

Additives for Superconformal Gold Feature Filling

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ABSTRACT

An overview of the effect of additives on Au electrodeposition from $\text{Na}_3\text{Au}(\text{SO}_3)_2$ based electrolytes is presented with an emphasis on filling of fully metallized recessed surface features such as trenches and vias. The impact of heavy metals additives Tl^+ , Pb^{2+} , and Bi^{3+} is reviewed and accompanied by a brief survey of the effects of Sb^{3+} , Te^{4+} , SeCN^- , 3-mercaptopropylsulfonic acid (MPS) and polyethyleneimine (PEI) additions. The addition of Tl^+ , Pb^{2+} , Bi^{3+} or Sb^{3+} accelerates the kinetics of $\text{Au}(\text{SO}_3)_2^{3-}$ reduction to Au, as manifest in hysteretic voltammetry and rising chronoamperometric transients, and yields bright specular deposits. Gold deposition with Pb^{2+} addition exhibits superconformal filling in sub-micrometer trenches while Bi^{3+} addition induces a more extreme bottom-up filling, but Tl^+ and Sb^{3+} additions yield essentially conformal deposition for the conditions examined. Modest acceleration and hysteresis observed with Te^{4+} addition reflect roughening due to limited nucleation, 3D growth and delayed coalescence, rather than catalysis, and are associated with conformal feature filling. Unlike the other additives, SeCN^- , MPS and PEI inhibit the deposition kinetics. Breakdown of suppression during deposition in micrometer size trenches is biased toward recessed surfaces where the flux of suppressor is constrained, yielding localized deposition and superconformal filling.

INTRODUCTION

Gold electroplating has been widely applied in applications ranging from fabrication of micro and nanoscale devices to artwork. In many cases a bright specular surface finish and specific metallurgical properties are needed, and the impact of ionic and molecular additives on both has received significant attention. Electrolytes based on the $\text{Au}(\text{CN})_2^-$ anion have been widely used in commercial gold electroplating although efforts to mitigate the environmental risk associated with cyanide chemistry have resulted in the development of alternative chemistries, including sulfite, thiosulfate and hydantoin^{1,2}. Important discoveries, disclosures and insights into the use of heavy metal surfactants as brightening additives for Au cyanide electroplating are well captured in the important work of McIntyre and Peck³ along with further studies by a number of other groups⁴⁻²⁵. In these works, electroanalytical studies find that micromolar concentrations of heavy metal additives such as Tl^+ , Pb^{2+} , Bi^{3+} and Sb^{3+} depolarize, i.e., accelerate, the Au deposition (and dissolution) reaction and yield bright electrodeposits. The depolarization induced by heavy metal adsorption reflects disruption of CN^- based overlayers that form during operation in the neat electrolyte; the result is acceleration of both Au deposition and dissolution. The surfactant quality of these low surface tension metals is reflected in underpotential deposition on Au surfaces and is widely examined in electrolytes ranging from acid to alkaline.^{24,25}

Integration challenges combined with operational restrictions for fabrication of microsystems by through-mask Au electroplating in patterned photoresist have motivated a shift from cyanide to sulfite or thiosulfate electrolytes for operations at neutral pH values.^{1,2,26-33} While applications still generally require smooth deposit surfaces, limited information is available as to the identity and

operation of brightening additives used in these electrolytes. Despite limited mechanistic insight into their operation, attention remains largely focused on the low surface tension heavy metals and other metal cations. The impact of Pb, Tl and Bi (as well as Ce and W) on surface smoothness as captured in **Figure 1** has been widely noted.

The benefits afforded to interconnect fabrication by superconformal *copper* deposition processes that allow void-free filling of high aspect ratio embedded damascene structures such as trenches and vias^{34,35} motivate the examination of additives for superconformal *gold* deposition for void-free filling of metallized features. Applications range from metallization for optoelectronics to microsystems and X-ray gratings, with the high density of gold underpinning the latter two technologies. Recent advances in processes for superconformal Au deposition that are key to achieving fully dense deposits are reviewed herein, noting commonalities with behaviors seen in cyanide chemistries and highlighting new insights and opportunities relevant to both existing and emerging technological opportunities. An effort is made to place these results in the context of known superconformal deposition mechanisms, i.e., the curvature enhanced accelerator coverage (CEAC) mechanism and the inhibitor-induced S-shaped negative differential resistance (S-NDR) mechanism, previously uncovered in electroplating studies of other metals including Cu, Ag, Ni and Co. The prospect of new mechanisms for superconformal growth is discussed in the context of the recently discovered bottom-up filling and self-terminating Au deposition process that, to date, has enabled the filling of trenches having aspect ratios (height/width) exceeding 55!

The CEAC mechanism³⁶⁻³⁸ presumes the rate of metal deposition scales with coverage of surfactant accelerator that itself responds to area change during metal deposition on non-planar surface segments. On planar surfaces such as rotating disk electrodes (RDE) progressive adsorption of accelerator leads to hysteretic cyclic voltammetry and rising chronoamperometric

transients that can be used extract kinetics for the accelerator adsorption, consumption, and impact on metal deposition rate. With these values in hand CEAC-based feature filling models enable accurate prediction of superconformal Cu deposition in damascene features and microvias from additive-containing acid sulfate electrolytes³⁵⁻⁴¹, superconformal Ag deposition in trenches and vias⁴²⁻⁴⁷ from SeCN^- accelerated cyanide electrolytes and Au filling from both KAu(CN)_2 and near neutral $\text{Au(SO}_3)_2^{3-}$ electrolytes containing Pb^{2+} accelerator.^{19,20,48} At larger length scales, the S-NDR mechanism couples suppressor transport and adsorption to the impact of adsorbate coverage on the metal deposition rate and consumption of the adsorbate through that metal deposition. With kinetics derived from studies on planar substrates, models based on the S-NDR mechanism enable accurate prediction of superconformal filling of tall and high aspect ratio features with Cu⁴⁹⁻⁵² and Zn⁵³ from sulfate electrolytes, Co⁵⁴ and Ni^{55,56,57} from mixed sulfate and chloride electrolytes and Au^{58,59} from sulfite electrolytes containing a variety of suppressing additives.

EXPERIMENTAL DETAILS

Unless noted otherwise depositions detailed in this work used an industrial sodium gold sulfite source ($\text{Na}_3\text{Au(SO}_3)_2$, Technic Gold-25F concentrate) containing 2 troy ounces of gold per liter, equivalent to $0.32 \text{ mol}\cdot\text{L}^{-1}$ ($197 \text{ g}\cdot\text{mol}^{-1}$ gold and $31.1 \text{ g} = 1 \text{ troy ounce}$). This solution was diluted to the stated concentrations using $18 \text{ M}\Omega\cdot\text{cm}$ water, with Na_2SO_3 added as a supporting electrolyte as indicated and deposition conducted in anywhere from 40 mL to 100 mL of room temperature ($\approx 23^\circ\text{C}$) electrolyte. Concentrations of Ti_2SO_4 , $\text{Pb(ClO}_4)_2$, and KSeCN were added using aliquots drawn from dilute stock solutions ($1 \text{ mmol}\cdot\text{L}^{-1}$ Ti_2SO_4 , $1 \text{ mmol}\cdot\text{L}^{-1}$ $\text{Pb(ClO}_4)_2$, $2.6 \text{ mmol}\cdot\text{L}^{-1}$ KSeCN). Concentrations of Sb^{3+} , Te^{4+} and Bi^{3+} were obtained by suspending a piece of the respective element in the electrolyte and passing the anodic charge through it, assuming 100 %

Faradaic dissolution efficiency to the specified ion. Concentrations obtained using this approach are taken as upper bound estimates of the actual concentrations. Electrolyte pH was determined using a pH electrode calibrated to buffer solutions of pH 7.00 and pH 10.01. Where noted, electrolytes were sparged with nitrogen or argon prior to use in order to remove dissolved oxygen and the same gas was used to cover the electrolyte during depositions. Cyclic voltammetry was performed using an RDE of 1.0 cm diameter composed of electrodeposited Au on the end of a Ag rod embedded in epoxy unless indicated otherwise. The RDE was polished to 1200 grit SiC paper before each experiment, and current densities are obtained from the deposition current using the projected electrode area; deposition currents are cathodic, regardless of the sign used for plotting.

Feature filling experiments were generally conducted on 3 mm × 11 mm, or similar size, fragments of patterned wafers. The substrates were rotated during deposition about a Pt spindle, oriented in analogy to a helicopter blade, with the patterned surface upward and the spindle masked by electroplaters tape to reduce extraneous currents. Rotation rates, ranging from 100 rpm (200π rad·min⁻¹) to 1600 rpm, were used to define and enhance the transport of the $\text{Au}(\text{SO}_3)_2^{3-}$ to the workpiece. A saturated Hg/Hg₂SO₄/saturated K₂SO₄ reference electrode (SSE), used for all experiments, was connected to the working electrode compartment via a fritted bridge filled with saturated solution of potassium sulfate, while a platinum counter electrode was held in a frit-separated cell immersed within the main cell.

RESULTS AND DISCUSSION

Addition of Tl⁺

Thallium (Tl⁺), associated with the production of bright surface, is probably the most studied additive for Au plating in both cyanide and sulfite electrolytes.^{6,23,24} Voltammetry of Au deposition

from sulfite electrolyte in the presence of micromolar quantities of Tl^+ exhibits accelerated deposition (i.e., depolarization) associated with adsorption of the additive. Concentration and transport dependence of hysteretic voltammetry (**Fig. 2**) as well as rising chronoamperometric transients manifest the adsorption. Bright specular Au films are observed following deposition potentials at least as negative as -0.95 V .⁶⁰ Deposition in patterned trench arrays is largely conformal, albeit with some evidence of modest superconformal deposition at more positive potentials and conditions of higher transport as in **Fig. 3**. Growth on planar section, as on the field adjacent to the filled features, is extremely smooth for these conditions.

Interestingly, the non-monotonic dependence of deposition rate on overpotential, the current density decreasing and then increasing before decreasing again on the return scans at more negative potentials in **Fig. 2**, is correlated with monotonically increasing adsorbate coverage⁶⁰. This non-monotonic dependence of deposition rate on both potential and Tl coverage is analogous to behavior reported for cyanide electrolytes and summarized in **Figure 4**.

The acceleration provided by the Tl adsorbate at low coverages and more positive potentials yields bright Au deposits through CEAC *smoothing*^{62,63} (i.e., filling sub-micrometer size furrows and divots instead of larger trenches and vias). The strongest indication of superconformal filling is evident for deposition at -0.85 V (**Fig. 3c**), where the dynamic range of the voltammetric current is substantial, making this a fertile region for further exploration. However, the limited potential range over which Tl seems able to induce superconformal filling of micrometer sized features by the CEAC mechanism suggests the adsorbate is a less than ideal surfactant for this application.

In fact, at the higher coverages associated with more negative potentials an inversion in behavior occurs such that increasing coverage of the surfactant begins to suppress deposition. This inversion induces growth instabilities, area expansion on convex surfaces diluting the coverage of

the suppressing adsorbate and thereby enhancing growth at the tips of asperities. The different growth morphologies for the low and high coverage behaviors are captured schematically in **Figure 5**. The instability at high Tl coverages manifests in the growth of single crystal whiskers, aligned along the $\langle 110 \rangle$ directions, that are especially striking compared to the smooth deposit obtained at more positive potential in the same figure. The actual chemical state of the Tl precursor, the adsorbate and its dependence on coverage and crystal orientation in neutral to alkaline media remains a challenging subject.^{24,25}

Addition of Pb^{2+}

The generality of the CEAC mechanism, namely the evolution of coverage of a surfactant adsorbate with local area change, developed for Cu sulfate electrolytes, was quickly extended to demonstrate and then quantify Ag as well as Au superfilling of trenches using SeCN^- and Pb^{2+} additions, respectively, in cyanide-based electrolytes.^{19,20,42-47} The rising current transients on planar substrates induced by Pb^{2+} addition to cyanide electrolyte composed of $0.02 \text{ mol}\cdot\text{L}^{-1} \text{KAu(CN)}_2 + 0.1 \text{ mol}\cdot\text{L}^{-1} \text{KOH} + 0.1 \text{ mol}\cdot\text{L}^{-1} \text{KCN}$ with $\text{Pb(NO}_3)_2$ additive are shown in **Fig. 6**. Superconformal Au filling of sub-micrometer trenches achieved by preadsorbing the accelerating Pb onto patterned substrates from additive-containing electrolyte and then conducting Au deposition in additive-free electrolyte is also shown. The simulations generated by a CEAC-based model, derived using kinetics extracted from fits to the current transients, capture the impact of Pb coverage enrichment that is driven by area change during growth on concave surface segments and predict the resulting superconformal feature filling.

The addition of Pb^{2+} , in this case $\text{Pb(ClO}_4)_2$, to sulfite electrolyte composed of $0.080 \text{ mol}\cdot\text{L}^{-1} \text{Na}_3\text{Au(SO}_3)_2 + 0.32 \text{ mol}\cdot\text{L}^{-1} \text{Na}_2\text{SO}_3$ yields rising chronoamperometry, shown in **Fig. 7**, that is

analogous to that observed in the cyanide electrolyte. Similar effects have been reported for chronopotentiometric experiments.^{17,18} Absent additives, deposition remains minimal almost to the -1.3 V switching potential in the associated voltammetry, shown in the same figure, and hysteresis is modest and due to roughening at the most negative potentials. The addition of Pb^{2+} increases deposition currents on the negative-going scan, with further increase on the return scan yielding hysteresis in the cyclic voltammograms. Higher additive concentration results in progressively greater depolarization on both scans.

Superconformal Au filling of patterned features in the electrolyte-additive system shown in the same figure is visually consistent with filling through the CEAC mechanism³⁵⁻³⁸. In particular, the deposition rate is initially uniform (conformal) and slow, increases first at the bottom corners of the trenches, then accelerates from the bottom more broadly, doing so more rapidly in narrower features. Furthermore, deposition continues and even accelerates over the full surface of the specimen, including the sidewalls of the trenches and overlying field, albeit not as much as from the trench bottoms. As with Tl^+ , the parallels between the impact of Pb^{2+} addition to cyanide and sulfite electrolytes speak to a similarity of the interactions between the heavy metal adsorbate, linear Au complexes and passivating surface analogs in the respective electrolytes.

