Electrodeposition of nanomaterials

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# Electrodeposition of Nanomaterials

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Introduction:

Electrodeposition

• has long history
Miniature mask from Loma Negra, Moche culture, northern Peru: 100 B.C. – 800 A.D.

Au applied to Cu by displacement plating.

Introduction:

Electrodeposition

- has long history
- is an important current technology
Metal interconnects in ultra large scale integrated circuits

- electrodeposited Cu has replaced Al in ULSI
- higher conductivity – better electromigration resistance


Cu interconnects on IBM chip
Introduction:

Electrodeposition

- has long history
- is an important current technology
- will play pivotal role in nanofabrication
Topics:

- Controlling morphology
- The dual-damascene method
- Electroless deposition
- Multilayer electrodeposition
Topics:

• Controlling morphology
• The dual-damascene method
• Electroless deposition
• Multilayer electrodeposition
Why do electrodeposited thin films become rough?

AFM image of film electrodeposited from 0.3M CuSO$_4$ / 1.2M H$_2$SO$_4$, 4 mA cm$^{-2}$, $t=6$ mins
• Random fluctuations $\rightarrow$ noise

• Surface tension leads to smoothening

$$\mu = \mu_{eq} + \Gamma \kappa \nu_m$$

• Can incorporate these ideas in equation of motion for surface e.g.

$$\partial h(x, t) / \partial t = -c \nabla^4 h(x, t) + \eta(x, t)$$
- Mass transport is by diffusion → *Laplacian instability*

Peaks grow faster than valleys
Further consequences of diffusion:

- Diffusion limited current $\propto -D \frac{C_{bulk}}{\delta}$
- $\delta$ depends on convection
Complex non-linear system *but* simple power law behaviour (scaling)

- *Local* roughness scales as $t^{\beta_{loc}}$.
- *Large-scale* roughness ($w_{sat}$) scales as $t^{\beta + \beta_{loc}}$.
• Can change current density, electrolyte concentration, temperature

• Only $\beta_{loc}$ changes.

• $\beta_{loc}$ depends on ratio of current to diffusion-limited current – Laplacian instability

This is a useful result:

- Only 5 numbers (scaling exponents and pre-factors) needed to describe roughness on any length-scale of film of any thickness

- 2 are invariant, 2 can be determined from a single film.
Example: deposition on patterned electrodes

- selective method
- widely used in microfabrication (‘through-mask plating’)
Example: deposition on patterned electrodes

Electrodeposited Co-Ni alloy pillars for patterned media studies. Patterning used interference lithography.

(Collaboration with C. A. Ross et al., M.I.T.)
Example: deposition on patterned electrodes

- edge $\rightarrow$ greater current density
- what happens to roughness?
• Edge significantly rougher than centre:

• *but* same scaling exponent $\beta + \beta_{\text{loc}}$

*R. Cecchini, J. J. Mallett and W. Schwarzacher
Tools for controlling morphology:

- Pulse electrodeposition
- High current density for ‘on’-pulse → high nucleation density
- Complexing agents and additives
Influence of additives

- When textured substrate used, Cl⁻ has major effect

13.5 min

Cu-on-Si substrate
No Cl⁻
Influence of additives

- When textured substrate used, Cl\(^{-}\) has major effect

Cu-on-Si substrate
0.25mM Cl

13.5 min
Topics:

- Controlling morphology
- The dual-damascene method
- Electroless deposition
- Multilayer electrodeposition
Metal interconnects in ultra large scale integrated circuits

- Electrodeposited Cu has replaced Al in ULSI
- Higher conductivity – better electromigration resistance

Through-mask plating

1 patterning

2 electrodeposition

3 seed layer etching

Damascene plating

1 patterning

2 electrodeposition

3 planarization
‘Superfilling’ needed to avoid defects

Early stages of plating

- Subconformal

Late stages of plating

- Void
- Conformal
- Superconformal (‘superfilling’)
- Defect-free
- Seam
Requires appropriate additives

- 1.8 M H$_2$SO$_4$
- 0.25 M CuSO$_4$
- 1 mM NaCl
- 88 µM PEG (M$_w$=3,400) n=77
- ~5 µM SPS/MPSA

D. Josell, B. Baker, D. Wheeler, C. Witt and T.P. Moffat,
Simple model:

- Additives act to block deposition
- Additive diffusion to recesses slow

Unfortunately this model is wrong!
Curvature Enhanced Accelerator Coverage Mechanism

- Metal deposition rate *increases* with catalyst coverage
- Local catalyst coverage increases as local area decreases - converse also true.

