Survey of P-Block Metal Additives for Superconformal Cu Deposition in an Alkaline Electrolyte

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ABSTRACT

Catalysis of Cu deposition from a near-neutral Cu²⁺ complexed electrolyte is examined using Bi³⁺, Pb²⁺ and Tl⁺ additives that were selected based on their known ability to accelerate Au deposition in near neutral pH gold sulfite electrolytes. Where appropriate, the ability of these electrolytes to yield superconformal filling of recessed features is also briefly examined. Voltammetry reveals strong acceleration of Cu deposition by Bi³⁺ additions while indication of superconformal filling accompanied by unusual microstructural transitions are evident in cross-sectioned specimens examined by scanning electron microscopy. Results are discussed in the context of behaviors observed for the same heavy metal additives in gold sulfite electrolytes.

INTRODUCTION

Electrochemical deposition of copper is used to fabricate defect-free interconnects in devices with dimensions spanning multiple length scales. Two different processes, known in the electroplating vernacular as through-mask plating and Damascene processing, are possible. Through-mask deposition¹ typically entails electrical contact made to a common backplane of a substrate that is covered with a patterned 2D insulating mask that serves as a template that guides the propagation of metal deposition from the bottom of the feature. Alternatively, Damascene

processing², involves the filling of a recessed 3-D templated volume whose surface is metallized for conductivity and whose recessed features are filled in a void-free manner by additive-derived superconformal^{3,4,5} deposition processes that emphasize deposition toward, or at, the bottoms of the features; planarization of the substrate surface after filling yields electrical isolation of the embedded metal filled features. Superconformal filling of sub-micrometer on-chip Damascene Cu features using competitive adsorption of deposition-accelerating and suppressing additives has been used industrially for more than two decades to produce multilevel structures of arbitrary connectivity through repeated cycles of templating, filling and planarization. Understanding of Cu filling in these small features is provided by models that capture the interplay between strongly adsorbed accelerating additives and evolving surface area within filling features, i.e., the Curvature Enhanced Accelerator Coverage (CEAC) mechanism³⁻⁶. Models based on the same mechanism have also been successfully applied to understand filling in larger vias of relatively low aspect ratio.⁷⁻¹¹ However, even more extremely localized, bottom-up filling of larger features can be obtained in electrolytes containing strongly adsorbed suppressing additives that yield S-shaped Negative Differential Resistance (S-NDR) evident during suppression breakdown in voltametric studies.¹²⁻¹⁴ The evolution of feature filling, including dependence on applied potential, transport and electrolyte composition observed in the electrolytes used for filling of large vias and through vias is well explained by bifurcation models that couple slow localized suppression breakdown with the much faster electrical response evident in the S-NDR signature¹²⁻²².

Recently, an electrodeposition process yielding bottom-up Au filling that is visually similar to that obtained by S-NDR suppressor containing Cu electrolytes was detailed.^{23,24} In place of deposition rate suppressing molecular additives it uses a deposition rate accelerating Bi^{3+} additive in near neutral Na₃Au(SO₃)₂ + Na₂SO₃ electrolyte, and in the most recent applications it has

achieved filling of trenches as deep as 300 µm and with aspect ratios (height divided by width) exceeding 65.²⁵⁻²⁸ Key features of the bottom-up filling process include: an "incubation period" of slow, conformal deposition that increases at more positive potentials; subsequent activation and rapid localized deposition on the bottom surface of the feature that enables defect-free filling of high aspect ratio features; and, finally, re-passivation of the active surface once filling reaches a certain distance from the feature opening that is defined by the applied potential. It is noteworthy that an incubation period of conformal growth is also observed with accelerator-based CEAC filling, where it reflects the time required for accelerating additives to adsorb before they can have an impact on filling evolution, while self-passivation near the surface is observed in S-NDR systems, where it reflects increased suppressor transport nearer the feature opening.

