Modeling Of Feature Scale Transients During Electrochemical Deposition

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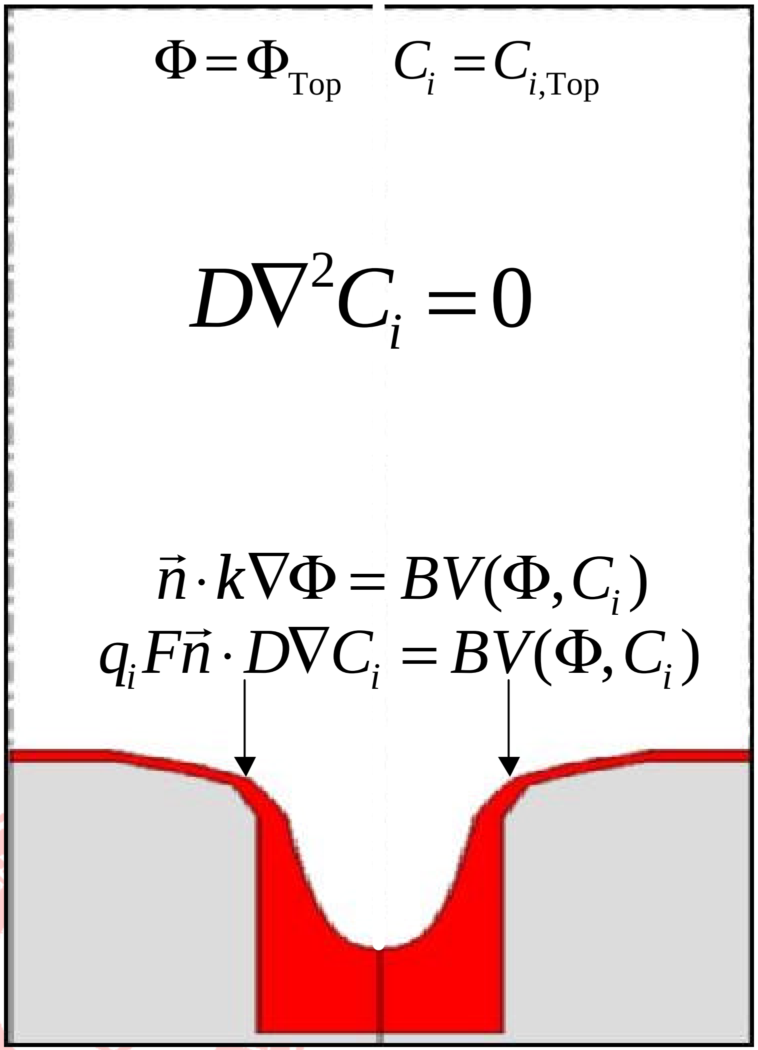
Objectives

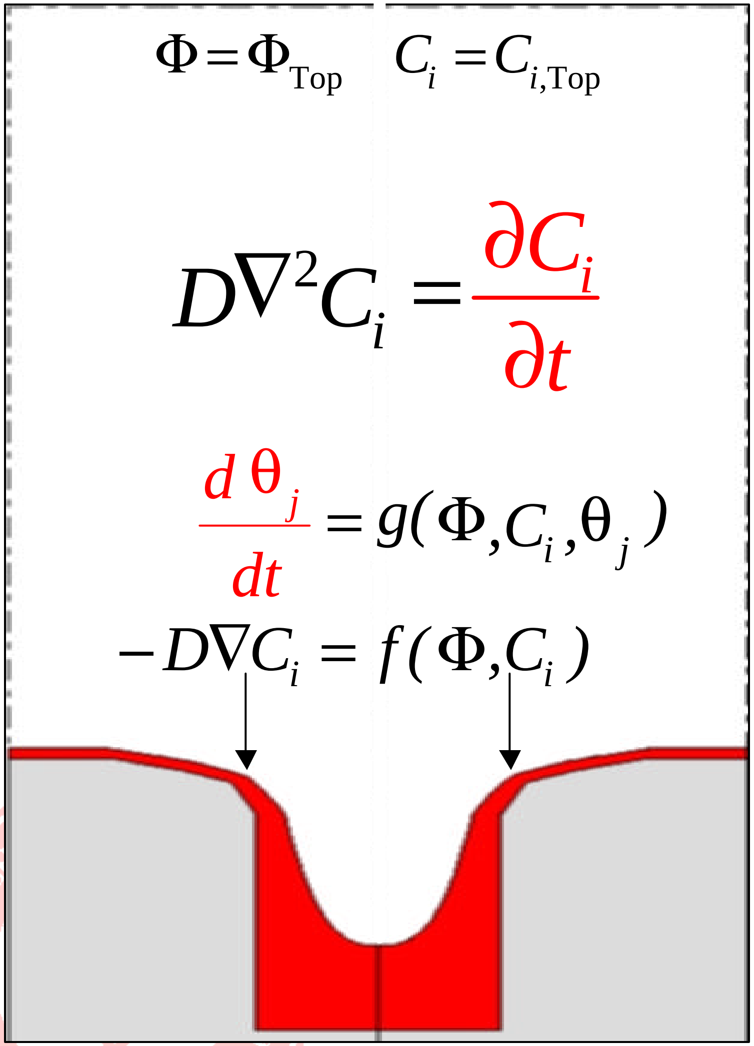
- To develop a software tool to study feature scale transients behavior in electrochemical deposition (ECD) processes.
- We consider 2 applications of our transient simulator to Cu ECD processes.
  - Pulsed plating in which the voltage is varied; it has an “on interval”, an “off interval” and a “de-plating interval”
  - Superconformal deposition using accelerator species, which can produce bumps at the top of a filled feature.

