



Superconformal Electrodeposition Using Derivatized Substrates

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This paper demonstrates superconformal electrodeposition of copper in trenches using a two-step process. The substrate is first derivitized with a submonolayer coverage of catalyst and then transferred for electroplating in a cupric sulfate electrolyte containing an inhibitor. For an optimum catalyst coverage, superconformal, “bottom-up” filling of trenches and vias is observed. If the catalyst coverage is too low or too high, conformal or subconformal deposition occurs, resulting in void formation during feature filling. The filling behavior of the derivitized electrodes is analogous to that obtained using a single (conventional) electrolyte containing both catalytic and inhibiting species. Restricting the catalyst to the surface by derivitization prior to metal deposition provides strong support for the curvature-enhanced accelerator coverage mechanism of superconformal film growth. From a technical perspective, the two-step process offers an interesting solution to the difficult control issues associated with catalyst destruction and related aging effects known to occur in the “conventional” single-electrolyte superfilling process.

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The use of electrodeposited copper in integrated circuits is due, in part, to the ability of the deposition process to fill high aspect ratio features superconformally. Understanding the “superfilling” process has been complicated by the presence of both deposition-rate suppressing (inhibitor) and deposition-rate accelerating (catalyst) additives in the electrolytes. Initially, efforts were made to extend leveling theory, whereby inhibitor depletion in the electrolyte within patterned features results in a nonuniform deposition rate and smoothing of the surface profile. However, it was found that this formalism failed to explain the filling process in submicrometer features and an empirically modified constitutive equation was required to simulate feature filling.¹⁻³ In the first such efforts the constitutive fitting equation provided the sole distinction between leveling and superfilling. Subsequently, an attempt to reconcile superfilling with a more robust description of the traditional leveling model was published.⁴ Nonetheless, comparison between these models and experimental observations revealed that superfilling could not be explained by an inhibition or leveling model.⁵⁻⁸

In the last two years, a curvature-enhanced accelerator coverage (CEAC) mechanism has been shown to quantitatively describe superconformal film growth. In this model, the accelerator, or catalyst, is considered to displace the inhibiting halide-cuprous-polyether species from the interface and remain segregated at the interface during metal deposition. Because the growth rate is directly proportional to the catalyst coverage, these stipulations naturally give rise to “bottom-up” or superfilling of submicrometer features as the catalyst coverage and metal deposition rate steadily increase during conformal growth on a concave surface such as the bottom of a filling feature. The CEAC mechanism has been incorporated into several different shape change models⁹⁻¹² and successfully predicts the initial incubation period of conformal deposition, the superconformal bottom-to-top filling itself, and the subsequent “momentum plating” or bump formation over filled features that are commonly observed. None of these aspects of filling could be explained by the leveling models.⁵⁻⁸ The CEAC models allow filling over the entire experimental parameter space, *i.e.*, catalyst precursor concentration, overpotential, and feature aspect ratio, to be explored for both trench and via geometries. Furthermore, these predictions are made with no fitting parameters; all kinetic factors are obtained from deposition studies conducted on planar substrates. More recently, the generality of the CEAC model has been demonstrated by successfully describing superconformal electrodeposition of silver from a selenium catalyzed electrolyte¹³⁻¹⁵ as well as iodine catalyzed copper chemical vapor deposition.¹⁶

An alternative model of superfilling based on accumulation of

catalyst at the bottoms of features has also been published.¹⁷ In contrast to the CEAC mechanism, it is premised on the initial interface condition being equilibrated with the electrolyte additives and the simulation required tuning of parameters to experimental feature filling results in order to fit the fill results obtained for a single electrolyte composition and deposition current.

One difficulty in the utilization and study of “superfilling” cupric sulfate electrolytes has been aging effects associated with disulfide/thiol catalyst chemistry. This has resulted in speculation as to the role of homogeneous electrolyte chemistry in the superfilling process. In this paper we demonstrate that these effects are not responsible for superfilling. Specifically, superconformal filling of a patterned electrode is demonstrated by first derivitizing the electrode with a submonolayer quantity of catalyst followed by transferring to a catalyst-free inhibited electrolyte for electroplating. For an optimum surface coverage, superfilling occurs in complete agreement with the CEAC model. These experiments also suggest a new strategy for circumventing electrolyte aging effects and the associated process control difficulties.

