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Superconformal Bottom-Up Gold Deposition in High Aspect Ratio Through Silicon Vias

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Abstract

This work presents superconformal, bottom-up Au filling of high aspect ratio through silicon vias (TSVs) along with a predictive framework based on the coupling of suppression breakdown and surface topography. The work extends a previous study of superconformal Au deposition in lower aspect ratio TSVs. Deposition was performed in a Na_3AuSO_3 electrolyte containing a branched polyethyleneimine (PEI) deposition-rate suppressing additive. Voltammetric measurements using a rotating disk electrode (RDE) were used to assess the impact of the PEI suppressor concentration and transport on the rate of metal deposition, enabling the interplay between metal deposition and suppressor adsorption to be quantified. The positive feedback associated with suppression breakdown gives rise to an S-shaped negative differential resistance (S-NDR). The derived kinetics for suppressor adsorption and consumption were used in a mass conservation model to account for bottom-up filling of patterned features. Predictions, including the impact of deposition potential and additive concentration on feature filling, are shown to match experimental results for filling of TSVs. This further generalizes the utility of the additive derived S-NDR model as a predictive formalism for identifying additives capable of generating localized, void-free filling of TSVs by electrodeposition.

INTRODUCTION

While Cu is now the dominant metal used for on-chip interconnects, Au is still the metal of choice for contacts to wide bandgap semiconductors. Through-mask plating is widely used for forming these simple Au structures, deposition proceeding from a common back contact with a layer of patterned photoresist defining the plated area^{1–3}. However, processes that achieve superconformal filling of damascene patterned features, such as those that dominate manufacture of on-chip Cu interconnects from the nanoscale^{4,5} to the microscale^{6–8}, are desirable because of the versatility offered by the Damascene process to build dense 3-D metallization networks of arbitrary complexity. Superconformal Au filling of micrometer size trenches has, in fact, been demonstrated using processes based on the use of a rate suppressing additive guided by the linear theory of leveling⁹ as well as the curvature enhanced accelerator coverage (CEAC) mechanism that involves competition between rate suppressing and accelerating additives^{10,11}. More recently, an effort to fill much larger TSVs using an electrolyte that exhibited non-linear S-shaped Negative Differential Resistance (S-

NDR) was reported. The system gives rise to distinctive partitioning of the work piece into active and passive regions whence, for 3-D patterned structures, deposition on the free surface is blocked while Au is actively deposited within the recessed features, the transition from passive to active behavior within the filling features being a sensitive function of the process control parameters.¹² Previously, the S-NDR mechanism has been shown to explain extreme bottom-up filling of Cu^{6,13–16} as well as the sidewall passive-to-active transition in Zn²⁰, Co²¹, and Ni²², including accurate quantitative prediction. However, no quantitative modeling has been applied to the Au system.

Transport, adsorption, deactivation and surface area change all can impact the coverage of adsorbed additives that more broadly underlie superconformal feature filling. However, S-NDR based models implemented thus far only required the first three effects to accurately predict the temporal and spatial evolution of deposition.^{17–19} The superconformal filling profiles associated with S-NDR systems arise from competition between metal passivation by suppressor adsorption and surface activation through suppressor deactivation. The resulting nonlinear dependence of suppressor coverage on suppressor concentration²³ couples with a gradient of suppressor concentration down filling features to localize deposition at, or toward, the bottoms of filling features. Both the side-wall passive-to-active transition and exclusive bottom-up geometries may be captured by S-NDR models, with critical behavior associated with the suppression breakdown underlying the highly nonlinear dependence of deposition rate on position in all cases. Importantly, such highly localized, sharp transitions cannot be derived from older leveling models based on linear relationships between deposition rates, suppressor coverage and suppressor concentration.^{24,25}

This study uses the same Na₃AuSO₃ electrolyte used in our previous Au feature filling work¹². Likewise, the additive branched polyethyleneimine (PEI) is used as the suppressor; however, in the present case a five-fold larger molecular mass (10,000 g/mol) is used. Electroanalytical measurements are used to parameterize an S-NDR model that enables quantitative prediction of the onset geometry of significant Au deposition within TSVs. This understanding is then combined with a programmed potential step wave form to achieve nearly void-free Au filling of the TSVs. Based on previous work with the Na₃AuSO₃-PEI electrolyte system, significant porosity evident in the microstructure can negatively impact the mechanical properties, including crack formation and propagation. Thus close attention will be given to the impact of PEI on the microstructure of the deposits.

