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The Suppression Induced S-NDR Mechanism for Defect-Free Filling of High Aspect Ratio Features

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Abstract

Superconformal electrodeposition in Through Silicon Vias for multiple metal systems is summarized and explained using models based on suppressor-induced, S-shaped negative differential resistance (S-NDR). Recent results for Ni are detailed, and the filling morphology is compared to previously published observations of superconformal Au, Cu and Zn in TSVs. Voltammetric measurements for quantifying the kinetics and interactions of metal deposition and suppressor adsorption are shown. Dependence of the superconformal filling behavior on deposition conditions including suppressor concentration, transport and deposition potential are described. S-NDR models based on fractional coverage of adsorbed suppressor capture experimental trends and predict the filling geometries. The results demonstrate the generality of the S-NDR mechanism for achieving void-free filling of large features by electrodeposition and the power of S-NDR based models for prediction of filling evolution and process design.

Background

Superconformal feature filling by additive-based electrodeposition is key for filling of patterned high aspect ratio features from deep-submicrometer trenches and vias to much larger Through Silicon Vias (TSVs). In larger features in particular, suppressor containing electrolytes that exhibit suppressor induced critical behavior (i.e., S-shaped Negative Differential Resistance, S-NDR) have been used to obtain bottom-up Cu filling of TSVs (1–4). Suppressor-containing electrolytes exhibiting S-NDR have also been used to obtain localized, superconformal filling of features with Ni and Ni alloys (5–8), Au (9) and Zn (10). Two types of filling evolution are observed, with complete bottom-up deposition and TSV filling achieved at a single potential with Cu (1) that contrasts with a passive-active transition at a distance down the filling feature, the position dictated by the applied potential and the suppressor concentration, exhibited by Au (9) and Ni (8). Nonetheless, both geometries have been quantitatively predicted using models based on the suppression breakdown derived S-NDR mechanism (8,11–13). Both filling morphologies arise from the critical behavior associated with suppression breakdown that manifests as S-NDR in cyclic voltammetry studies corrected for potential drop across cell resistance (*iR*-corrected), and both differ from the smooth, monotonic dependence of deposition rate on distance down filling features predicted by leveling models based on a fixed rate of additive consumption that is first order in coverage (14,15).

This paper describes TSV filling results that capture the key differences between singular bottom-up growth versus side-wall passive-active transitions of deposition within the vias

that are exhibited by different metal systems. Electroanalytical measurements are used to quantify the S-NDR superconformal filling mechanism that underlies the feature filling dynamics. Filling simulations from S-NDR based models incorporating kinetics from the electroanalytical measurements are shown to predict TSV filling geometries as well as trends with processing conditions.

Experimental results

While some studies have utilized combinations of additives, many of the cited studies, use only a single suppressing additive (i.e., suppressor), which greatly simplifies the assessment of its nature. Figure 1 shows cyclic voltammograms (CVs) for Ni, Au and Cu that capture the critical breakdown in deposition suppression exhibited by S-NDR filling electrolytes for Ni, Au and Cu.

The S-NDR is evident with full correction for iR loss (1a and 1d). Rotating disk electrode (RDE) studies assess the impact of the suppressor on the kinetics of metal deposition rate. Figure 1a captures the more negative onset potential of suppression breakdown that accompanies increased suppressor concentration. Rotation rate can also be used to control the flux of suppressor to the RDE surface (Fig. 1b). Fitted curves are used to acquire kinetics for modeling of feature filling.

Representative filling in suppressor-containing electrolytes is captured in Fig. 2. The bottom-up deposition exhibited by Cu leads to void-free feature filling when the applied potential (not iR corrected) is held constant (Fig. 2a). In contrast, with Ni there is minimal deposition above the region of the passive-active transition with uniform deposition beneath it (Fig. 2b); longer deposition time merely thickens the deposit, the position of the passive-active transition remaining nearly unchanged with time. Adjustment of the deposition potential can be used to shift the active-passive transition within the TSV (Fig. 2c). Analogous behavior is observed with Au, albeit with less effective suppression in the passive range such that visible deposition is evident, while greater metal ion depletion in the actively plating via also yields a visible thickness gradient (Fig. 2d).

S-NDR Modeling

Modeling of both electroanalytical data and feature filling assumes that the fractional suppressor coverage θ evolves through adsorption of additive from the electrolyte and deactivation of adsorbate during deposition according to

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

where k_+ and k_- are kinetic rate constants defining the suppressor adsorption and deactivation, respectively, and local suppressor concentration C_s (8). The metal deposition rate v is assumed to be a linear function of the suppressor coverage

$$v=v_{\theta=0}(1-\theta)+v_{\theta=1}\theta \quad [2]$$

expressed here in terms of the deposition rates on unsuppressed ($\theta = 0$) and suppressed ($\theta = 1$) surfaces. Fitting of voltammetry and feature filling prediction also requires evaluation of additive and metal ion transport. Equations 1 and 2 yield coverage evolution that is nonlinear in adsorbate coverage and, with mass balance of adsorption and transport, in local suppressor concentration as well.