Two-Step Process

Step 1: Electrode derivitization.—Electrode derivitization is a subject that has received wide study in the last 15 years with the adsorption of thiol/disulfide molecules on noble metals being a model system. In this work, a wafer patterned with a repeating trench test structures, with a copper seed already deposited, was provided by International Sematech. It was sectioned to obtain test specimens that were approximately 15 × 20 mm. The accelerator (*i.e.*, catalyst) was first attached to the copper surface by immersion in a stagnant 1.8 mol/L H₂SO₄ solution containing 0.5, 5, 50, 500, or 1000 μmol/L of the catalyst precursor, either SPS (Na₂(SO₃(CH₂)₃S)₂) or MPSA (NaSO₃(CH₂)₃SH). The specimens were removed after 30 s, rinsed with distilled water, and dried with a tetrafluoroethane duster. For reference, derivitization in 1000 μmol/L MPSA for 60 s or longer was found, using X-ray photoelectron spectroscopy, to yield time-independent coverage of catalyst; this maximum value is deemed to be “saturation” coverage. Derivitization in 0.5, 5, 50, or 500 μmol/L SPS and 1000 μmol/L MPSA for 30 s, yielded surface coverages θ estimated to be 0.002, 0.02, 0.17, 0.84, and 0.97 of the saturated value, respectively. In the adsorption process with these catalysts, the disulfide or thiol head group interacts strongly with the copper substrate while the sulfonate end-group remains intact; in this paper we do not distinguish between thiolate *vs.* disulfide formation at the interface. The following results indicate that when the specimen is transferred to the plating electrolyte the adsorbed, sulfonate-terminated catalyst hin-

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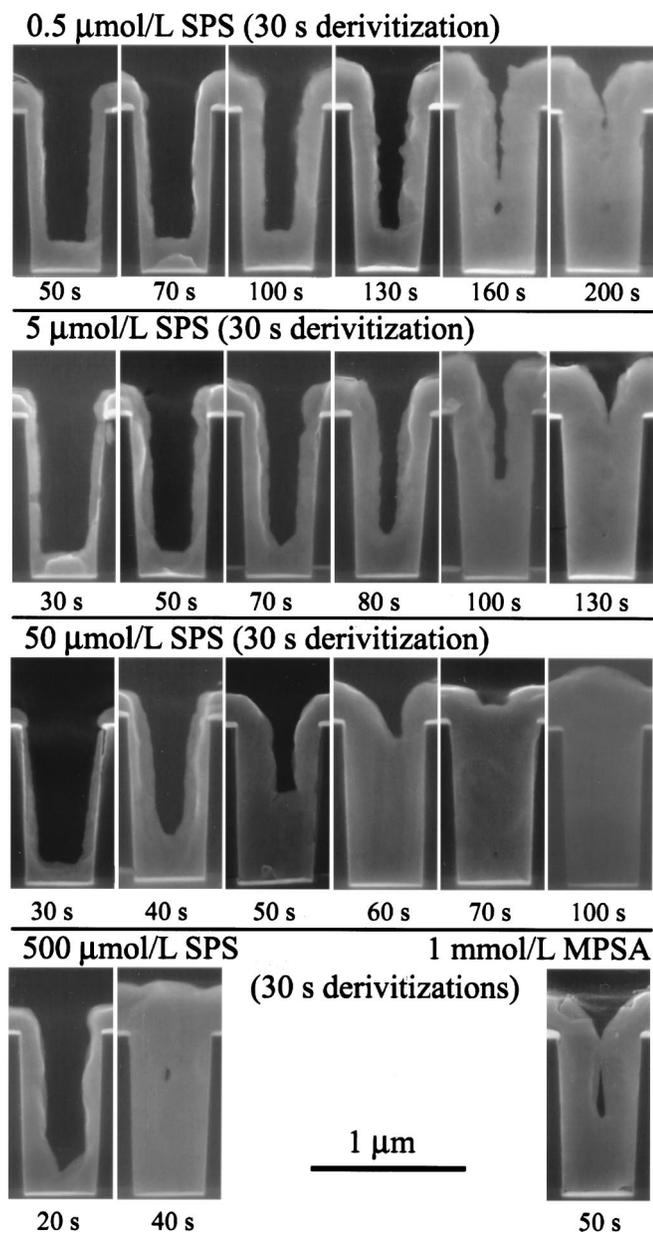