EXPERIMENTAL DETAILS

Depositions were conducted at room temperature in a cell containing 35 mL of 0.32 mol/L Na₃AuSO₃ electrolyte of pH 9.0. Additive was introduced to the electrolyte from a master solution of 10 mmol/L PEI of 10,000 molecular mass (Alfa Aesar^{*}) in 18 MΩ-cm water. The electrolyte was sparged with argon between electrochemical measurements to reduce the impact of dissolved oxygen. A Hg/Hg₂SO₄/saturated K₂SO₄ reference electrode (SSE) was connected to the working electrode compartment via a fritted salt bridge filled with saturated solution of K₂SO₄. All experiments were conducted without compensation for cell

^{*}Corporate and product names are included for completeness of description and do not constitute endorsement.

resistance, with all potentials relative to this reference. A platinum counter electrode was held in a frit-separated cell immersed within the main cell.

Voltammetry was conducted on a Au rotating disk electrode (RDE) of 1.0 cm diameter (area 0.78 cm²). The RDE was polished with 1200 grade SiC paper and rinsed with 18 M Ω -cm water prior to each experiment. Voltammetry was performed at 2 mV/s at different RDE rotation rates: 25 rpm, 100 rpm, 400 rpm and 1600 rpm. Currents in electroanalytical measurements are converted to current densities using the projected RDE geometric area. However, as will be seen, the deposit area is generally ill-defined beyond suppression breakdown. Specifically, deposition in the additive-containing electrolyte is not uniform so that the “current density” reported under such circumstance can represent a lower bound for active areas. Conversely, the measured currents can also be increased through enhanced deposition on deposit roughness that projects beyond the boundary layer.

Feature filling was performed using fragments of wafers patterned with ≈ 56 μ m deep TSVs of annular cross-section (courtesy of IBM) having a 1 μ m thick Cu seed in the field and a lesser amount on the side walls. To give definition to the metal ion and additive transport, the patterned substrates rotated about one end from a Pt spindle during deposition, like a helicopter blade, the patterned surface facing upwards. Based on the ≈ 1 cm distance between the features and rotational axis for most of the imaged TSVs, the 100 rpm (200 π rad/min) rotation rate corresponds to an estimated 10 cm/s flow rate over the surface. Pre-wetting with ethyl alcohol was used to displace air bubbles that were otherwise trapped in the TSVs during immersion in the electrolyte for Au deposition. Following immersion, the specimens were rotated at open circuit for 2 min prior to starting the metal deposition in order to displace the alcohol from the TSV by mixing with the bulk electrolyte. In most cases a 5 s voltage pulse at -1.5 V was then applied, just prior to feature filling, to improve nucleation on the Cu seeded TSVs.

The TSVs were imaged optically after embedding them in epoxy and then cross-sectioning and polishing them on diamond lapping films down to 0.1 μ m grit size using standard techniques and equipment. A subset of specimens was also examined by scanning electron microscopy. These specimens were subjected to an additional cleaning of the surface using oblique 4 keV Ar⁺ to remove residual surface damage from the mechanical polishing prior to imaging.

DEPOSITION ON PLANAR AND PATTERNED SUBSTRATES

Figure 1 shows cyclic voltammograms (CVs) that capture the suppression induced by the introduction of the PEI additive as well as the concentration-dependence (Fig. 1a) and the transport-dependence (Fig. 1b) of the potential at which suppression is lifted. Suppression is seen to lift at more negative potentials, the threshold value increasing with both PEI concentration and RDE rotation rate. Following suppression breakdown, the current-voltage response merges with the response of the additive-free electrolyte. The gradual increase of current in the passive region, i.e. at potentials positive of the suppression breakdown, suggests a leakage process associated with metal deposition and/or some parasitic contribution from water reduction. Deposition currents on the return sweeps remain

accelerated to more positive potentials than the suppression breakdown potentials, leading to hysteretic responses. Analogous behavior has been seen for all the previously cited electrolytes exhibiting superconformal metal deposition in TSVs by the S-NDR mechanism. Examination of the electrode surface after cycling reveals a swirl pattern comprised of active and passive regions. For 20 $\mu\text{mol/L}$ PEI the pattern is especially clear at higher rotation rates as shown in the optical micrograph of the RDE center that is inset in Fig. 1a. Similar swirl patterns have been reported in RDE studies of other metal-additive S-NDR systems.^{26–28}

Figure 2 shows cross sectioned annular TSV's following Au deposition from a 20 $\mu\text{mol/L}$ PEI-containing electrolyte at the indicated applied potentials. The specified potentials are all positive of the critical potential that defines the hysteretic voltammetric loop for deposition on a planar electrode (Fig. 1). Accordingly, the free the surfaces of the TSV patterned work pieces are in the passive state while a transition to active metal deposition is evident within the recessed vias. The transition from the passive state to active deposition expressed as the distance from the field to the location where the maximum Au deposit thickness is first achieved, d_s , is seen to increase at more positive potentials. An analogous dependence, as well as an increase of d_s with suppressor concentration, has been detailed with the Ni and Co systems exhibiting suppression breakdown induced S-NDR. Longer deposition times at more positive potentials (see Fig. 2) are necessary to provide visible deposits due to the slower potential activated deposition rate. The figure also implicitly captures the minimal impact of deposition time on the passive distance d_s , consistent with behavior observed with the Ni and Co systems from the onset of breakdown all the way to impingement of the deposits on the opposing sidewall.