Simulations for different values of the adsorption and deactivation kinetics yield a range of predicted filling behaviors based on the kinetics for Cu deposition in the presence of a polyether (11,12). As shown in Fig. 3, a variety of different growth contours develop for different kinetic parameters. The results are similar to the filling behaviors exhibited by Cu as well as Ni and Au. Horizontal growth contours alone indicate bottom-up filling. Deposition initially below a location within the TSV captures the passive-active transition; subject to metal ion depletion, pinch-off of the sidewall deposits ultimately leaves a keyhole void with deposition predicted to progress upward only after pinch-off. In both cases a gradient of suppressor concentration down the feature coupled with the nonlinear evolution equation yields the localized deposition and nonlinear dependence of deposition rate on position.

The exhibition of bottom-up filling versus passive-active deposition is thus related to the kinetics of suppressor adsorption and deactivation in the system. Other impacts of the kinetics are found in Fig. 4 where the Ni deposition rate in the actively depositing region is independent of suppressor concentration, but not potential, while the bottom-up Cu growth rate increases as the front moves upward is relatively insensitive to potential and suppressor concentration. The filling profiles and simulations indicate that the bottom-up Cu deposition rate comes from transport-limited metal ion flux whereas the Ni filling is associated with minimal or comparatively modest metal ion depletion. Both growth modes involve near transport-limited suppressor flux to the upper region of the growing deposit.

Exploration of the kinetic parameter space of the full spatial and temporal S-NDR based models, developed to explain bottom-up Cu filling (11–13), are also able to explain the passive-active transition characteristic seen during Ni and Au deposition in TSVs. The models capture the depletion of suppressor concentration down the feature, which underlies models of leveling as well (14,15), coupled with the critical behavior of the nonlinear electrolyte-suppressor system. Simpler S-NDR models capture the localized deposition of the active-passive transition geometry, comparison of prediction and experiment showing reasonable agreement (Fig. 5).

Improved understanding of the system kinetics permits development of potentiodynamic protocols that progressively advance the location of the passive-active transition upwards to enable void-free filling. Figure 6 shows examples of partly filled TSVs obtained using potential histories that progressively turn on deposition higher in the TSVs to enable void-

free filling. The stepped potentials are analogous to galvanodynamic processes proposed for Cu TSV filling (16).

Conclusions

Models based on the S-NDR mechanism explain both the bottom-up filling of TSVs exhibited by suppressor-containing Cu electrolyte and the side-wall passive-active transitions exhibited by suppressor-containing Ni and Au electrolytes. Experiment and model indicate the same underlying mechanism, the different filling modes arising from differences in the system-dependent kinetics. Processes that achieve superconformal, void-free filling are possible with systems exhibiting either growth mode.

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Figure 1.

Voltammetry for a) Ni deposition from 1 mol/L NiSO_4 + 0.2 mol/L NiCl_2 + 0.5 mol/L H_3BO_3 with different 1800 MW polyethyleneimine (PEI) concentrations and b) modeling fits to data (8), c) Au deposition from 0.32 mol/L $\text{Na}_3\text{Au}(\text{SO}_3)_2$ with overlaid current density values from early and late plateaus in chronoamperometric data capturing passive and active states (9) and d) impact of iR -correction on Cu deposition from 1.0 mol/L CuSO_4 + 0.5 mol/L H_2SO_4 + 0.001 mol/L NaCl with 60 $\mu\text{mol/L}$ suppressor (1). More detailed information is given in the references.

Figure 2.

SEM images of cross-sectioned 56 μm deep annular TSVs a) Cu filled for the indicated deposition times at fixed potential (1), b) Ni filled for the indicated deposition times at fixed potential (8), c) Ni deposited for 10 min at the indicated potentials (8) and d) square cross-section TSVs with Au deposited for 1 hour at -1.26 V, -1.25 V and -1.24 V (top row from left) and -1.20 V and -1.19 V (bottom row from left) versus a Hg/Hg₂SO₄/saturated K₂SO₄ reference (9). Electrolytes, suppressor additives and unspecified deposition conditions are detailed in referenced publications.

Figure 3.

Predicted contours during filling of annular TSVs (radial cut) for: (top) $k_+ = 340 \text{ m}^3/\text{mol}\cdot\text{s}$ and (bottom) $130 \text{ m}^3/\text{mol}\cdot\text{s}$ and (left) $k_- = 26.4 \times 10^6 \text{ 1/m}$ and (right) $37.9 \times 10^6 \text{ 1/m}$. For additional model parameters see Ref. 12.

Figure 4.

a) Ni deposition rate below the passive-active transition in 56 μm deep TSVs in electrolyte containing indicated suppressor concentrations (8) and b) Cu deposition rate under with the indicated suppressor concentrations and potentials defined relative to a mercury/mercurous sulfate/saturated potassium sulfate reference electrode (SSE) (1).

Figure 5.

Experimental and predicted distance from the top of 56 μm deep annular TSVs to the location at which maximum Ni deposition rate is (first) achieved for indicated suppressor concentrations and applied potentials (data adapted from Ref. 8).

Figure 6.

Ni deposition in 56 μm deep TSVs: a) for 20 min at -1.23 V and then at -1.27 V and b) 10 min at potentials stepped in -20 mV increments from -1.21 V to -1.31 V. Electrolyte containing 20 $\mu\text{mol/L}$ PEI. Substrates rotating at $10/3 \pi$ rad/s (100 rpm); electrolyte as in Ref. 8 with 20 $\mu\text{mol/L}$ suppressor.