Addition of Bi^{3+}

The addition of Bi^{3+} to gold sulfite electrolytes generates substantial acceleration, manifest in the hysteretic cyclic voltammetry and rising chronoamperometry shown in **Fig. 8**. The hysteretic response reflects positive feedback due to self-catalyzing activation. With potential at and negative of -0.95 V the system exhibits monotonic acceleration with Bi^{3+} concentration and fluid flow in both voltammetric and chronoamperometric analysis in a manner typical of other systems that

exhibit CEAC behavior. In contrast, at more positive potentials where the voltammetric current on the return scan is in steep decline, chronoamperometry reveals a highly nonlinear and non-monotonic dependence on RDE rotation rate as shown in **Fig. 9**. The superconformal deposition in patterned features obtained in the Bi^{3+} containing electrolytes at -0.9 V and more positive potentials is also highly nonlinear, exhibiting an extended incubation period before the onset of a bottom-up filling dynamic. The incubation period is associated with nominally uniform passive deposition, and its duration depends on potential, feature depth, additive concentration and electrolyte pH. Activation, under appropriate conditions, manifests in the extreme bottom-up filling shown in **Fig. 10**.^{61,64-67} The superconformal, bottom-up void-free filling has been achieved and detailed in trenches having aspect ratios as high as 56 and across 10 cm diameter wafers patterned with arrays of trenches of aspect ratio over 40.⁶⁷ No less remarkable is the fact that the bottom-up evolution self-passivates at a controllable distance from the field under appropriate conditions. Incubation, activation and passivation are all evident in distinctive rising and self-terminating chronoamperometric transients associated with the filling of patterned specimens, two examples of filled trench arrays and the associated transients being shown in **Fig. 11**. The transients exhibit extended periods of slow passive deposition before rapidly increasing current marks the inception and continuation of bottom-up filling across each substrate. The final decrease of current back to the minimal level of early times reflects passivation of the upward moving deposit at a distance from the field that is captured in the accompanying cross-sectioned specimens. Slightly more negative potentials, used early in each process, were to shorten the incubation period of passive deposition. The mechanism behind this unusual filling evolution clearly lies beyond the purview of both the CEAC and S-NDR mechanisms. Whether other mechanistic paths to critical behavior, for example the impact of physical shear on additive adsorption, consumption and the

rate of metal deposition⁶⁸ or pH gradients, long discussed for superfilling ferrous systems⁶⁹⁻⁷¹, play any role in passivation of the field or the localization and bottom-up filling in this system remains to be investigated.

Addition of Sb³⁺

Cyclic voltammetry with 80 mmol·L⁻¹ Na₃Au(SO₃)₂ + 0.64 mol·L⁻¹ Na₂SO₃ electrolyte containing the indicated micromolar concentrations of Sb³⁺ is shown in **Figure 12a**. Absent the additive, the current density remains below 0.1 mA·cm⁻² on the negative-going scan to the -1.1 V switching potential, and there is minimal hysteresis. Addition of Sb³⁺ accelerates deposition on the initial negative-going scan, with further acceleration on the positive-going return scan yielding significant hysteresis. Higher Sb³⁺ concentrations yield higher current densities that reach saturation on the positive going scan for concentrations beyond 10 μmol·L⁻¹ Sb³⁺. With the data replotted on a logarithmic scale in **Fig. 12b** it is evident that accelerated deposition on the negative-going scan begins at approximately -0.85 V and exhibits a complex dependence on potential at more negative values. Saturation on the return sweep at potentials positive of -0.9 V is evident for concentrations as low as 3 μmol·L⁻¹ Sb³⁺.

The impact of the Sb³⁺ additive is very sensitive to electrolyte aging, presumably due to oxidation of Sb³⁺ to Sb⁵⁺ species. Stability of the Sb³⁺ additive required N₂ or Ar sparging of the electrolyte between experiments and a sustained gas flow over the electrolyte during experiments. Absent sparging the additive-accelerated current density dropped by roughly one-half every hour toward the additive-free value. Sparging substantially slowed the loss of efficacy. Redosing an electrolyte from which acceleration had been lost by extended (e.g., overnight) air exposure with an identical increment of Sb³⁺ concentration yielded voltammetric response identical to the

original. A white precipitate that accumulated at the bottom of the cell with repeated dosing suggests oxidation of the Sb^{3+} to Sb^{5+} exceeds the solubility threshold for Sb_2O_5 .

Trench filling in electrolytes containing various Sb^{3+} concentrations is shown in **Figure 13**. The features to be filled, electroplated first with a thin Au layer from additive-free solution to cover the original sputtered Cu seed layer prior to electrodeposition in the additive-containing electrolyte, are shown in **Fig. 13a**. Filling for 15 min at -0.9 V in electrolyte containing 2 $\mu\text{mol/L}$ Sb^{3+} is shown in **Fig. 13b**; filling under identical conditions but with 5 $\mu\text{mol/L}$ Sb^{3+} , shown in **Fig. 13c**, captures increased acceleration at higher additive concentrations. The surfaces are smooth in both cases, other than residual cusps over the trenches. Filling at progressively more negative potentials, from -0.85 V to -0.9 V and -0.95 V (**Fig. 13d-f**), yields progressively faster deposition, with increasingly large keyhole shaped voids despite lower Sb^{3+} concentration at the more negative potentials. However, deposition remains essentially conformal beyond the impact of metal ion depletion.

The mirror-like finish of the surfaces is, as with the other accelerating heavy metal adsorbates, in accord with the CEAC smoothing mechanism that applies even under conditions that reduce its effectiveness for superconformal filling of microscale size features (e.g., adsorbate consumption over lengths scales smaller than the feature size or surface diffusion that is rapid compared to filling times).^{62,63} The RDE also exhibited mirror-like deposits after the voltammograms in **Fig. 12** despite deposition rates approaching substantial fractions of the transport limit.

Addition of Te^{4+}

Cyclic voltammograms obtained from 80 $\text{mmol}\cdot\text{L}^{-1}$ $\text{Na}_3\text{Au}(\text{SO}_3)_2$ + 0.32 $\text{mol}\cdot\text{L}^{-1}$ Na_2SO_3 electrolyte containing the indicated micromolar concentrations of Te^{4+} are shown in **Figure 14a**.

The additive increases the deposition rate on the negative-going sweep beginning somewhat negative of -0.9 V. The logarithmic scale in **Fig. 14b** captures a linear dependence at more positive potentials on both the negative-going initial scan and positive-going return scan that is consistent with Butler-Volmer kinetics having different charge transfer coefficients. Distinct acceleration of deposition begins near -0.9 V on the negative-going scan. The return scan tracks the negative-going scan positive of the switching potential over a potential range that increases with Te^{4+} concentration before hysteretic behavior begins, with an additional subtle inflection near -0.85 V.

Cross sections of damascene trenches after deposition from electrolytes containing different Te^{4+} concentrations in **Figure 15** are consistent with acceleration due to the additive. The deposit at -0.9 V thickens as the additive concentration increases from $2 \mu\text{mol}\cdot\text{L}^{-1} \text{Te}^{4+}$ to $3 \mu\text{mol}\cdot\text{L}^{-1} \text{Te}^{4+}$ and $10 \mu\text{mol}\cdot\text{L}^{-1} \text{Te}^{4+}$ even as the deposition time decreases for the last; the deposit obtained after just 3 min in electrolyte containing $18 \mu\text{mol}\cdot\text{L}^{-1} \text{Te}^{4+}$ (**Fig. 15d**) indicates further increase of the deposition rate at this concentration. However, deposition is conformal in all cases. Deposition at -1.0 V, negative of the activation potential in the voltammetry, with $6 \mu\text{mol}\cdot\text{L}^{-1} \text{Te}^{4+}$ is conformal as well. The acceleration of deposition on the patterned specimens, like the acceleration indicated by the hysteresis in **Fig. 14**, is modest as compared to that seen with both Sb^{3+} and Pb^{2+} , and filling is essentially conformal. However, close examination of the images captures a fine scale roughness on all the deposits. This roughness, although at a length scale too small to be visible to the unassisted eye, increases the surface area and likely contributes to, or entirely underlies, the increased current density in the voltammetry and deposit thickness on the features.

Addition of Polyethyleneimine

Unlike the acceleration provided by heavy metal ions, N-bearing polymers such as PEI suppress gold deposition to values even below that of additive-free, intrinsically suppressed sulfite electrolytes^{58,59,72}. The polarization reflecting this enhanced suppression can exceed several hundred millivolts in cyclic voltammograms with $0.32 \text{ mol}\cdot\text{L}^{-1} \text{ Na}_3\text{Au}(\text{SO}_3)_2$ with PEI of 1800 molecular mass as shown in **Figure 16**. In contrast to the hysteretic voltammetry observed with the heavy metals, the hysteresis induced by PEI arises from lower current density on the negative going scan with, following suppression breakdown, the return scan approaching that of additive-free electrolyte. Post experiment correction of the potential for iR ohmic losses with current flow across the cell reveals an S-shaped inversion at the potentials where the breakdown of suppression occurs, consistent with operation of the S-NDR mechanism at potentials within the hysteretic range of the appropriate additive concentration. The inset shows the RDE surface after completion of one voltammetric cycle in electrolyte containing $20 \text{ }\mu\text{mol}\cdot\text{L}^{-1}$ PEI. The swirl captures coexistence of regions of passive and active deposition that develop during passage through the hysteretic potential ranges of the negative-going and positive-going scans, respectively. The RDE flow field helps organize the active and passive domains seen in **Fig. 16**; on static planar electrodes the domains of active deposition are circular in shape and more randomly distributed, at least during the early stages of the bifurcation.⁴⁹

During deposition on patterned substrates within the hysteretic potential region the spatial variation of suppressor transport causes the regions of active deposition to be biased toward more recessed surface segments as seen in the square through silicon vias (TSV) in **Figure 17**. The depth down the vias at which active deposition begins is a function of both the PEI concentration and the applied potential. Under potentiostatic control the relatively sharp transition between active and passive deposition is marked by the bulge in the deposit profile. The passive deposition

process, and in particular the transition point between the passive and active state, is also marked by significant additive incorporation within the gold deposit that is evident as nanoscale pores. These are especially numerous in the thin and conformal passive deposit. In smaller trenches the transition from passive to active deposition plays out against the full height of the feature, **Figure 18**, the wedge-shaped deposit capturing the gradient of suppressor concentration. Higher magnification makes the porous nature of the deposits clear.

The S-NDR behavior can be characterized by the suppression breakdown and its dependence on suppressor concentration and transport. A selection of results shown in **Figure 19** allows extraction of kinetics to be used for modeling of experimental Au deposition in annular through silicon vias (TSV) shown in **Figure 20**. The model is effective at predicting the potential-dependent deposition rates on the passive and active surfaces as well as the depth within the vias at which the transition between the two occurs as summarized in **Figure 21**. Importantly, knowledge of the potential dependence of this transition depth permits dynamic control of the applied potential to achieve superconformal deposition for nominally void-free filling of the entire feature as shown in **Figure 22**. Higher magnification images in the same figure again make clear the porosity that exists in the deposits, especially the passive deposits on the sidewalls and field. The nanoscale porosity also provides verification of the consumption model and, depending on the application, either a limitation or a unique aspect of the PEI additive system.

Addition of 3-mercapto-1-propanesulfonic acid

With copper deposition from acid sulfate electrolytes the additive MPS behaves as an accelerator when used in conjunction with chloride and a suppressor additive.³⁵ In contrast, with Au deposition from sulfite electrolyte containing a thallium accelerator MPS behaves as a

suppressor, as shown by voltammetry in **Figure 23**. The extent of inhibition increases with MPS concentration before saturating with a 300 mV offset with a similar voltametric slope suggestive of a simple site blocking model. Trench filling begins with formation of a v-notch bounded by the vertical trench sidewalls before seam-free filling and growth of a uniform overburden. Deposition in micrometer size trenches from electrolyte without the MPS is conformal or subconformal depending on the imposed current density, consistent with the general absence of superconformal deposition noted earlier in the presence of Tl^+ alone. Deposition in electrolyte containing MPS (and Tl^+) exhibits a gradient of thickness that is suggestive of the S-NDR based filling of trenches obtained using PEI (**Figures 18** and **22**). Whether the Tl^+ influences the surface roughness in this combined additive system is not known.

Addition of $SeCN^-$

The impact of $SeCN^-$ addition as well as variation in supporting electrolyte concentration on Au deposition was examined with $80 \text{ mmol}\cdot\text{L}^{-1} \text{ Na}_3\text{Au}(\text{SO}_3)_2 + x \text{ mol}\cdot\text{L}^{-1} \text{ Na}_2\text{SO}_3$ electrolytes. Voltammograms for electrolytes containing $0 \text{ }\mu\text{mol}\cdot\text{L}^{-1}$ to $4 \text{ }\mu\text{mol}\cdot\text{L}^{-1} \text{ SeCN}^-$ and $0.32 \text{ mol}\cdot\text{L}^{-1} \text{ Na}_2\text{SO}_3$ are shown in **Figure 24a-d** while the effect of increasing the supporting electrolyte to $0.64 \text{ mol}\cdot\text{L}^{-1} \text{ Na}_2\text{SO}_3$ in the presence of $4 \text{ }\mu\text{mol}\cdot\text{L}^{-1} \text{ SeCN}^-$ and $6 \text{ }\mu\text{mol}\cdot\text{L}^{-1} \text{ SeCN}^-$ is shown in **Fig. 24e,f**. The deposition current increases modestly and some hysteresis develops with $1 \text{ }\mu\text{mol}\cdot\text{L}^{-1} \text{ SeCN}^-$ in the electrolyte. However, the Au deposit is copper colored upon completion of the voltametric cycle. The voltammograms with $2 \text{ }\mu\text{mol}\cdot\text{L}^{-1} \text{ SeCN}^-$ exhibit increased hysteresis at all three rotation rates, the Au deposit on the RDE dark again. As with the PEI, and unlike the heavy metal additives, the voltammograms show this hysteresis arises from enhanced suppression on the negative scan

due to SeCN^- adsorption combined with the return scan tending toward behavior characteristic of the additive-free case. With $4 \mu\text{mol}\cdot\text{L}^{-1}$ SeCN^- suppression increases further such that deposition remains suppressed on both the negative and positive going scans at the two higher rotation rates. With higher Na_2SO_3 concentration the $4 \mu\text{mol}\cdot\text{L}^{-1}$ SeCN^- also induces suppression on the negative-going scans, but suppression breakdown is evident on the return scan at 1600 rpm, occurs just negative of -1.1 V on the negative scan at 400 rpm and is minimal at 100 rpm. However, with increase of the SeCN^- concentration to $6 \mu\text{mol}\cdot\text{L}^{-1}$ suppression is reasserted for the entire scan at 1600 rpm, fails only at the -1.2 V switching potential at 400 rpm, with NDR on the return scan, and persists to a potential negative of -1.1 V at 100 rpm.