EVALUATION OF KINETIC PARAMETERS

Both fitting of the electroanalytical measurements and feature fill prediction presume fractional suppressor coverage θ evolving through accumulation and deactivation according to

$$\frac{d\theta}{dt} = k_+ C_s (1 - \theta) - k_- \theta v(\theta, \eta) \quad [1]$$

where C_s is the suppressor concentration at the electrolyte/deposit interface. The deposition rate $v(\theta)$ is assumed to be a linear function of the suppressor coverage θ and metal ion concentration at the interface, thus

$$v(\theta, \eta) = \frac{\Omega}{nF} \frac{C_{Au}}{C_{Au}^0} (j_{\theta=0}(1 - \theta) + j_{\theta=1}\theta) \equiv v_0(1 - \theta) + v_1\theta \quad [2]$$

The current densities on unsuppressed ($J_{\theta=0}$) and suppressed ($J_{\theta=1}$) surfaces are those associated with the metal deposition only and have been related to the metal deposition rate through Faraday's constant $F = 96485 \text{ C/mol}$, n the ionic charge and Ω the molar volume of solid Au. The current densities are assumed to exhibit the conventional exponential

dependence on overpotential η (relative to the reversible potential of ≈ -0.37 V estimated from the CVs)

$$j_{\theta=0,1} = j_{\theta=0,1}^o e^{-\frac{\alpha_{\theta=0,1} F \eta}{RT}} \quad [3]$$

where the back reaction has been neglected in light of the high overpotentials used in the feature filling experiments. As defined using Eq. 2, the exchange rate constants $j_{\theta=0,1}^o$ for the bare, $\theta=0$, and fully inhibited, $\theta=1$, surface are for bulk metal ion concentration C_{Au}^o at the interface.

Values for $j_{\theta=0}^o$ and $\alpha_{\theta=0}$ are given in Table I with other parameters that will be discussed. The values were determined by fitting voltammetric data from additive-free electrolyte; the fitted curves are overlaid on the experimental data in Fig. 3a; the CVs and fitted curves for non-zero suppressor concentrations in Fig. 3b-c are discussed later. The similar experimental current densities prior to suppression breakdown at the higher PEI concentrations in Fig. 1 suggest that the surfaces in these PEI-containing electrolytes are saturated with PEI prior to the suppression breakdown event.

Parasitic processes such as water reduction that can reduce the current density associated with the metal deposition below the measured current density are taken to be negligible in this system. The values of $j_{\theta=1}^o$ and $\alpha_{\theta=0}$ were therefore obtained directly from the fit to the negative-going sweeps up to the critical potential. The difference of $\alpha_{\theta=1}=0$ from $\alpha_{\theta=0}$ is not expected from a simple blocking mechanism.

Fitting of the CVs to obtain the remaining kinetic parameters k_+ and k_- involves integrating Eq. 1 for $\theta(t)$, subject to Eqs. 2 and 3, and mass balance between suppressor diffusion across the boundary layer and its adsorption onto the surface expressed as

$$D_s \frac{C_s^o - C_s}{\delta} = \Gamma k_+ C_s (1 - \theta) \quad [4]$$

Values for the areal density of sites Γ , suppressor diffusion coefficient D_s and boundary layer thickness δ (scaling with the rotation rate as $\omega^{-0.5}$) were estimated (see Table I). Metal ion depletion across the boundary layer, more significant here than our recent Ni and Co studies with higher metal ions concentrations, was accounted for by balancing the molar volume weighted ion flux across the boundary layer with the deposition rate

$$\Omega D_{Au} \frac{C_{Au}^o - C_{Au}}{\delta} = v_{\theta=0} (1 - \theta) + v_{\theta=1} \theta \quad [5]$$

where the right side of Eq. 5 also depends on the metal ion concentration at the surface, C_{Au} , through Eq. 2. This balance is most relevant when deposition approaches the metal ion transport limit with $C_{Au} \rightarrow 0$.

