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

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Abstract

This work demonstrates void-free cobalt filling of 56 μm tall, annular Through Silicon Vias (TSVs) using a mechanism that couples suppression breakdown and surface topography to achieve controlled bottom-up deposition. The chemistry, a Watts electrolyte containing a dilute suppressing additive, and processes are described. This work extends understanding and application of the additive-derived S-shaped Negative Differential Resistance (S-NDR) mechanism, including previous demonstrations of superconformal filling of TSVs with nickel, copper, zinc and gold.

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 larger features in particular, experimentally observed bottom-up copper electrodeposition in TSVs (1–4) using electrolytes containing only a single deposition rate suppressing additive has been quantitatively predicted using models based on the suppression breakdown derived, S-shaped Negative Differential Resistance (S-NDR) mechanism (5–7). In addition, Au (8) and Ni (9) have been shown to 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, that has also been quantitatively predicted using S-NDR models. Both filling morphologies are seen in electrolytes exhibiting critical behavior associated with suppression breakdown that manifests as a negative differential resistance in iR-corrected cyclic voltammetry studies. Both 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 (10,11).

Superconformal cobalt and cobalt-iron deposition have been demonstrated in submicrometer features in electrolytes containing the suppressing additive 2-mercapto-5-benzimidazolesulfonic acid (12). Both electroanalytical measurements and the geometry of feature filling indicate the S-NDR mechanism. This paper uses polyethyleneimine (PEI) for filling of much larger TSVs because it enables localized, superconformal filling of TSVs (9) and microcracks (13,14) with ferrous metals including Ni and Ni-alloys (15). It shows a subset of experimental results from a study that follows the path of the Ni study, including electroanalytical measurements and Co deposition in TSVs using a $\text{CoSO}_4 + \text{CoCl}_2 + \text{H}_3\text{BO}_3$ electrolyte with the branched PEI suppressor.

Experimental results

Rotating disk electrode (RDE) studies were used to assess the impact of the suppressing PEI on the metal deposition rate. Figure 1 shows typical results, with deposition suppressed on the negative-going sweep until suppression breakdown at a potential defined by the suppressor concentration and RDE rotation rate that control the flux of suppressor to the RDE surface. Deposition is unsuppressed on the return sweep. This behavior is analogous to that exhibited by Cu, Au and Ni systems that also exhibit suppression breakdown induced S-NDR (the suppression is somewhat less, suppression breakdown potential more positive, than that of Ni electrolyte with the same PEI concentration (9)).

Figure 2 shows the associated impact of applied potential on TSV filling. A passive-active transition, with minimal deposition above, is evident. More positive deposition potential shifts the transition lower down the TSV, as does higher PEI concentration (not shown). Similar to results obtained with Ni, deposition rates below the transition are clearly independent of position at the less negative potentials. Figure 3 shows that the transition does not move during filling. In addition, it makes clear that deposition rates below the passive-active transition are also uniform at more negative potentials before increasing deposit thickness begins to impede metal ion transport down the TSV.

Interestingly, after the sidewall deposits impinge (creating a keyhole void in the lower portion of the TSV), deposition begins to move upward. The lower magnification optical image in Fig. 4 captures a change of contrast in an imperfectly filled TSV after extended deposition. The contrast change is well above the location of the original passive-active transition. Scanning electron microscope (SEM) images of the deposit on the field and at the location of the contrast change within the TSV make clear that the change in optical contrast corresponds to a change from dense Co to a porous deposit. Deposition contours predicted by a S-NDR based model capture the passive-active transition approximately halfway up the TSV, entrapment of a keyhole shaped void through sidewall impingement and post-pinchoff upward deposition with v-notch shape. Although predicted, the post-pinchoff growth had not been previously noted in experiments with other metal systems.