Deposition from electrolytes containing SeCN^- into patterned features seen in **Figure 25** reveals extremely rough and porous deposits. Nevertheless, for certain conditions deposition is localized to the trenches and, aside from porosity, is superconformal in nature for the more positive potentials of -1.05 V and -1.00 V. Both transport and potential likely contribute to the localization within the recessed surface area.

Considered as a whole, the results indicate that the modest increase of deposition current and associated hysteresis with $1 \mu\text{mol}\cdot\text{L}^{-1}$ SeCN^- arise largely from roughening that accompanies localized breakdown of the adsorbed SeCN^- suppressor. Greater inhibition is associated with higher additive concentrations and increased hydrodynamic transport, the impact of both evident in shifting of suppression breakdown to more negative potentials. The results with $4 \mu\text{mol}\cdot\text{L}^{-1}$ SeCN^- and both $0.32 \text{ mol}\cdot\text{L}^{-1}$ and $0.64 \text{ mol}\cdot\text{L}^{-1}$ Na_2SO_3 suggest that the presence of additional free sulfite hinders the competitive adsorption and/or function of the more suppressing SeCN^- adsorbate.

DISCUSSION

A cursory survey and review of the effects of a limited selection of heavy metal and molecular additive on Au deposition from $\text{Na}_3\text{Au}(\text{SO}_3)_2 + \text{Na}_2\text{SO}_3$ as well as cyanide electrolytes is presented. Voltammetric and feature filling behavior are examined under defined hydrodynamic conditions. Feature filling using the additives Tl^+ , Pb^{2+} , Bi^{3+} , and MPS (this last with Tl^+) has been previously explored and described in varying degrees of detail. The use of Sb^{3+} , Te^{4+} and SeCN^- for feature filling in sulfite electrolytes has not been described before, and interesting variation from cyanide chemistry³ was noted for Sb^{3+} additions. All the electrolyte-additive systems examined exhibit hysteresis in cyclic voltammetry on planar RDE, with the possible exception of the MPS (with Tl^+) system for which the return sweep was not reported. The individual additives differ significantly in that Pb^{2+} , Tl^+ , Bi^{3+} and Sb^{3+} unambiguously accelerate Au deposition from the sulfite electrolyte (producing smooth and bright surfaces), Te^{4+} does so modestly or not at all, while PEI, MPS and SeCN^- suppress deposition. The additives also differ significantly in the nature of feature filling they enable. Electrolytes containing Te^{4+} and Sb^{3+} yield conformal deposition; filling with Tl^+ is at most slightly superconformal; Pb^{2+} yields superconformal filling, with clear similarity to behavior in cyanide electrolytes; and Bi^{3+} , PEI and SeCN^- permit superconformal filling but with strong localization of activated deposition. Of the last three, electrolytes containing Bi^{3+} yield dense deposits and void-free filling of extremely high aspect ratio feature while PEI and SeCN^- give rise to dendritic and porous deposits, SeCN^- especially so.

Superconformal feature filling using Pb^{2+} additive in sulfite electrolyte has been examined in only modest detail. However, both electroanalytical measurements on RDE and feature filling on patterned substrates show similarity to corresponding results in cyanide electrolyte. The behavior in that system has been shown to be quantitatively consistent with the CEAC formalism; kinetics

from chronoamperometry on planar RDE permit reasonably accurate prediction of experimental feature filling.

The acceleration provided by TI^+ , well recognized in the literature, as well as Sb^{3+} , is clear in the respective voltammetry. The extremely smooth deposits obtained with both additives are consistent with the CEAC smoothing mechanism and similar in this respect to deposition from electrolyte containing Pb^{2+} . Despite this acceleration, only conformal feature filling is obtained with Sb^{3+} , and essentially the same is obtained with TI^+ , behavior differing substantially from the CEAC-derived superconformal feature filling demonstrated using Pb^{2+} . While these differences still require quantitative explanation, it is recognized that coverage dependent acceleration of the additives is also subject to other system specific effects; effective CEAC-derived smoothing at very fine length scales suggests that adsorbate incorporation, desorption or surface diffusion limit prevent superconformal filling of the relatively larger features.^{62,63} The transition of TI^+ from an accelerator to a suppressor with higher coverages obtained at more negative potentials, observed in both voltammetry and feature filling, appears to be distinct among this group of additives. While this behavior does not seem useful for void-free feature filling it may serve for exploring nanowire growth modalities.

In the case of inhibiting additives, a variety of different control schemes can be used to enable feature filling. The PEI system is representative of one limiting case of S-NDR behavior where the passive-active transition is localized to a given feature depth. When combined with a potentiodynamic program that advances the potential to more negative values, the passive-active transition can be made to propagate toward the free-surface to achieve effective filling of features. Optimization of suppressor concentration and applied potential is necessary for initiating Au deposition at the bottoms of different features. This macromolecular additive comes with the

strong caveat that significant incorporation of PEI into the deposit occurs. Likewise, the rich behavior observed in voltammetry with SeCN^- manifests another caveat where, although localization of the deposition within patterned features occurs, the deposit is extremely rough, exhibiting highly lenticular or dendritic aspects at a finer length scale. Analogous localization through the S-NDR mechanism, coupled with rough and porous deposits, has also been demonstrated during Cu deposition in alkaline electrolytes containing suppressing additives.^{74,75} Roughening at nanometer length scales most likely also underlies the comparatively modest increase of current during voltammetry in gold deposition with the Te^{4+} additive; absent acceleration (or suppression) of the actual kinetics, deposition in patterned features is, unsurprisingly, conformal. Details regarding Au deposition using MPS plus TI^+ are insufficient to rationalize the observed superconformal filling, but the finding should inspire further investigations.

Extension and applicability of the CEAC and S-NDR mechanisms to superconformal gold deposition has been demonstrated for a number of different systems. More interesting is that the journey has uncovered new phenomena that promise new mechanisms for extreme bottom-up filling in both high and low aspect ratio features. Of specific interest is the substantial acceleration induced by Bi^{3+} that, under appropriate conditions, leads to dense Au deposition localized to the most remote surface segments as well as a growth front that self-terminates at a controllable distance from the free surface. The system has enabled superconformal filling of the highest aspect ratio features with Au (or any other metal) that have been described to date, and the results suggest better to come. It is said that one learns even from failures, but it is premature to declare *any* of the systems examined herein as such, given that impact of two (or more) additives may convert some

of the “failures” detailed herein into entirely new processes for superconformal deposition bases on new ideas that refine present understanding.

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FIGURE CAPTIONS

Figure 1: a) Microbumps fabricated using through mask deposition in lithographically patterned photoresists. Surface morphology critical for application is seen to be influenced by the concentration of the supporting electrolyte. A) $0.05 \text{ mol}\cdot\text{L}^{-1}$, B) $0.15 \text{ mol}\cdot\text{L}^{-1}$ and C) $0.3 \text{ mol}\cdot\text{L}^{-1}$. D) The patterned surface is seen prior to photoresist removal for the highest concentration. b) Surface morphology of the microbumps as a function of additive and concentration. Basic bath

composition and operating conditions: $0.06 \text{ mol}\cdot\text{L}^{-1} \text{Na}_3[\text{Au}(\text{SO}_3)_2] + 0.60 \text{ mol}\cdot\text{L}^{-1} \text{Na}_2\text{SO}_3 + 0.30 \text{ mol}\cdot\text{L}^{-1} \text{H}_3\text{PO}_3 + 1000 \text{ ppm PEG-1000}$, pH 8.0, temperature 60°C , current density $0.5 \text{ A}\cdot\text{dm}^{-2}$ and mechanical agitation (Figures from Reference 33 with permission)

Figure 2. Cyclic voltammetry for $80 \text{ mmol}\cdot\text{L}^{-1} \text{Na}_3\text{Au}(\text{SO}_3)_2 + 0.64 \text{ mol}\cdot\text{L}^{-1} \text{Na}_2\text{SO}_3$ electrolyte of pH 9.5 containing $1 \text{ }\mu\text{mol}\cdot\text{L}^{-1} \text{Tl}^+$, $4 \text{ }\mu\text{mol}\cdot\text{L}^{-1} \text{Tl}^+$ and $6 \text{ }\mu\text{mol}\cdot\text{L}^{-1} \text{Tl}^+$ at RDE rotation rates of a) 100 rpm, b) 400 rpm, c) 1600 rpm. d) Voltammetry for electrolyte containing $6 \text{ }\mu\text{mol}\cdot\text{L}^{-1} \text{Tl}^+$ at different RDE rotation rates. Current densities are obtained from measured current using the nominal RDE surface area and scan rates are as indicated.

Figure 3: Gold deposition in trenches from $80 \text{ mmol}\cdot\text{L}^{-1} \text{Na}_3\text{Au}(\text{SO}_3)_2 + 0.64 \text{ mol}\cdot\text{L}^{-1} \text{Na}_2\text{SO}_3$ electrolyte of pH 9.5 with Tl^+ additive. a) 20 min at -0.95 V in electrolyte containing $2 \text{ }\mu\text{mol}\cdot\text{L}^{-1} \text{Tl}^+$ with substrate rotation rate 1600 rpm. b-f) Electrolyte containing $6 \text{ }\mu\text{mol}\cdot\text{L}^{-1} \text{Tl}^+$ with rotation rates b) 100 rpm, c-d) 400 rpm and e-f) 1600 rpm. Potentials are -0.90 V except for c), which is at -0.85 V . Deposition times 20 min except for e), which is 10 min. Deposition is subconformal at 100 rpm, suggestive of metal ion depletion. Deposition is modestly superconformal at higher rotation rate and less negative potential, partly obscured by outward bulging of the lower sidewalls. (Figure from Reference 61)

Figure 4: The effect of electrode pre-exposure in a $0.02 \text{ mol}\cdot\text{L}^{-1} \text{KAu}(\text{CN})_2 + 0.1 \text{ mol}\cdot\text{L}^{-1} \text{KCN} + 0.1 \text{ mol}\cdot\text{L}^{-1} \text{KOH}$ solution containing $20 \text{ mmol}\cdot\text{L}^{-1} \text{TlNO}_3$. a) linear voltammograms after exposure times of 1) 0.5 s, 2) 10 s, 3) 20s, 4) 40 s, 5) 80 s, 6) 320 s. Scan 7), in TlNO_3 -free electrolyte, is independent of pre-exposure time. Current density is higher for intermediate (40 s) exposure time than for shorter or longer exposure times. b) current density at -0.75 V as a function of the pre-exposure time, i.e., adsorbate coverage. (Figures from Reference 13 with permission)

Figure 5: a) A schematic of the non-monotonic influence of adsorbed TI on the Au electrodeposition rate in sulfite electrolyte. At lower coverages where the surfactant accelerates deposition, the CEAC mechanism of smoothing yields preferential deposition toward the bottoms of recessed surface features by enriching the accelerating surfactant on concave surfaces. At higher coverages where the surfactant suppresses deposition, area expansion on convex surfaces dilutes the suppressing adsorbate yielding enhanced growth at the tips of asperities. b) cross section views of Au deposition in $80 \text{ mmol}\cdot\text{L}^{-1} \text{ Na}_3\text{Au}(\text{SO}_3)_2 + 0.64 \text{ mol}\cdot\text{L}^{-1} \text{ Na}_2\text{SO}_3$ electrolyte of pH 9.0 for a) 13 min at -0.8 V in electrolyte containing $10 \text{ }\mu\text{mol}\cdot\text{L}^{-1} \text{ TI}^+$ and b) 3 min at -1.0 V in electrolyte containing $20 \text{ }\mu\text{mol}\cdot\text{L}^{-1} \text{ TI}^+$. Both were preceded by Au deposition for 10 s at -1.5 V to protect the Cu seed layer. (Figures from Reference 60)

Figure 6: a) Current transients during Au deposition at -0.95 V in $0.02 \text{ mol}\cdot\text{L}^{-1} \text{ KAu}(\text{CN})_2 + 0.1 \text{ mol}\cdot\text{L}^{-1} \text{ KOH} + 0.1 \text{ mol}\cdot\text{L}^{-1} \text{ KCN}$ electrolyte containing the indicated concentrations of $\text{Pb}(\text{NO}_3)_2$ additive without agitation. The bold curves are fits used to extract kinetics used in CEAC modeling. b) Trenches of three different widths with just the evaporated Ti/Au seed are seen in the top row. Filling of the same size trenches is shown after 100 s in agitated $0.02 \text{ mol}\cdot\text{L}^{-1} \text{ KAu}(\text{CN})_2 + 0.1 \text{ mol}\cdot\text{L}^{-1} \text{ KOH} + 0.1 \text{ mol}\cdot\text{L}^{-1} \text{ KCN}$ electrolyte for seed layer improvement, 60 s in stagnant electrolyte containing also $10 \text{ }\mu\text{mol}\cdot\text{L}^{-1}$ of $\text{Pb}(\text{NO}_3)_2$ for surface derivatization and then deposition for the indicated times at -0.95 V in agitated Pb-free electrolyte. All three steps were conducted at -0.95 V. c) Simulations of the experimental filling using an estimated initial Pb coverage of 0.15 monolayers in a CEAC-based model with kinetics derived from the chronoamperometric fitting. (Figures from Reference 20)

