Electrodeposition of nanomaterials

W. Schwarzacher
H. H. Wills Physics Laboratory,
University of Bristol

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Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
00 JUN 2003	**N/A**	-

4. TITLE AND SUBTITLE
Electrodeposition of Nanomaterials

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Physics Laboratory,University of Bristol

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release, distribution unlimited

13. SUPPLEMENTARY NOTES
See also ADM001697, ARO-44924.1-EG-CF, International Conference on Intelligent Materials (5th) (Smart Systems & Nanotechnology)., The original document contains color images.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			
unclassified	**unclassified**	**unclassified**	**UU**	**47**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

Introduction:

Electrodeposition

- has long history

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

Au applied to Cu by displacement plating.

From: ‘Pre-Columbian Surface Metallurgy’, H. Lechtman, Sci. Am. (1984).

Introduction:

Electrodeposition

- has long history
- is an important current technology

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Metal interconnects in ultra large scale integrated circuits

Cu interconnects on IBM chip

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

P. C. Andricacos, Interface, ***8****(1) (1999).*

Introduction:

Electrodeposition

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

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Topics:

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

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Topics:

- Controlling morphology
- The dual-damascene method
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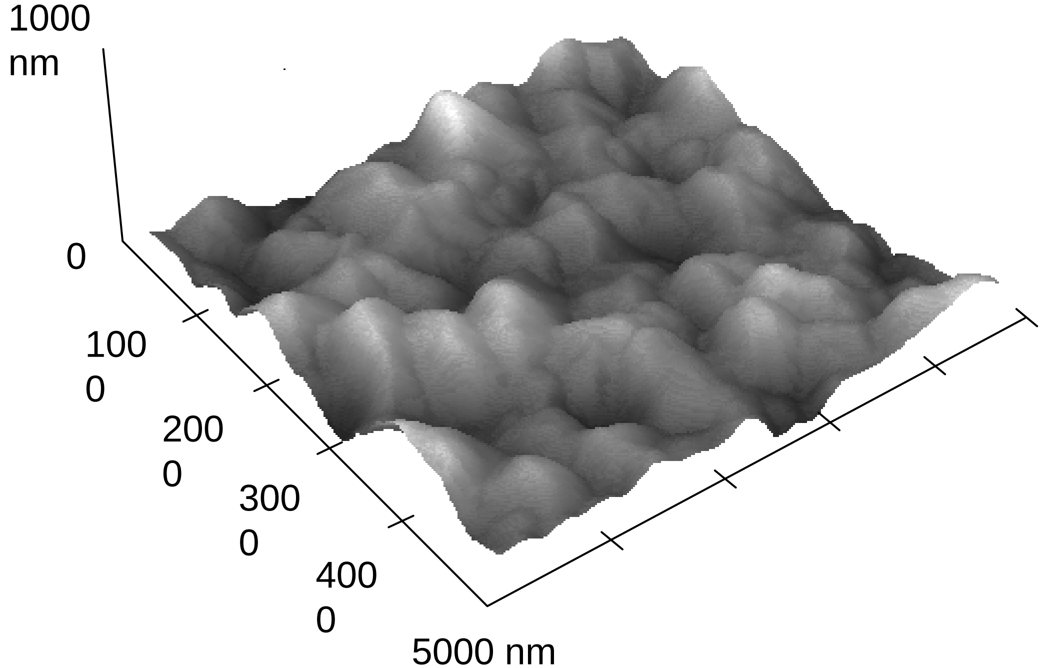
Why do electrodeposited thin films become rough?



AFM image of film electrodeposited from 0.3M $CuSO_4$ / 1.2M H_2SO_4, 4 mA cm^{-2}, *t=6 mins*

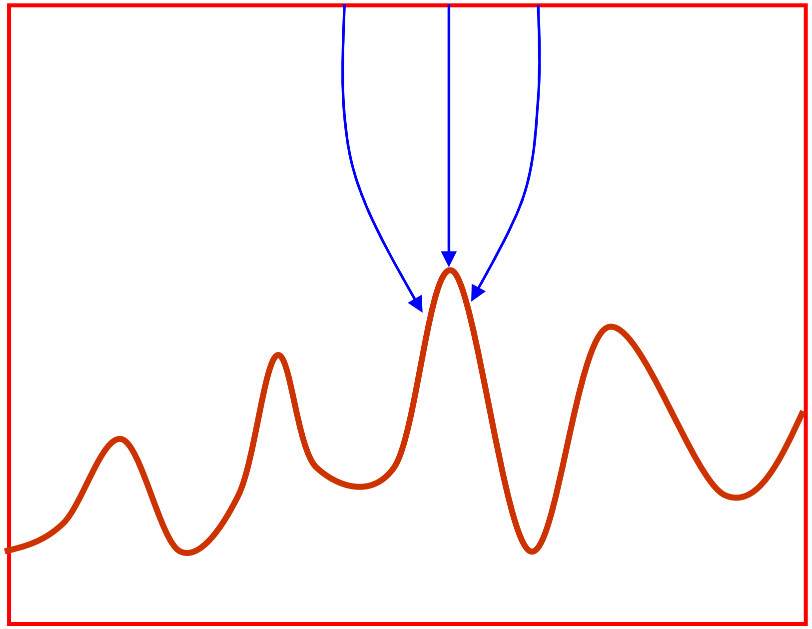
- Random fluctuations → noise
- Surface tension leads to smoothening

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

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

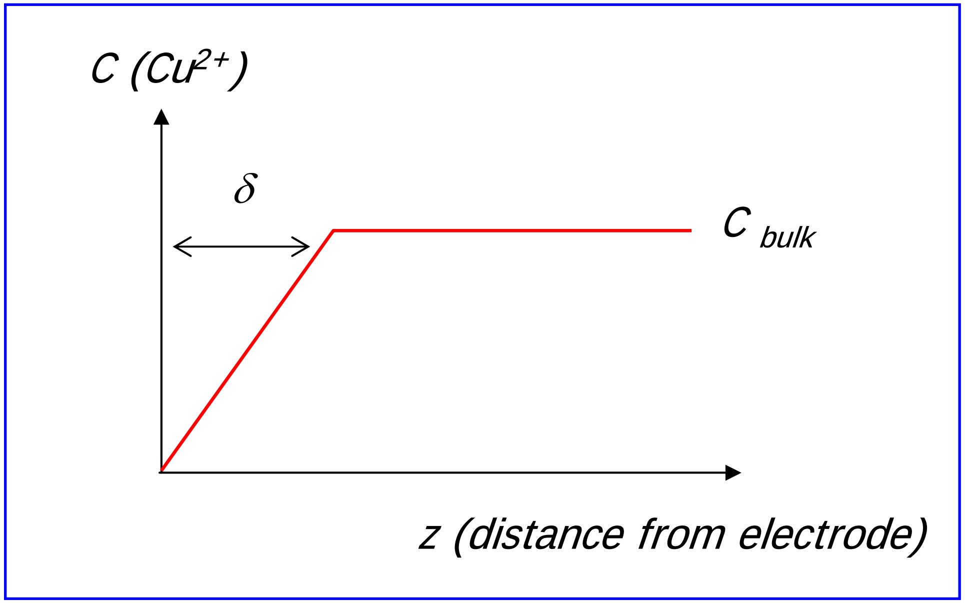
$$\partial h(\mathbf{x},t)/\partial t = -c\nabla^4 h(\mathbf{x},t) + \eta(\mathbf{x},t)$$

