I describe bottom-up gold filling of through silicon vias (TSV) over 50 micrometers tall in a sulfite electrolyte\(^1\) and compare the results to recent results for copper\(^2\). Both processes use a single deposition suppressing additive, polyethyleneimine (PEI) for the Au case. With the gold, deposition transitions from slow suppressed deposition to faster unsuppressed deposition over a distance of approximately 5 \(\mu\)m down the TSV (Fig. 1); the transition for the Cu case is sharper and more extreme, yielding deposition that is entirely localized to the bottom surface of the TSV.

The growth dynamics of these systems cannot be accounted for using shape change models based only on suppressor consumption induced gradients (traditional leveling) or area change coupled with adsorbate coverage (the Curvature Enhanced Accelerator Coverage mechanism of damascene superfill\(^3\)). Rather, both cases can explained using a quantitative model of feature filling in chemical systems exhibiting unstable deposition characterized by S-shaped negative differential resistance (S-NDR) where deposition is also limited by resistivity of the electrolyte\(^4\). A critical potential manifesting such S-NDR, previously detailed for the Cu electrolyte yielding TSV fill in Fig. 1, is evident with the Au electrolyte as well (Fig. 2).

I detail electrochemical studies including cyclic voltammetry and chronoamperometry on planar substrates to understand the phenomenon, explaining how parameters for modeling by the resistivity stabilized S-NRD mechanism can be extracted from such studies. I explain the role of geometry, kinetics, and experimental conditions on the nature of predicted feature filling. Anticipated deposition profiles range from extreme bottom-up filling with growth fully localized to the bottom surface (as with Cu) to the more relaxed version of superfilling where significant sidewall deposition attenuates with height in the feature (as with Au).

Finally, I detail experiments whereby operational conditions are modified to permit controlled deposition within the TSV, including the vertical placement of the transition from suppressed to unsuppressed deposition within the TSV (Figs. 3 and 4). Experimental results, including in submicrometer damascene features, are placed in the context of model predictions.

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