Figure 7: Gold deposition in N_2 sparged $80 \text{ mmol}\cdot\text{L}^{-1} \text{ Na}_3\text{Au}(\text{SO}_3)_2 + 0.32 \text{ mol}\cdot\text{L}^{-1} \text{ Na}_2\text{SO}_3$ electrolyte of pH 9.5 containing the indicated concentrations of Pb^{2+} . a) Acceleration in

chronoamperometry and b) hysteresis in cyclic voltammetry caused by the indicated concentrations of $\text{Pb}(\text{ClO}_4)_2$ in the electrolyte. The cyclic voltammograms were acquired at a scan rate of $2 \text{ mV}\cdot\text{s}^{-1}$. c) The evolution of superconformal filling of submicrometer size trenches in Au sulfite electrolyte as indicated. (Figures from Reference 48)

Figure 8: a) Cyclic voltammetry in $0.16 \text{ mol}\cdot\text{L}^{-1} \text{ Na}_3\text{Au}(\text{SO}_3)_2 + 0.64 \text{ mol}\cdot\text{L}^{-1} \text{ Na}_2\text{SO}_3$ electrolyte of pH 9.5 containing the indicated Bi^{3+} concentrations. The data was acquired at a scan rate of $2 \text{ mV}\cdot\text{s}^{-1}$ with the RDE rotating at 100 rpm for all. b) Chronoamperometric transients for electrolyte containing $10 \text{ }\mu\text{mol}\cdot\text{L}^{-1} \text{ Bi}^{3+}$ for different RDE rotation rates showing more rapid increase with faster transport at -0.95 V , behavior typical of accelerating adsorbates. (Figures from Reference 61)

Figure 9: A) Chronoamperometric transients in electrolyte containing $10 \text{ }\mu\text{mol}\cdot\text{L}^{-1} \text{ Bi}^{3+}$ at the stated potential and RDE rotation rates. The RDE remains passivated both under stagnant conditions as well as at the highest RDE rotation rate, but deposition accelerates at intermediate potentials. b) The value of current density from the transients shown in A) evaluated at 1000 s and plotted as a function of rotation rate. (Figures from Reference 61)

Figure 10: a) Bottom-up Au deposition in fully metallized trenches at the indicated deposition times. The sequence captures the evolution of filling in electrolyte containing $4 \text{ }\mu\text{mol}\cdot\text{L}^{-1} \text{ Bi}^{3+}$ at applied potential of -0.90 V . (Figure from Reference 61). b) Au filling in $5.5 \text{ }\mu\text{m}$ deep, $0.65 \text{ }\mu\text{m}$ wide trenches after the indicated deposition times at -0.86 V with the specified Bi^{3+} concentrations. (Figure from Reference 64). Deposition in all cases in $80 \text{ mmol}\cdot\text{L}^{-1} \text{ Na}_3\text{Au}(\text{SO}_3)_2 + 0.64 \text{ mol}\cdot\text{L}^{-1} \text{ Na}_2\text{SO}_3$ electrolyte with the patterned substrates rotating at 400 rpm.

Figure 11: Scanning electron microscope images of Au electrodeposits of cross-sectioned gratings after two-step Au deposition in approximately $85 \text{ }\mu\text{m}$ deep $3 \text{ }\mu\text{m}$ pitch, $1.5 \text{ }\mu\text{m}$ wide trenches for

4 h at -0.75 V followed by 27 h at -0.73 V in electrolyte with initial pH 8.96 and in nominally 60 μm deep 3 μm pitch, 1.5 μm wide trenches for 1 h 40 min at -0.75 V followed by 5 h at -0.73 V in electrolyte with initial pH 9.46. Higher magnification images highlight the passivated deposits at the tops of the trenches. The current transients and potential histories associated with the potentiodynamic controlled filling of the two specimens are shown beneath. An incubation time of ≈ 3 h before bottom-up filling begins is seen for filling of the 60 μm deep trenches in the higher pH electrolyte. An incubation time of 18 h is seen with the 85 μm deep trenches in the lower pH electrolyte. Both in $0.16 \text{ mol}\cdot\text{L}^{-1} \text{Na}_3\text{Au}(\text{SO}_3)_2 + 0.64 \text{ mol}\cdot\text{L}^{-1} \text{Na}_2\text{SO}_3$ electrolyte containing $40 \mu\text{mol}\cdot\text{L}^{-1} \text{Bi}^{3+}$ at a rotation rate of 300 rpm. (Figures from Reference 67)

Figure 12: a) Cyclic voltammetry in $80 \text{ mmol}\cdot\text{L}^{-1} \text{Na}_3\text{Au}(\text{SO}_3)_2 + 0.64 \text{ mol}\cdot\text{L}^{-1} \text{Na}_2\text{SO}_3$ electrolyte of pH 9.5 containing the indicated concentrations of Sb^{3+} . b) The data replotted on a logarithmic scale. Current densities are obtained from measured current using the nominal RDE surface area of 0.79 cm^2 with scan rate and rotation rate as indicated. Data was acquired without compensation for the estimated 6Ω cell resistance.

Figure 13: a) Trenches 0.5 μm deep of various aspect ratio with only the bilayer seed of Au on Cu prior to Au electrodeposition. Au deposition in $80 \text{ mmol}\cdot\text{L}^{-1} \text{Na}_3\text{Au}(\text{SO}_3)_2 + 0.64 \text{ mol}\cdot\text{L}^{-1} \text{Na}_2\text{SO}_3$ electrolyte: 15 min at -0.90 V with b) $2 \mu\text{mol}\cdot\text{L}^{-1} \text{Sb}^{+3}$ and c) $5 \mu\text{mol}\cdot\text{L}^{-1} \text{Sb}^{+3}$; and d) 25 min at -0.85 V with $5 \mu\text{mol}\cdot\text{L}^{-1} \text{Sb}^{+3}$, e) 30 min at -0.90 V with $3 \mu\text{mol}\cdot\text{L}^{-1} \text{Sb}^{+3}$, and f) 25 min at -0.95 V with $3 \mu\text{mol}\cdot\text{L}^{-1} \text{Sb}^{+3}$. All depositions were at rotation rate of 50 rpm and were preceded by 10 s of Au deposition an additive-free electrolyte at -1.2 V to eliminate pinholes in the evaporated Au seed layer.

Figure 14: a) Cyclic voltammetry in $80 \text{ mmol}\cdot\text{L}^{-1} \text{Na}_3\text{Au}(\text{SO}_3)_2 + 0.32 \text{ mol}\cdot\text{L}^{-1} \text{Na}_2\text{SO}_3$ electrolyte of pH 9.5 containing the indicated concentrations of Te^{4+} . b) The data replotted on a logarithmic

scale. Current densities are obtained from measured current using the nominal RDE surface area of 0.79 cm^2 . RDE rotation rate and scan rate as indicated. Software compensation for 70 % of the measured 6.5Ω cell resistance (i.e., leaving $\approx 2 \Omega$ of uncompensated cell resistance).

Figure 15: Au deposition in trenches of various aspect ratio from $80 \text{ mmol}\cdot\text{L}^{-1} \text{ Na}_3\text{Au}(\text{SO}_3)_2 + 0.32 \text{ mol}\cdot\text{L}^{-1} \text{ Na}_2\text{SO}_3$ electrolyte with Te^{4+} concentrations and deposition times as indicated. In each case filling was immediately preceded by 8 s deposition at -1.5 V to reduce corrosion of the Cu seed layer. All depositions were at rotation rate of 100 rpm.

Figure 16: Cyclic voltammetry of Au deposition in $0.32 \text{ mol}\cdot\text{L}^{-1} \text{ Na}_3\text{Au}(\text{SO}_3)_2$ electrolyte containing the indicated concentrations of $10,000 \text{ g}\cdot\text{mol}^{-1}$ PEI additive with RDE rotation rate 100 rpm. Experimental currents, converted to current densities using RDE area, are plotted against the applied potential without correction for cell impedance. The insert shows the inhomogeneous “swirl” deposit on the RDE surface after cycling in electrolyte containing $20 \mu\text{mol}\cdot\text{L}^{-1}$ PEI at rotation rate of 1600 rpm. (Figure from Reference 49)

Figure 17: Partial filling of square cross-sectioned TSV filled in $0.32 \text{ mol}\cdot\text{L}^{-1} \text{ Na}_3\text{Au}(\text{SO}_3)_2$ electrolyte containing $110 \mu\text{mol}\cdot\text{L}^{-1}$ of $1800 \text{ g}\cdot\text{mol}^{-1}$ PEI is seen at deposition potentials across the hysteretic range observed in cyclic voltammetry. From left to right: top row ($-1.26, -1.25, -1.24$) V and bottom row ($-1.20, -1.19$) V. The deposition time is 1 h in all cases. Active deposition begins at a depth controlled by the potential, with metal ion depletion responsible for decreasing deposition rate farther down. The dark speckle is embedded grit from polishing. (Figure from Reference 58)

Figure 18: Partial filling of trenches in $0.32 \text{ mol}\cdot\text{L}^{-1} \text{ Na}_3\text{Au}(\text{SO}_3)_2$ electrolyte containing $110 \mu\text{mol}\cdot\text{L}^{-1}$ of $1800 \text{ g}\cdot\text{mol}^{-1}$ PEI after 30 s of deposition at -1.275 V in trenches of two different width.

The transition from passive to active deposition yields a wedge shaped profile that reflects the gradient of suppressor concentration. (Figure from Reference 58)

Figure 19: Experimental and simulated voltammetry of Au deposition in $0.32 \text{ mol}\cdot\text{L}^{-1}$ $\text{Na}_3\text{Au}(\text{SO}_3)_2$ electrolyte with additive concentrations a) $0 \text{ }\mu\text{mol}\cdot\text{L}^{-1}$, b) $10 \text{ }\mu\text{mol}\cdot\text{L}^{-1}$ and c) $20 \text{ }\mu\text{mol}\cdot\text{L}^{-1}$ of $10,000 \text{ g}\cdot\text{mol}^{-1}$ PEI at the indicated scan rate and RDE rotation rates. The lifting of suppression on the initial negative-going scans in PEI-containing electrolytes occurs at more negative potentials than the reassertion of suppression on the return scans. Simulations of suppression breakdown are based on the kinetics extracted from the fits. Experimental currents are converted to current densities using the 0.78 cm^2 RDE area. The data was collected without compensation for iR potential drop across the cell resistance R, but the simulations account for the associated deviation from the applied scan rate. Both experimental and simulated voltammetry are plotted against the applied potential. (Figures from Reference 59)

Figure 20: Optical images of cross-sectioned annular TSV after Au deposition in $0.32 \text{ mol}\cdot\text{L}^{-1}$ $\text{Na}_3\text{Au}(\text{SO}_3)_2$ electrolyte containing $20 \text{ }\mu\text{mol}\cdot\text{L}^{-1}$ of $10,000 \text{ g}\cdot\text{mol}^{-1}$ PEI for the indicated deposition times and applied potentials. Except for the two most negative potentials, the deposits were preceded by a 5 s pulse at -1.5 V to improve nucleation on the Cu seeded surface. The patterned substrates were rotating at 100 rpm during deposition. (Figure from Reference 59)

Figure 21: a) The passive deposition rate on the field and the active deposition rate from the deposit thickness just below the passive-to-active transition within the TSV in **Figure 20**. All are nominal rates determined from the deposit thickness and deposition time without consideration of the deposit density. The solid lines represent predicted rates based on the deposition kinetics obtained from the cyclic voltammetry for a fully dense deposit; the dashed lines represent rates accounting for the indicated volume fraction of porosity. b) The distance d_s from the field down

the TSV to where the maximum deposition rate is achieved. Experimental distances from the field to the depth in the TSV where the maximum deposit thickness is first obtained are plotted versus the applied potential. The bars show the maximum and minimum values obtained from all TSVs examined on each specimen. The predictions are the distance down the TSV to the location where the deposition rate achieves 99 % of its unsuppressed value for the $20\ \mu\text{mol}\cdot\text{L}^{-1}$ concentration of $10,000\ \text{g}\cdot\text{mol}^{-1}$ PEI of the filling experiments. Simulations and data are plotted against applied potential. (Figures from Reference 59)

Figure 22: Cross-sectioned annular TSV after Au deposition in $0.32\ \text{mol}\cdot\text{L}^{-1}$ $\text{Na}_3\text{Au}(\text{SO}_3)_2$ electrolyte containing $20\ \mu\text{mol}\cdot\text{L}^{-1}$ of $10,000\ \text{g}\cdot\text{mol}^{-1}$ PEI showing progression of superconformal filling for different ranges of ramped potential. (a, d, g) 50 min total: ramped at $0.02\ \text{mV}\cdot\text{s}^{-1}$ from $-1.09\ \text{V}$ to $-1.15\ \text{V}$. (b, e, h) 100 min total: ramped at $0.02\ \text{mV}\cdot\text{s}^{-1}$ from $-1.09\ \text{V}$ to $-1.21\ \text{V}$. (c, f) 127 min total: ramped at $0.02\ \text{mV}\cdot\text{s}^{-1}$ from $-1.09\ \text{V}$ to $-1.21\ \text{V}$ then at $0.025\ \text{mV}\cdot\text{s}^{-1}$ from $-1.21\ \text{V}$ to $-1.25\ \text{V}$. Deposition was preceded by a 5 s pulse at $-1.5\ \text{V}$ to improve nucleation on the Cu seeded surface. (a, b, c) Higher magnification views near the position of the deposits at the via midline. (c) The microstructural boundary between side wall growth and advancing bottom-up growth front is evident. (g, h) Passive deposition on the field. The patterned substrate was rotating at 100 rpm during deposition. (Figure from Reference 59)