- Mass transport is by diffusion → *Laplacian instability*



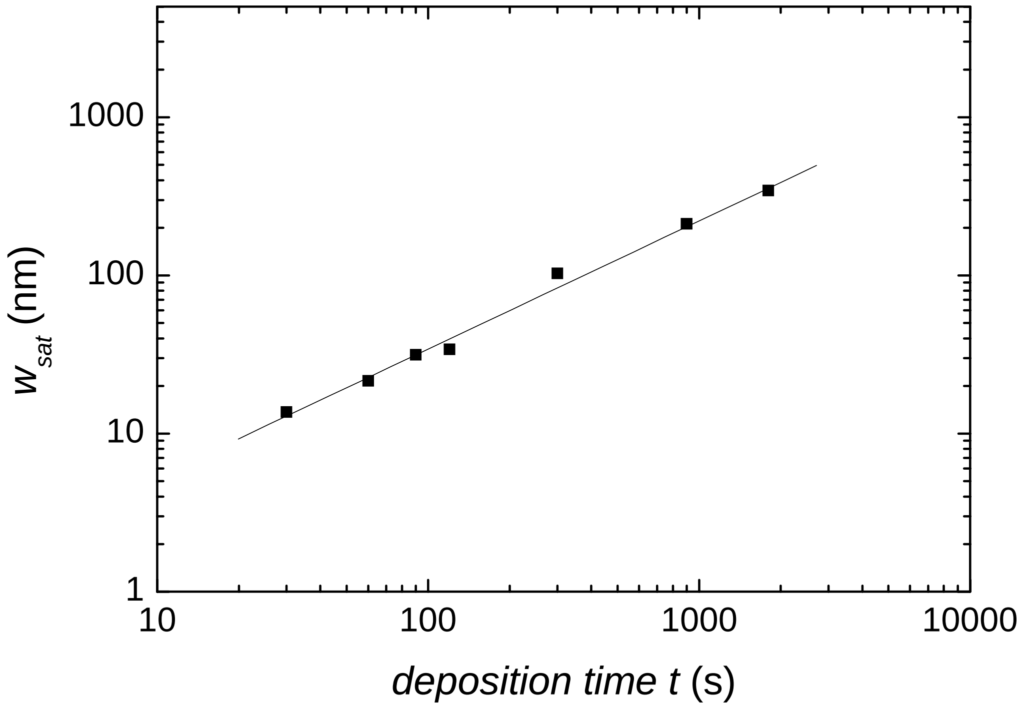
Peaks grow faster than valleys

Further consequences of diffusion:



- Diffusion limited current $\propto -D\dfrac{C_{bulk}}{\delta}$
- δ 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 β_{loc} changes.

- β_{loc} depends on ratio of current to diffusion-limited current – Laplacian instability

S. Huo and W. Schwarzacher, Phys. Rev. Lett. ***86****, 256 (2001)*

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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.

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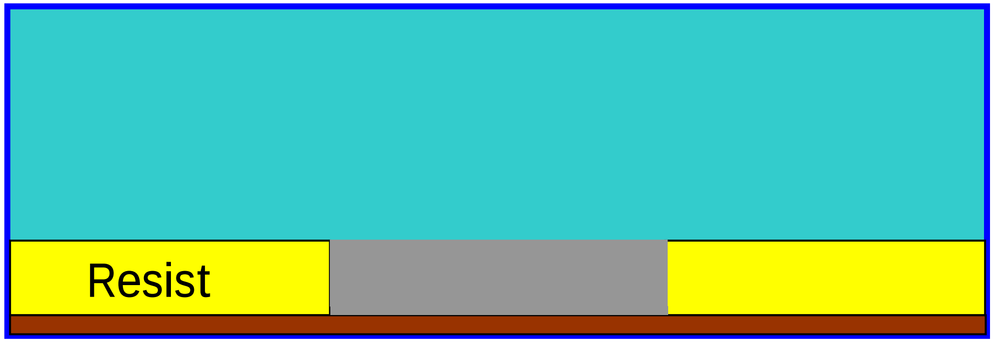
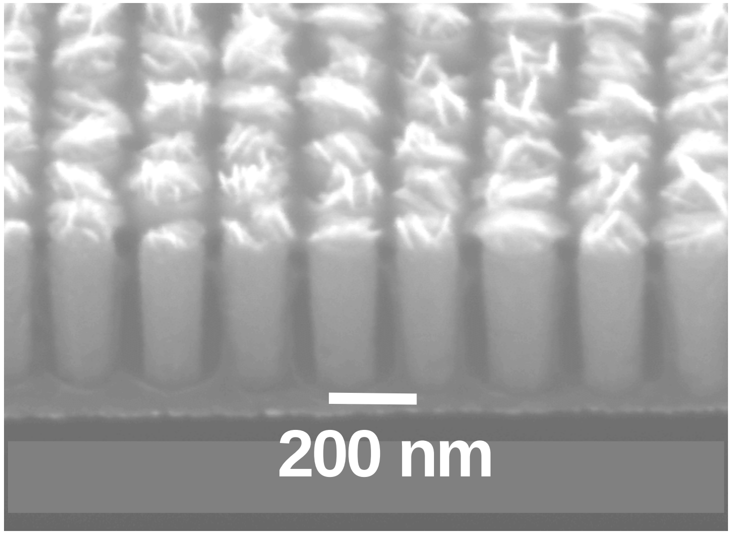
Example: deposition on patterned electrodes



- selective method
- widely used in microfabrication ('through-mask plating')

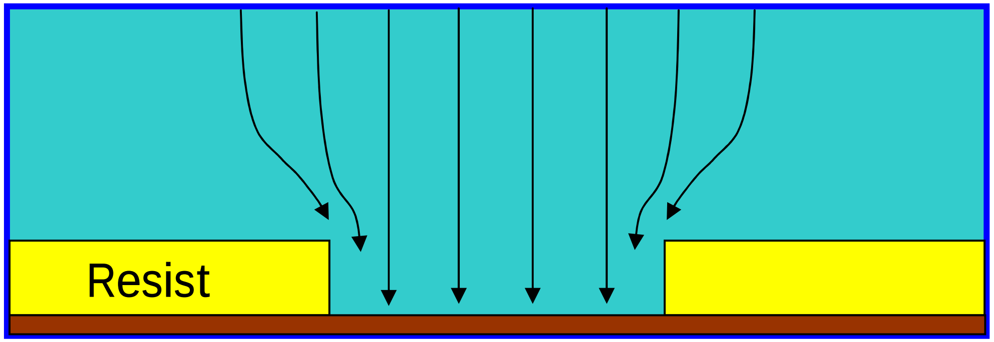
Example: deposition on patterned electrodes



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

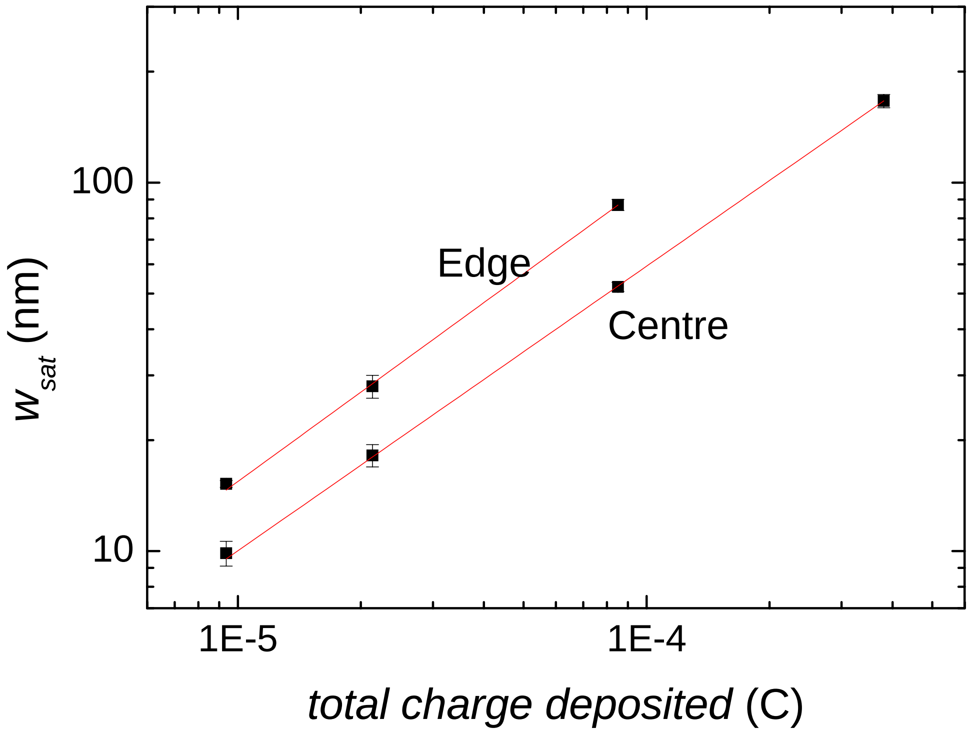
(Collaboration with C. A. Ross et al., M.I.T.)

Example: deposition on patterned electrodes



- edge → greater current density
- what happens to roughness?