Figure 1. Cross sectioned trenches showing the time evolution of feature filling as a function of electrode derivitization, *i.e.*, pretreatment. The concentration of SPS or MPESA catalyst used for the 30 s surface derivitization steps are indicated. All specimens were transferred to the acidified PEG-Cl cupric sulfate for copper deposition at an overpotential of -0.25 V.

ders the formation of the passivating halide-cuprous-polyethylene glycol layer. The hindrance of passivation increases monotonically with local coverage of adsorbed catalyst.

Step 2: Electrodeposition.—The derivitized specimens were immediately transferred to an electrochemical cell containing an electrolyte of 0.24 mol/L CuSO_4 , 1.8 mol/L H_2SO_4 , 88 $\mu\text{mol/L}$ poly(ethylene glycol) (3,400 Mw), and 1 mmol/L NaCl; all copper deposition was done in this electrolyte. The specimens were inserted vertically into the stagnant electrolyte at an overpotential of -0.25 V, which was applied prior to immersion. They were subsequently removed after predetermined deposition times, rinsed in deionized water, and dried. They were then cross sectioned for viewing by scanning electron microscopy using standard techniques. Figure 1 shows the time evolution of feature filling for the five different

derivitization conditions indicated. In the following text discussing these experimental results the specimens are identified by the catalyst precursor concentration used in the derivitization step (*i.e.*, step 1).

Discussion

For the specimen derivitized in 0.5 $\mu\text{mol/L}$ SPS, deposition proceeds conformally and the surface roughens with increasing film thickness. This eventually results in void formation, when the side walls impinge, and formation of a deep cusp above the trench. Identical behavior was observed for substrates which had not been derivitized, *i.e.*, $\theta_{\text{SPS}} = 0$, (not shown). For the 5 , 50 and 500 $\mu\text{mol/L}$ SPS derivitizations, the initial increment of growth is still conformal. However, it is followed by acceleration of growth at the concave (bottom) corners characteristic of the inception of the superconformal deposition process. This yields the V-shaped bottom apparent in the specimens plated for 70 , 40 , and 20 s, following derivitizations in 5 , 50 , and 500 $\mu\text{mol/L}$ SPS, respectively. Upon further deposition, the V-shaped bottoms become flat. Between 80 and 100 s the 5 $\mu\text{mol/L}$ derivitized specimens exhibit rapid bottom-up filling, a hallmark of the superfilling process. However, by 130 s the sidewalls impinge just before the rapidly advancing trench bottom reaches the top of the trench. In contrast, the 50 $\mu\text{mol/L}$ specimens exhibit near optimum superfilling behavior with rapid bottom-up filling occurring between 50 and 70 s with negligible sidewall motion. An inversion of the growth front curvature is evident at 70 s, and, by 100 s, a large bump is seen above the trench. For the 500 $\mu\text{mol/L}$ SPS and 1 mmol/L MPESA specimens, the surface coverage is effectively saturated at the start of metal deposition and geometrically driven changes in catalyst coverage associated with the CEAC mechanism are minimal. Additionally, the universally rapid copper deposition results in substantial depletion of the cupric species, which induces the void formation evident in the 40 s 500 $\mu\text{mol/L}$ SPS and 50 s 1 mmol/L MPESA specimens. Several important observations follow from this simple experiment.

1. The shape evolution observed during the superfilling process is qualitatively indistinguishable from results obtained in a single electrolyte containing both catalyst and suppressor.⁹⁻¹⁶

2. The transition from conformal to superconformal to subconformal filling with increasing catalyst coverage is analogous to the identical transitions observed as a function of SPS or MPESA concentration in an electrolyte containing both catalyst and suppressor.⁹⁻¹²

3. The shape evolution and growth transitions observed are all predicted by the CEAC mechanism; as in these experiments, the first simulations of trench filling using the CEAC mechanism assumed that all the catalyst was present on the surface at $t = 0$ with no catalyst in the electrolyte.⁹

4. The time required to fill a given trench decreases with the initial catalyst coverage, as expected due to the underlying role of catalyst in the CEAC mechanism. Indeed, the geometrically differentiated surface reactivity predicted by the CEAC model can dominate filling behavior in spite of substantial metal ion concentration gradients associated with the faster deposition at higher catalyst coverage. For the 50 $\mu\text{mol/L}$ SPS sample, in particular, superconformal filling occurs with deposition on the free surface proceeding at $>80\%$ of the diffusion limited current density.