Figure 23: Cathodic polarization due to addition of MPS to a sulfite-based gold electrolyte (Sel-Rex Neutronex 309i) that contains gold sulfite, sodium sulfite, a pH buffer and thallium with, and without, addition of a liquid MPS additive (Aldrich). A) Linear-scan voltammetry for MPS concentrations: a) $0\ \text{mL}\cdot\text{L}^{-1}$, b) $0.3\ \text{mL}\cdot\text{L}^{-1}$, c) $1.2\ \text{mL}\cdot\text{L}^{-1}$, d) $2.4\ \text{mL}\cdot\text{L}^{-1}$ and e) $4.8\ \text{mL}\cdot\text{L}^{-1}$. Scan rates $5\ \text{mV}\cdot\text{s}^{-1}$ and RDE rotation rate of 100 rpm. The electrode potential at current density of $5\ \text{mA}\cdot\text{cm}^{-2}$ is plotted as a function of the additive concentration. C) Cross sectioned trenches showing

the evolution of Au filling: A) before Au electrodeposition and after B) 0.23 μm , C) 0.47 μm , D) 0.55 μm and E) 2.0 μm of Au deposition in electrolyte containing 3 $\text{mL}\cdot\text{L}^{-1}$ MPS. The deposition process is not detailed. (Figures from Reference 73 with permission)

Figure 24: Cyclic voltammetry in 80 $\text{mmol}\cdot\text{L}^{-1}$ $\text{Na}_3\text{Au}(\text{SO}_3)_2$ + 0.32 $\text{mol}\cdot\text{L}^{-1}$ Na_2SO_3 electrolyte of pH 9.5 containing a) 0 $\mu\text{mol}\cdot\text{L}^{-1}$ SeCN^- , b) 1 $\mu\text{mol}\cdot\text{L}^{-1}$ SeCN^- , c) 2 $\mu\text{mol}\cdot\text{L}^{-1}$ SeCN^- and d) 4 $\mu\text{mol}\cdot\text{L}^{-1}$ SeCN^- each at the indicated RDE rotation rates. Cyclic voltammetry in 80 $\text{mmol}\cdot\text{L}^{-1}$ $\text{Na}_3\text{Au}(\text{SO}_3)_2$ + 0.64 $\text{mol}\cdot\text{L}^{-1}$ Na_2SO_3 electrolyte of pH 9.5 containing e) 4 $\mu\text{mol}\cdot\text{L}^{-1}$ SeCN^- and f) 6 $\mu\text{mol}\cdot\text{L}^{-1}$ SeCN^- each at the indicated RDE rotation rates. Current densities are obtained from measured current using the nominal RDE surface area of 0.79 cm^2 at the indicated scan rate using software compensation for 70 % of the measured 6.5 Ω cell resistance (i.e., leaving $\approx 2 \Omega$ of uncompensated cell resistance).

Figure 25: Partial filling of Au-seeded trenches 3 μm deep and of aspect ratio 1.5 in 80 $\text{mmol}\cdot\text{L}^{-1}$ $\text{Na}_3\text{Au}(\text{SO}_3)_2$ + 0.64 $\text{mol}\cdot\text{L}^{-1}$ Na_2SO_3 electrolyte containing a,b) 4 $\mu\text{mol}\cdot\text{L}^{-1}$ SeCN^- for 10 min and c) 6 $\mu\text{mol}\cdot\text{L}^{-1}$ SeCN^- for 30 min at the indicated potentials and rotation rates.

FIGURES

Figure 1:

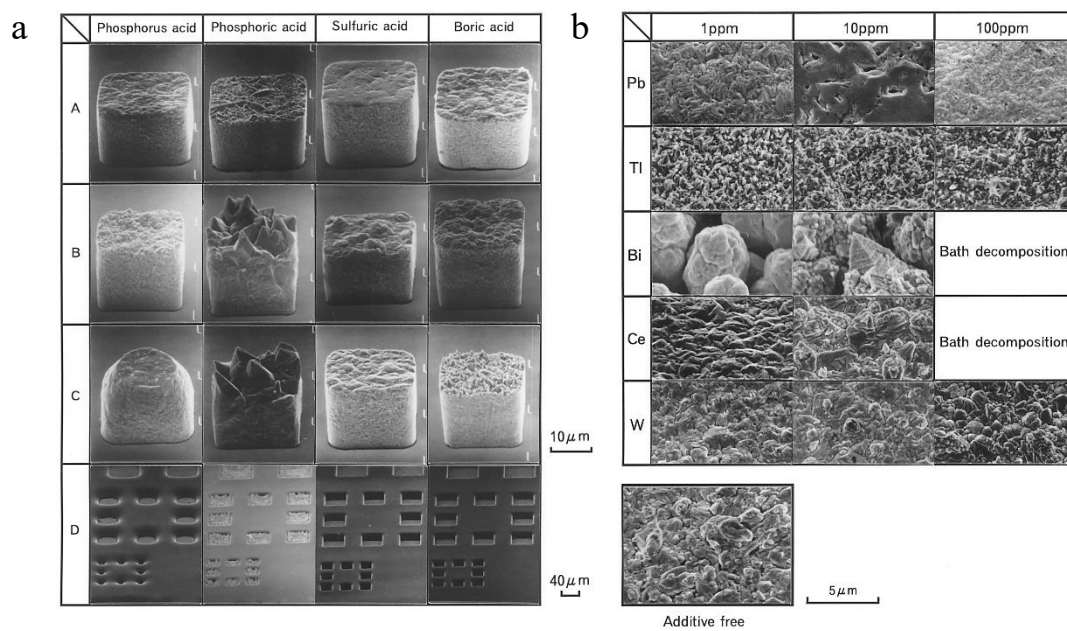


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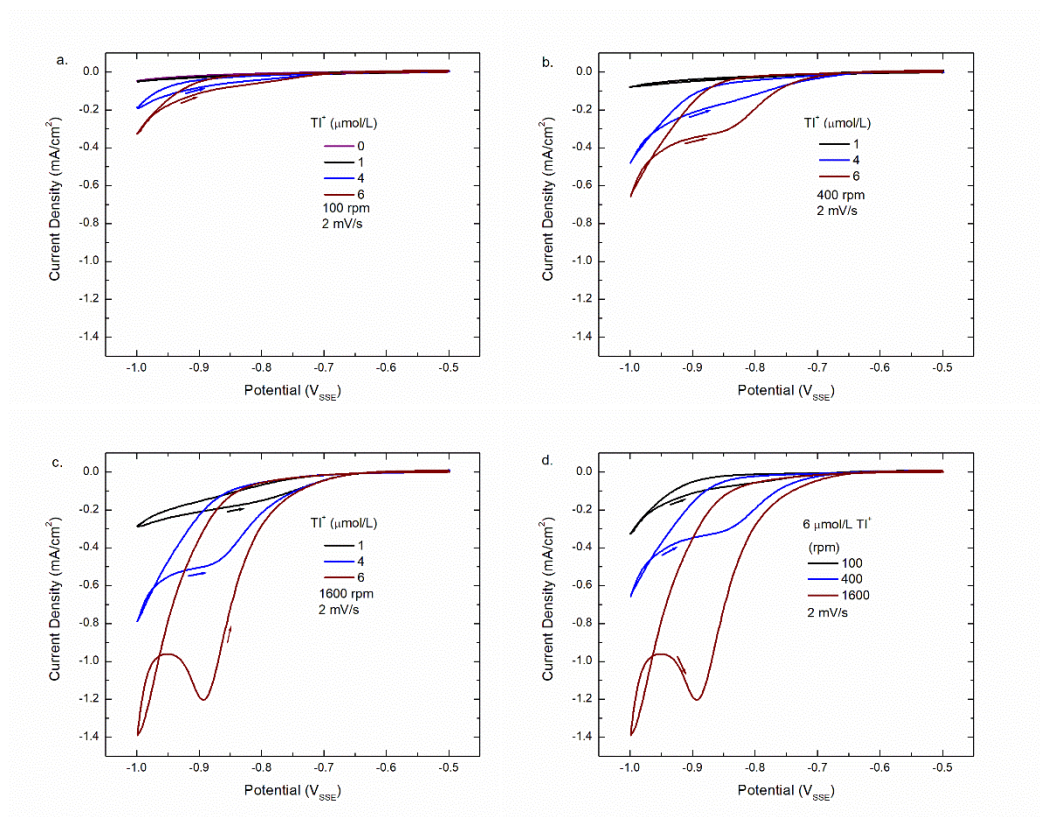


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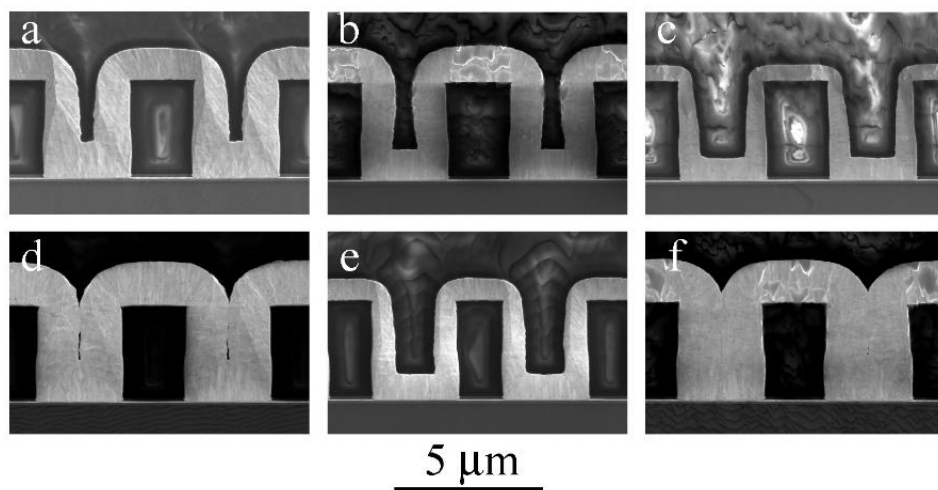


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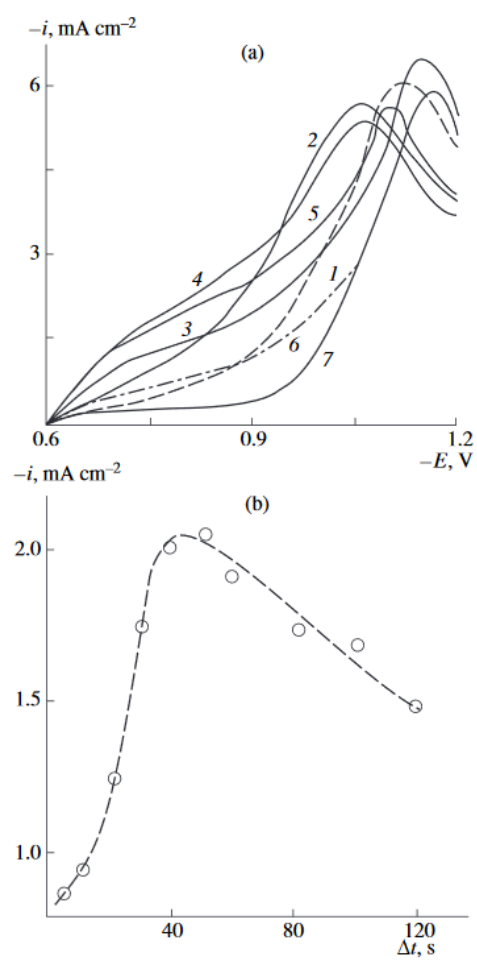


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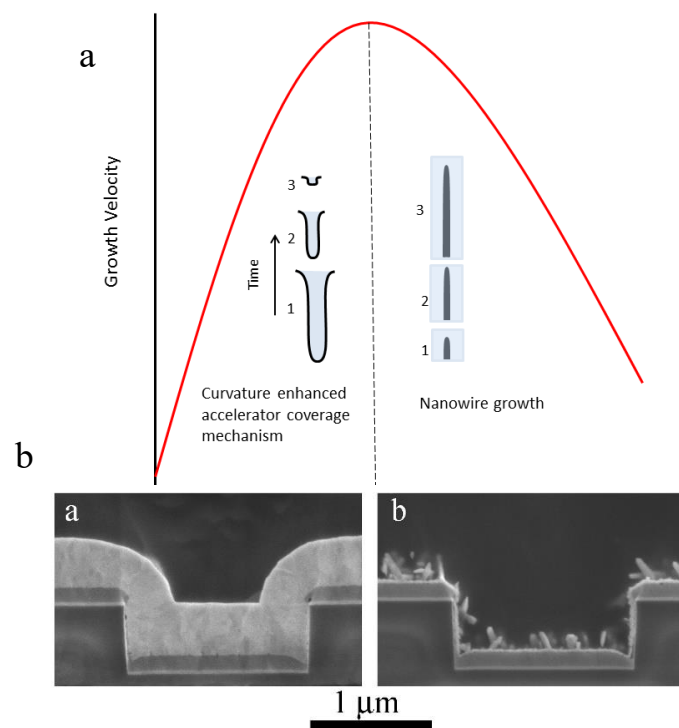


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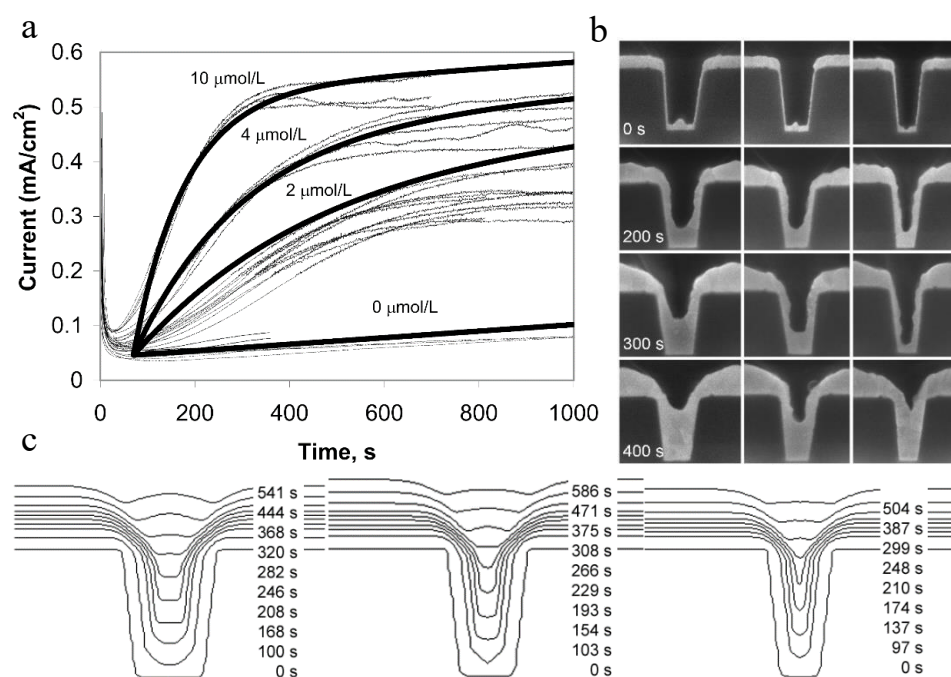