Pseudo-Steady Feature Scale Models



- Assumes fast redistribution of surface species and fluid concentrations compared to film growth – at least on the time frame of the process.
- Can just solve Laplace's equation in fluid, match rates to fluxes at surface.

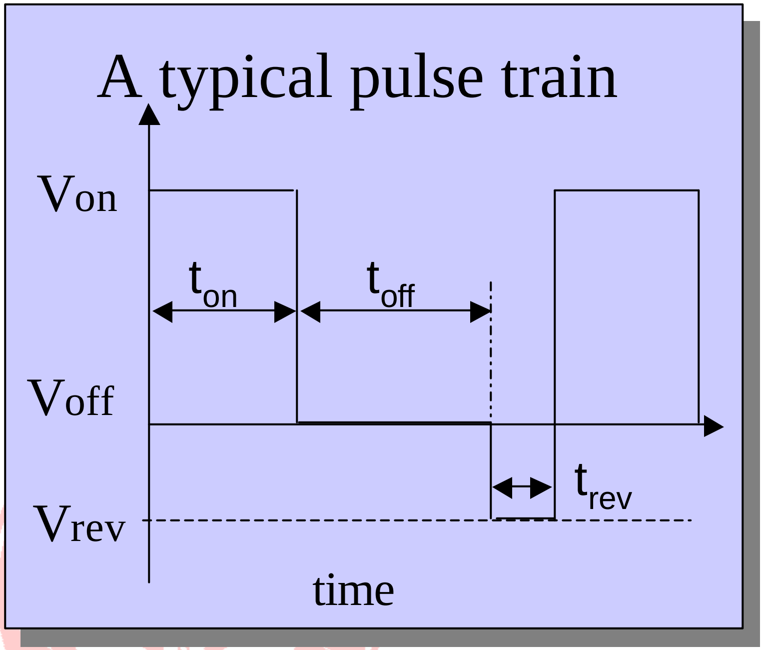
Non-Steady Feature Scale Models

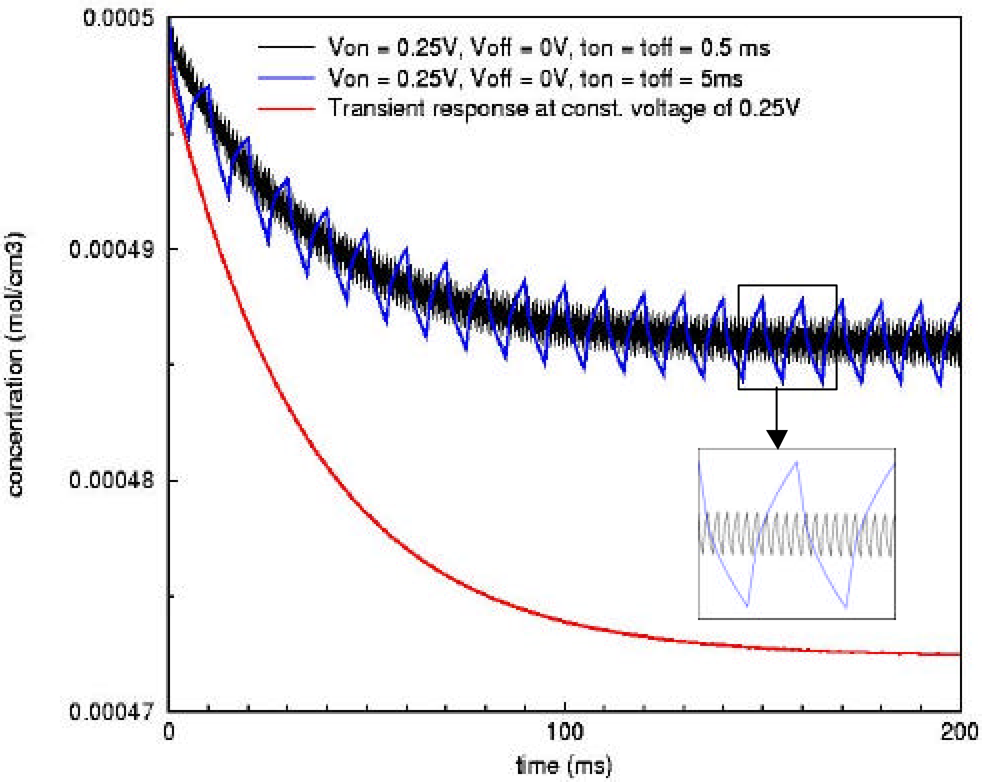


- Pseudo-steady not adequate if conditions change faster than concentrations can respond, i.e. rapidly changing potential, slow changes in concentrations.
- Must solve Poisson’s equation.
- Must keep state between time steps, and figure out how to “pass the information along”.

Pulse Plating

- During the off –time following an on-time in a pulse, the concentration fields relax and make the concentration more uniform inside and outside the features, which results in more conformal deposition profiles