- Edge significantly rougher than centre:

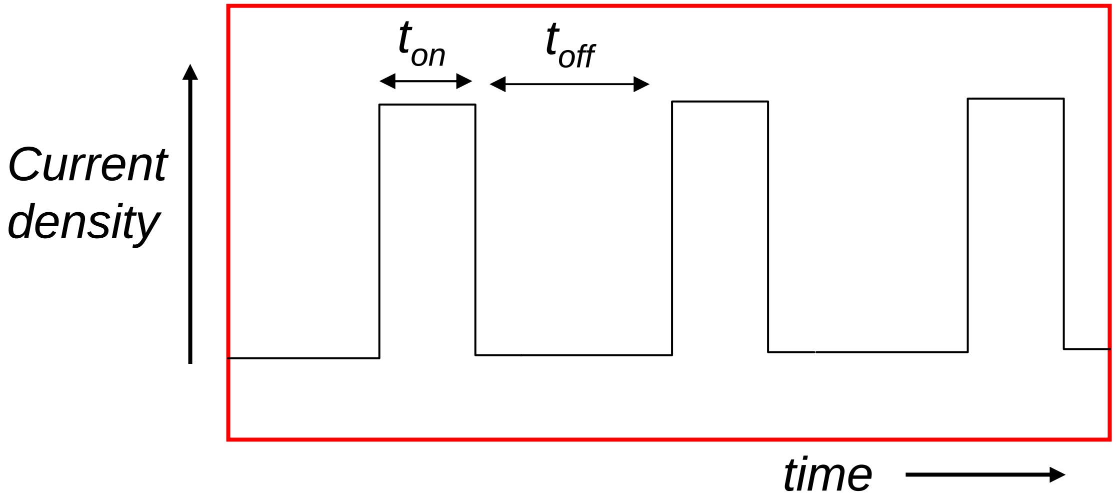


- *but* same scaling exponent $\beta+\beta_{loc}$

R. Cecchini, J. J. Mallett and W. Schwarzacher
(Electrochem. Sol. State Lett., in press)

Tools for controlling morphology:

- Pulse electrodeposition



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

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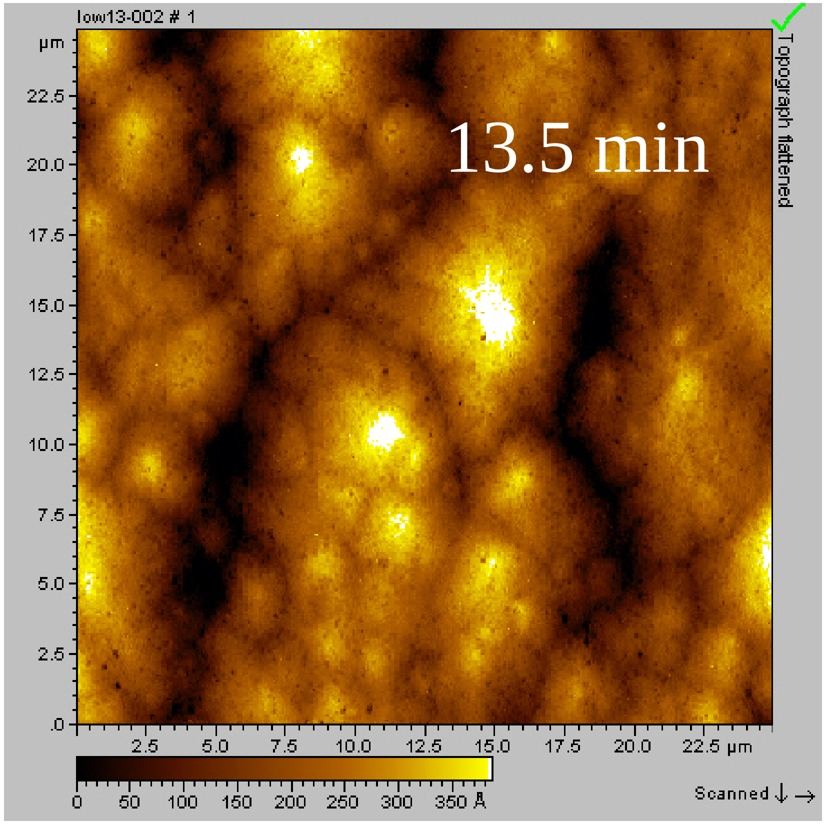
Influence of additives

- When textured substrate used, Cl^- has major effect



Cu-on-Si substrate
No Cl^-

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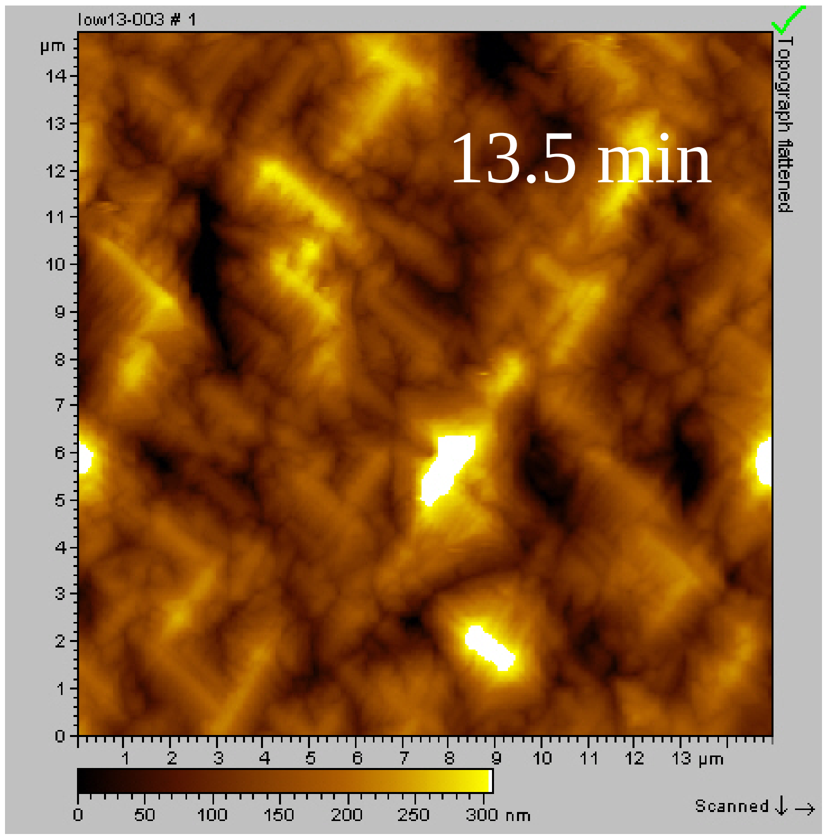
Influence of additives

- When textured substrate used, Cl^- has major effect



Cu-on-Si substrate
0.25mM Cl

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Topics:

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

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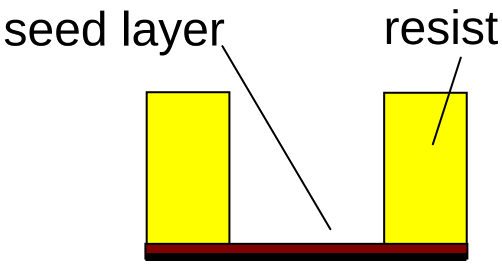
Metal interconnects in ultra large scale integrated circuits

Cu interconnects on IBM chip

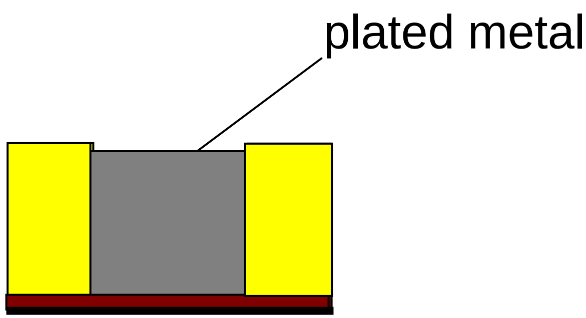
- electrodeposited Cu has replaced Al in ULSI
- higher conductivity – better electromigration resistance

