



Superconformal Deposition by Surfactant-Catalyzed Chemical Vapor Deposition

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The curvature enhanced accelerator coverage (CEAC) mechanism recently proposed to explain superconformal filling of fine trenches during copper electrodeposition is shown to also explain superconformal filling and roughness evolution during iodine-catalyzed chemical vapor deposition of copper. As with electrodeposition, the coverage of adsorbed catalyst changes with surface area during interface evolution. The surface area decreases along the bottoms of submicrometer features, leading to increased coverage, thus increasing local deposition rates and thereby enabling superconformal filling. This result shows that this CEAC mechanism may be generally applied to understand interface evolution in surfactant mediated film growth processes.

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Recent publications have described the curvature enhanced accelerator coverage (CEAC) mechanism,^{1,2} and successfully used it to predict superconformal filling of fine features during copper electrodeposition in both trenches¹⁻⁴ and vias⁵ in a previously described electrolyte.⁶ This mechanism presumes that a catalyst remains segregated on the growth surface. It further presumes that reduction (increase) of local surface area during growth on rough or patterned surfaces results in a local increase (decrease) of coverage of the catalyst. This leads directly to spatially varying deposition rates, with higher rates in concave features, and thus superconformal film growth within submicrometer trenches and vias. When optimized, superconformal deposition may be used to completely fill submicrometer features having vertical sidewalls and high aspect ratios (height/width). This is in contrast to the formation of a void or seam that necessarily accompanies conformal or subconformal film growth in any feature with an aspect ratio greater than 0.5. Quantitative predictions were made for filling over a wide range of electrolyte compositions, deposition voltages, and trench aspect ratios using kinetic parameters obtained from voltammetric studies on planar substrates.¹⁻⁵ The predictions accurately described all aspects of superconformal filling experiments, including the initial "incubation period" of conformal growth, when bottom-to-top "superfill" itself occurred or did not occur, and subsequent development of an overfill bump, a manifestation of so-called momentum plating.

This paper shows how the same CEAC mechanism explains recently disclosed results stating superconformal filling during iodine catalyzed chemical vapor deposition in vias up to aspect ratios of four.⁷⁻⁹ In the process, this paper makes the significant conclusion that any chemical vapor deposition (CVD) or electrodeposition process can, in principal, be made to yield superconformal deposition if a surface segregating catalytic species exists. In addition, based on results for copper electrodeposition, superconformal CVD might be further enhanced through appropriate use of a rate-suppressing additive in addition to the dilute, more surface active, rate-accelerating catalyst.¹⁻⁵

Modeling Feature Filling with the CEAC Mechanism

Modeling of interface evolution during catalyzed CVD can be performed using algorithms previously used to simulate CEAC during copper electrodeposition.¹⁻⁵ In this paper, the filling of trenches by catalyzed CVD is explored using a string model¹ while a simplified geometrical description is used for examining growth in vias.⁵ The only distinction between the CVD model and the prior electrodeposition models is the expression used to describe the coverage dependence of the interface kinetics. Complete simulation of filling also requires consideration of mass transport of copper and iodine precursors in the gaseous medium above and within the trench.

However, chemical vapor deposition processes typically provide near-conformal deposition in fine features, due to insignificant gradients of metal precursor down such features. Thus, metal and catalyst precursor depletion within features is ignored in the simulations presented below. Failure to fill will therefore manifest as formation of a seam, characteristic of conformal growth,¹ rather than as a void within the feature,² created by significantly faster deposition at the top of the feature in the event of such depletion. Conditions for optimal filling have been shown to be only modestly affected by this approximation.^{2,3} As this paper focuses on filling, modeling assumes the existence of a lithographically defined feature that is already covered by a smooth copper seed layer. All issues associated with deposition of such a seed layer are ignored.