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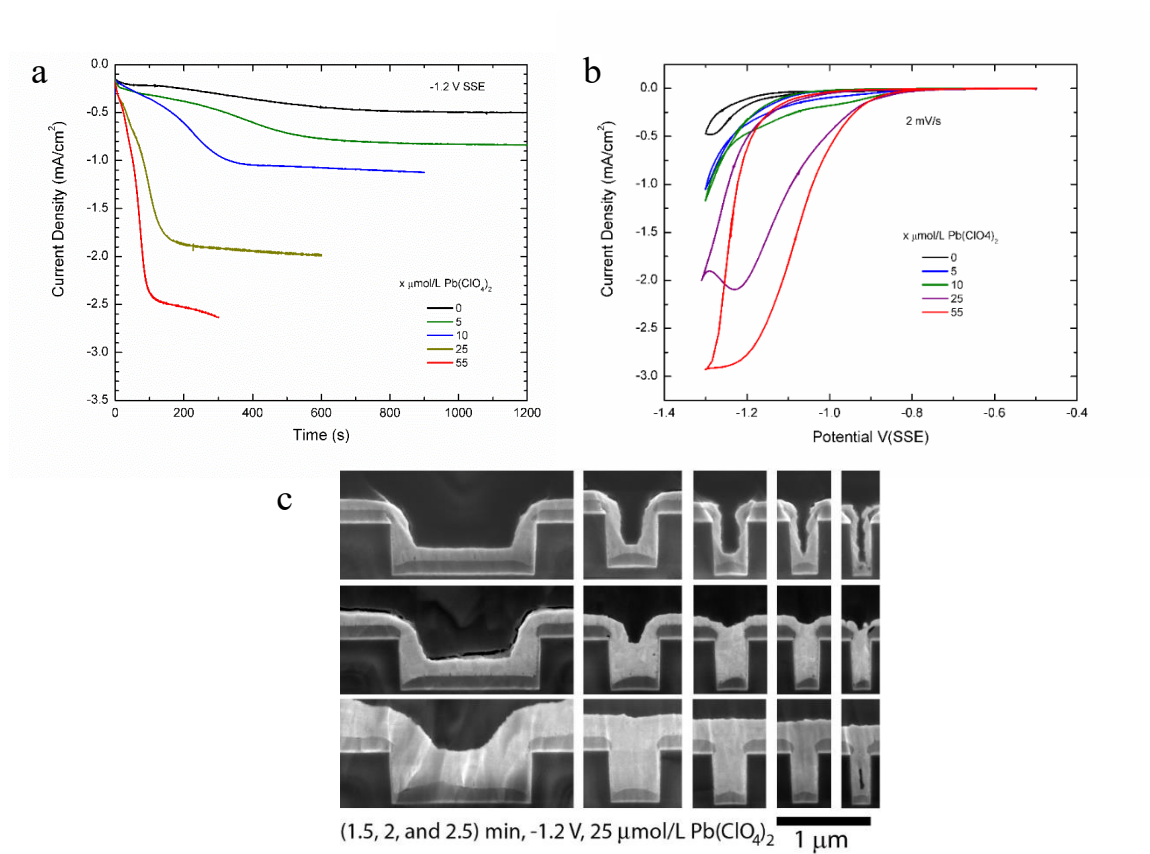


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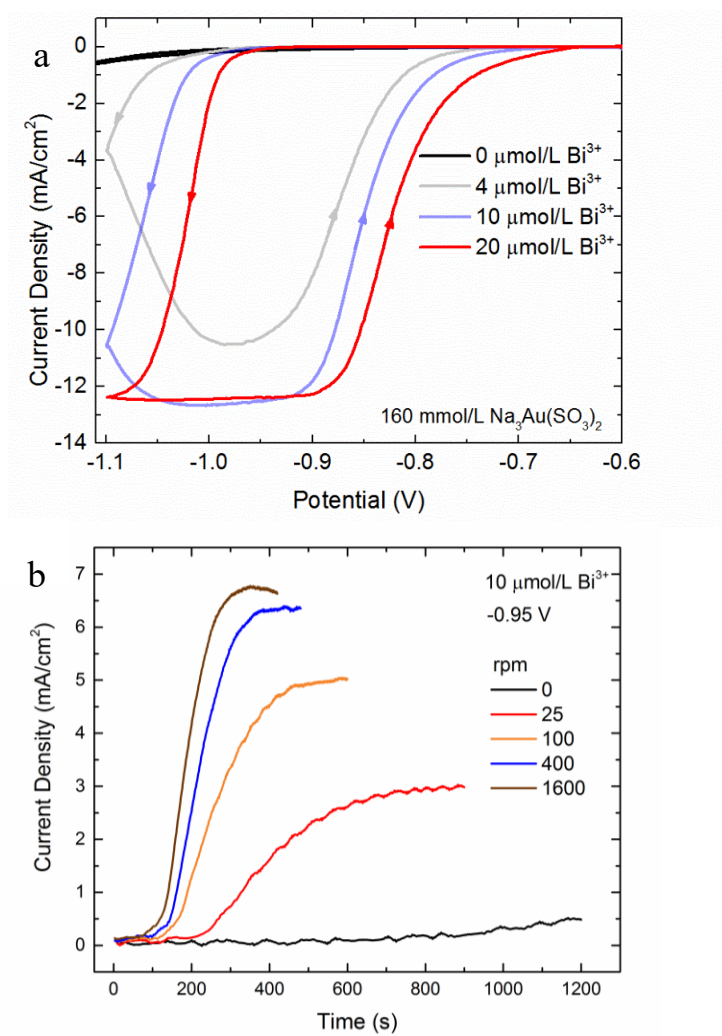


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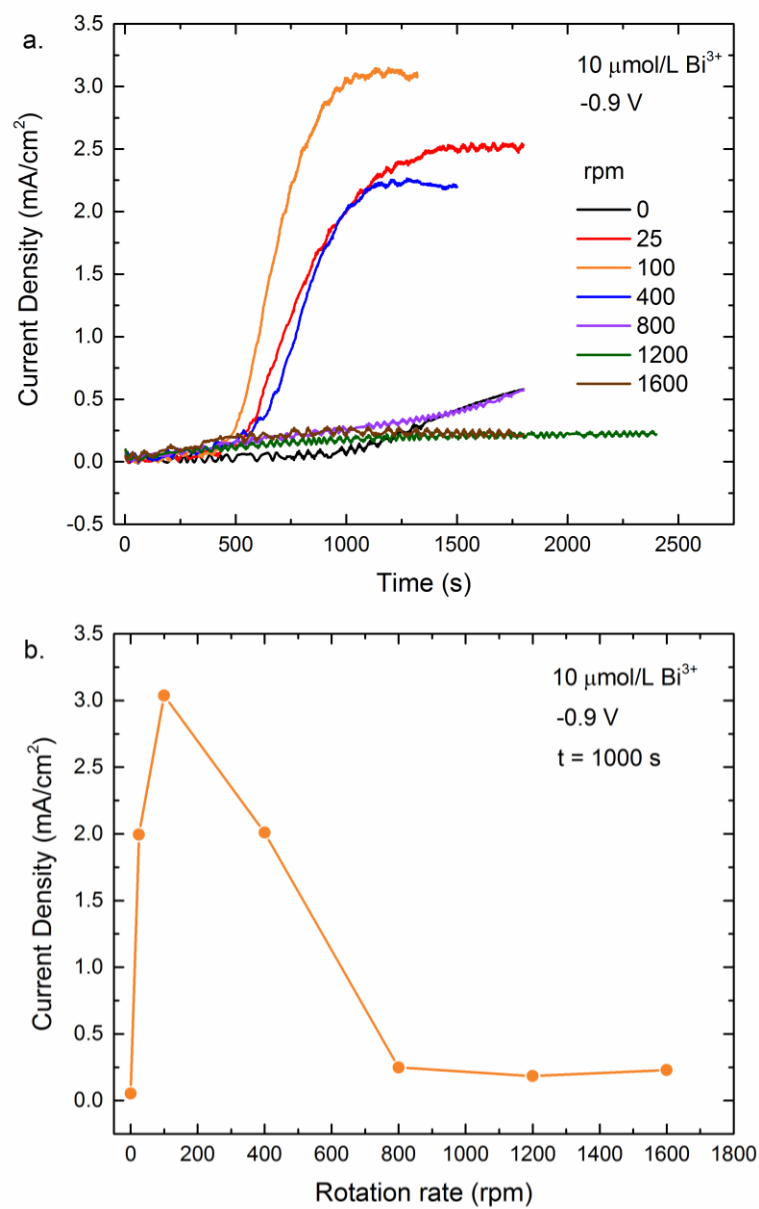


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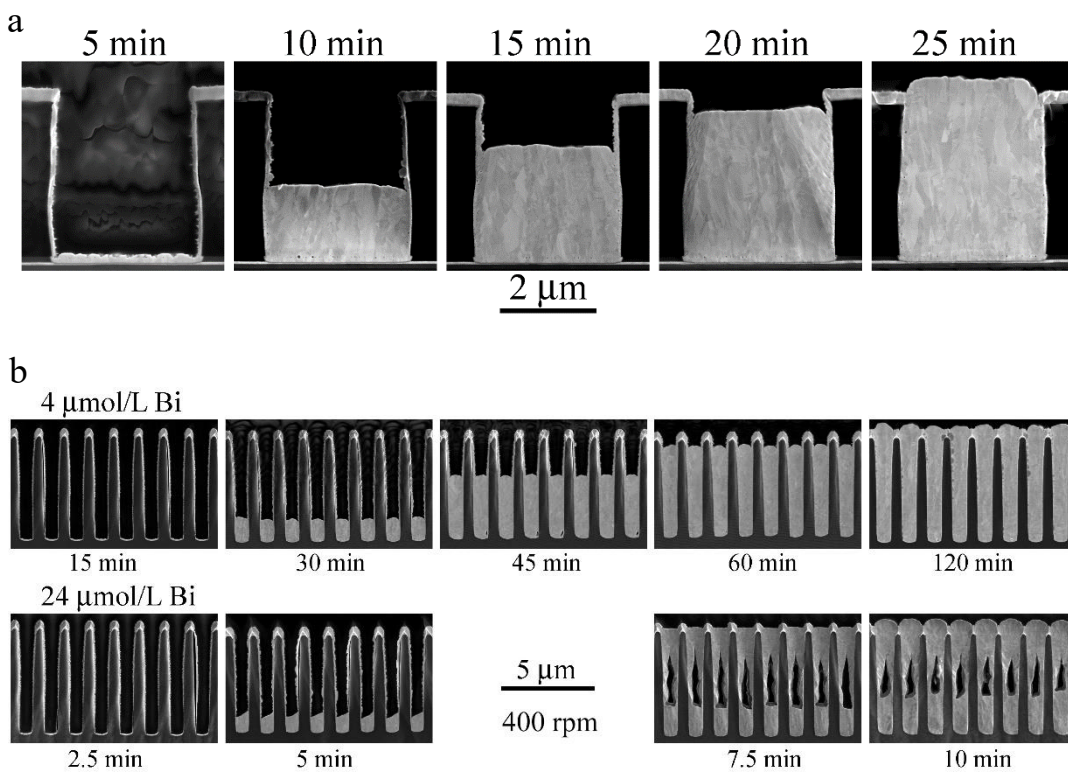