5. Derivitization followed by metal deposition in a catalyst-free electrolyte allows the consumption of catalyst to be systematically studied. Furthermore, it permits an upper bound for the quantity of thiolate/disulfide incorporated during electroplating to be established, *i.e.*, no more than the submonolayer quantity of catalyst is occluded within the bulk electrodeposition.

6. Finally, these experiments demonstrate that the differential reactivity responsible for superfilling in the system studied has little to do with homogeneous chemistry involving thiol/disulfide nor the transport of inhibiting species, Cl-PEG.

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References

1. P. C. Andricacos, C. Uzoh, J. O. Dukovic, J. Horkans, and H. Deligianni, *IBM J. Res. Dev.*, **42**, 567 (1998).
2. H. Deligianni, J. O. Dukovic, P. C. Andricacos, and E. G. Walton, in *Electrochemical Processing in ULSI Fabrication and Semiconductor/Metal Deposition II*, P. C. Andricacos, J. L. Stickney, and G. M. Oleszak, Editors, PV 99-9, p. 52, The Electrochemical Society Proceedings Series, Pennington, NJ (2000).
3. M. Georgiadou, D. Veyret, R. L. Sani, and R. C. Alkire, *J. Electrochem. Soc.*, **148**, C54 (2001).
4. A. C. West, *J. Electrochem. Soc.*, **147**, 227 (2000).
5. J. Reid and S. Mayer, in *Advanced Metallization 1999, Proceedings of the Conference*, MRS, p. 53 (2000).
6. T. Ritzdorf, D. Fulton, and L. Chen, in *Advanced Metallization 1999, Proceedings of the Conference*, MRS, p. 101 (2000).
7. E. Richard, I. Vervoort, S. H. Brongersma, H. Bender, G. Beyer, R. Palmans, S. Lagrange, and K. Maex, in *Advanced Metallization 1999, Proceedings of the Conference*, MRS, p. 149 (2000).
8. T. P. Moffat, J. E. Bonevich, W. H. Huber, A. Stanishevsky, D. R. Kelly, G. R. Stafford, and D. Josell, *J. Electrochem. Soc.*, **147**, 4524 (2000).
9. T. P. Moffat, D. Wheeler, W. H. Huber, and D. Josell, *Electrochem. Solid-State Lett.*, **4**, C26 (2001).
10. D. Josell, D. Wheeler, W. H. Huber, and T. P. Moffat, *Phys. Rev. Lett.*, **87**, 016102 (2001).
11. D. Josell, D. Wheeler, W. H. Huber, J. E. Bonevich, and T. P. Moffat, *J. Electrochem. Soc.*, **148**, C767 (2001).
12. D. Josell, D. Wheeler, and T. P. Moffat, *Electrochem. Solid-State Lett.*, **5**, C49 (2002).
13. T. P. Moffat, B. Baker, D. Wheeler, J. E. Bonevich, M. Edelstein, D. R. Kelly, L. Gan, G. R. Stafford, P. J. Chen, W. F. Egelhoff, and D. Josell, *J. Electrochem. Soc.*, **149**, C423 (2002).
14. D. Josell, B. Baker, C. Witt, D. Wheeler, and T. P. Moffat, *J. Electrochem. Soc.*, In press.
15. B. Baker, M. Freeman, B. Melnick, D. Wheeler, D. Josell, and T. P. Moffat, *J. Electrochem. Soc.*, Accepted for publication.
16. D. Josell, D. Wheeler, and T. P. Moffat, *Electrochem. Solid-State Lett.*, **5**, C44 (2002).
17. A. C. West, S. Mayer, and J. Reid, *Electrochem. Solid-State Lett.*, **4**, C50 (2001).