In thermally activated CVD, the deposition rate (*i.e.*, local growth velocity v) may be expressed as the product of the concentration of the metal precursor at the interface and a thermally activated kinetic factor

$$k = k_0 \exp\left(-\frac{\Delta G^*}{RT}\right) \quad [1]$$

For copper CVD, a variety of organometallic precursor compounds have been identified with particular interest focused on ligand-stabilized copper(I) β -diketonate compounds.¹⁰ Deposition occurs through dissociative adsorption followed by a disproportionation reaction. Manipulation of crystal growth processes through the use of surfactants has become generic across many fields in the last decade. The one result of central importance to this paper is the report that iodine catalyzes the decomposition of hexafluoroacetylacetonate vinyltrimethylsilane, CuI (hfac)(vtms), and enhances copper deposition rates.^{8,11} The kinetics of the copper deposition rate were measured for a reported iodine coverage of ≈ 0.1 monolayers (coverage determined relative to Cu (111)).¹¹ It is worth noting that low energy electron diffraction (LEED) and scanning tunneling microscopy (STM) studies reveal that iodine forms a close packed ($\sqrt{3} \times \sqrt{3}$) R 30° structure corresponding to a coverage of 0.3 monolayers.¹²⁻¹⁴

In this paper, the copper deposition rate v is presumed to scale linearly with the catalyst coverage with the rate varying between that determined for an iodine-free surface and that corresponding to a coverage of ≈ 0.1 monolayers. For the remainder of this paper, coverage is expressed in terms of the fraction θ of the ≈ 0.1 monolayers reported coverage. Lacking additional kinetic data, the deposition rate is also presumed to be maximized at this coverage. The dependence of velocity on coverage is thus expressed as

$$v(\theta, T) = (1 - \theta)v(0, T) + \theta v(1, T) \quad [2]$$

for $\theta: [0,1]$ with the temperature dependent deposition rates on un-

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catalyzed and fully catalyzed surfaces, $v(0,T)$ and $v(1,T)$, respectively, taken from Ref. 11. Using the published values, Eq. 2 can be rewritten

$$v(\theta,T) = (1 - \theta)k' \exp\left(-\frac{\Delta G'}{RT}\right) + \theta k'' \exp\left(-\frac{\Delta G''}{RT}\right) \quad [3]$$

with $k' = 1.55 \times 10^7$ nm/s, $k'' = 5.6 \times 10^3$ nm/s, $\Delta G' = 6.4 \times 10^4$ J/mol, and $\Delta G'' = 2.5 \times 10^4$ J/mol. Equation 3, with the stated kinetic parameters, quantitatively captures the impact of catalyst coverage on the rate of the copper deposition for temperatures between approximately 100 and 300°C. This equation is not presumed to necessarily capture the exact form of that relationship for intermediate values of coverage θ but is used in the absence of experimental data. Note that the acceleration associated with catalyst coverage, expressed as the ratio $v(1,T)/v(0,T)$, decreases from ≈ 90 down to only 1 as the temperature increases from 100 and 300°C.

Conservation of the adsorbed iodine catalyst, including any time-dependent accumulation, is summarized in

$$\frac{d\theta}{dt} = \kappa v\theta + C_{\text{Iodine}}^i k^*(1 - \theta) \quad [4]$$

The first term accounts for coverage change caused by the changing area, the rate of local area change being equal to the local curvature κ times the normal velocity v , hence the name of the curvature enhanced accelerator coverage mechanism. The second term accounts for accumulation from the gas phase with concentration of the catalyst precursor C_{Iodine}^i at the interface and adsorption rate constant k^* . An additional term that characterizes the effect of consumption, desorption, or deactivation can be added although its effect is reported to be negligible for iodine-catalyzed copper CVD.^{8,11} Consumption was also neglected in modeling superconformal copper electrodeposition.^{1,5}

In light of the minimal consumption or deactivation of adsorbed iodine during copper CVD, superconformal film growth can be implemented either by establishing a fixed initial surface coverage on the copper seed layer prior to the metal deposition or, alternatively, by inclusion of a small quantity of the catalyst precursor with the metal precursor to allow continuous dosing during film growth. Simulations in this paper use the first growth scheme, $C_{\text{Iodine}}^i = 0$, and are thus analogous to the earliest modeling of the CEAC mechanism for copper electrodeposition.¹