Evolution of current density and adsorbate coverage through Eqs. 1–5 depends on a number of parameters. However, with values for the other parameters either known or otherwise estimated, k_+ and k_- were adjusted to capture the dependence of the suppressor breakdown potential on the suppressor flux to the interface, as manifest in the concentration and RDE rotation rate dependences. Significantly, simulations over a wide range of k_+ values can exhibit similar suppression breakdown potential if k_- is scaled appropriately. This is clearest for the case of near ideal suppression (i.e., $v_{\theta=0} \gg v_{\theta=1} \rightarrow 0$) for which the unsaturated steady state suppressor coverage, obtained from solution of Eqs. 1 and 3 with $\frac{d\theta}{dt}=0$, is

$\theta = \frac{k_+}{k_-} \frac{C_S}{v_{\theta=0}}$, so that k_+ and k_- enter explicitly only in the ratio $\frac{k_+}{k_-}$. However, the coverage also depends on the suppressor and metal ion concentrations at the electrolyte/metal interface (C_S and $v_{\theta=0}$, respectively) and thus the boundary layer thickness through Eqs. 4 and 5. Simultaneous fitting of the suppression breakdown potentials at the four rotation rates therefore further restricts the range of k_+ and k_- values.

Fitting of the suppression breakdown observed in the cyclic voltammetry for two different suppressor concentrations and four different rotation rates is shown in Fig. 3b and 3c. The emphasis was on capturing the suppression breakdown potentials, with no effort to fit the slope of the data at more negative potentials in light of the evolving and unquantified surface area, and thereby current density, associated with active regions of the bifurcating electrode. The k_+ and k_- values, derived from the simultaneous fitting of all eight curves, are indicated in Table I. As the data acquisition was performed without iR compensation, a corresponding $-iR$ potential offset is included in the overlaid simulations. Both the cell resistance and metal ion transport limit have only a modest impact on fitting of the suppression breakdown due to the low currents, well below the transport limit, prior to suppression breakdown. At potentials negative of suppression breakdown, the current densities generally fall below the predicted values, suggesting incomplete activation of the RDE surface (Fig. 1a inset).

TSV FILLING SIMULATIONS

The distinct breakdown of inhibition in the voltammetric curves reflects the emergence of a two state active–passive system, the critical potential representing the limiting condition for balance between the concentration-dependent rate of suppressor adsorption onto the uniform, planar surface and the potential-dependent rate of adsorbate deactivation (Eq. 1). Decrease of the suppressor concentration within recessed features effectively introduces a position-dependent positive shift of the critical potential from that at the free-surface. For experiments of most interest the passive-to-active transition occurs at the location within the feature where the critical potential equals the actual applied potential.

Previous models of Cu bottom-up TSV filling through the additive derived S-NDR mechanism evaluated both the metal ion and the suppressor concentration distributions within the boundary layer and the TSV, capturing experimental observations^{17,18}. These entailed full spatial and temporal analysis¹⁸ or a pseudo steady state, one-dimensional

analysis¹⁷ that took advantage of experimental TSV fill times that were substantially longer than diffusional relaxation times. This study, like the earlier Co²¹ and Ni²² studies, also uses the pseudo steady state approach, neglecting the impact of the transient and spatial evolution of the actual current distribution. Likewise, although this is a less robust approximation due to the lower metal ion concentration in the present Au electrolyte, metal ion depletion is again neglected in the simulations yielding the location of the passive-to-active transition. The general uniformity of the metal deposited with the TSV at less negative potentials (Fig. 2) indicates that this is good approximation for the less negative applied potentials in the study. Thus, simple evaluation of the suppressor concentration C_s as a function of distance down the TSV permits the position of the passive-to-active transition within TSV to be predicted as a function of applied potential (and suppressor concentration) using only the voltammetrically measured critical potential.

Figure 4 shows schematic representations of the geometry utilized in the simulations. Summarizing the relevant equations (as previously detailed²²), for inner radius r_i and outer radius r_o of the annular TSV, mass balance of the divergence of suppressor flux down the cross sectional area $a_f = \pi(r_o^2 - r_i^2)$ and the rate of suppressor adsorption on the surrounding sidewall perimeter $p_f = 2\pi(r_o + r_i)$ yields

$$a_f D_s \frac{d^2 C(z)}{dz^2} = p_f \Gamma C(z) k_+ (1 - \theta) \quad [6]$$

where z is the distance from the field down the TSV. Equating the flux across the linear gradient of the boundary layer to the sum of adsorption on the field around the TSV and that going down the TSV gives

$$a_s D_s \frac{C_s^\infty - C(0)}{\delta} = (a_s - a_f) \Gamma C(0) k_+ (1 - \theta) + a_f D_s \left. \frac{dC}{dz} \right|_{z=0} \quad [7]$$

where the concentration at the boundary layer-substrate interface equals that at the top of the TSV. For boundary layer thickness δ that is less than the spacing of the TSVs as in the experiments, the mass balance is invoked over the square area $a_s = \delta^2$ around each TSV. Finally, mass balance at the bottom of the TSV requires the suppressor flux and rate of suppressor adsorption satisfy

$$\Gamma C(-h) k_+ (1 - \theta) = D_s \left. \frac{dC}{dz} \right|_{z=-h} \quad [8]$$