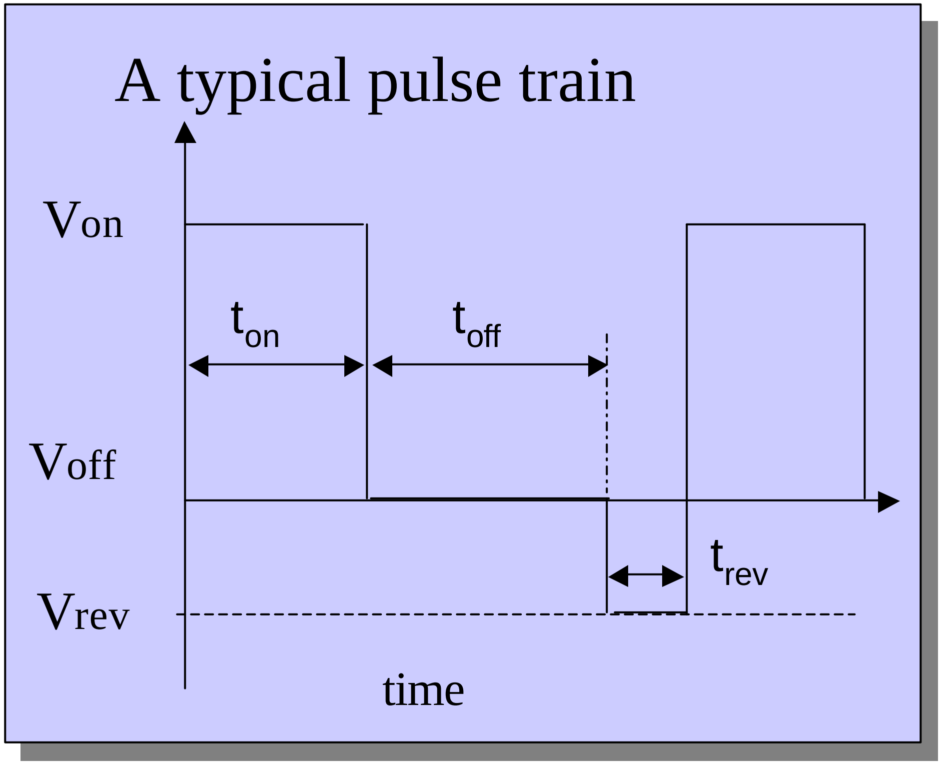




Averaging over a pulse

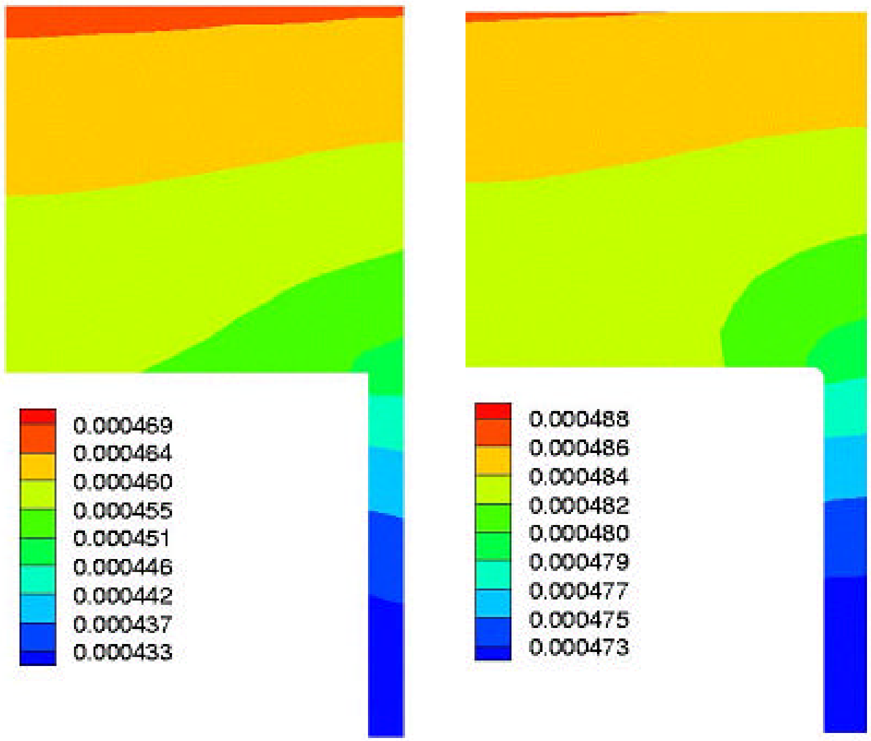
- Integrate deposition rates over each pulse segment divide by total pulse width to get average rate.

$$\overline{\mathrm{R}} = \frac{1}{t_{\mathrm{pulse}}} \int_{\mathrm{pulse}} R(t)\,dt$$



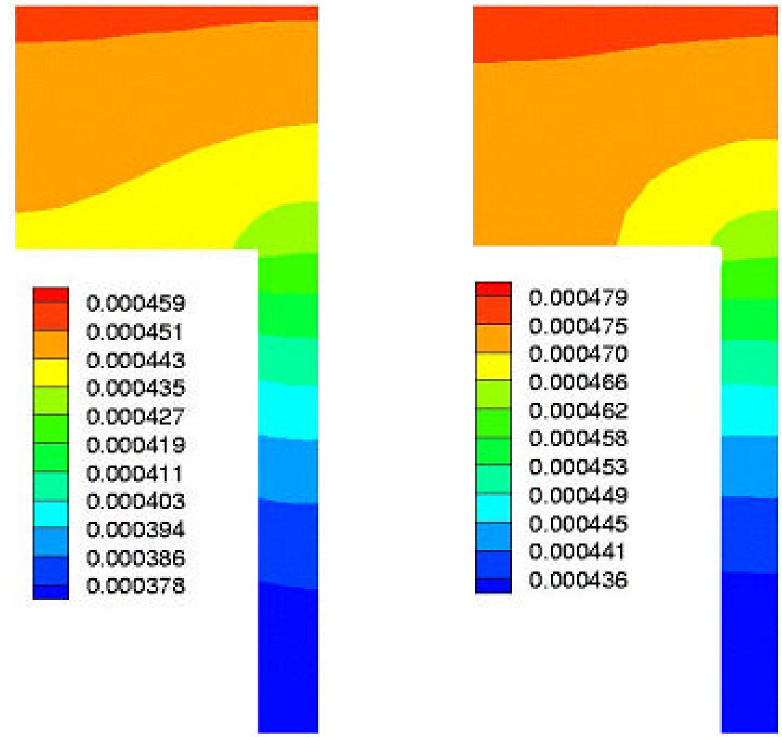
Copper Ion Concentration

Feature: 0.25µ wide AR=2 trench.