Given the impact of Bi³⁺ on deposition of the noble metal Au in sulfite electrolyte, the present work uses electroanalytical measurements to explore its impact on Cu deposition and trench filling in near-neutral electrolyte based on EDTA complexed Cu²⁺. EDTA has a substantial history as a complexing agent for Cu²⁺ in alkaline solution used for electroless deposition processes. This includes several reports of superconformal filling of submicrometer size features.²⁹⁻³⁵ Likewise, Bi³⁺ as well as Pb²⁺ and Tl⁺, for that matter, are all well-known accelerators of Au deposition³⁶ in sulfite (and cyanide) electrolytes that have been shown to yield superconformal feature filling^{37,38}, with Pb²⁺ additions being more effective for trench filling while Tl⁺ additions generating bright surfaces. In moderately acidic complexing Cu electrolytes, Pb²⁺ has been reported to yield indications of superconformal feature filling³⁹, albeit as a modest suppressor. Accordingly, a limited survey of the impact of Tl⁺ and Pb²⁺ on Cu deposition and feature filling was performed.

EXPERIMENTAL DETAILS

An ethylenediaminetetraacetic acid (EDTA, $C_{10}H_{16}N_2O_8$) complexed cupric sulfate electrolyte, 50 mmol·L⁻¹ CuSO₄·5H₂O + 100 mmol·L⁻¹ C₁₀H₁₆N₂O₈, was used for all experiments. The electrolyte was constituted by dissolving the respective salts in 18 MΩ·cm water. The pH was adjusted from the as-mixed value to near neutral 9.1 and 10.0 through the addition of sodium hydroxide, and all experiments were performed at room temperature. All potentials stated in this work were measured, and are quoted, relative to a Hg/Hg₂SO₄/saturated K₂SO₄ reference electrode (SSE). Dilute concentration of the Bi³⁺ additive was introduced by anodic dissolution of 99.999 (mass) % Bi metal into the electrolyte in the working electrode compartment at a potential of -0.70 V. The possibility of parasitic oxidative processes makes the stated Bi³⁺ concentrations upper bounds. The other heavy metal additives were introduced by titration of aliquots of 1 mmol·L⁻¹ Tl₂SO₄ or 1 mmol·L⁻¹ Pb(ClO₄)₂ aqueous solution prepared from the respective salts.

Electroanalytical experiments in the electrolytes were conducted using a rotating disk electrode (RDE) comprised of a 0.5 cm diameter oxygen-free high conductivity copper disk encapsulated in epoxy. The surface of the RDE was polished to 1200 grit silicon carbide paper to obtain nominally identical surfaces prior to each experiment. Voltammetry was acquired using iR, i.e., current multiplied by resistance, compensation for 85 % of the measured 50 Ω resistance between the working electrode contact and SSE reference electrode. Reductive, cathodic currents are plotted as positive.

Copper feature filling in the electrolyte was examined using fragments of trench-patterned substrates. The patterned wafers were cleaved into fragments approximately 3 mm \times 12 mm in size for the exploratory study. Electrodeposition on the wafer fragments was conducted with the specimens rotating about one end from a Pt spindle (like a helicopter blade) in the electrolyte with the resulting flow nominally parallel to the patterned surfaces; as with the voltammetry, the

cathodic currents are plotted as positive. Significant deposition within the slot in the spindle in which the wafer fragment substrates were clamped precludes quantitative evaluation of deposition charge. Unlike the voltammetry, no attempt was made to compensate for potential drop within the electrolyte or workpiece contacts during the feature filling experiments. The filled specimens were subsequently cross sectioned for imaging by scanning electron microscope (SEM). Further details on trench fabrication and metallurgical cross-sectioning can be found in previous publications.^{23,24}

CYCLIC VOLTAMMETRY

Cyclic voltammetry in the additive-free 50 mmol·L⁻¹ CuSO₄ + 100 mmol·L⁻¹ C₁₀H₁₆N₂O₈ electrolyte captures the onset of significant metal deposition negative of -1.35 V, as shown in Fig. 1. The RDE exhibited a dull copper deposit upon completion of the cycle. The small, approximately constant background current density at more positive potentials may reflect a parasitic process. Deposition stops at approximately -1.28 V on the return scan from the -1.6 V switching potential, resulting in slight hysteresis. With the addition of micromolar concentration of Bi³⁺ additive, no discernable impact on the potential at which the RDE surface activates on the negative-going scan is evident although the steeper rise in current after activation for Bi3+ concentration of 20 μ mol·L⁻¹ and higher suggests more rapid activation of the full RDE surface. This becomes even more evident during the positive-going return scan. Indeed, the current density increases with Bi³⁺ concentration to the extent that current continues to rise even as the potential moves positive from -1.45 V to -1.3 V. For electrolyte containing 50 µmol/L Bi³⁺ the plateau-like response around 9 mA·cm⁻² persists over several hundred millivolts, suggesting that Cu deposition is close to the transport limit for the complexed Cu ions, this potential regime overlapping the region where deposition was entirely passivated on the negative-going scan. The range of the