The differential equation and boundary conditions in Eqs. 6–8 and suppressor adsorption and metal deposition interactions defined by Eqs. 1–4 permit simulation of deposition profiles using the kinetic parameters obtained from the RDE experiments (Table I). Suppressed deposition is predicted in the upper portion of the TSVs with a micrometer scale transition to unsuppressed deposition in the lower portion of the TSV at depth d_s down the

TSV that is consistent with experimental observations (and analogous to model predictions detailed previously with Ni filling).

Figure 5a compares deposition rates obtained from the specimens shown in Fig. 2 with values predicted using the CV-derived kinetics in Table I, both as functions of the applied potential. The nominal deposit rate of the porous deposits is significantly faster than that predicted from the current density in the voltammetry. However, the data is consistent with predictions assuming 50 % volume of incorporated porosity. The thickness of the deposits immediately below the passive-to-active transition indicates deposition faster than that expected from the voltammetry (as seen by favorable comparison to another prediction for 50 % porosity). However, just a few micrometers below the bulging deposits (see Fig. 2) that yielded these high rates, thicknesses vary minimally with depth and the measured deposition rates are consistent with expectations.

Figure 5b compares the experimental and predicted values of the passive-to-active transition depth d_s as functions of the applied potential. The predictions of the simple, 1D, single component model does a good job anticipating the experimental dependence of the transition depth on applied potential. The iR drop across the $\approx 11 \Omega$ cell resistance, based on measured deposition currents on the small patterned substrates, ranges from 2 mV at -1.09 V to less than 7 mV at -1.29 V and is ignored in both figures.

POTENTIAL MEDIATED TSV FILLING PROCESSES

Because the applied potential determines the location where suppression fails within the filling feature, metal deposition can be localized toward the bottom of the TSV and run at the transport limit without risk of pinch-off from deposition higher up. As demonstrated previously with Ni and Co, void-free filling can be accomplished by adjusting the applied potential over time in order to progressively actuate deposition higher in the TSV as appropriate for the evolution of filling farther down. As in the ferrous metal studies, both stepped and ramped potentials are examined here.

Figure 6 shows partial filling obtained using a stepped potential where deposition times were progressively shortened as the potential was stepped to more negative values. While an overall v-shaped profile is evident, the Au deposition differs from that detailed with both Co and Ni in three significant aspects. First, while the surface of the passive deposit is smooth (Fig. 6b), that of the active deposit is quite rough (Fig. 6c). Second, there is an especially pronounced build-up of deposit immediately below the passive-to-active transition (see Fig. 2) that substantially exceeds the thickness only a few micrometers farther down the feature; potential stepping thus yields the observed wavy deposit on the sidewalls. Third, substantial passive deposit on the sidewalls higher in the feature accumulates during sequential filling of the lower regions, similar to that on the field and consistent with the relatively large leakage currents as compared to the active deposition rates (Fig. 1).

These three differences have significant impact on the nature of filling and the deposit itself. The deposit roughness is a source of nanoscale voids within the deposit and where the sidewall deposits impinge (Figs. 6d and 6e). The waviness serves as a potent source of more

substantial voids where impingement of the sidewall deposits occurs. The passive deposit, while not expected to prevent superconformal filling, e.g., through keyhole void entrapment, is highly porous and likely the cause of deposit cracks in the earlier Au TSV filling study. Significantly, analogous porosity and cracking in passive deposits was also detailed in the study of S-NDR Co filling of TSVs. The porosity in both systems suggests suppressor deactivation occurs through incorporation whereby a substantial quantity of organic suppressor is embedded in the slowly growing metal deposit.

Figure 7a contrasts the partial filling already shown in Fig. 6 with that obtained using longer deposition times at the potential steps (Fig. 7b). While the TSV is nominally filled in less than 2 hr, voids along the center line are evident. A more smoothly graded potential step waveform should reduce the incremental region that is activated with each potential step and thus the amplitude and impact of the previously noted undulations of deposit thickness underlying these voids. Halving the size of the potential steps, as well as using longer deposition time at each step to more fully fill the lower regions prior to activating deposition higher up, yields a center-line seam that can only be seen in the electron microscope (Fig. 7c).