(a) ~ 7% depletion (b) ~ 2% depletion

Feature: 0.25µ wide AR=4 trench.



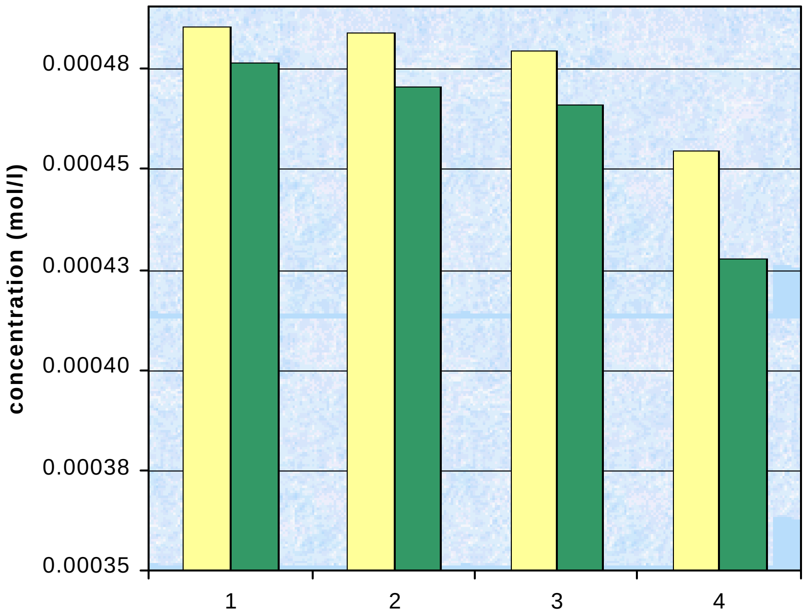
(a) ~ 20% depletion (b) ~ 7% depletion

(a) With constant voltage 0.25 V

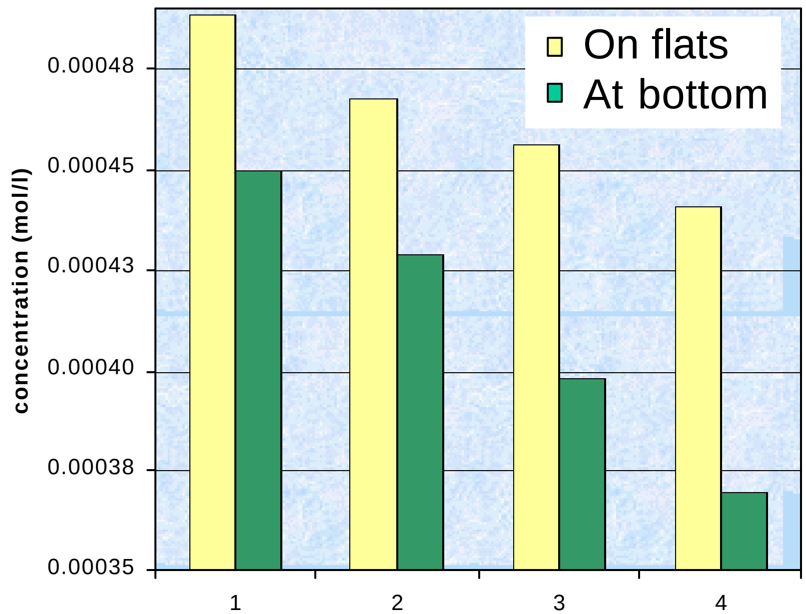
(b) With pulsed voltage sequence of 0.25V:5ms, 0.0V:5ms. (The concentrations shown are the values at the end of a deposition pulse, near the beginning of deposition – before the feature has changed.)

Note: Figures are not to scale; Concentrations in mol/cm^3

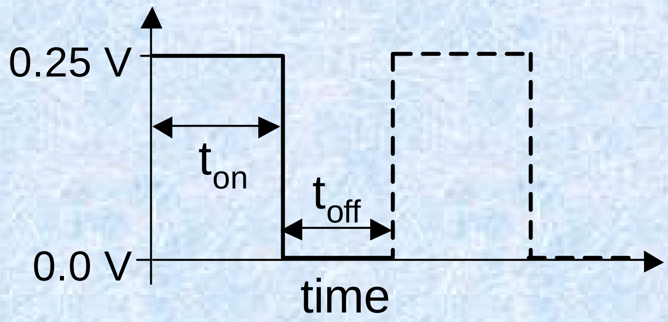
Copper Ion Concentrations



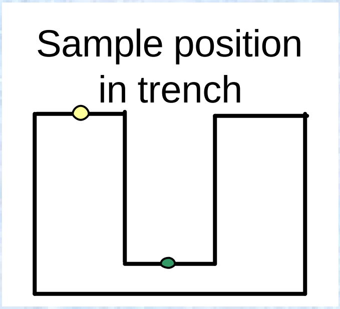
0.25 μm wide, 0.5 μm deep,
0.75 μm pitch trench



0.25 μm wide, 1.0 μm deep,
0.75 μm pitch trench

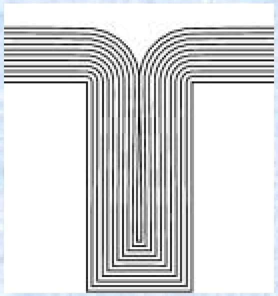


1: t_{on} = 5 ms, t_{off} = 10 ms
2. t_{on} = 5 ms, t_{off} = 5 ms
3. t_{on} = 5 ms, t_{off} = 1 ms
4. V = 0.25 volts



