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Electrochemistry for Materials Technology

Chapter 1. Fundamentals of Electrodeposition

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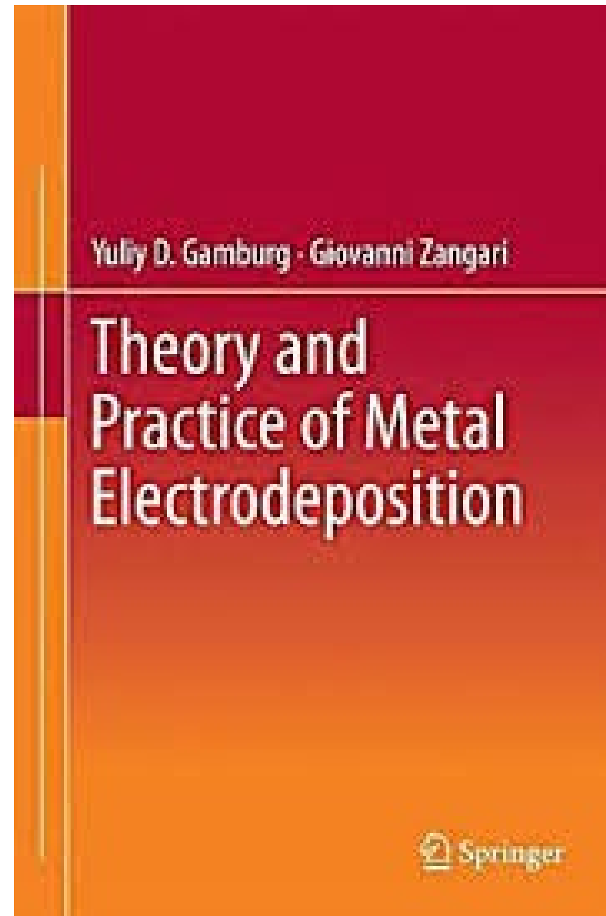

Theory and Practice of Metal Electrodeposition (English) , 2011

Yuliy D. Gamburg , Giovanni Zangari Springer

1. Electrolytic plating (electroplating)

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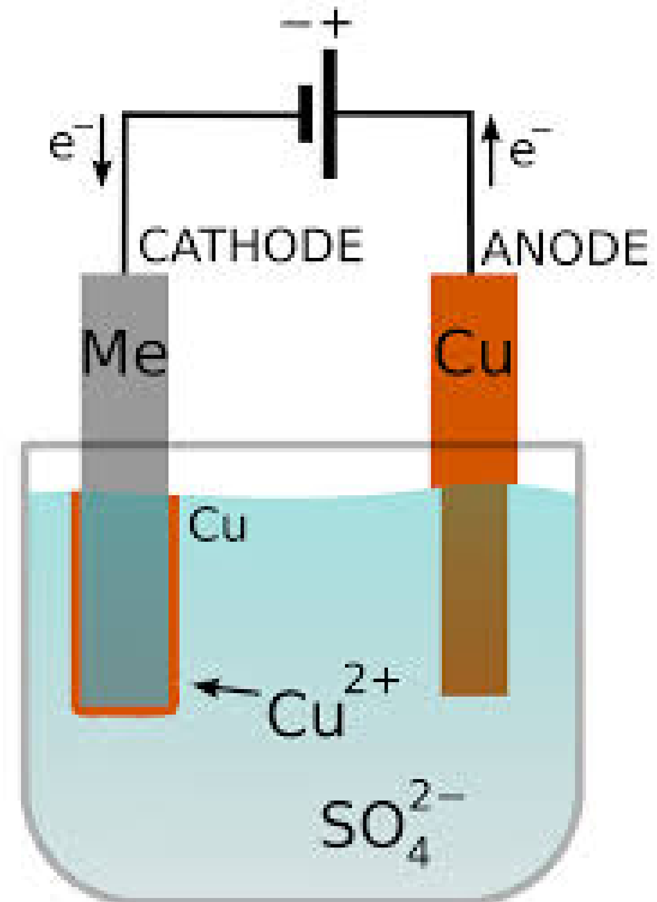
- Uses electrical current to reduce metal ions (drive chemical reaction)
- All features need to be electrically connected
- Allows control of the plating process