hysteretic behavior extends to progressively more positive potentials with increasing additive concentration, expanding from a maximum width of approximately 70 mV for the additive-free electrolyte to ≈ 160 mV for 10 µmol·L⁻¹ Bi³⁺ and nearly 400 mV for 50 µmol·L⁻¹ Bi³⁺, the highest concentration examined. A slight cloudiness extending several millimeters out from the Cu RDE onto the surrounding epoxy was noted, indicating that some additional deposition (or precipitation) process is triggered by homogeneous chemistry within the boundary layer adjacent to the RDE at the more negative potentials.

Two successive voltage cycles without interruption in electrolyte containing 30 μ mol·L⁻¹ Bi³⁺ are shown in Fig. 2a. The second cycle begins with suppression that is nominally identical to that at the beginning of the first negative-going scan, but deposition activates at a potential approximately 150 mV positive of the potential at which activation occurred on the first cycle. The current density then increases toward a nominal plateau near 9 mA·cm⁻² with the second return scan nominally duplicating the first thereafter. Consistent with the passivation observed by -0.9 V on return scans in Fig. 1, cycling to -0.8 V in the first of the cycles in Fig. 2a evidently reverses, to a great extent, modification of the electrode surface that underlies the preceding additiveinduced increase of current. Similarity of the return scans after both cycles indicates surface roughening is not the source of increased current density on the return scans, reinforcing the role of potential-dependent additive adsorption in the enhanced deposition current. The increase in current at potentials negative of -1.5 V that was not observed in Fig. 1 is associated with more extended electrolysis of this bath. Adjusting the negative vertex potentials to more positive value reveals strong hysteretic response that develops immediately following the onset of suppression breakdown. Positive feedback evident as a negative differential resistance (NDR) is particularly strong on the return scans for switching potentials of -1.375 V and -1.4 V that are just negative of the sharp uptick that marks activation with the onset of suppression breakdown in the negativegoing scans (**Fig. 2b**).

Chronoamperometric measurements using the RDE at potentials in the hysteretic range exhibit an incubation period of passive deposition before a transient rise of deposition current, as shown in **Fig. 3**. The rising transients correspond to highly localized deposition that initiates in scratches and other surface defects on the RDE as seen in the inset micrograph for deposition at -1.23 V. The rising transients reflect the inception of localized active deposition and the associated increase of active area. The rising current finds analogy in the increasing current on the negative going scans and NDR on the return scans in the voltammetry that likewise reflect not only Cu deposition kinetics but also progressive activation of the RDE surface area.

As previously noted, localization in recessed regions and an incubation period prior to the activation of deposition are signatures of the Bi³⁺ accelerated bottom-up feature filling Au electrolytes (and more generally for deposition from suppressed electrolytes exhibiting S-NDR). It is not unreasonable to imagine that the localization observed on the RDE surface in the Bi³⁺- accelerated Cu system has analogous implications for selective deposition in engineered recessed features, i.e., trenches and vias.

As with the Bi^{3+} additive, cyclic voltammetry for Cu deposition from the EDTA electrolytes containing Pb^{2+} or Tl^+ was briefly surveyed. In addition to EDTA being a strong complexing agent for Cu^{2+} it is also a well-known chelating agent for heavy metals. The formation constants log K₁ are 18.7 to 18.8 for Cu^{2+} , 22.8 to 27.9 for Bi^{3+} , 18.3 to 18.04 for Pb^{2+} , 22.3 for Tl^{3+} and 6.53 for Tl^{+} .^{40,41} The impact of the respective heavy metals on the Cu deposition rate was briefly examined as a function of salt additions up to 50 µmol·L⁻¹. As shown in **Fig. 4a**, Pb additions up to 20 µmol·L⁻¹ have no impact on the voltametric hysteresis beyond that evident for the base electrolyte. In

contrast, Tl⁺ additions, as shown in **Fig. 4b**, lead to a monotonic positive shift in the onset potential for deposition and slight acceleration of the deposition during the negative-going voltammetric scan, while the return scans merge together and/or cross over the negative-going scan at current density $< 2.5 \text{ mA} \cdot \text{cm}^{-2}$. Visible roughening apparent after the voltammetric cycle makes it difficult to assign the relative contributions of catalysis versus area expansion to the overall response. In any case the results for both systems contrast with the strong acceleration observed for the Bi³⁺dosed electrolyte. As such, filling experiments were not performed for either system.