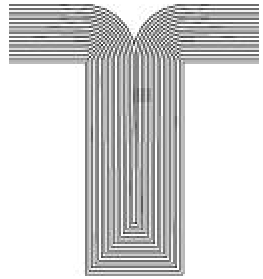
Effect of Pulsing on Trench-Filling

Constant potential ECD
(0.25V)



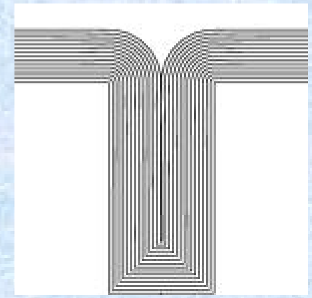
5 % void

Pulsed ECD, no de-plating
(0.25V:5 ms, 0.0V:5 ms)



3 % void

Pulsed ECD, with de-plating
(0.25V:5 ms, 0.0V:5 ms, -0.2V:1 ms)

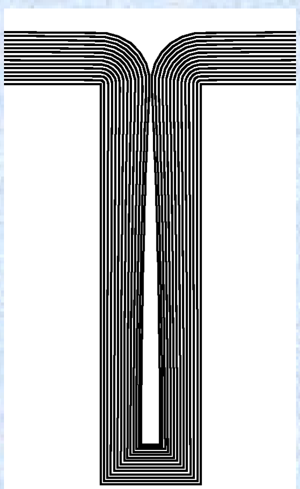


1.4% void

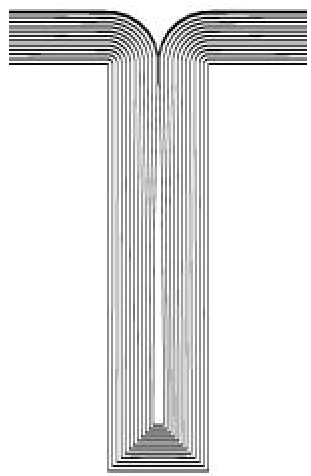
0.25 μm x 0.5 μm trenches

/est *et al*., 145(9)
ECS,1998

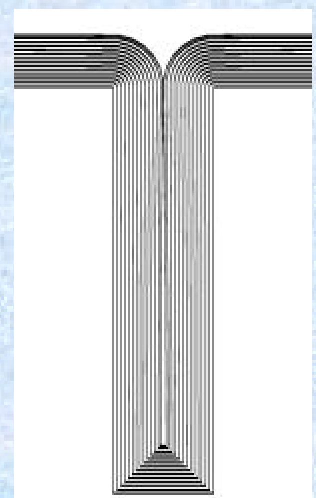
0.25 μm x 1.0 μm trenches



19 % void



10% void

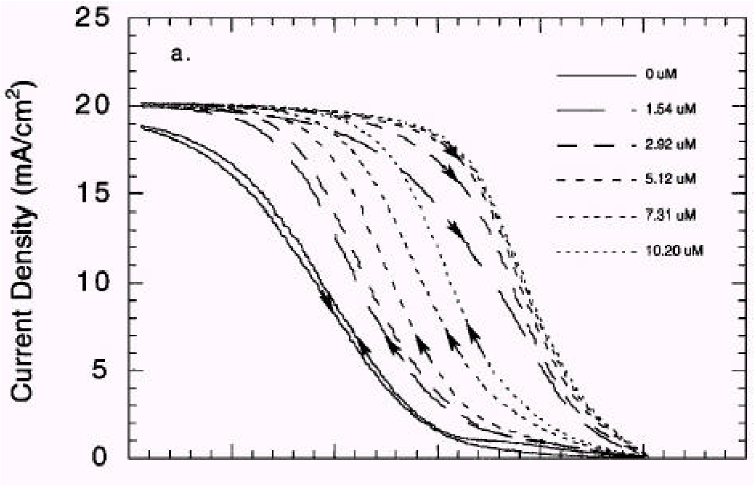


5% void

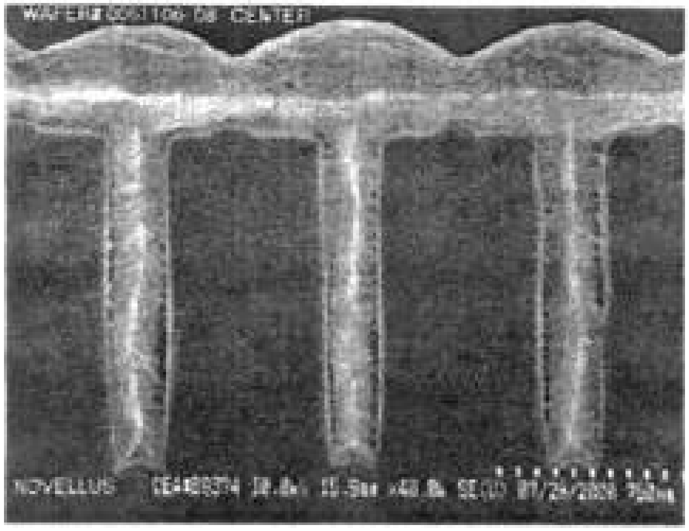
% void = width of void at bottom after deposition divided by initial feature width time 100

Superconformal ECD Using Accelerators

- Experimentally, systems show definite hysteresis.
  - Cyclic voltammetry
  - “Bumping” during deposition
- Recent models attribute behavior to accumulation of a species which blocks adsorption of inhibitor [West *et al.*].
- Curvature-based accumulation can account for bottom-up filling of features.
- Because material is accumulating on the surface, it must be tracked over time.
- Liquid concentrations respond quickly and *can* be viewed as at steady-state.