Figure 8 shows the evolution of filling when the applied potential is ramped rather than stepped. The apparently smooth increase of deposit thickness with depth throughout filling (Fig. 8d–f) eliminates the large voids seen along the center line in Fig. 7. The higher magnification images in Fig. 8a–c show micrometer size grains in the regions filled by active deposition, with only a small fraction of nanoscale porosity incorporated during growth due to the dendritic deposit surface. A well-defined layer of darker, highly porous material is evident adjacent to the sidewalls in Figs. 8b and 8c. The images capture the sharply defined interface between this passive deposit and the overlying active deposit, as well as its increasing thickness toward the TSV top. The passive deposit manifests the significant leakage current (Fig. 1), its variation with position and deposition time reflecting the increasingly long period of (passive) deposition the farther the deposit has moved up from the TSV bottom. Images of the free surface at yet higher magnification in Fig. 8g – h highlight the highly porous passive deposit without overlying active deposits.

DISCUSSION

The superconformal Au deposition in the PEI-containing sulfite electrolyte shows localized deposition exhibiting a passive-to-active transition going down the TSVs. Unsuppressed “active” metal deposition starts at a distance down the filling feature that is defined by the suppressor concentration and applied potential, metal deposition associated with a slower leakage through the suppressor layer occurring at the slower “passive” rate above this location. The geometry is analogous to that previously noted during Au deposition in lower aspect ratio square TSVs as well as Ni and Co deposition in similar annular TSVs, all using a smaller PEI suppressor.^{12, 21, 22} The S-NDR model previously applied to both the Ni and Co systems once again provides reasonably accurate prediction of the position of the passive-to-active transition as a function of the applied potential. Also as previously demonstrated with those systems, waveforms that progressively move the active region further up the feature enable filling of the TSVs without the keyhole voids that would

otherwise result from filling near the metal-ion transport limit. It is expected that filling times can be reduced below those shown for both the stepped and ramped cases by further optimization of the waveforms.

Regarding the quality of the Au deposits, growth in the neat sulfite electrolyte is generally rough and dendritic. While potential control of the passive-to-active transition associated with the S-NDR mechanism of superconformal filling prevents pinch-off and macroscale void formation, the intrinsically rough active deposits in the essentially suppressor-free lower portion of the TSV do incorporate nanoscale porosity. Furthermore, as seen previously with the Co S-NDR filling system, the material deposited on passivated surfaces is highly porous. This last, coupled with the not insignificant passive deposition rate in the PEI-containing electrolyte, yields a significant thickness of porous Au on the sidewalls higher in the TSV. Nonetheless, this work demonstrates yet again the broad applicability of superconformal S-NDR based feature filling processes, the power of S-NDR based models for predicting the feature filling evolution and electroanalytical analysis techniques that can be used to assess systems for improved feature filling and deposit quality.

CONCLUSIONS

Superconformal Au deposition in annular TSVs has been experimentally demonstrated and predicted using a simple S-NDR model. These results extend previously demonstrated superconformal deposition in the PEI-containing sulfite electrolyte to higher aspect ratio features and demonstrate that the filling can be quantitatively predicted using kinetics acquired from simple electroanalytical measurements using a rotating disk electrode. The cyclic voltammetry, was used to assess the impact of PEI concentration and transport on the suppression breakdown potential. The results were analyzed to obtain kinetics used in an S-NDR based model to simulate superconformal Au deposition in the annular TSVs. The model predicts the experimentally observed passive-to-active transition within the TSVs, including its location as a function of both suppressor concentration and applied potential. Void-free feature filling, not possible for fixed potential deposition, was achieved using potential waveforms that take advantage of the potential-dependent suppression depth and geometric leveling to produce superconformal filling. These results, combined with previously detailed superconformal Cu, Zn, Ni and Au filling of TSVs, demonstrate the broad applicability of the S-NDR based mechanism for superconformal feature filling and S-NDR based models for prediction of feature filling.

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References

1. Osaka T, Koder A, Misato T, Homma T, Okinaka Y. *J Electrochem Soc.* 1997; 144:3462.
2. Watanabe H, Hayashi S, Honma H. *J Electrochem Soc.* 1999; 146:574.
3. Honma H. *Electrochim Acta.* 2001; 47:75.
4. Andricacos PC, Uzoh C, Dukovic JO, Horkans J, Deligianni H. *IBM J Res Dev.* 1998; 42:567.
5. Moffat TP, Wheeler D, Edelstein MD, Josell D. *IBM J Res Dev.* 2005; 49:19.

