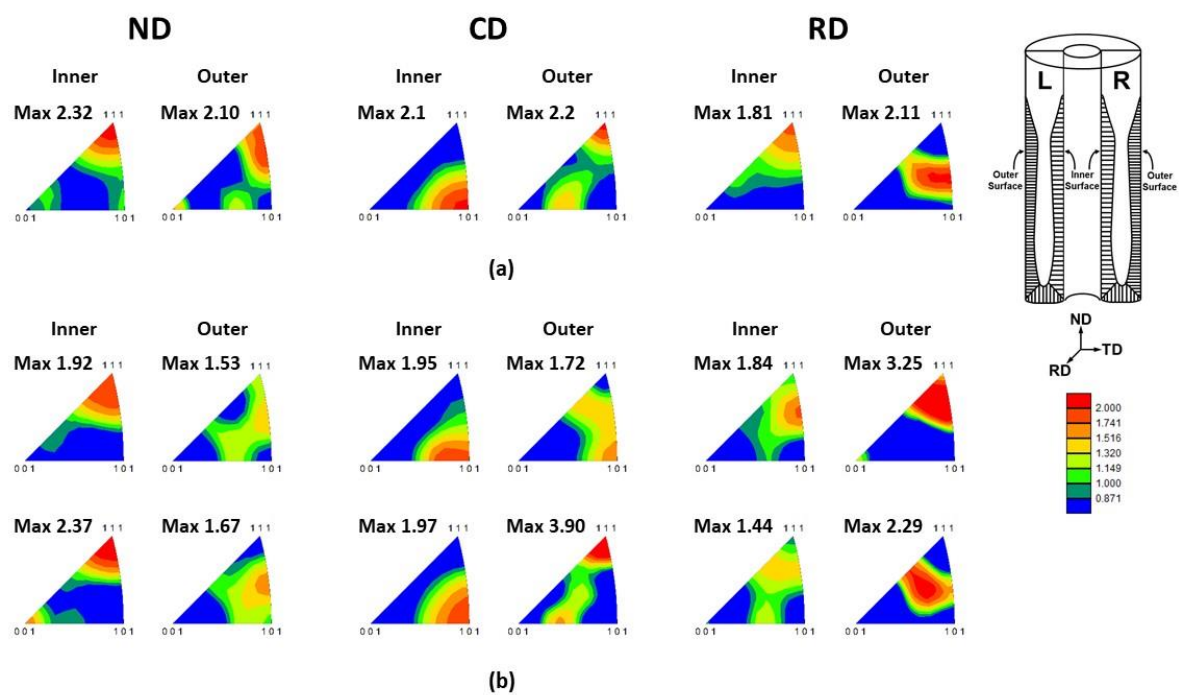


Figure S-2. IPF images for inner and outer sidewalls. (a) Left pattern and (b) right patterns

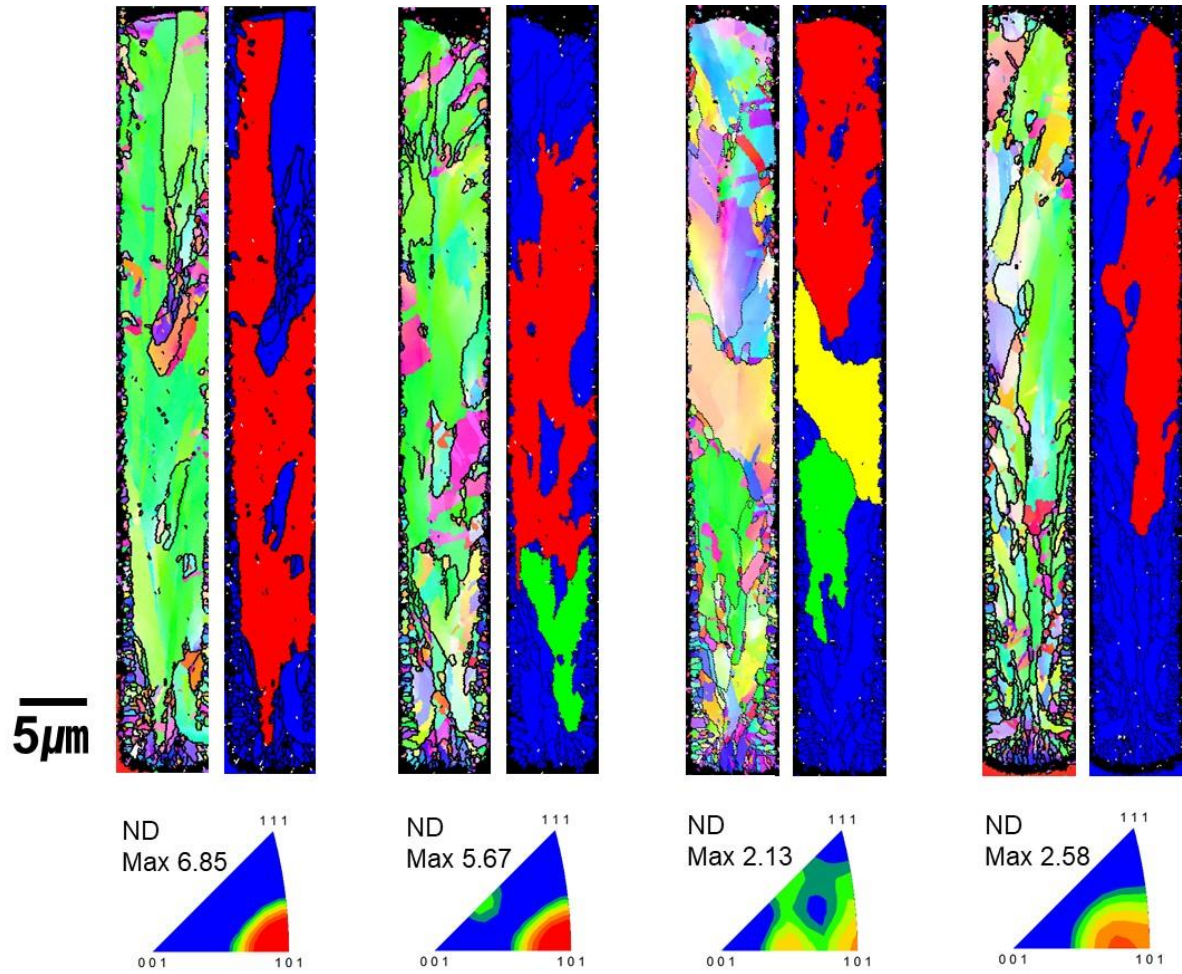


Figure S-3. EBSD ND and grain size maps for cross-sections of two different annular vias after Cu deposition in the electrolyte containing 12 $\mu\text{mol/L}$ TET at $-0.64 V_{\text{SSE}}$ for 12 min. The corresponding IPF for the EBSD maps reveal the bias towards $\langle 110 \rangle$. The grain size color maps treat grains containing $\Sigma 3$ boundaries, i.e., twinned orientations, as single entities, indicated by the red, yellow and green, that can span a considerable volume within the TSV.