The simulation in Fig. 4 assumes fractional suppressor coverage θ evolves 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. With v assumed to scale linearly with the coverage θ , e.g.,

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

the combined equations yield coverage evolution that is nonlinear in the coverage. Concurrent solutions of additive and metal ion transport in the electrolyte and mass

conservation at the moving interface are also required for evaluation of both voltammetry and feature fill modeling. The result is that coverage is also nonlinear in suppressor concentration. Figure 5 shows simulations of Ni deposition in TSVs obtained using a pseudo steady state analysis, the electrolyte-additive system exhibiting critical behavior in voltammetry and passive-active transition within filling TSVs similar to those detailed here for Co. The plots capture the nonlinear variation of deposition rate with distance down the feature that can arise from the nonlinear relationships between suppressor concentration, adsorbate coverage and metal deposition rate (9), thereby predicting the passive-active transition observed experimentally with both Ni and Co.

The potential dependence in Fig. 2 suggests the use of a potential step waveform to obtain void-free Co filling of the TSVs. Figure 6 shows an example of filling through such a process, the stepped potential progressively turning deposition on higher up, thereby minimizing metal ion depletion and creating a v-shaped growth surface that enables void-free filling by geometrical leveling. This approach has been demonstrated previously for void-free TSV filling with Ni (9).

Conclusions

Electroanalytical measurements in a Co electrolyte exhibit suppression breakdown induced S-NDR while a passive-active transition is observed within TSVs during Co deposition. Superconformal, void-free Co filling of TSVs is achieved using a stepped potential that takes advantage of localized growth derived from the S-NDR mechanism to progressively move active deposition up the feature for void-free filling. For deposition at fixed potential, predicted upward motion of the growth front from the passive-active transition after impingement of the sidewall deposits is also noted for the first time. The results demonstrate the broad applicability of S-NDR based models for understanding feature filling in a number of suppressor-containing electrolytes.

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Figure 1.

Cyclic voltammograms in electrolyte containing 2 $\mu\text{mol/L}$ PEI (no iR correction for cell resistance). Current density shown as positive here corresponds to Co deposition. RDE rotation rates are indicated, the voltammetry scan rate 2 mV/s for all. Deposition is suppressed on initial negative-going scans. (100 rpm = $10/3 \pi$ rad/s)

Figure 2. Cross-sectioned 56 μm deep annular TSVs after 10 min Co deposition at the indicated potentials in electrolyte containing 20 $\mu\text{mol/L}$ PEI, the substrates rotating at 100 rpm. Suppression breakdown on the planar surface is negative of -1.31 V for this PEI concentration.

Figure 3. Cross-sectioned 56 μm deep annular TSVs after Co deposition for the indicated times at -1.29 V in electrolyte containing $20\text{ }\mu\text{mol/L}$ PEI, the substrates rotating at 100 rpm .

Figure 4.

Low magnification optical image and higher magnification SEM images of a cross-sectioned 56 μm deep annular TSV after Co deposition for 3.5 hours at -1.29 V in electrolyte containing 20 $\mu\text{mol/L}$ PEI, the substrate rotating at 100 rpm. The simulation shows predicted growth contours in the annular TSVs for $k_+ = 130\text{ m}^3/\text{mol}\cdot\text{s}$ and $k_- = 37.9 \times 10^6\text{ 1/m}$. Other model parameters can be found in Ref. 6.

Figure 5.

Simulations of Ni deposition in TSVs with 10 $\mu\text{mol/L}$ PEI in the electrolyte for deposition at -1.26 V including a) deposition rate and adsorbate coverage and b) suppressor concentration and consumption (or deactivation) rate as functions of distance from the top of the TSV (curve colors same as appropriate vertical axis). Other model parameters as detailed in source publication (from Ref. 9).

Figure 6.

Co deposition in 56 μm deep TSVs using 5 min deposition at potentials starting at -1.19 V and moving in -20 mV intervals across the indicated potential ranges in electrolyte containing $20\text{ }\mu\text{mol/L}$ PEI. The higher magnification images of the specimen stepped through -1.31 V show only a few small, circular voids toward the bottom of the TSV; shallow features above the voids are an artifact of the ion milling process used for surface preparation. Substrates were rotating at 100 rpm.