6. Moffat TP, Josell D. *J Electrochem Soc.* 2012; 159:D208.
7. Hayashi T, Kondo K, Saito T, Takeuchi M, Okamoto N. *J Electrochem Soc.* 2011; 158:D715.
8. Fan C, Le Corre A, Yon D. *Microelectronic Eng.* 2011; 88:749.
9. Hu Z, Ritzdorf T. *J Electrochem Soc.* 2006; 153:C467.
10. Josell D, Wheeler D, Moffat TP. *J Electrochem Soc.* 2006; 153:C11.
11. Josell D, Moffat TP. *J Electrochem Soc.* 2013; 160:D3009.
12. Josell D, Moffat TP. *J Electrochem Soc.* 2013; 160:D3035.
13. Wang, Lee, SWR. *Proceedings ASME 2011 International Mechanical Engineering Congress & Exposition (IMECE2011)*; November 11–17, 2011; Denver, Colorado. 2011. p. 855
14. Kim MJ, Kim HC, Choe S, Cho JY, Lee D, Jung I, Cho WS, Kim JJ. *J Electrochem Soc.* 2013; 160:D3221.
15. Hayase M, Nagao M. *J Electrochem Soc.* 2013; 160:D3216.
16. Jin SY, Wang G, Yoo BY. *J Electrochem Soc.* 2013; 160:D3300.
17. Josell D, Wheeler D, Moffat TP. *J Electrochem Soc.* 2012; 159:D570.
18. Wheeler D, Moffat TP, Josell D. *J Electrochem Soc.* 2013; 160:D3260.
19. Yang L, Radisic A, Deconinck J, Vereecken PM. *J Electrochem Soc.* 2013; 160:D3051.
20. Josell D, Moffat TP. *J Electrochem Soc.* 2015; 162:D129.
21. Josell D, Silva M, Moffat TP. *J Electrochem Soc.* 2016; 163:D809.
22. Josell D, Moffat TP. *J Electrochem Soc.* 2016; 163:D322.
23. Roha D, Landau U. *J Electrochem Soc.* 1990; 137:824.
24. Madore C, Matlosz M, Landolt D. *J Electrochem Soc.* 1996; 143:3927.
25. West AC. *J Electrochem Soc.* 2000; 147:227.
26. Hill MRH, Rogers GT. *J Electroanal Chem.* 1978; 86:179.
27. Lee MG, Jorne J. *J Electrochem Soc.* 1992; 139:2841.
28. Jorne J, Lee JG. *J Electrochem Soc.* 1996; 143:865.

Figure 1.

Cyclic voltammetry of Au deposition a) in electrolytes containing the indicated concentrations of PEI additive with RDE rotation rate 100 rpm ($10\pi/3$ rad/s) and b) in electrolyte containing 10 $\mu\text{mol/L}$ PEI at the indicated RDE rotation rates. 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 measured cell resistance R, measured values of which ranged between 6 ω and 9 ω , and the data is plotted against the applied potential. The insert shows the inhomogeneous “swirl” deposit on the RDE surface after cycling in electrolyte containing 20 $\mu\text{mol/L}$ PEI for rotation rate of 1600 rpm.

Figure 2.

Optical images of cross-sectioned annular TSVs after Au deposition in electrolyte containing 20 μmol/L PEI concentrations 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 3.

Experimental and simulated voltammetry of Au deposition in electrolytes with additive concentrations a) 0 $\mu\text{mol/L}$ PEI, b) 10 $\mu\text{mol/L}$ PEI and c) 20 $\mu\text{mol/L}$ PEI at the indicated 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. The simulations of suppression breakdown, detailed later in the text, are based on the kinetics in Table I. 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 . The simulations account for the associated deviation from the applied 2 mV/s potential scan rate. Both experimental and simulated voltammetry are plotted against the applied potential.

Figure 4.

Schematic of the geometry used to model Au deposition with the annular TSVs: a) cross section of a TSV showing the domain for the simulations, b) half TSV with full top indicating the inner and outer radii that define the perimeter p_f and open area a_f , c) planview of TSV array with area δ^2 supplying suppressor flux to the underlying field and embedded TSV demarcated and d) cross section through a row of TSVs with height of the boundary layer indicated.

Figure 5.

a) The passive deposition rate on the field and the active deposition rate from the deposit thickness just below the passive-to-active transition as well as farther down the TSV. 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, summarized in Table I, for a fully dense deposit; the dashed lines represent rates accounting for the indicated volume fractions 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. The simulations are for the 20 $\mu\text{mol/L}$ PEI concentration of the filling experiments, using the kinetics in Table I. Simulations and data are plotted against applied potential.