Simulations of trench filling were performed using Eq. 3 and 4, in an interface tracking string model.¹ Behavior varied according to the initial catalyst coverage, θ_0 , growth temperature and aspect ratio (trench height/width), see Fig. 1 and 2. Superconformal filling occurs in Fig. 1a, b, c, d, e, and g for deposition at 273 K and in Fig. 2a, b, d, e, and g at 373 K. “Superfill” is achieved because the catalytic iodine coverage becomes sufficiently high at the bottom of the trench that rapid bottom-up filling occurs, following an initial period of conformal growth, with relatively little sidewall motion. As the growth front approaches the top of the trench an inversion of the interface curvature occurs, forming a bump visible above the trench. If θ_0 is too high or the aspect ratio too large, the differential velocity along the surface profile is too small and the sidewalls impinge before the bottom of the trench can escape. A vertical seam then forms in the center of the trench, leaving a cusped surface profile (see Fig. 1f, h, and i and Fig. 2c, f, h, and i). The simulations show that lower θ_0 enables filling of higher aspect ratio trenches. This is not surprising, as it clearly maximizes the differential velocity that can be obtained from Eq. 2. Practically, however, one is limited in how low θ_0 can be, because the growth kinetics, and thus predicted deposition times, increase by orders of magnitude as θ_0 decreases. As the deposition temperature rises, the maximum aspect ratio that can be filled decreases (Fig. 3). This is due to the decrease of the ratio $v(1,T)/v(0,T)$ with increasing temperature. Importantly,

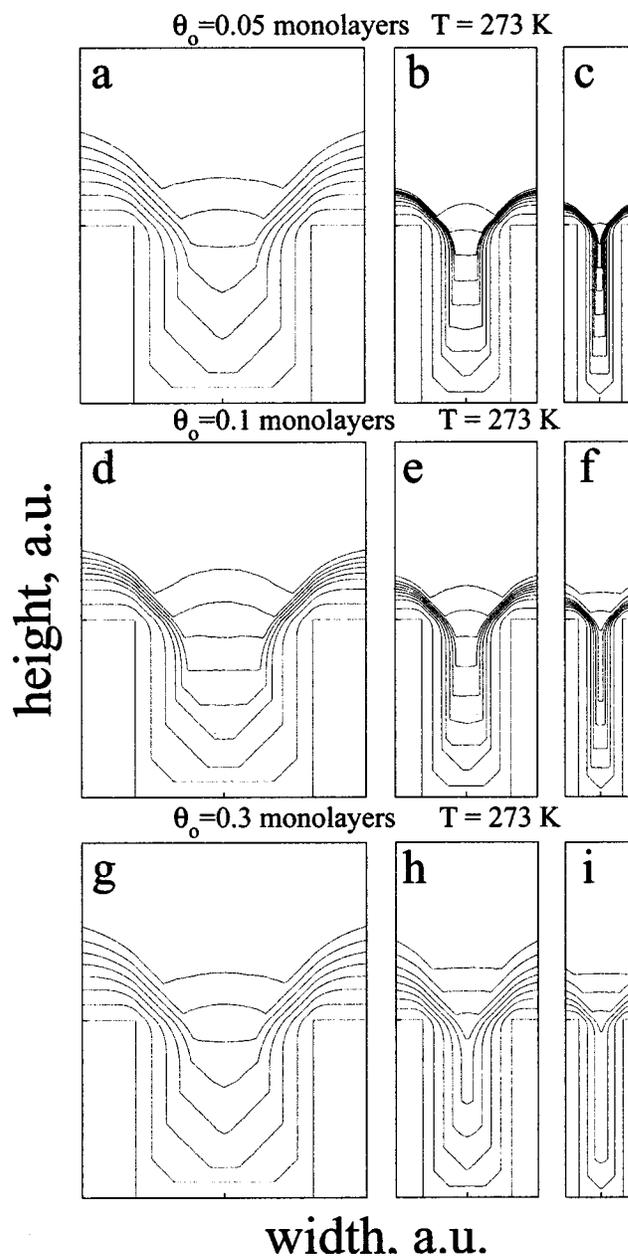


Figure 1. Growth contours of copper CVD in trenches with aspect ratios of 1, 2, and 4 for initial accelerator coverages of 0.05, 0.1, and 0.3 monolayers (top to bottom). All simulations use kinetics at 273 K. Superconformal filling occurs in features a, b, c, d, e, and g. The absolute dimensions affect only the time for filling.