Figure 11

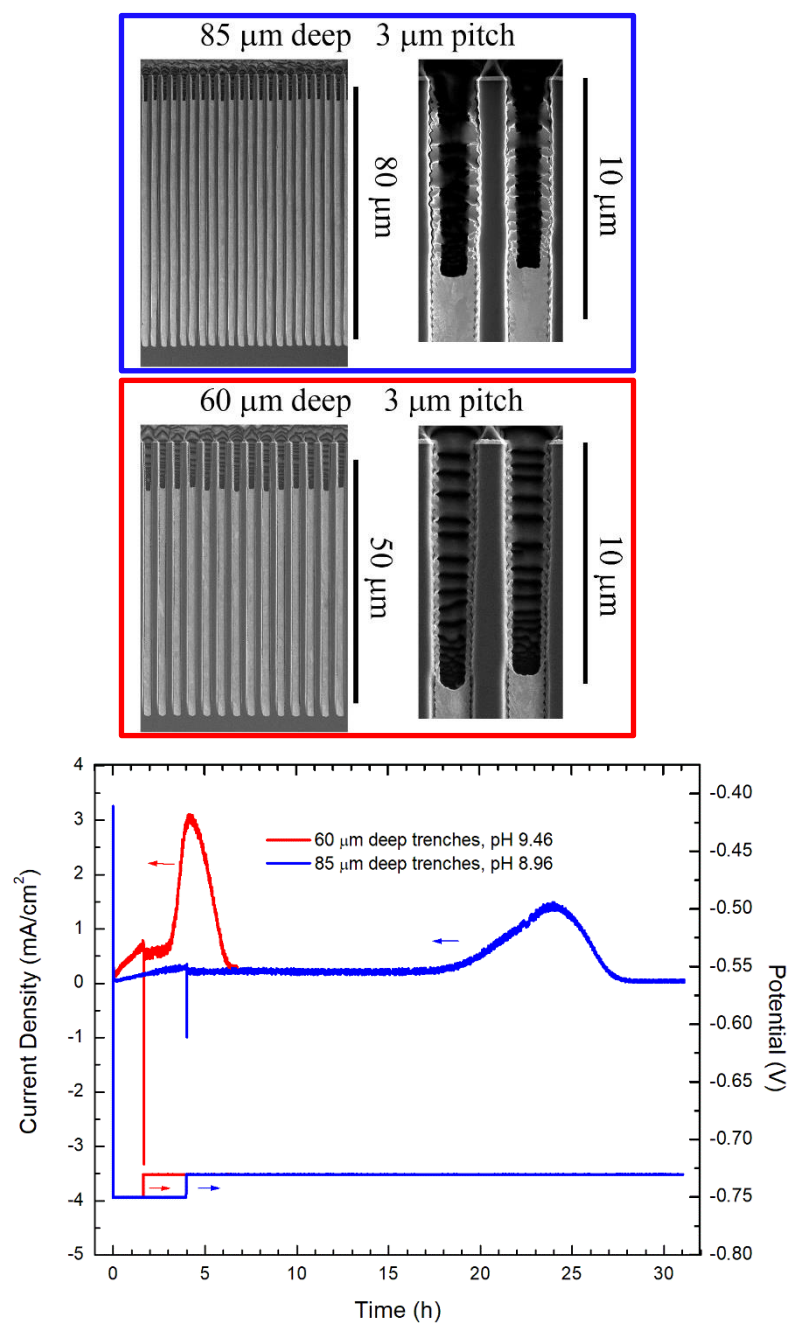


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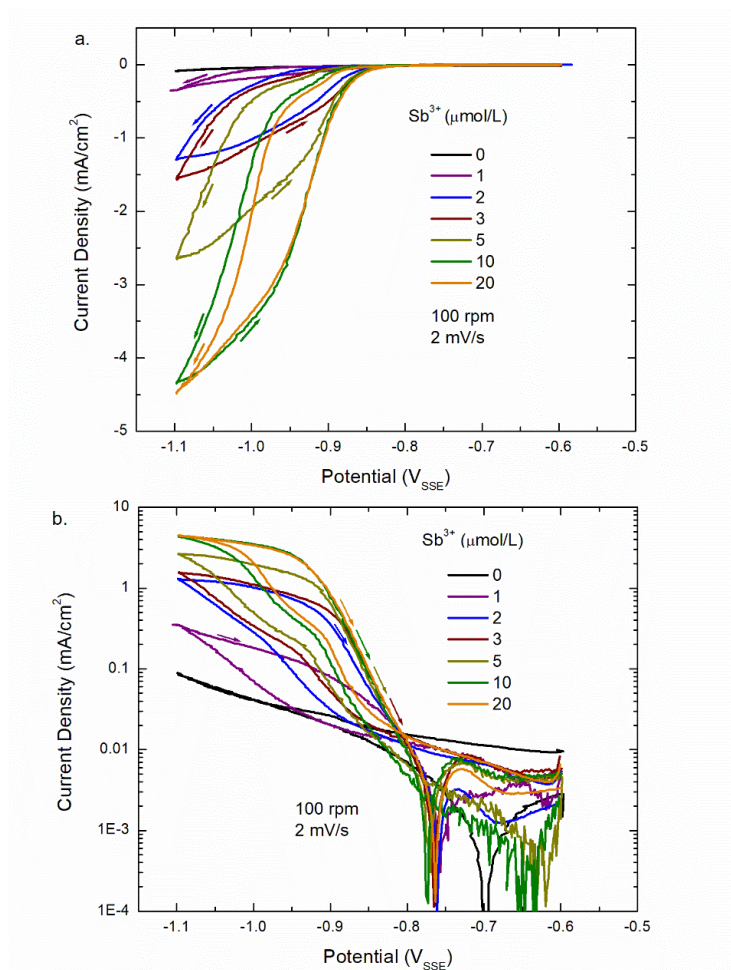


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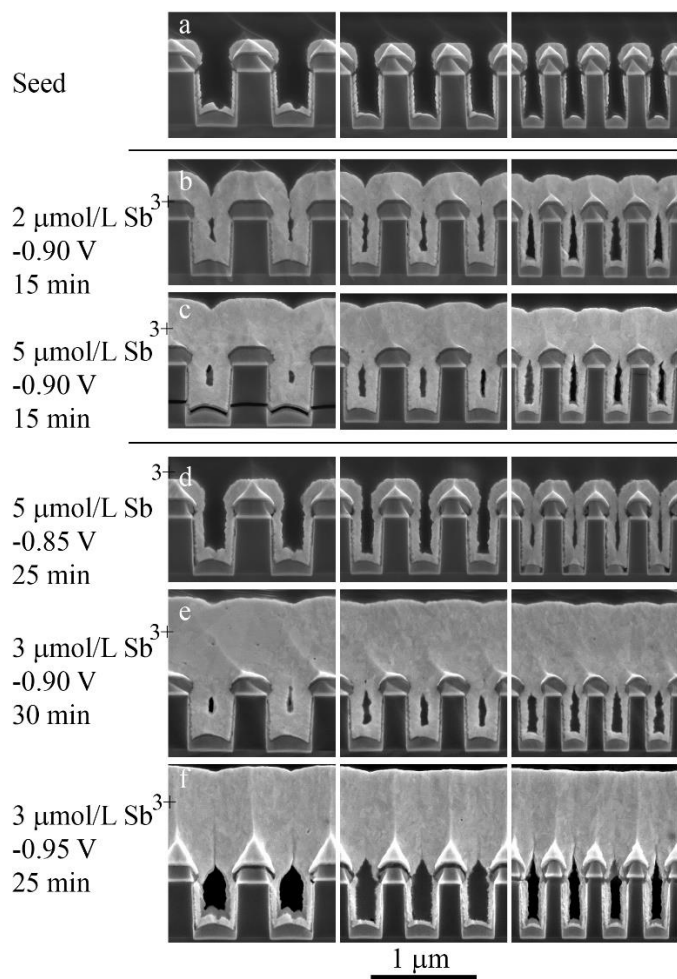


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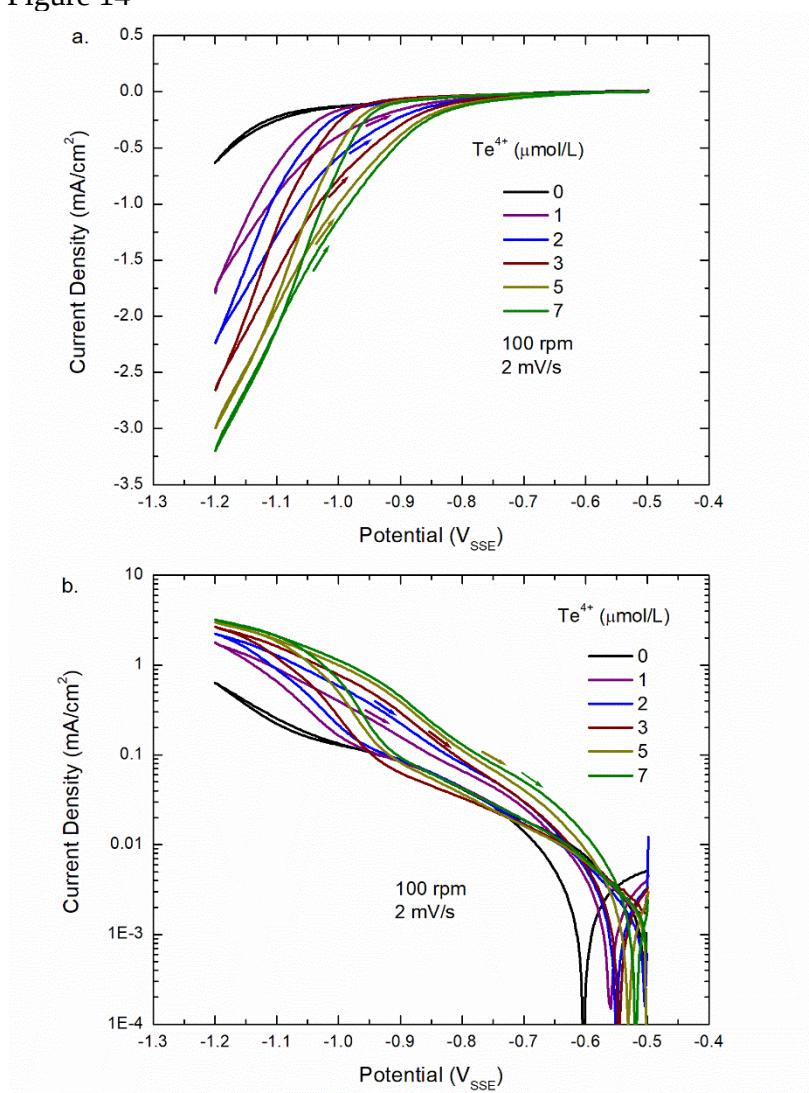


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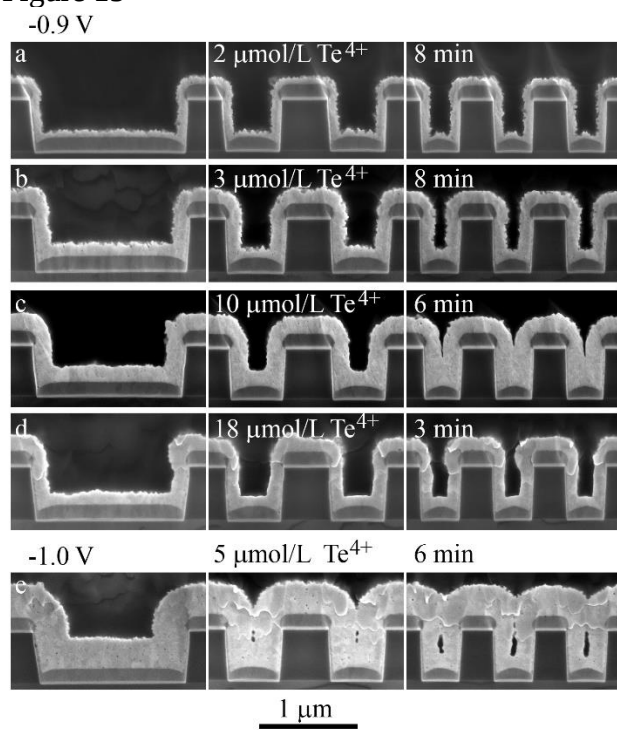


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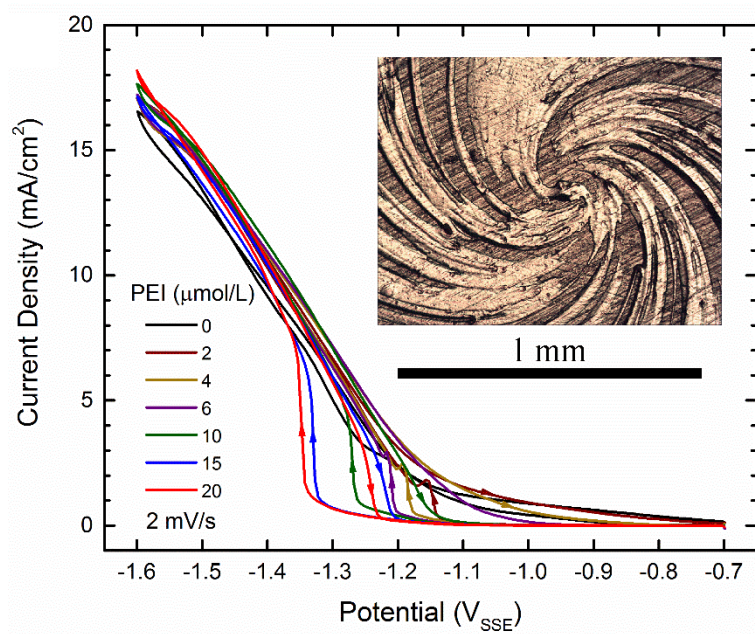


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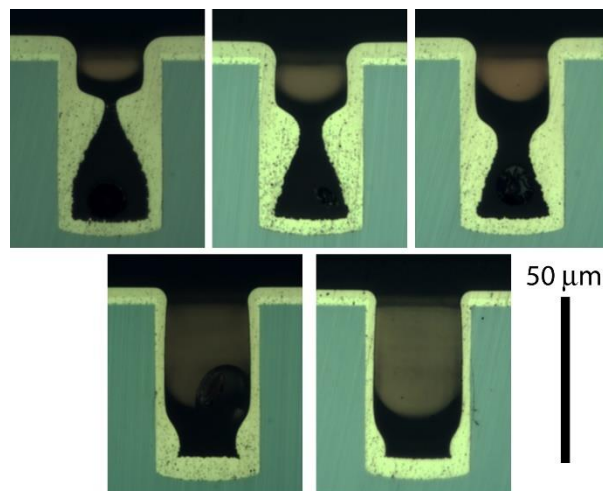