P. C. Andricacos, Interface, ***8****(1) (1999).*

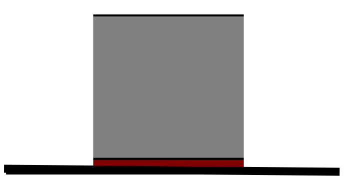
Through-mask plating



1 patterning

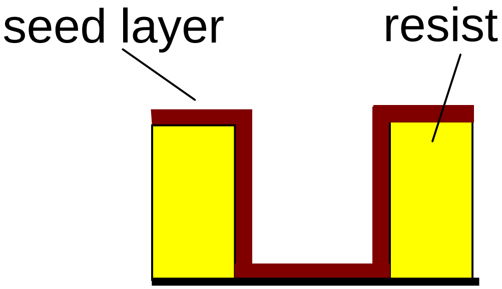


2 electrodeposition

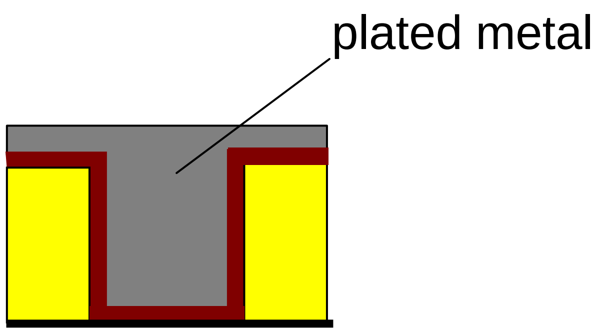


3 seed layer etching

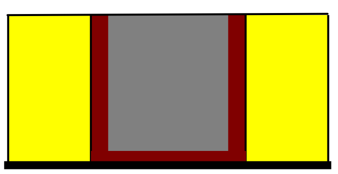
Damascene plating



1 patterning

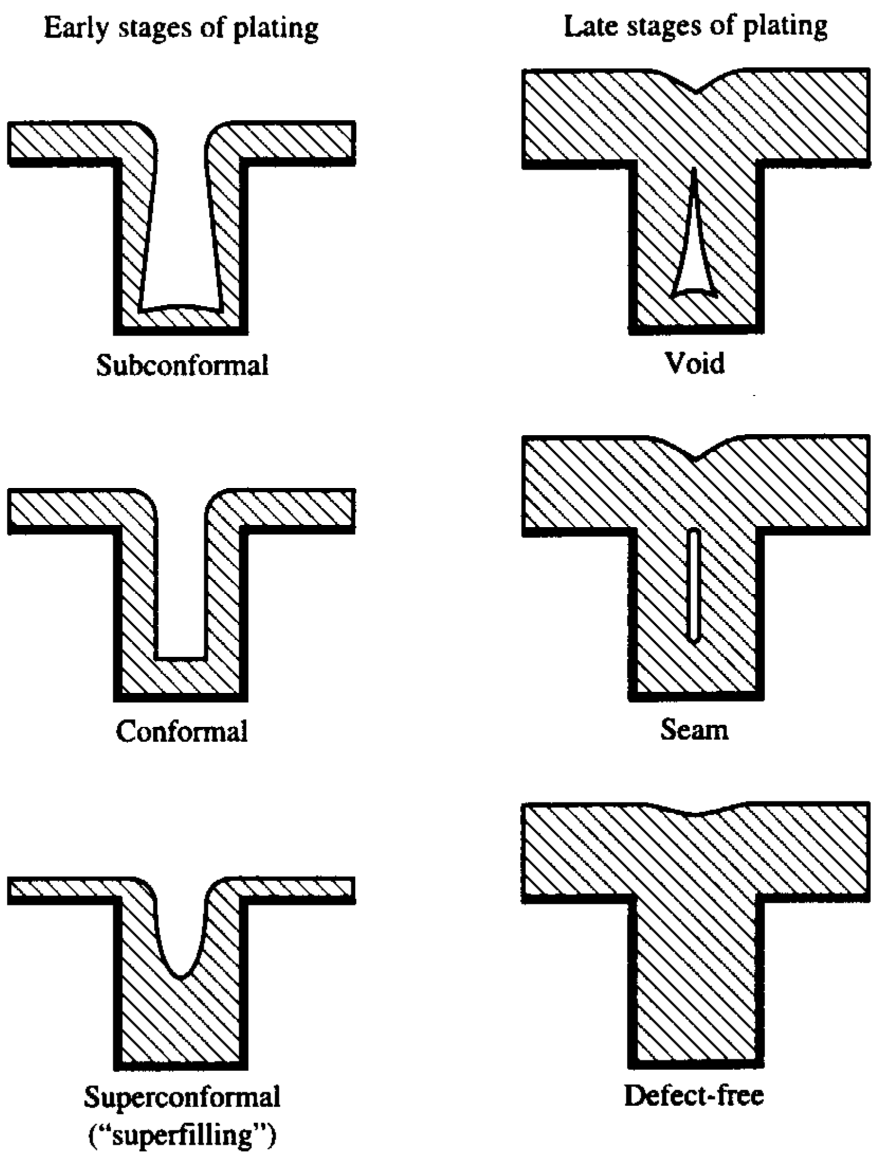


2 electrodeposition

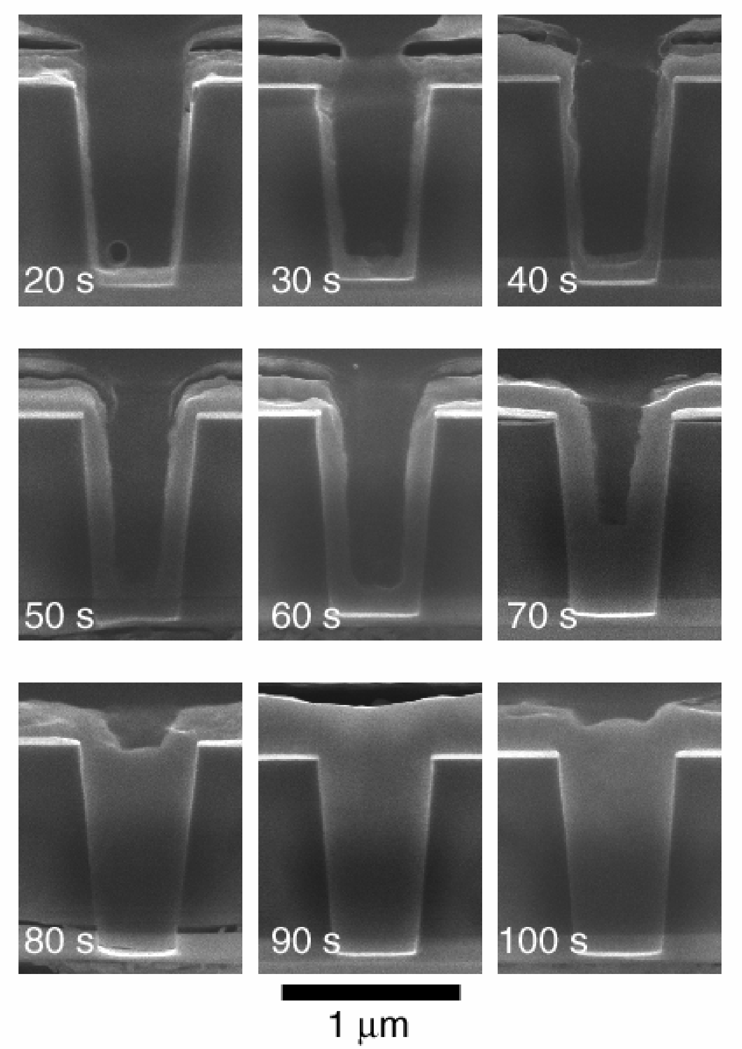


3 planarization

‘Superfilling’ needed to avoid defects



Requires appropriate additives

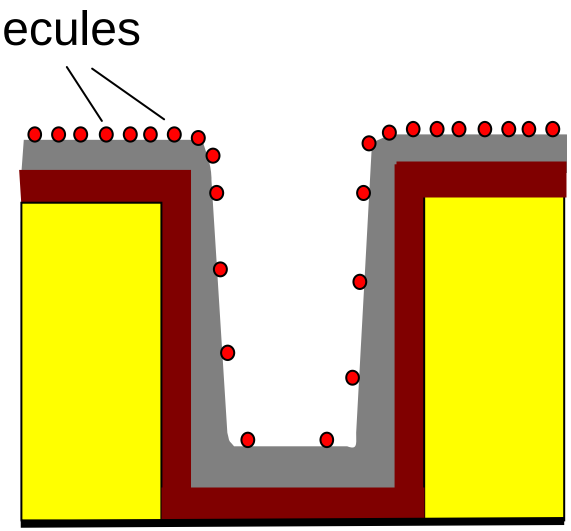


- 1.8 M H_2SO_4
- 0.25 M $CuSO_4$
- 1 mM NaCl
- 88 μM PEG (M_w=3,400) n=77
- ~ 5 μM SPS/MPSA