tantly, the simulations are consistent with recently described CVD filling experiments including both the maximum aspect ratios filled^{8,9} and the observation of improved filling with decreasing deposition temperature.⁹ We do, however, add the caveat that the experimentally observed trend with temperature likely also reflects increasing mobility of the adsorbed catalyst with increasing temperature. Surface mobility of the catalyst, beyond that needed to avoid incorporation during deposition, leads to more uniform catalyst coverage. Such mobility thus negates local coverage changes induced by the CEAC mechanism that are responsible for superconformal filling.

The kinetic formulation in Eq. 3 was also used in a simple model that was originally designed to capture the CEAC effect during filling of vias by electrodeposition⁵ to obtain predictions of the maximum aspect ratio that can be filled as a function of temperature for

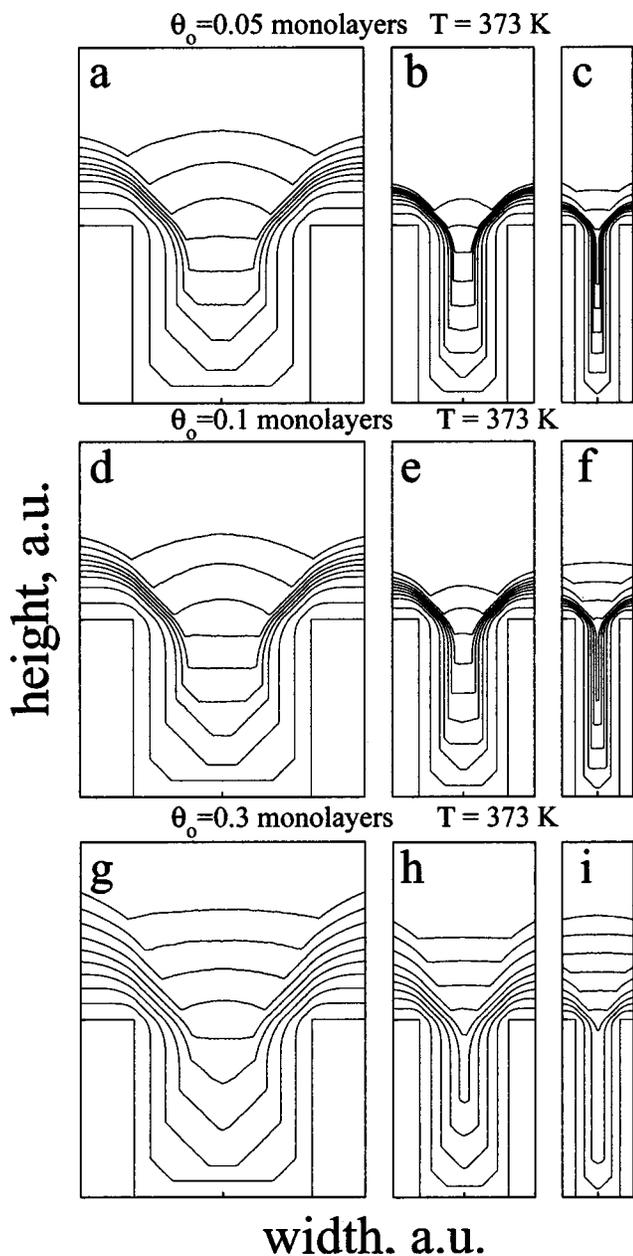


Figure 2. Growth contours of copper CVD in trenches with aspect ratios of 1, 2, and 4 for initial accelerator coverages of 0.05, 0.1, and 0.3 monolayers (top to bottom). All simulations use kinetics at 373 K. Superconformal filling occurs in features a, b, d, e, and g. The absolute dimensions affect only the time for filling.

different starting coverage (Fig. 4). That model uses a geometrical simplification to replace the curved growth surface and the curvature term in Eq. 4. This is accomplished by using straight segments for the sidewalls and bottom surface and allowing instantaneous redistribution of catalyst from eliminated sidewall area on the bottom surface. A sufficiently high diffusion coefficient for transport of the copper precursor to the surface was used in the model to make depletion both above and within the via insignificant.