Figure 6.

Cross-sectioned annular TSV after Au deposition; the dark spots on the Au in the optical image are diamond particles pulled from the lapping paper by the ductile metal. Deposition was conducted in electrolyte containing 20 $\mu\text{mol/L}$ PEI concentrations. The applied potential was stepped in 20 mV increments from -1.09 V to -1.29 V, the deposition times being 10 min at the first three potentials and decreasing by 1 min for each step thereafter to end at -1.31 V for 1 min. Deposition was preceded by a 5 s pulse at -1.5 V to improve nucleation on the Cu seeded surface. Representative regions of the central optical image, its length scale below, were imaged by scanning by electron microscope. The length scale above the central image is indexed for these electron micrographs. The patterned substrate was rotating at 100 rpm during deposition.

Figure 7.

Cross-sectioned annular TSV after Au deposition in electrolyte containing 20 $\mu\text{mol/L}$ PEI concentrations showing superconformal filling for three progressively longer stepped sequences of applied potential. Top row are optical images with the corresponding SEM images shown below. a) Deposition time 75 min total: stepped in 20 mV increments from -1.09 V to -1.31 V with 10 min at each of the first three potentials and decreasing by 1 min at each potential thereafter. b) Deposition time 116 min total: stepped in 20 mV increments from -1.09 V to -1.33 V with 12 min at each of the first seven potentials followed by (10, 8, 5, 4, 3, 2) min at the subsequent potentials. c) Deposition time 161 min total: stepped in 10 mV increments from -1.09 to -1.33 V with 8 min at each of the first fourteen potentials then 7 min at the next three potentials followed by (5, 4, 3, 2, 1) min each at two sequential potentials. Deposition was preceded by a 5 s pulse at -1.5 V to improve nucleation on the Cu seeded surface. The patterned substrate was rotating at 100 rpm during deposition.

Figure 8.

Cross-sectioned annular TSV after Au deposition in electrolyte containing 20 μmol/L PEI concentrations showing the progression of superconformal filling for progressively larger ranges of the ramped applied potential. (a, d, g) 50 min total: ramped at 0.02 mV/s from -1.09 V to -1.15 V. (b, e, h) 100 min total: ramped at 0.02 mV/s from -1.09 V to -1.21 V. (c, f) 127 min total: ramped at 0.02 mV/s from -1.09 V to -1.21 V then at 0.025 mV/s from -1.21 V to -1.25 V. Deposition was preceded by a 5 s pulse at -1.5 V to improve nucleation on the Cu seeded surface. (a, b, c) Higher magnification views near the position of the deposit at the via midline. (g, h) Passive deposition on the field. The patterned substrate was rotating at 100 rpm during deposition.

Table 1

Values for feature geometry, metal cation and suppressor transport, and the metal deposition and suppressor adsorption/desorption kinetics for the simulations presented in this study. Values for k_+ and k_- are from simultaneous fitting of the voltammetry for the PEI concentrations 10 $\mu\text{mol/L}$ and 20 $\mu\text{mol/L}$ as shown in Figs. 3b and 3c. Voltammetry is fit assuming 100 % current efficiency for the active ($j_{\theta=0}^o$), and suppressed ($j_{\theta=1}^o$) metal deposition rate and a reversible potential of -0.37 V.

Parameter	Name	Units	Value
TSV inner radius	r_i	m	4×10^{-6}
TSV outer radius	r_o	m	9.5×10^{-6}
TSV height	h	m	56×10^{-6}
Diffusion coefficient, suppressor	D_s	m^2/s	9.2×10^{-11}
Bulk concentration, Au	C_{Au}^o	mol/m^3	320
Boundary layer thickness for rotation rate $\omega = 50\pi$ rad/min (25 rpm)	δ	m	80×10^{-6}
Saturation suppressor coverage	Γ	mol/m^2	2.5×10^{-7}
Suppressor adsorption kinetics	k_+	$\text{m}^3/\text{mol}\cdot\text{s}$	8×10^4
Suppressor burial kinetics	k_-	$1/\text{m}$	1×10^8
Unsuppressed Au exchange rate constant	$j_{\theta=0}^o$	A/m^2	1×10^{-5}
Suppressed Au exchange rate constant	$j_{\theta=1}^o$	A/m^2	3×10^{-5}
Unsuppressed charge transfer coefficient	$\alpha_{\theta=0}$	-	0.45
Suppressed deposition charge transfer coefficient	$\alpha_{\theta=1}$	-	0.35
Au ionic charge	n	-	1
Au molar volume	ω	m^3/mol	10.21×10^{-6}