Figure 18

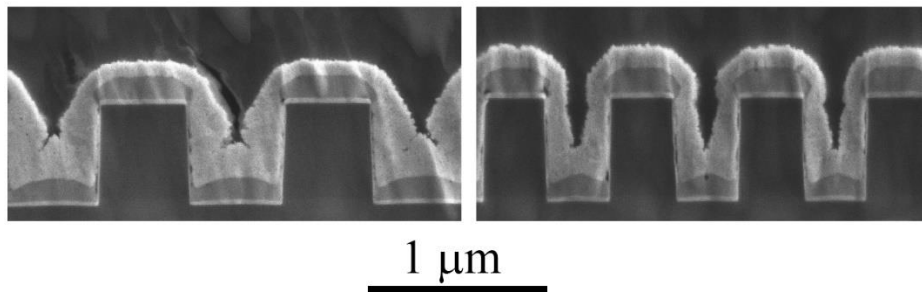


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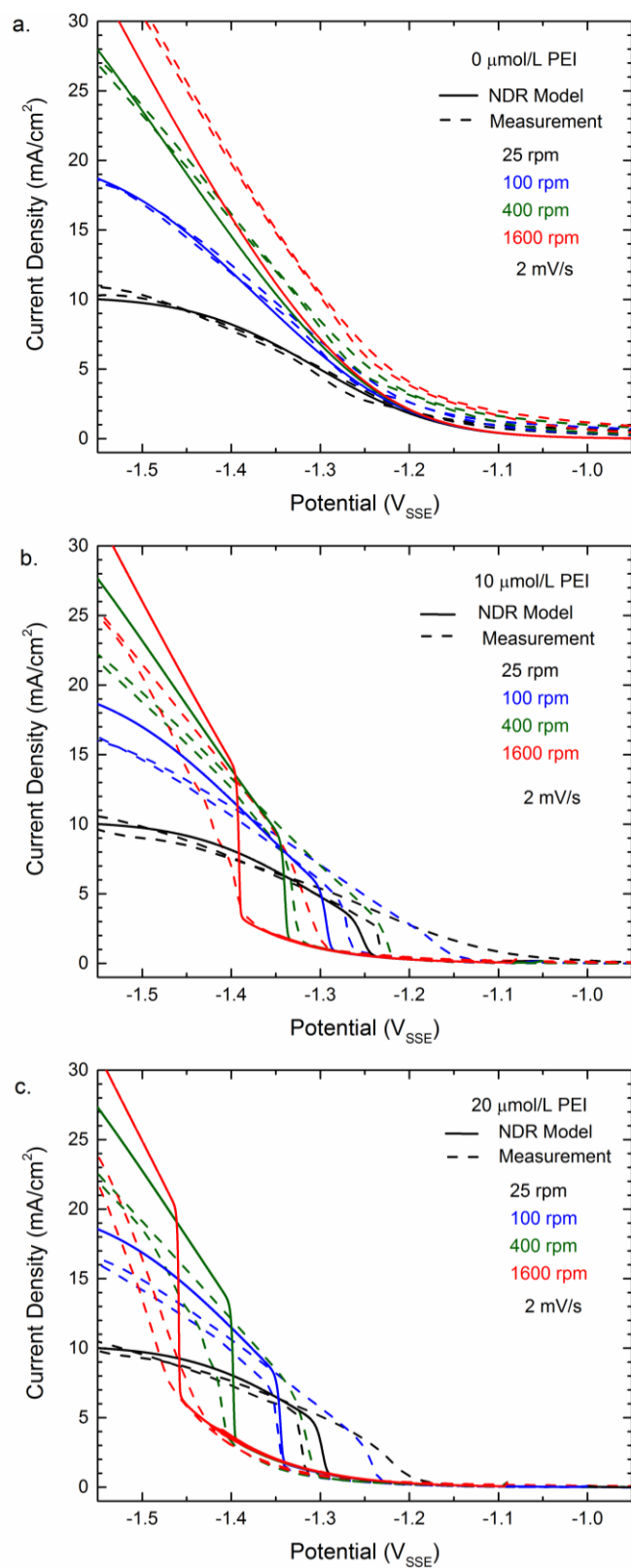


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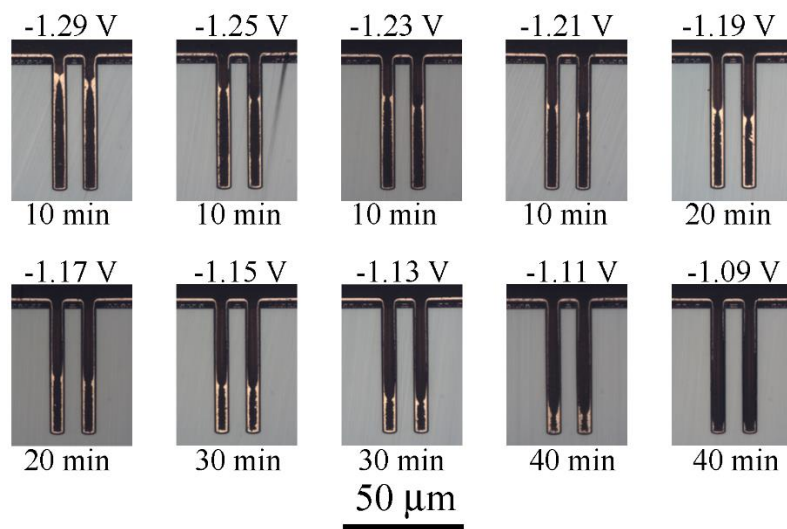


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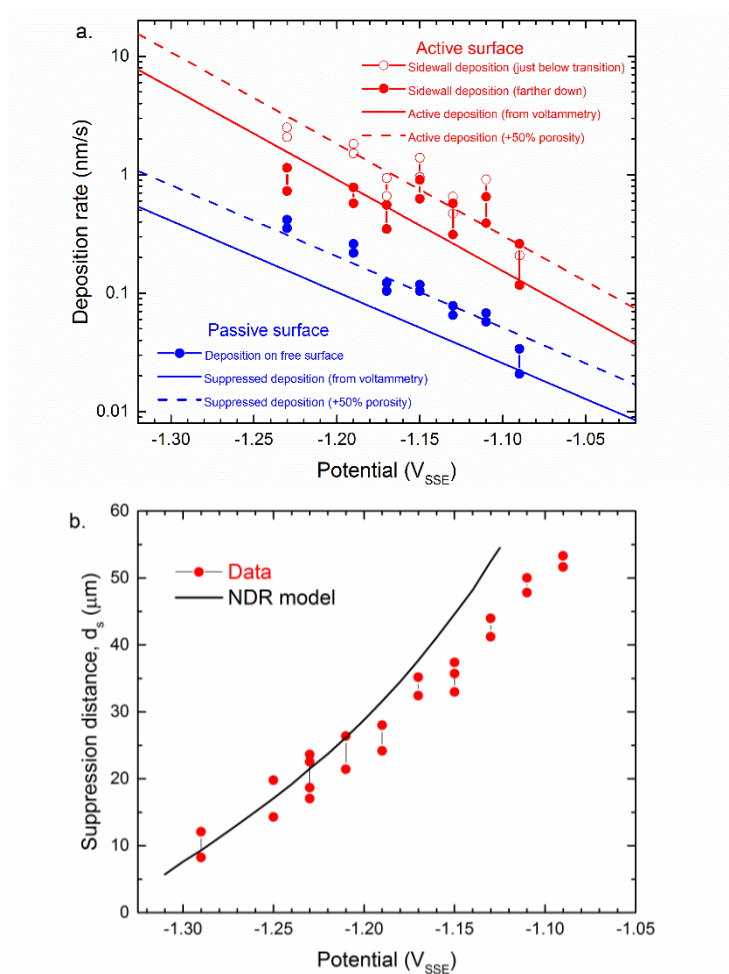


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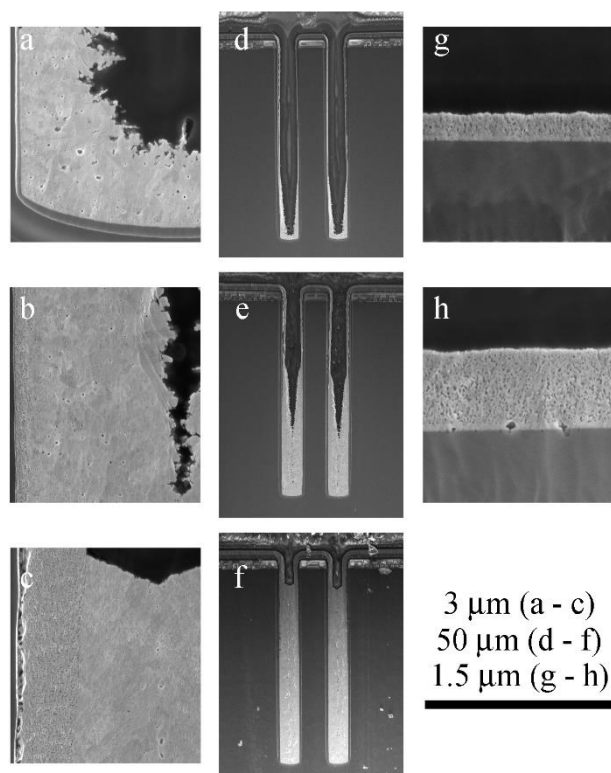


Figure 23

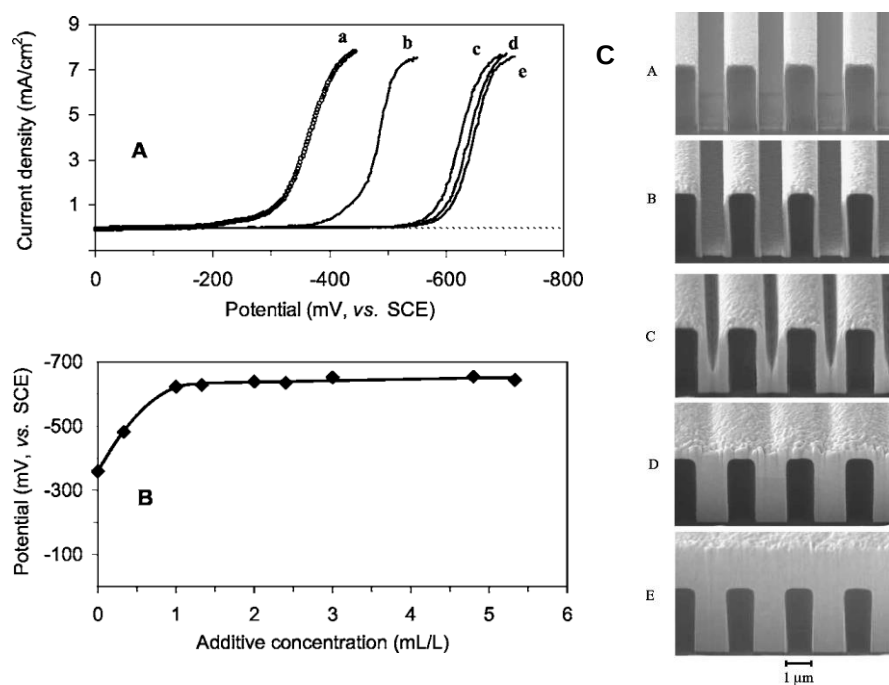


Figure 24

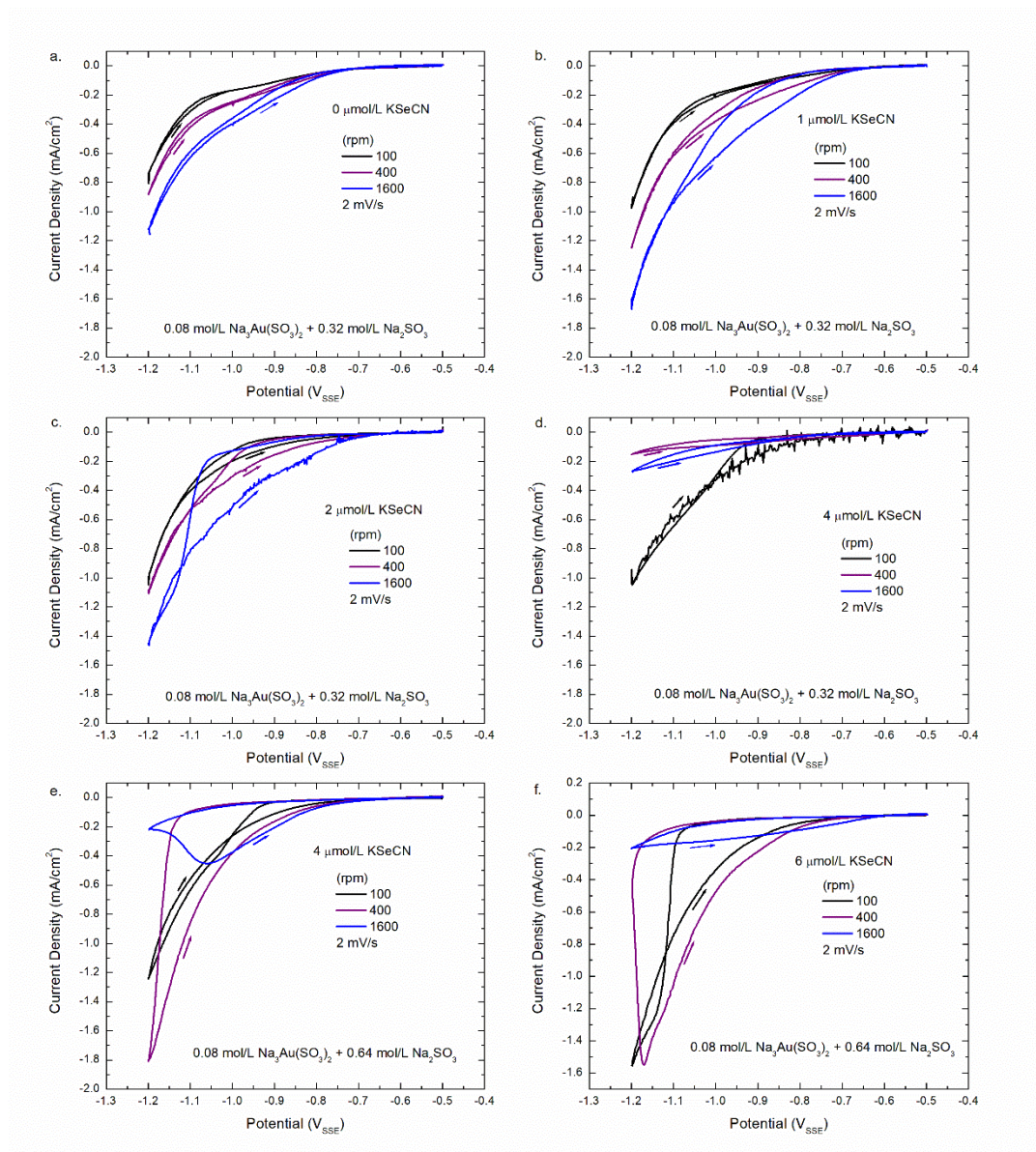


Figure 25