D. Josell, B. Baker, D. Wheeler, C. Witt and T.P. Moffat,
J. Electrochem. Soc. **149**, C637 (2002).

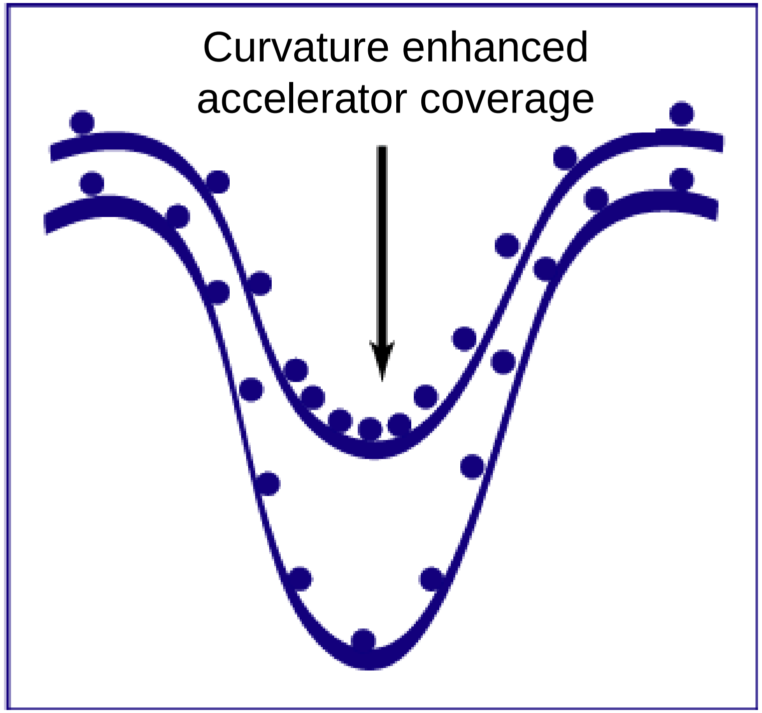
Simple model:

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



Unfortunately this model is wrong!

Curvature Enhanced Accelerator Coverage Mechanism

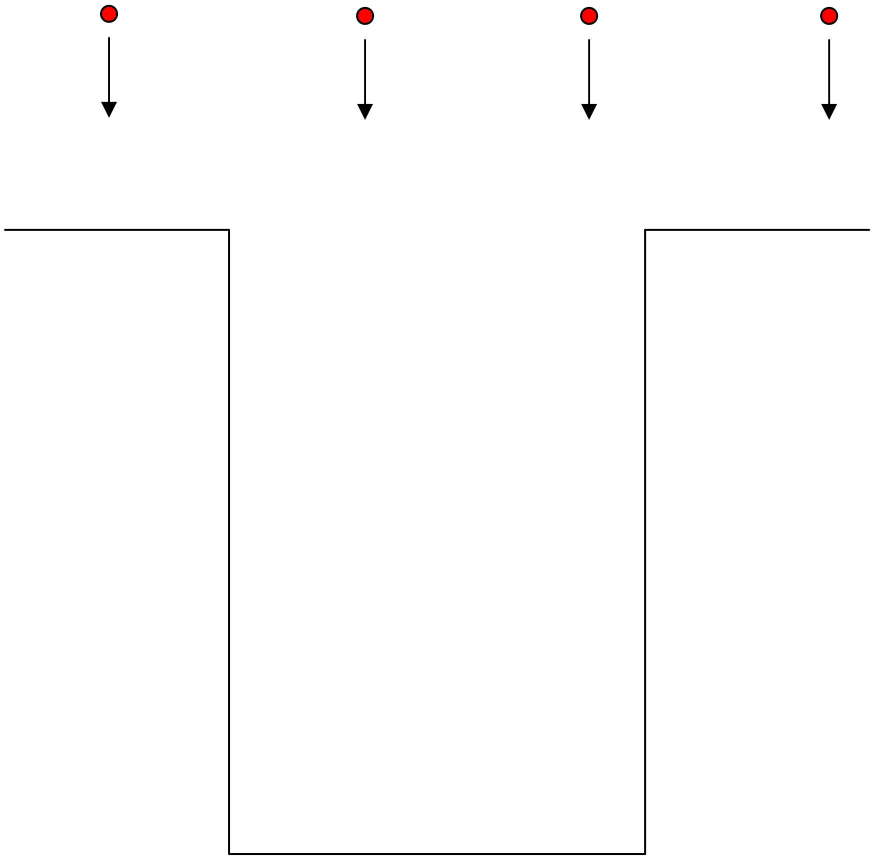


- Metal deposition rate *increases* with catalyst coverage
- Local catalyst coverage increases as local area decreases - converse also true.

T.P. Moffat, D. Wheeler, W.H. Huber and D. Josell, Electrochemical and Solid-State Letters **4**, C26 (2001).

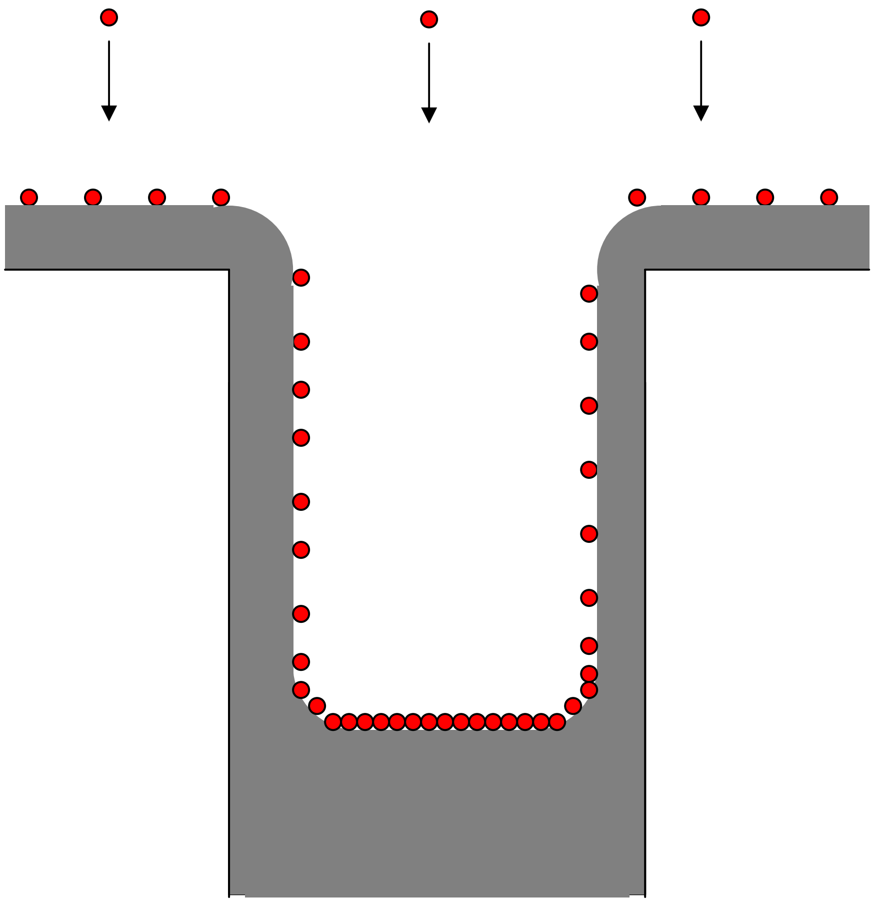
Curvature Enhanced Accelerator Coverage Mechanism

- Initial condition - catalyst coverage $\theta = 0$
- Catalyst accumulates from reaction with precursors in electrolyte