TRENCH FILLING

Representative images of deposition after 10 min and 30 min at -1.35 V in 3 μ m deep, 2 μ m and 4 μ m wide trenches in electrolyte containing 10 μ mol·L⁻¹ Bi³⁺ are shown in **Fig. 5**. The applied potential is just positive of the value yielding suppression breakdown on the planar RDE (**Fig. 1**). The Cu deposit is highly porous and essentially conformal in the narrower trenches, reaching a thickness of approximately 0.4 μ m after 30 min deposition; the porosity may be related to electrolyte pH and possibly H₂ generation. In contrast, much more substantial deposition occurs on the sidewalls and bottom of the wider trench. Active deposition is already underway at 10 min on the trench bottom and extending all way up the sidewalls to just below the field. The wider trench is nearly, albeit irregularly, filled by 30 min, the volume of the active deposit being free of the nanoscale porosity that is characteristic of the passive deposit seen in the narrower trench.

Deposition was also examined in deeper trenches in an electrolyte containing 20 μ mol·L⁻¹ Bi³⁺ The current transients for deposition in 7 μ m deep, 0.65 μ m wide trenches are shown in **Fig. 6** for different potentials. As with the planar RDE (**Fig. 3**), the lower initial current density corresponds to slow and conformal passive deposition that yields a fragile and porous microstructure. The nominal passive current density is higher than on the RDE due to the larger actual surface area of the patterned substrate given the fairly high aspect ratio of the trenches (as well as some contribution from deposition in the holder). Inset micrographs of the respective cross-sectioned trenches reveal active Cu deposition approximately 2 μ m below the trench openings of the specimens deposited at -1.28 V and -1.25 V. The rising transients reflect the degree of activation, although the relatively gradual rise of the current transient at -1.22 V was not associated with obvious activation of deposition, at least in the trenches within the region of the specimen examined.

Motivated by the prior observation of the strong influence of pH on the rate of Bi³⁺ stimulated Au deposition in sulfite media²⁴, the effect of shifting the pH from 9.1 to 10 on the Bi^{3+} stimulated deposition process was briefly examined as shown in Fig. 7. As with the lower pH electrolyte, the acceleration of Cu deposition by the Bi³⁺ additive begins at the same potential as the onset of deposition in the additive-free electrolyte, reflecting the role of Bi³⁺ in stimulating the growth process. In contrast to impact of pH seen in the Bi³⁺ stimulated Au deposition from sulfite electrolytes, close examination of the voltammetry at pH 9.1 in Fig. 1, and pH 10 in Fig.7 reveals no significant difference. Likewise, the pH change does not substantially impact the localized superconformal deposition observed during trench filling at potentials in the hysteretic voltammetric region. Cross-sectioned trenches after Cu deposition shown in Fig. 8 reveal dense deposits growing on top of the porous conformal deposits that line the low aspect ratio trenches. The porous and dense microstructures once again reflect the passive and active deposition states respectively, that are manifest in the hysteretic voltammetry. The more complete filling of trenches with the dense (active) deposits at more negative potentials is consistent with shortening of the incubation period as well as potential-dependent deposition kinetics of the active state (Fig. 7).

The three spherically shaped occluded regions of low-density deposit within the trenches filled at -1.39 V, **Fig. 8c**, and the similar porous region observed with the filling trench at 1.41 V, **Fig. 8df**, are an additional curiosity in the filling process. Their spherical nature and low density suggest the possibility of a homogenous precipitation process that might also be related to the cloudy deposits on the epoxy surface surrounding the RDE noted earlier. Not shown here, conformal porous deposits are obtained in narrower trenches as with the lower pH electrolyte. Deposition at -1.41 V (and at a somewhat higher rotation rate) exhibits increased variability in the extent of trench filling that dovetails with the variations observed in microstructural evolution implicit for the three trenches examined from the same specimen (**Fig. 8d-f**). The images also capture a bias towards inception of active deposition in the bottom corners.