Use of a growth rate-coverage relationship other than the linear form in Eq. 2 would be expected to change the maximum aspect ratio of a feature that can be filled at a given temperature and starting coverage. It would not, however, significantly alter the arguments or conclusions made here concerning the mechanism behind superconformal feature filling.

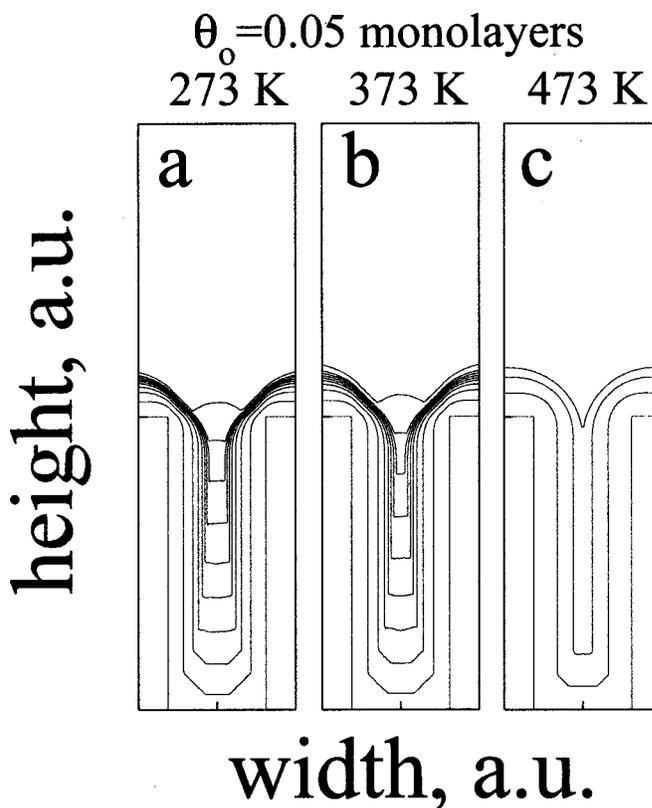


Figure 3. Growth contours for copper CVD in trenches with aspect ratio 3 at three different temperatures for an initial catalyst coverage of 0.05 monolayers. Note that superconformal filling occurs only at the two lower temperatures.

Surface Smoothing by the CEAC Mechanism

Surface smoothing during iodine catalyzed copper CVD has been noted by the same groups that noted superconformal filling.^{8,9,11} Interestingly, the publications that first presented and applied the CEAC mechanism to explain superconformal electrodeposition explicitly noted the significance of the mechanism for surface smoothing.^{1,2} By accelerating deposition on concave surfaces (valleys) and slowing deposition on convex surfaces (hills), Eq. 2 natu-

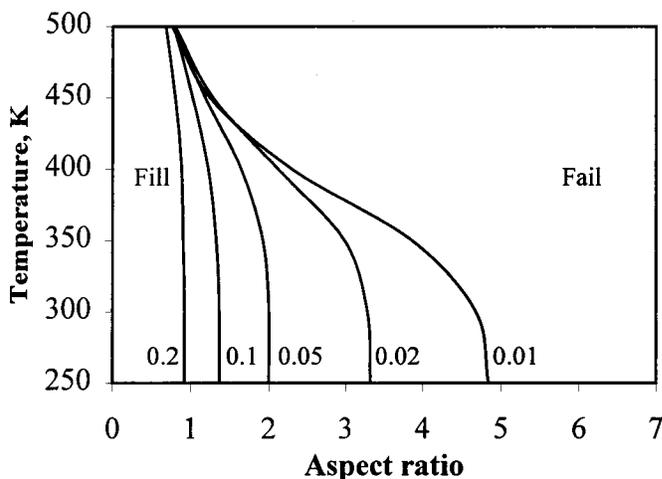


Figure 4. Curves indicating predicted maximum aspect ratios of vias that can be filled, for given initial coverage of catalyst, as functions of deposition temperature. Values of the initial coverage are given next to each curve.