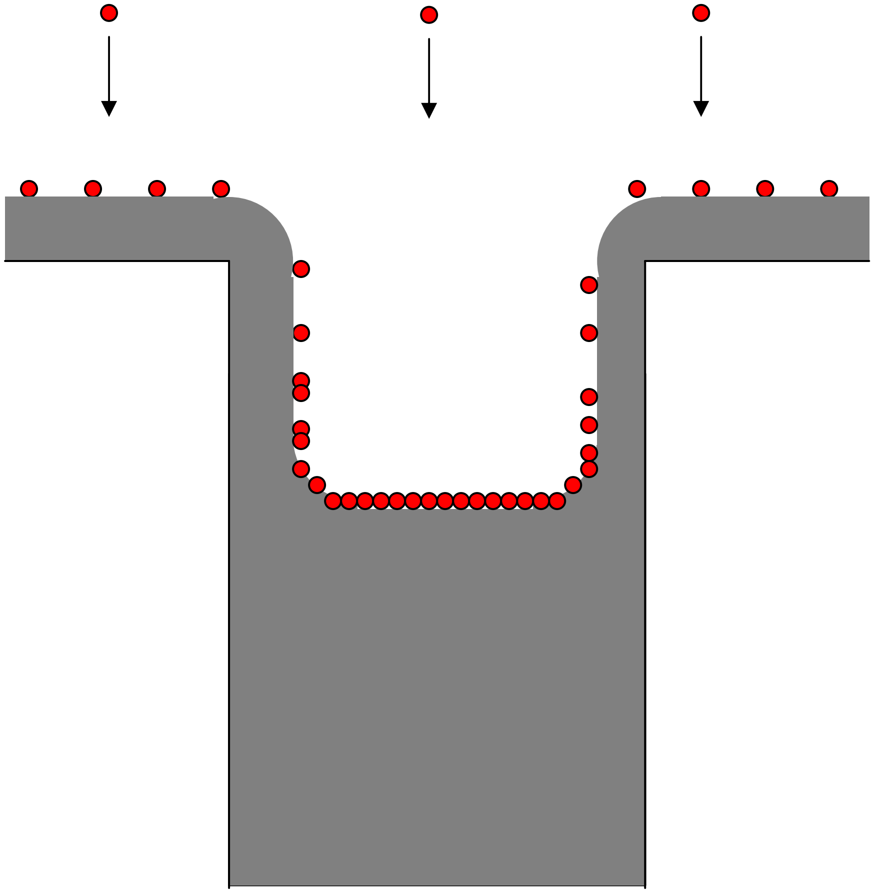
Curvature Enhanced Accelerator Coverage Mechanism

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



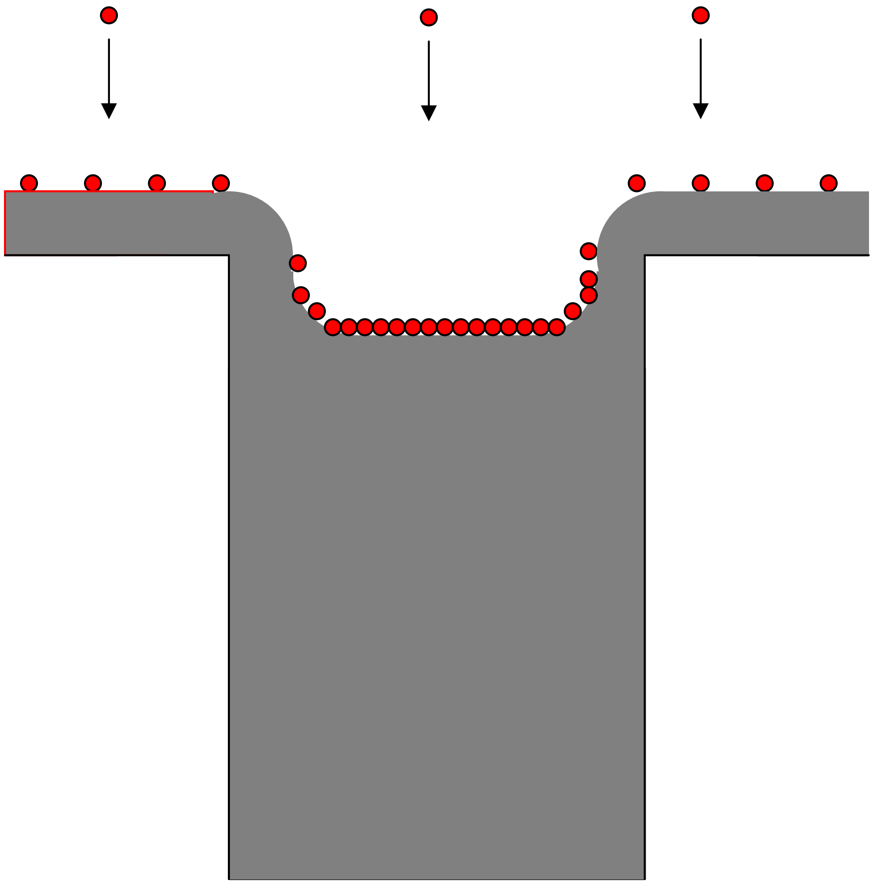
Curvature Enhanced Accelerator Coverage Mechanism

- 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



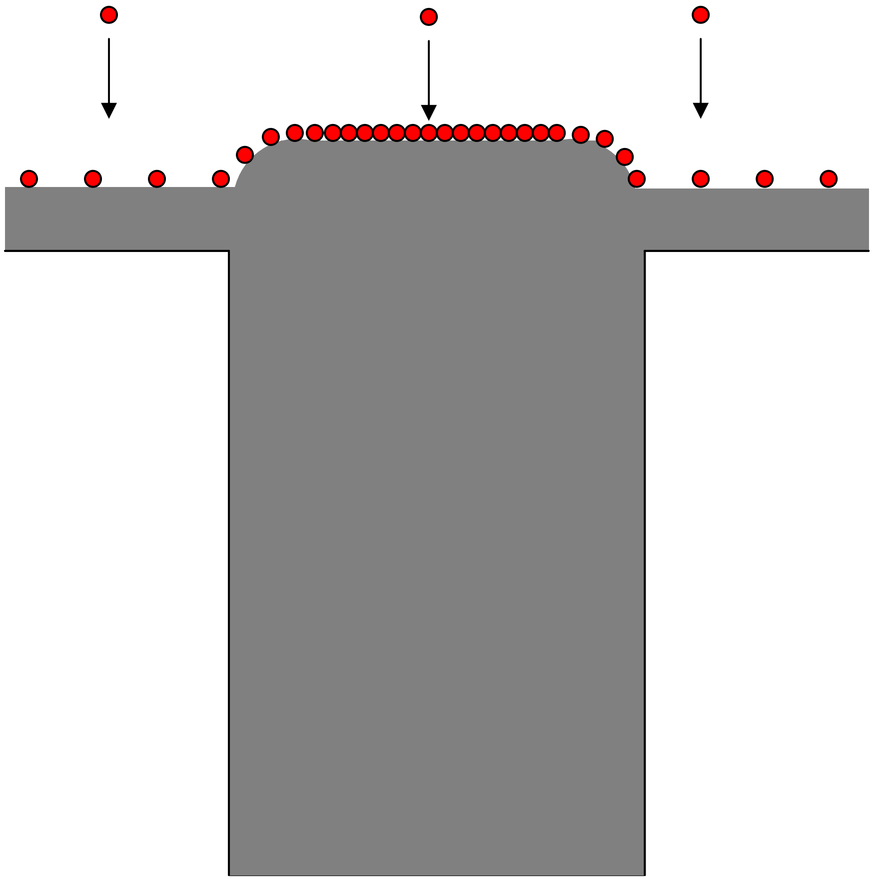
Curvature Enhanced Accelerator Coverage Mechanism

- Inversion of curvature

  ‘Bottom’ is above trench.