Josell *et al.* PRL (87) 1,2001



West *et al.* ESL (4) 7,2001

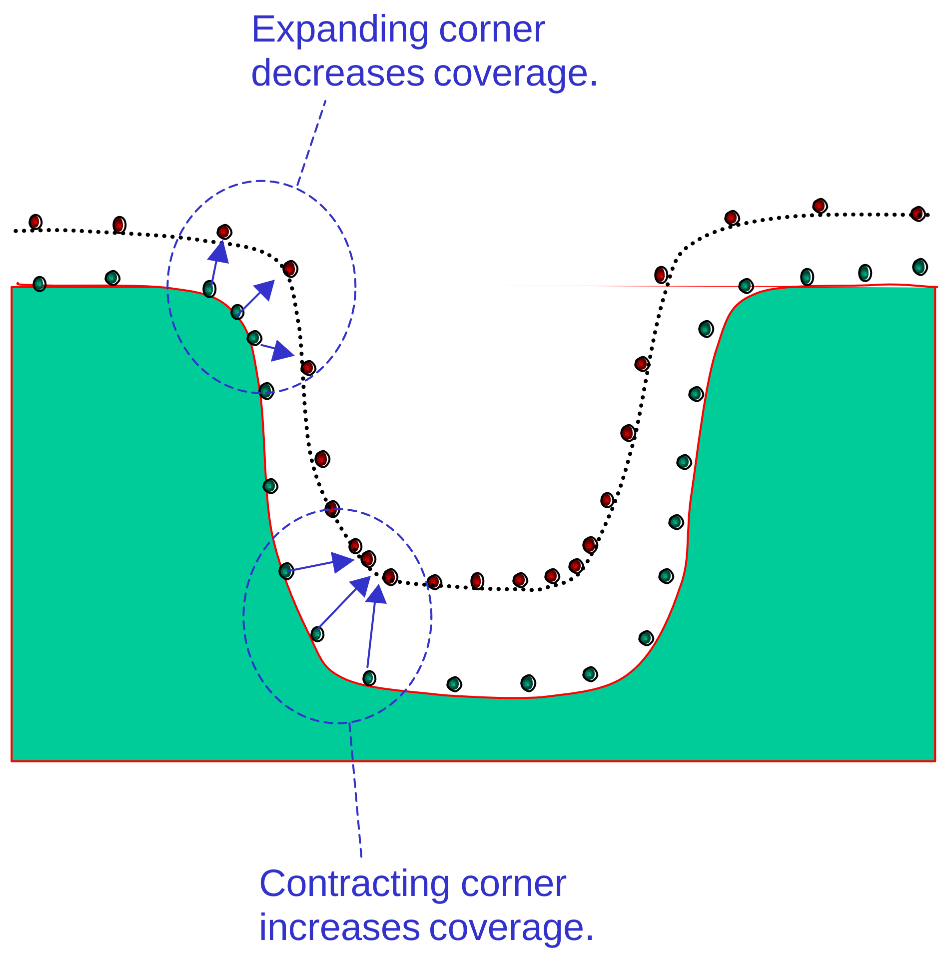
Superconformal ECD Using Additives

Consider 3 species system :

- **Cu^{2+}** undergoes single step charge transfer reaction at electrode.
- **Accelerator** adsorbs and is locally concentrated by growth. Rate of change of coverage depends on local curvature term and on an adsorption term.
- **Suppressor** reacts by adsorption. It inhibits copper deposition by blocking surface sites for reaction. Adsorbtion rate depends on accelerator surface coverage.

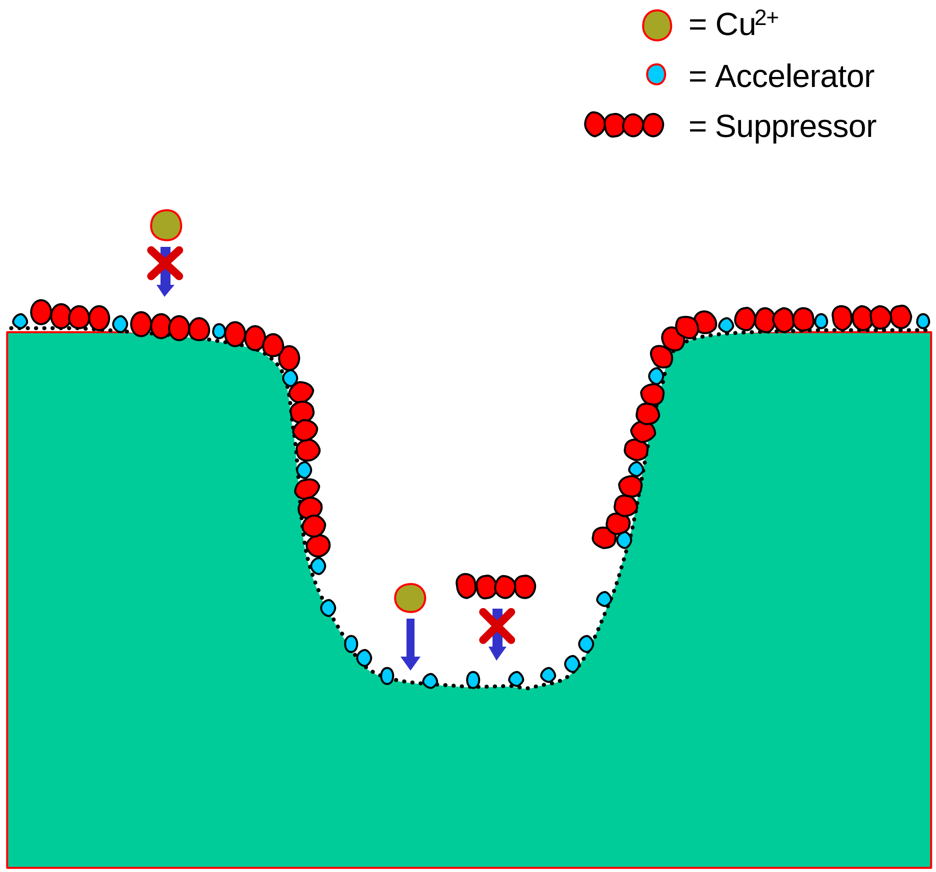
Accelerator Reaction Mechanism

- The accelerator catalyzes the Cu deposition reaction and inhibits leveler action by blocking sites.
- In areas of positive curvature, species on surface get crowded together as surface advances.
- In areas of negative curvature, the expanding surface decreases coverages.