Curvature Enhanced Accelerator Coverage Mechanism

- Initial condition - catalyst coverage $\theta = 0$
- Catalyst accumulates from reaction with precursors in electrolyte
Curvature Enhanced Accelerator Coverage Mechanism

- Catalyst coverage increases on bottom, concave surface, may decrease on top, convex corners.
- Deposition rate highest at bottom of feature.
Curvature Enhanced Accelerator Coverage Mechanism

- Catalyst coverage maximized on bottom surface
- Metal deposition rate at bottom is accelerated.
Curvature Enhanced Accelerator Coverage Mechanism

- Catalyst coverage maximized on bottom surface.
- Metal deposition is highest on bottom.
Curvature Enhanced Accelerator Coverage Mechanism

- Inversion of curvature
  ‘Bottom’ is above trench.
  ‘Momentum plating’

- Catalyst coverage $\theta$ decreases as bump area increases
Topics:

- Controlling morphology
- The dual-damascene method
- Electroless deposition
- Multilayer electrodeposition
No need for electrical contact to substrate!

- Conventional electrodeposition: electrons that reduce metal ions in solution supplied from external circuit
- Electroless deposition: electrons generated at substrate by chemical reducing agent
- Need catalytically active surface
Example: electroless Cu

Typical electrolyte: 0.04 M CuSO$_4$, 0.08 M EDTA (ethylenediaminetetraacetic acid - complexing agent), 0.24M HCHO (formaldehyde - reducing agent), 0.4 mM 2,2’-bipyridyl (stabilizer)

\[
2 \text{ HCHO} + 4 \text{ OH}^- \rightarrow 2 \text{ HCOO}^- + 2 \text{ H}_2\text{O} + \text{ H}_2 + 2 \text{ e}^- \\
\]

\[
\text{CuEDTA}^{2-} + 2 \text{ e}^- \rightarrow \text{Cu}^0 + \text{EDTA}^4_{\text{ADS}} 
\]
Mixed potential theory

\[ M^{z+} + ze \rightarrow M_{\text{lattice}} \]

catalytic surface

\[ \text{Re}_{\text{solution}} \rightarrow \text{Ox}_{\text{solution}} + ne \]

catalytic surface

Oxidation

Potential

Reduction

log i

metal dissolution

metal deposition

electron generation

electron consumption
• Electroless deposition can deposit single metals e.g. Cu, Ni, Au or alloys e.g. CoFeB
• Despite versatility, under-exploited in nanotechnology

Topics:

- Controlling morphology
- The dual-damascene method
- Electroless deposition
- Multilayer electrodeposition
Multilayer electrodeposition

- Use electrolyte containing ions of more than one metal: pulse deposition → multilayer

- Typical example: 0.05M Cu$^{2+}$; 2.3M Ni$^{2+}$; 0.4M Co$^{2+}$
  -0.2V → pure Cu
  -1.6V → ferromagnetic Co-Ni-Cu alloy
Multilayer electrodeposition

• For 1-2 nm layers, electrodeposited multilayers show Giant Magnetoresistance

• Even greater effect with multilayer nanowires prepared by template deposition:
Multilayer electrodeposition

- Over 110% GMR at 77K, over 55% at room temperature
Multilayer electrodeposition

- What happens as layer thickness further reduced?
- Multilayer → heterogeneous alloy

Electrodeposition Research Group
Multilayer electrodeposition

- Can control Cu-Ni alloy composition through lengths of Cu and Ni pulses

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Application: alloy/alloy superlattice

$100 \times (\text{Cu}_{0.19}\text{Ni}_{0.81} \ 6\text{nm/ Cu}_{0.79}\text{Ni}_{0.21} \ 2\text{nm})$ alloy/alloy multilayer
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