Published in final edited form as:

ECS Trans. 2016 ; 163(7): D322–D331. doi:10.1149/2.1151607jes.

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

D. Josell and T.P. Moffat

Materials Science and Engineering Division, NIST, Gaithersburg, MD 20899, USA

Abstract

This work demonstrates void-free nickel filling of 56 μm tall, annular Through Silicon Vias (TSVs) using a mechanism that couples suppression breakdown and surface topography to achieve controlled superconformal, void-free deposition. The chemistry, a Watts electrolyte containing a dilute suppressing additive, and processes are fully detailed. The impact of deposition potential and additive concentration on the filling of the patterned features is presented. Voltammetric measurements on planar substrates, including the impact of rotation rate and suppressor concentration on the rate of metal deposition and potential of suppression breakdown, are used to quantify the interplay between metal deposition and suppressor adsorption. The derived kinetics are then used to quantitatively predict the observed bottom-up filling in the TSVs using the S-shaped negative differential resistance (S-NDR) mechanism for superconformal deposition; the predictions capture the experimental observations. This work extends understanding and application of the additive-derived S-NDR mechanism developed with non-ferrous metals.

Background

Superconformal feature filling by additive-based electrodeposition is key for filling of patterned features from deep-submicrometer trenches and vias to much larger Through Silicon Vias (TSVs). In the TSVs, Cu exhibits bottom-up filling (1–4) from electrolytes containing only a single deposition rate suppressing additive that has been quantitatively predicted using models based on the suppression breakdown derived, S-shaped Negative Differential Resistance (S-NDR) mechanism (5–7). However, a number of metals, including Au (8) and, now, Ni (9) exhibit deposition where a passive-active transition exists at a distance down the filling feature, the distance being dictated by the applied potential and the suppressor concentration. This filling morphology, as that exhibited by Cu, is seen in electrolytes exhibiting critical behavior associated with suppression breakdown that manifests as a negative differential resistance in iR -corrected cyclic voltammetry studies. In all cases, the localized deposition profiles differ from the smooth dependence of deposition rate on distance down filling features predicted by leveling models based solely on additive depletion occurring at a fixed rate that is linear in coverage (10,11).

For the Watts $\text{NiSO}_4 + \text{NiCl}_2 + \text{H}_3\text{BO}_3$ electrolyte, suppressor induced critical behavior has been identified for a number of additives (12–14). Among these, polyethyleneimine (PEI) has been used to fill sub-micrometer trenches, to selectively fill microcracks with Ni by electrodeposition (15,16) and to obtain superconformal Ni-alloy deposition in TSVs (17). Critical behavior detailed in these works, linked to the breakdown of adsorbed suppressor,

underlies the deposition morphology. This paper further details Ni deposition in Watts electrolyte using branched PEI. It demonstrates electroanalytical measurements to quantify the impact of the PEI suppressor on the Ni deposition kinetics, including suppressor adsorption and deactivation kinetics that affect the critical behavior associated with suppression breakdown. It presents TSV filling results that demonstrate the impact of deposition potential and suppressor concentration on the position of the passive-active transition of metal deposition within the features. A simple S-NDR based model incorporating suppressor adsorption and deactivation from the electroanalytical measurements is shown to predict the TSV filling geometry as well as trends with suppressor concentration and deposition potential. The understanding thus obtained is then used to enable void-free filling of the TSVs with Ni.

Experimental results

Rotating disk electrode (RDE) studies assessed the impact of the suppressing PEI on the metal deposition rate; potentials are relative to a mercury/mercurous sulfate/saturated sulfate reference (V_{SSE}). Figure 1a captures the impact of the additive, with increased suppression (i.e., more negative potential for suppression breakdown) accompanying increased suppressor concentration. Figure 1b captures corresponding impact of RDE rotation rate that, like concentration, can be used to control the flux of suppressor to the RDE surface. Fitted curves are used to acquire parameters for modeling of feature filling.

The associated impacts of PEI concentration and deposition potential on feature filling are captured in Fig. 2. A clear active-passive transition is evident moving down the feature, with minimal Ni deposition above the transition. Increased suppressor concentration and/or more positive deposition potential shift the transition lower down the TSV. The potential dependence is analogous to Au TSV filling in an electrolyte that also exhibits critical behavior and hysteresis in cyclic voltammetry (8).

S-NDR Modeling

Modeling of both electroanalytical data and feature filling assume the fractional suppressor coverage θ evolves through adsorption from the electrolyte and deactivation 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, for metal deposition rate v and local suppressor concentration C_S (11). The metal deposition rate is assumed to be a linear function of the suppressor coverage θ , i.e.,

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

expressed here in terms of the deposition rates on unsuppressed ($\theta=0$) and suppressed ($\theta=1$) surfaces. The pair of equations combined yield coverage evolution that is nonlinear in the suppressor concentration and adsorbate coverage. Fitting of voltammetry and feature filling prediction also requires solution of additive and metal ion transport.

Simulations for different values of the adsorption and deactivation kinetics yield a range of filling behaviors that have been examined particularly for application to the bottom-up filling Cu system (5,6). Depending on the kinetics assumed, the simulations capture the bottom-up filling of the Cu system. However, as shown in Fig. 3, they also predict the passive-active transition observed in the Ni system. In particular, localized deposition is predicted to begin and remain below a particular location within the TSV (the location of this passive-active transition dictated by the applied potential and suppressor concentration). Deposition proceeds at all locations below this point, although subject to metal ion depletion that ultimately causes pinch-off of the sidewall deposits leaving a keyhole void beneath. It is only after pinch-off that deposition is predicted to progress upward. Importantly, it is the gradient of suppressor concentration down the feature coupled with the nonlinear coverage evolution equation that yields the localized deposition and nonlinear dependence of deposition rate on position evident in Fig. 2.