Suppressor Reaction Mechanism

- The suppressor inhibits the copper deposition reaction by blocking surface sites.
- The rate of adsorption decreases with increasing accelerator coverage.



Additive Coverage Evolution

$$\frac{dq_{\mathrm{sup}}}{dt} = -k_2\left(q_{\mathrm{sup}} - \mathrm{K}\left(1 - q_{\mathrm{acc}} - q_{\mathrm{sup}}\right)\right) \qquad K = 30\exp(-7\sqrt{q_{\mathrm{acc}}})$$

$$\frac{d\left(Aq_{\mathrm{acc}}\right)}{dt} = -k_1\left(q_{\mathrm{acc}} - q_{\mathrm{acc,eq}}\right) \Rightarrow \frac{dq_{\mathrm{acc}}}{dt} = \frac{\mathrm{i}\Omega}{\mathrm{nF}} k q_{\mathrm{acc}} - k_1\left(q_{\mathrm{acc}} - q_{\mathrm{acc,eq}}\right)$$

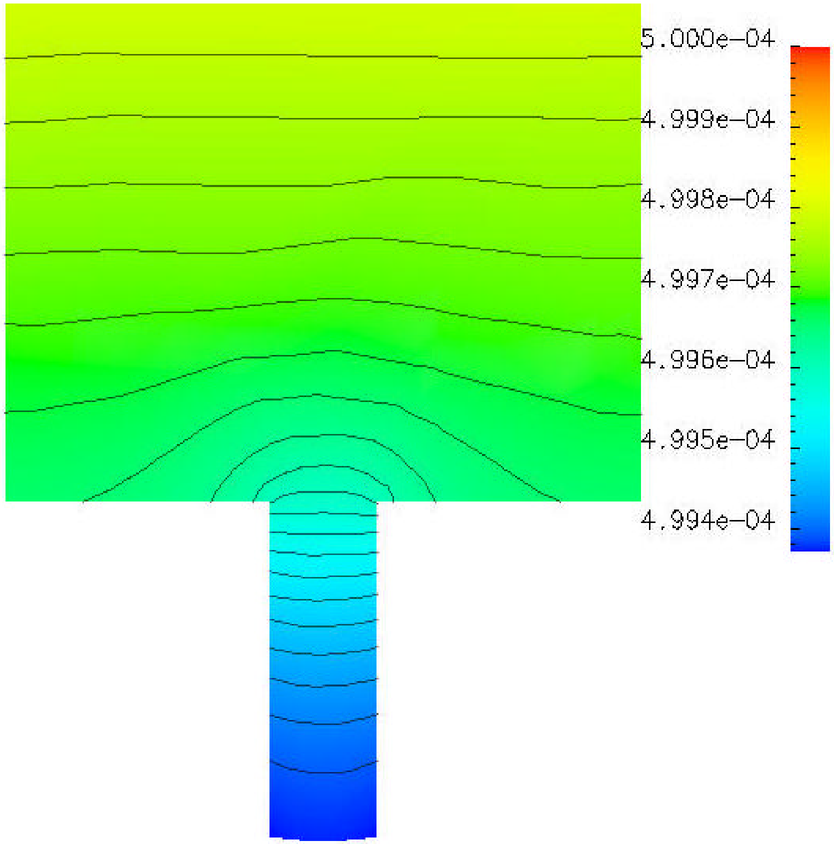
$$i = i_0\left(1 - q_{\mathrm{sup}}\right)$$

i = current density, O_{cu}= atomic volume of copper, ? = curvature, $?_{acc}$= surface coverage of accelerator, k_1, k_2 = rate constants of adsorption for accelerator and suppressor, $?_{sup}$= surface coverage of suppressor, K = equilibrium constant for adsorption of suppressor, i_0 = current in absence of suppresser