Successful filling of deeper trenches requires suppressing deposition on the sidewalls farther below the field. In the Bi^{3+} containing Au electrolytes this is accomplished using potentials closer to the positive potential end of the voltammetric hysteretic range. The result of an analogous shift to more positive potentials in the Bi^{3+} containing Cu electrolyte is shown in **Fig. 9**. Deposits in 56 µm deep annular vias filled at -1.10 V exhibit active deposition that is recessed essentially to the via bottom (**Fig. 9a,b**) albeit with activation higher in the vias that, with further deposition, would trap a void and truncate the bottom-up filling. Deposits in 45 µm deep, 4 µm wide trenches filled under the same conditions exhibit similar localization without activation on the upper sidewalls (**Fig. 9c,d**). Both the localization of Cu deposition at the feature bottoms and the incipient failure through sidewall activation following partial bottom-up Cu filling (i.e., truncated bottom-up filling) are observed during Au feature filling in Bi^{3+} containing Au electrolytes²³⁻²⁸. The similarity to Au fill is clear through comparison to the visually analogous examples of localized Au deposition exhibiting sub-optimal and true bottom-up filling in **Fig. 9c,f**. The sub-100 nm spherical precipitates adjacent to the lower surfaces in **Fig. 9c,d** suggest homogeneous nucleation in the electrolyte, or perhaps fragile debris from passive deposition on some portion of the workpiece, that has been captured during the epoxy infiltration step used to produce the cross-section.

DISCUSSION

Localized Cu filling of recessed surface features has been obtained using the single accelerating additive Bi³⁺ in a slightly alkaline EDTA-CuSO₄ electrolyte rather than the combined accelerating and suppressing additives typically used in acid Cu electrolytes for Damascene feature filling.³⁻¹¹ The process takes advantage of the intrinsic suppression associated with such chelated electrolytes. Likewise, whereas bottom-up Cu filling of larger TSV is possible with the co-adsorption of polyethers and halides to form a suppressor phase through the S-NDR mechanism,¹²⁻¹⁴ in the present work Bi serves as a surfactant on the advancing surface and activates the reduction of the Cu-EDTA complex. The surfactant quality is likely supported by the immiscible nature of Cu and Bi. As with the bottom-up Au filling that motivates this study the sharpness of the system response is suggestive of a critical phenomenon. Accordingly, the nature of coupling between the ohmic losses associated with current flow in the electrolyte and the interface kinetics through the NDR behavior indicated in **Fig. 1** and **Fig. 2** deserves further study.

Similarities aside, clear differences exist between the Bi-accelerated Cu system and the previously detailed Bi-accelerated Au system. The most significant is the inability of the Bi³⁺ additive to shift the potential associated with the onset of suppression breakdown in the Cu voltammetry whereas Bi³⁺ adsorption shifts suppression breakdown in the Au system by hundreds of millivolts. Despite this difference on the negative-going scans, the Bi³⁺ additive provides for

sustained acceleration of deposition over a broad range of potentials on the reverse scans in both systems as reflected in the substantial hysteresis in both systems: a range of ≈ 0.4 V for the Cu electrolyte versus ≈ 0.5 V for the Au electrolyte. Thus, Bi³⁺ can maintain growth on an actively advancing Cu deposit but has limited, if any, ability to nucleate destabilization of the original passive state formed during open circuit immersion. Despite this difference in the voltammetry, and regardless of its explanation, the Bi³⁺ additive enables localization during feature filling in the Cu system that is visually analogous to that obtained in the Au system even though it presently fails to fill features completely. Another similarity is the ability of more positive deposition potentials to shift active deposition farther from trench openings in higher aspect ratio trenches. The commonality of phenomena appears too numerous to be mere coincidence and suggest that, with further work, the promise of an alkaline electrolyte for filling high aspect features with Cu might be realized. Future efforts should include the study of higher metal ion concentration as well as different organic complexing agents, the latter to not only learn more about the passivation or inhibition of the deposition process but also about the complexation of the additives themselves and its impact on reactivity.

In contrast to the similarity evident between Bi^{3+} -accelerated Au deposition from the Na₃Au(SO₃)₂ electrolyte and Bi^{3+} -accelerated Cu deposition from the Cu-EDTA electrolyte, the same cannot be said for the other heavy metal additive additions Tl⁺ and Pb²⁺, at least for the conditioned examined herein.