Models based on the S-NDR mechanism predict the bottom-up filling geometry exhibited by the Cu system and passive-active transition characteristic of the Ni TSV filling geometry because they have the same origin. Specifically, the gradient of suppressor concentration down the feature, which underlies models of leveling as well (10,11), couples with the critical behavior of the nonlinear electrolyte-suppressor system. Comparison of prediction and experiment shows reasonable agreement (Fig. 4).

The understanding provided by both experiment and model permits development of potentiodynamic processes for void-free Ni TSV filling analogous to galvanodynamic processes proposed for Cu TSV filling (18). Figure 5 shows examples of partly filled TSVs obtained using potential histories that progressively turn on deposition higher in the TSVs to enable void-free filling.

Conclusions

Models based on the S-NDR mechanism are seen to capture the geometry of Ni deposition observed during filling of TSV in a PEI-suppressed Watts electrolyte. They capture trends of the filling geometry with suppressor concentration and applied potential. The models are the same as those that predict bottom-up filling in other suppressed systems. They differ principally in the values of the kinetic parameters for the particular electrolyte-additive system, consistent with observation of both the bottom-up and passive-active transition geometries during Cu and Zn filling of TSVs using different suppressors (1,5,6,19). Significantly, this understanding enables development of processes that achieve superconformal, void-free Ni filling of large features.

References

1. Moffat TP, Josell D. J Electrochem Soc. 2012; 159:D208.

2. Kim MJ, Kim HC, Choe S, Cho JY, Lee D, Jung I, Cho WS, Kim JJ. *J Electrochem Soc.* 2013; 160:D3221.
3. Hayase M, Nagao M. *J Electrochem Soc.* 2013; 160:D3216.
4. Jin SY, Wang G, Yoo BY. *J Electrochem Soc.* 2013; 160:D3300.
5. Josell D, Wheeler D, Moffat TP. *J Electrochem Soc.* 2012; 159:D570.
6. Wheeler D, Moffat TP, Josell D. *J Electrochem Soc.* 2013; 160:D3260.
7. Yang L, Radisic A, Deconinck J, Vereecken PM. *J Electrochem Soc.* 2013; 160:D3051.
8. Josell D, Moffat TP. *J Electrochem Soc.* 2013; 160:D3035.
9. Josell D, Moffat TP. *J Electrochem Soc.* 2016; 163:D322.
10. Madore C, Matlosz M, Landolt D. *J Electrochem Soc.* 1996; 143:3927.
11. West AC. *J Electrochem Soc.* 2000; 147:227.
12. Kim SK, Bonevich JE, Josell D, Moffat TP. *J Electrochem Soc.* 2007; 154:D443.
13. Lee CH, Bonevich JE, Davies JE, Moffat TP. *J Electrochem Soc.* 2008; 155:D499.
14. Lee CH, Bonevich JE, Davies JE, Moffat TP. *J Electrochem Soc.* 2009; 156:D301.
15. Zheng XG, Shi YN, Lu K. *J Electrochem Soc.* 2013; 160:D289.
16. Zheng XG, Shi YN, Lu K. *J Electrochem Soc.* 2015; 162:D222.
17. Lin YT, Huang HM, Wang HW, Dow WP, Lin JY, Chang PH, Lee HC. *ECS Electrochem Lett.* 2015; 4:D25.
18. Yang L, Radisic A, Deconinck J, Vereecken P. *J Electrochem Soc.* 2015; 162:D599.
19. Josell D, Moffat TP. *J Electrochem Soc.* 2015; 162:D129.

Figure 1.

a) Cyclic voltammetry in electrolyte with 1800 MW PEI concentrations ranging from 0 $\mu\text{mol/L}$ to 15 $\mu\text{mol/L}$ showing Ni deposition. b) Cyclic voltammetry in electrolyte with 1800 MW PEI of the indicated concentration, where the current, plotted here as positive, actually corresponds to Ni electrodeposition; fits to data were used to extract kinetics for modeling. Data was acquired with software correction for 80 % of the 9 Ω resistance between reference and RDE determined using the potentiometer's built in software. The acquired data has been corrected for the remaining 20 % of cell resistance. RDE rotation rates and voltammetry scan rate as indicated. (100 rpm = $10/3 \pi$ rad/s) (Figures from Ref. 9)

Figure 2.

Cross-sectioned 56 μm deep annular TSVs after 10 min Ni deposition at the indicated potentials and PEI concentrations.

Figure 3. Predicted contours during filling of annular TSVs for suppressor adsorption kinetics $k_+ = 130 \text{ m}^3/\text{mol s}$ and, from left to right, deactivation kinetics $k_- = (26.4, 37.9 \text{ and } 162.4) \times 10^6 \text{ 1/m}$. For other model parameters see Ref. 6.

Figure 4. Comparison of 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 (parameters in Ref. 9).

Figure 5. Ni deposition in 56 μm deep TSVs: a) for 20 min at -1.23 V and then -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 100 rpm; electrolyte same as in Ref. 9.