adapted from West *et. al.* ESL,4(7),C50,2001

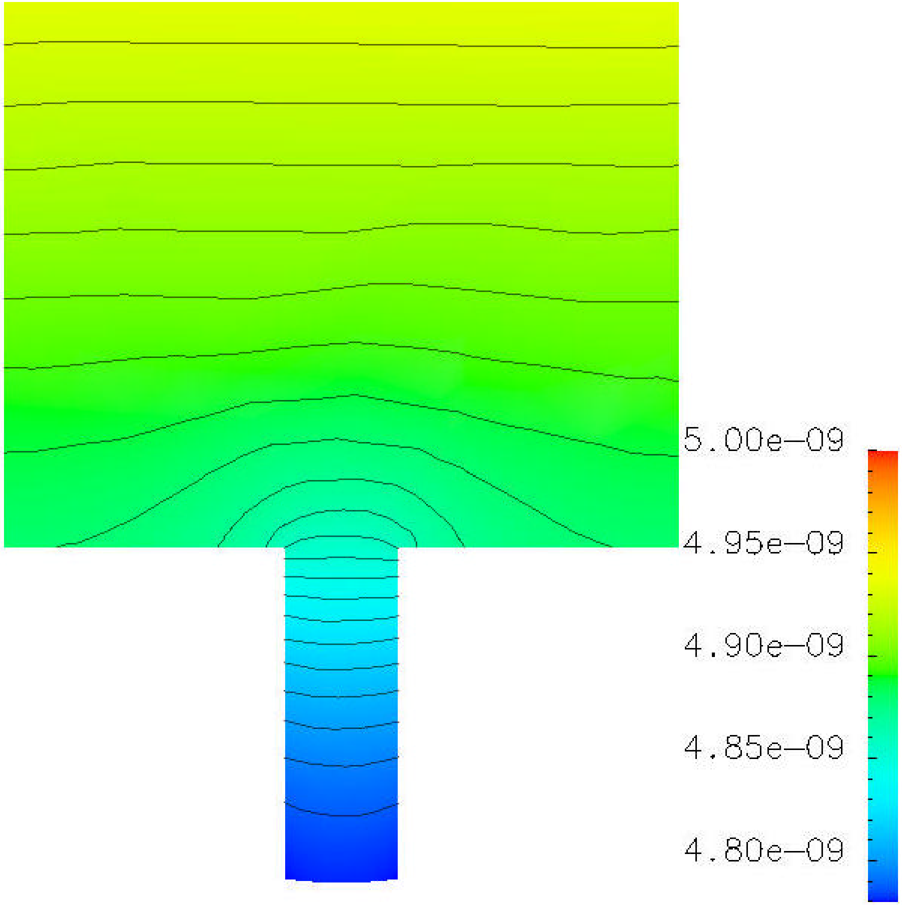
Copper Ion Concentration

- Finite element simulations show less than 0.1% depletion of copper down 0.6 μm, aspect ratio 3 trench at a current of 10 mA.
- Assumption that copper concentration is spatially uniform appears valid.

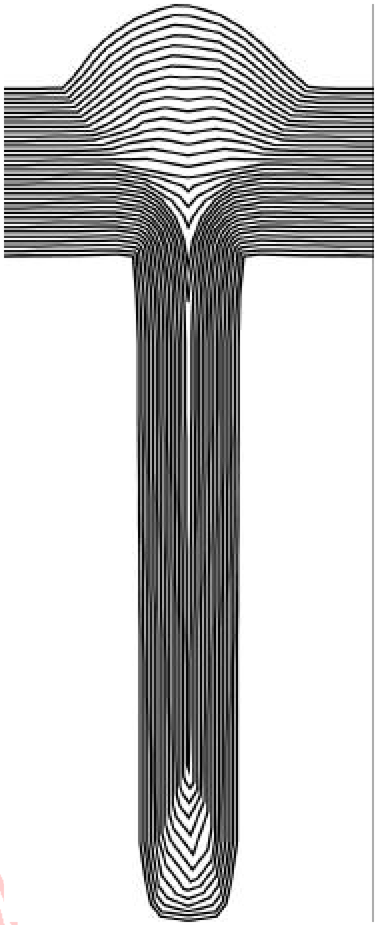


Accelerator Concentration

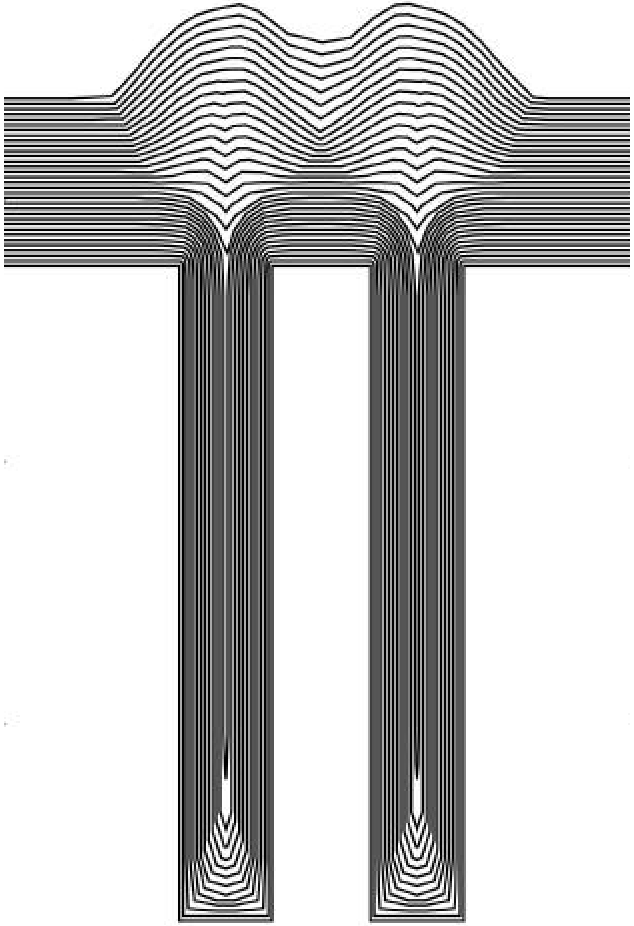
- Finite element simulations show there is about 1% depletion of accelerator down 0.6 μm, aspect ratio 3 trench.
- Our assumption that accelerator concentration is spatially uniform appears valid.



Deposition Into Trenches



Deposition into
digitized trench



2 neighboring AR 5
idealized trenches

Conclusions

- Demonstrated transient feature scale ECD simulator
- It is important to consider the effect of transients in the concentration fields with a pulsed voltage, which affects the final film profile evolution
- The transient dependence of reaction rate on the accumulation of the accelerator and suppressor is important to get bump formation, but copper and accelerator not necessarily depleted in the liquid phase.
- Tracking transient behavior may be the correct way to reproduce particular phenomena.