CONCLUSIONS

A brief survey is presented of the prospect of using micromolar concentrations of the heavy metal additive additions Tl⁺, Pb²⁺, and Bi³⁺ to generate superconformal and/or extreme bottom-up

filling of Cu from an alkaline 50 mmol·L⁻¹ CuSO₄ + 100 mmol·L⁻¹ EDTA electrolyte. The study is motivated by the success of these heavy metal additives in generating such behavior in gold deposition from near neutral Na₃Au(SO₃)₂ and cyanide electrolytes. Electroanalytical measurements captured substantial acceleration of the rate of Cu deposition by Bi³⁺ adsorption following activation of the Cu EDTA passivated surface. Acceleration is reflected in the strong positive feedback evident as a negative differential resistance during the return scans in cyclic voltammetry. However, unlike the Bi³⁺ accelerated Au sulfite system, where voltammetric activation is observed at potentials well positive of the onset of deposition in the additive-free electrolytes, the potential at which activation occurs in the present Cu system is unchanged from that in the additive-free electrolyte. The Bi^{3+} additive, while assisting in the maintenance of active deposition, appears to have difficulty destabilizing the passivated surface under the conditions examined. The feature filling results do demonstrate that destabilization does in fact occur at recessed surfaces, but the activation process is uneven. An additional drawback of the system, also evident in previous work with alkaline Cu systems, is that, while the active deposits appear to be quite dense, the passive deposits are both significant in volume for the filling conditions examined and highly porous. Further work will be required to overcome these challenges.

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FIGURES



Figure 1: Cyclic voltammetry for Cu deposition from 50 mmol·L⁻¹ CuSO₄ + 100 mmol·L⁻¹ $C_{10}H_{16}N_2O_8$ of pH 9.1 with the indicated Bi³⁺ concentrations. The applied potential was cycled

from -0.80 V SSE at 2 mV·s⁻¹, the RDE rotation rate is 100 rpm (200π rad·min⁻¹), data was acquired using iR compensation for 85 % of the measured 50 Ω cell resistance (i.e., leaving 8 Ω of uncompensated cell resistance). Cathodic currents are plotted positive, with current density obtained from measured current using the nominal area of the 0.5 cm diameter RDE. Potentials are referenced to a saturated mercurous sulfate (SSE) reference electrode.



Figure 2: Cyclic voltammetry for Cu deposition from 50 mmol·L⁻¹ CuSO₄ + 100 mmol·L⁻¹ $C_{10}H_{16}N_2O_8$ adjusted to pH 9.1 using NaOH. a) Multicycle voltammogram with electrolyte containing the specified 30 µmol·L⁻¹ Bi³⁺ concentration where the potential was cycled twice from -0.80 V to -1.6 V and back to -0.80 V at 2 mV·s⁻¹. b) Cyclic voltammograms with electrolyte containing 50 µmol·L⁻¹ Bi³⁺ for different switching potentials in the range -1.3 V to -1.5 V. Conditions where partial activation is achieved on the negative going scan initially exhibit rising current on the return scan, and thus negative differential resistance. The potential was cycled from -0.80 V at 2 mV·s⁻¹ with 85 % iR compensation while the RDE was rotated at 100 rpm. Cathodic currents are plotted positive, with current density obtained from measured current using the nominal area of the 0.5 cm diameter RDE.



Figure 3: Current transients for Cu deposition at the specified potentials on the RDE rotated at 100 rpm in 50 mmol·L⁻¹ CuSO₄ + 100 mmol·L⁻¹ C₁₀H₁₆N₂O₈ electrolyte of pH 9.1 containing 50 μ mol·L⁻¹ Bi³⁺. An "incubation period" of conformal, suppressed deposition precedes the onset of active deposition, its duration increasing at more positive potentials. Data was acquired using iR compensation for 85 % of the measured 50 Ω cell resistance. Cathodic currents are plotted positive, with current density obtained from measured current using the nominal area of the 0.5 cm diameter RDE. An inset image of the deposit grown on the RDE at -1.23 V for 720 s (area approximately 300 μ m × 230 μ m).