  ‘Momentum plating’

- Catalyst coverage θ decreases as bump area increases



Topics:

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

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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

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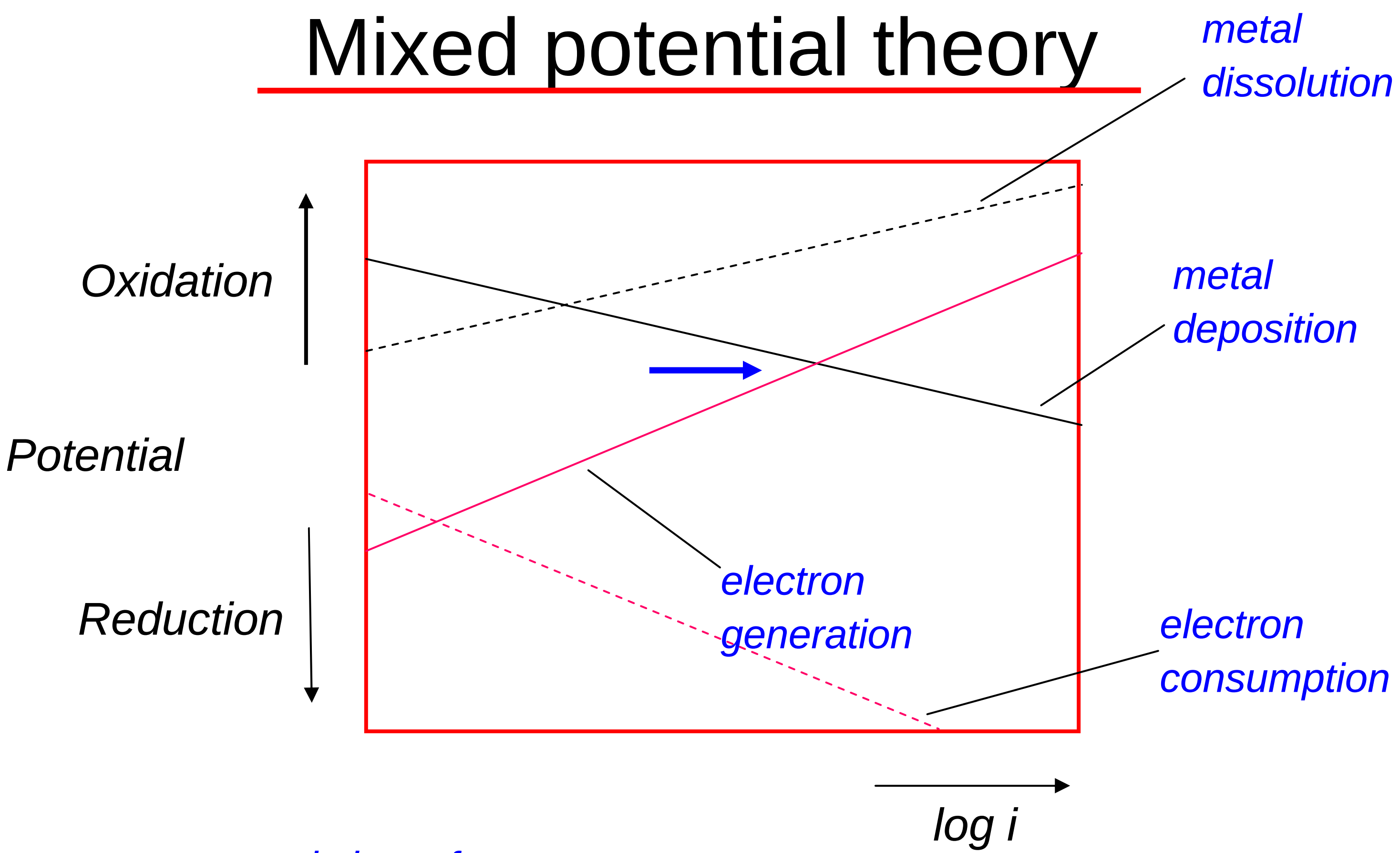
Example: electroless Cu

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)

$$2\ HCHO + 4\ OH^- \rightarrow 2\ HCOO^- + 2\ H_2O + H_2 + 2\ e^-$$

$$CuEDTA^{2-} + 2\ e^- \rightarrow Cu^0 + EDTA^{4-}{}_{ADS}$$

Mixed potential theory



$$M^{z+} + ze \xrightarrow{\text{catalytic surface}} M_{lattice}$$

$$Re_{solution} \xrightarrow{\text{catalytic surface}} Ox_{solution} + ne$$

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

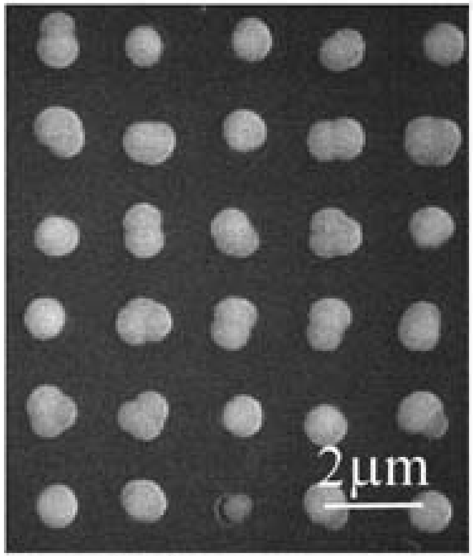


Fig.2 SEM micrograph of nickel dots on silicon wafer.

T.Osaka, N.Takano, S.Komaba; *Chem. Lett*., **7** 657 (1998)

Topics:

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- The dual-damascene method
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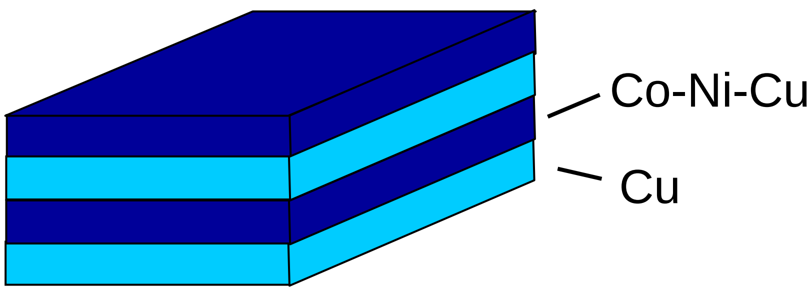
Multilayer electrodeposition

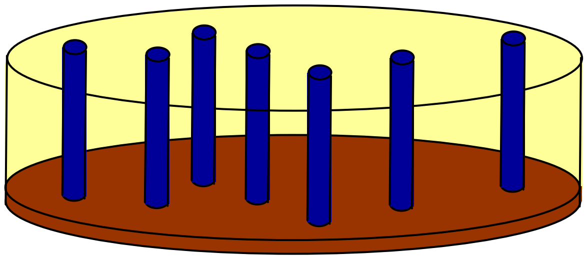
- Use electrolyte containing ions of more than one metal: pulse deposition → multilayer

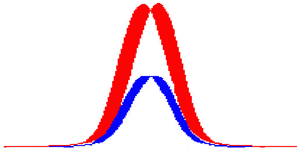
- Typical example: 0.05M Cu^{2+}; 2.3M Ni^{2+}; 0.4M Co^{2+}
  - -0.2V → pure Cu
  - -1.6V → ferromagnetic Co-Ni-Cu alloy



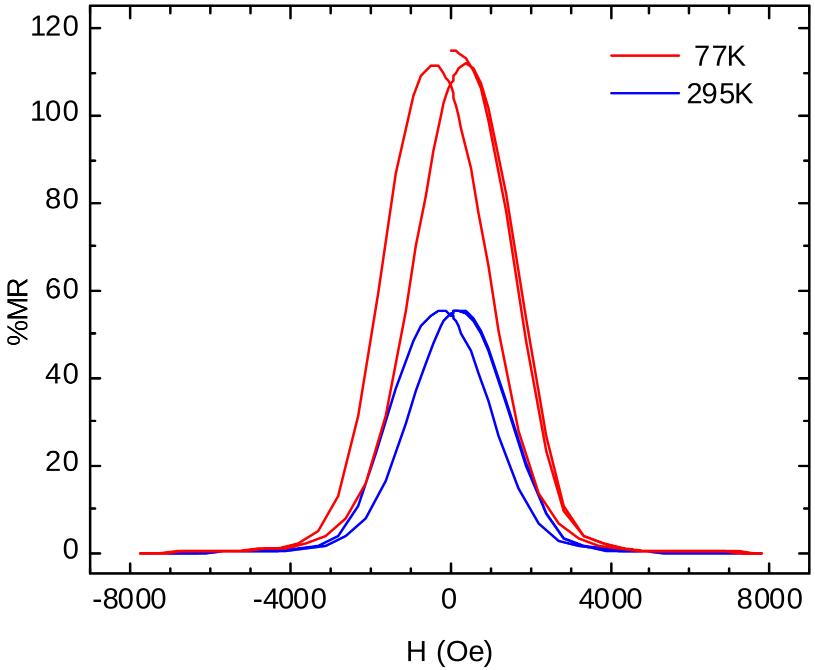
Multilayer electrodeposition

- For 1-2 nm layers, electrodeposited multilayers show *Giant Magnetoresistance*
- Even greater effect with multilayer nanowires prepared by template deposition:





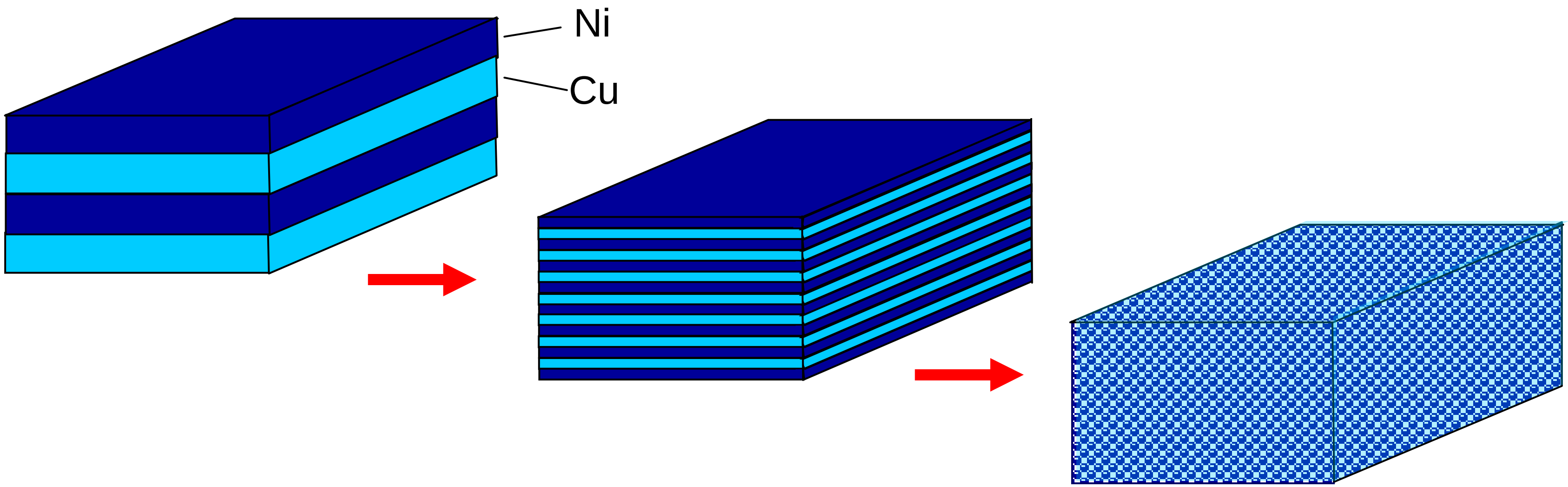
Multilayer electrodeposition



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

Multilayer electrodeposition

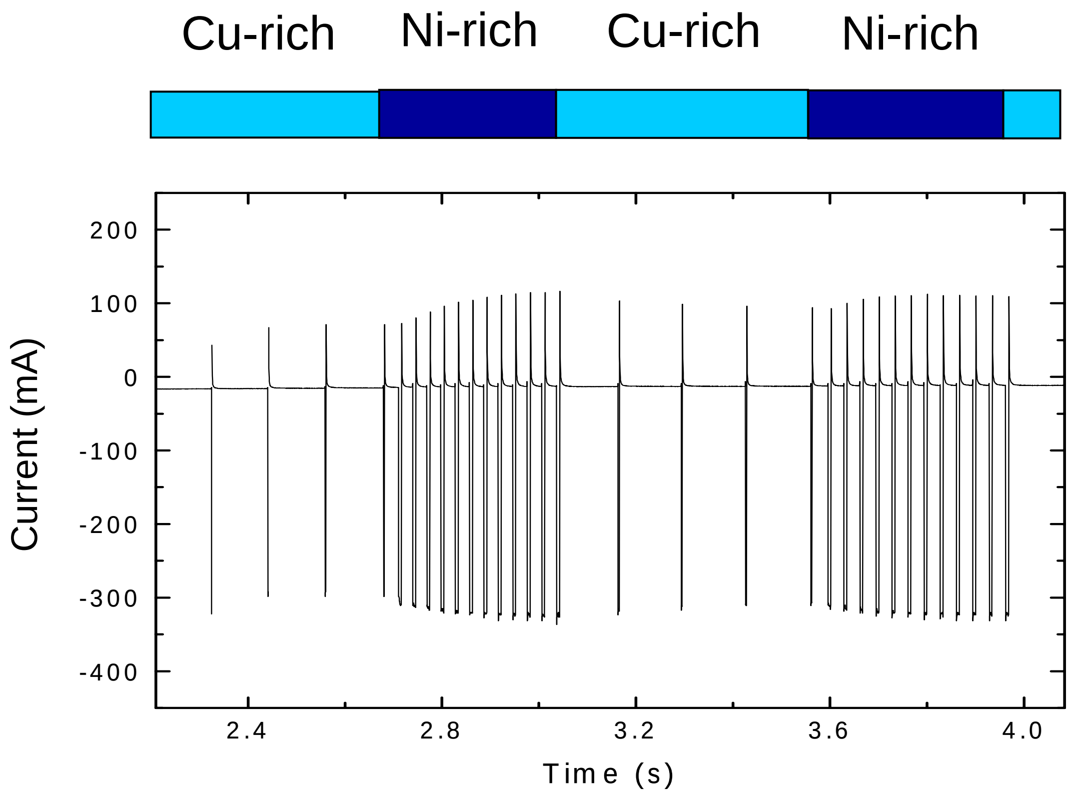
- What happens as layer thickness further reduced?
- Multilayer → heterogeneous alloy



Electrodeposition Research Group

Multilayer electrodeposition

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



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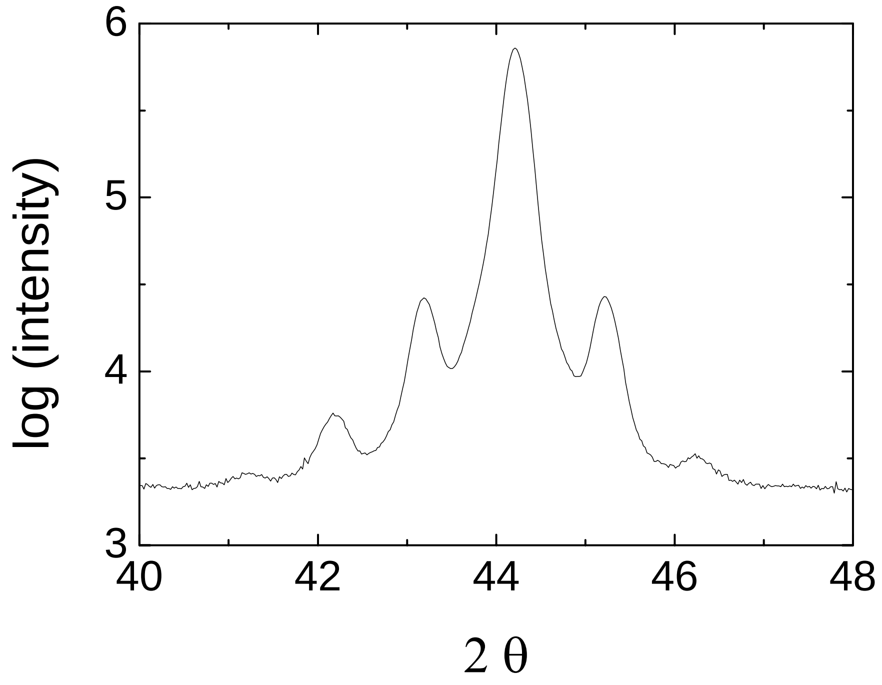
Application: alloy/alloy superlattice



100×($Cu_{0.19}Ni_{0.81}$ 6nm/ $Cu_{0.79}Ni_{0.21}$ 2nm) alloy/alloy multilayer

Acknowledgments:

S. Huo, J. J. Mallet, R.Cecchini and P. Evans (Bristol)

T. P. Moffat (NIST)

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