rally leads to smoothing of surfaces during growth; as recessed surface catches up with protruding regions overshoot can, however, occur as manifested by the overfill bump in trench filling. The increasing importance of the CEAC mechanism at the higher curvatures associated with smaller ($<1\ \mu\text{m}$) length scale roughness makes it clearly distinct from traditional leveling theories that predominate for roughness length scales comparable to diffusional length scales (10's to 100's of micrometers).

Conclusions

This work has demonstrated that the CEAC mechanism can be used to explain why copper deposition occurs predominantly at the bottoms of fine features during iodine-catalyzed CVD of copper resulting in superconformal filling. Along with results published earlier for copper electrodeposition, this work demonstrates that the same formalism can be used to describe two fundamentally different chemical reactions; (i) competitive adsorption between a dilute, rate-accelerating additive and a rate-suppressing additive in copper electrodeposition, and (ii) simple catalysis of deposition by an iodine additive in CVD. In both cases, superfilling results from increasing coverage of rate-accelerating catalyst, and thus metal deposition rate, at the bottoms of fine features due to decreasing surface area in those locations. This paper suggests that the CEAC-based model developed here, along with rigorous evaluation of the impact of catalyst coverage on deposition rate, will permit accurate prediction of superconformal CVD in a manner similar to that recently done for copper electrodeposition. Finally, the CEAC mechanism

has general implications for understanding the use of catalysts to produce smooth "bright" surfaces by chemical vapor deposition.

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References

1. T. P. Moffat, D. Wheeler, W. H. Huber, and D. Josell, *Electrochem. Solid-State Lett.*, **4**, C26 (2001).
2. D. Josell, D. Wheeler, W. H. Huber, and T. P. Moffat, *Phys. Rev. Lett.*, **87**, 016102 (2001).
3. D. Josell, D. Wheeler, W. H. Huber, J. E. Bonevich, and T. P. Moffat, *J. Electrochem. Soc.*, **148**, C767 (2001).
4. D. Wheeler, D. Josell, and T. P. Moffat, *J. Comput. Phys.*, Submitted.
5. D. Josell, D. Wheeler, and T. P. Moffat, *Electrochem. Solid-State Lett.*, To be published.
6. 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).
7. H. Park, W. Koh, S.-M. Choi, K.-C. Park, H.-K. Kang, J.-T. Moon, K. Shim, H. Lee, O. Kwon, and S. Kang, in *Proceedings of The IEEE 2001 International Technology Conference*, p. 12, IEEE, New York (2001).
8. E. S. Hwang and J. Lee, *Electrochem. Solid-State Lett.*, **3**, 138 (2000).
9. S. G. Pyo, W. S. Min, H. D. Kim, S. Kim, T. K. Lee, S. K. Park, and H. C. Sohn, in *Proceedings of the Advanced Metallization Conference*, Montreal, Canada. Oct 9-11 (2001), In press.
10. A. E. Kaloyeros and M. A. Fury, *MRS Bull.*, **18**, 22 (1993).
11. E. S. Hwang and J. Lee, *Chem. Mater.*, **12**, 2076 (2000).
12. P. H. Citrin, P. Eisenberger, and R. C. Hewitt, *Phys. Rev. Lett.*, **45**, 1948 (1980).
13. B. Di Cenzo, G. K. Wertheim, and D. N. E. Buchanan, *Surf. Sci.*, **121**, 411 (1982).
14. B. V. Andryushechkin, R. E. Baranovsky, K. N. Eltsov, and V. Y. Yurov, *Surf. Sci.*, **488**, L541 (2001).