Figure 4: Cyclic voltammetry for Cu deposition from 50 mmol·L⁻¹ CuSO₄ + 100 mmol·L⁻¹ $C_{10}H_{16}N_2O_8$ electrolyte of pH 9.1 for the specified a) Pb²⁺ or b) Tl⁺ concentrations. The potential was cycled from -0.80 V at 2 mV·s⁻¹, and the RDE rotation rate is 100 rpm. The data were collected using 85 % iR compensation for the 50 Ω cell resistance. Cathodic currents are plotted positive, with current density obtained from measured current using the nominal area of the 0.5 cm diameter RDE.



Figure 5: Scanning electron microscope images of Cu electrodeposits in cross-sectioned trenches on Au seeded wafer fragments patterned with 3 μ m deep trenches approximately 2 μ m and 4 μ m

wide after Cu deposition at -1.35 V at 100 rpm in 50 mmol·L⁻¹ CuSO₄ + 100 mmol·L⁻¹ C₁₀H₁₆N₂O₈ electrolyte containing 10 μ mol·L⁻¹ Bi³⁺ for the indicated periods of time.



Figure 6: Current transients associated with Cu electrodeposition at the indicated potentials on substrates patterned with 7 μ m deep, 0.65 μ m wide trenches seeded with Pt in 50 mmol·L⁻¹ CuSO₄ + 100 mmol·L⁻¹ C₁₀H₁₆N₂O₈ electrolyte of pH 9.1 containing 20 μ mol·L⁻¹ Bi³⁺. The substrates were rotated at 200 rpm. Cathodic currents are plotted positive, with the nominal current density obtained from measured current using the 3 mm × 12 mm planar area of the substrate. Transients acquired without compensation for cell resistance. Inset scanning electron microscope images of the Cu electrodeposits in the cross-sectioned trenches show active deposition at -1.28 V and -1.25 V localized ≈ 2 µm from the trench openings and entirely conformal deposition at -1.22 V; features farther down the trenches filled at -1.28 V are artifactual irregularities from the epoxy backfill process.



Figure 7: Cyclic voltammetry for Cu deposition from 50 mmol·L⁻¹ CuSO₄ + 100 mmol·L⁻¹ $C_{10}H_{16}N_2O_8$ of pH 10.0 containing the specified Bi³⁺ concentrations. The potential was cycled from -0.80 V at 2 mV·s⁻¹, and the RDE was rotated at 100 rpm. Data was acquired using software 85 % iR compensation of the measured 50 Ω cell resistance. Cathodic currents are plotted positive, with current density obtained from measured current using the nominal area of the 0.5 cm diameter RDE.



Figure 8: Scanning electron microscope images of Cu electrodeposits in cross-sectioned trenches on Au seeded wafer fragments patterned with 3 μ m deep, 4 μ m wide trenches after Cu deposition in 50 mmol·L⁻¹ CuSO₄ + 100 mmol·L⁻¹ C₁₀H₁₆N₂O₈ electrolyte of pH 10.0 containing 10 μ mol·L⁻

¹ Bi³⁺. Filling after a) 50 min at -1.35 V, b) 50 min at -1.37 V and c) 45 min at -1.39 V, all at 200 rpm. d-f) 38 min at -1.41 V at 400 rpm.



Figure 9: Scanning electron microscope images of Cu electrodeposits in cross-sectioned a) Cuseeded 56 mm deep annular vias after 2 h 30 min at -1.10 V with b) highlight of feature bottom and c) evaporated Au-on-atomic layer deposited Pt-seeded 45 μ m deep, 4 μ m wide trenches after 4 h at -1.10 V with d) highlight of feature bottom. The Cu was electrodeposited from 50 mmol·L⁻¹ CuSO₄ + 100 mmol·L⁻¹ C₁₀H₁₆N₂O₈ electrolyte of pH 10.0 containing 50 μ mol/L Bi³⁺ while the wafer fragment rotated at 300 rpm. The filling geometries are compared to Au filled Au-on-Ptseeded 45 μ m deep, 4 μ m wide trenches after e) 1 h 25 min at -0.82 V and f) 4 h at -0.80 V, both in 0.16 mol·L⁻¹ AuNa₃(SO₃)₂ +0.64 mol·L⁻¹ Na₂SO₃ electrolyte containing 4 μ mol Bi³⁺ while rotating at 400 rpm. The small spherical precipitates adjacent to the bottom surface in d) are suggestive of homogeneous nucleation in the electrolyte or perhaps friable passive deposit inserted/displaced during epoxy infiltration used for specimen cross-sectioning.