2. Immersion Plating (displacement reaction)

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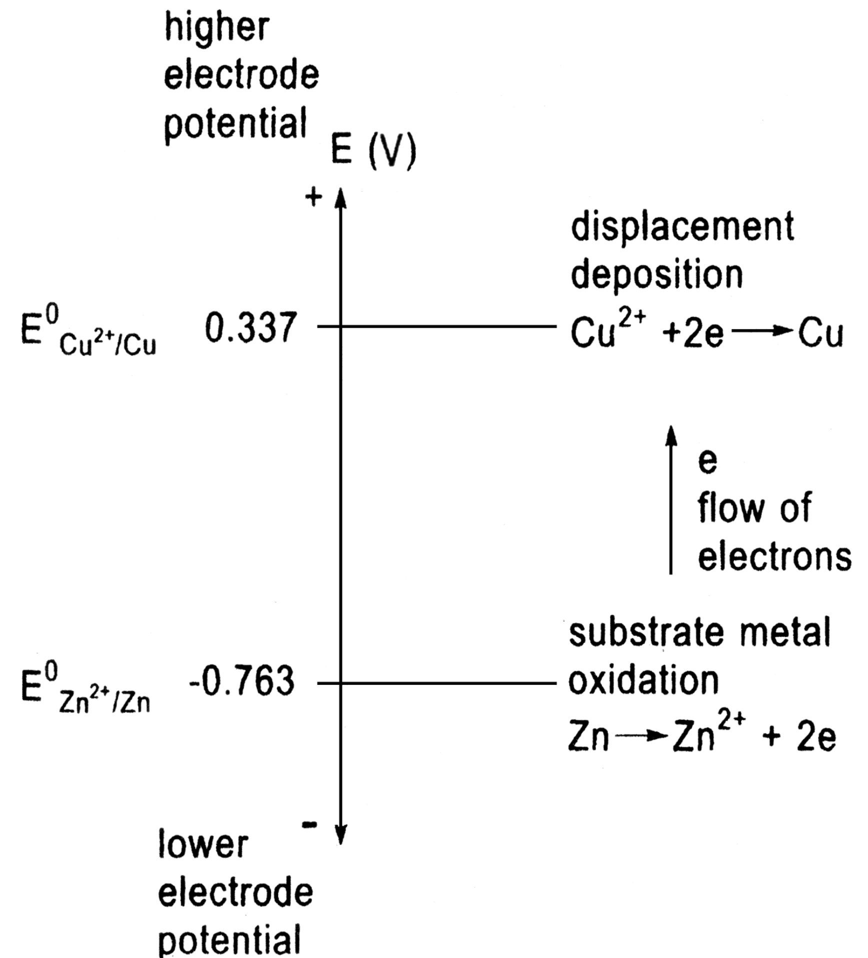
- Metal ion is reduced from solution by exchange with a metal atom from the substrate
- Type of metal deposited must be more noble : higher Electromotive Force (EMF, Eo) than the metal dissolved
- Deposition stops after few microns of deposition



3. Electroless Plating (autocatalytic)

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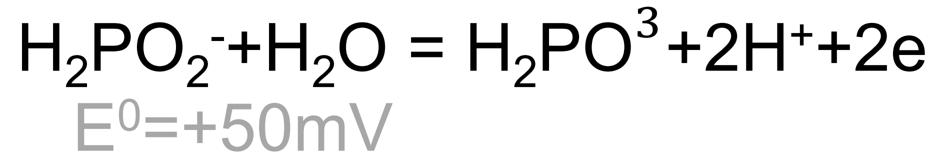
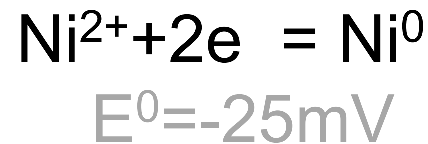
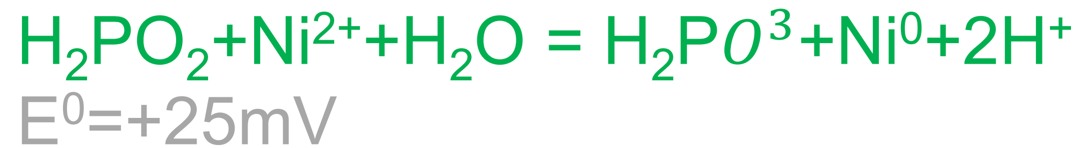
- Chemical reaction induces metal atom reduction
- Non-conductive substrates
- Features do not need to be electrically connected
- Difficult to control plating parameters
- Limited bath lifetime







Immersion versus electroless plating

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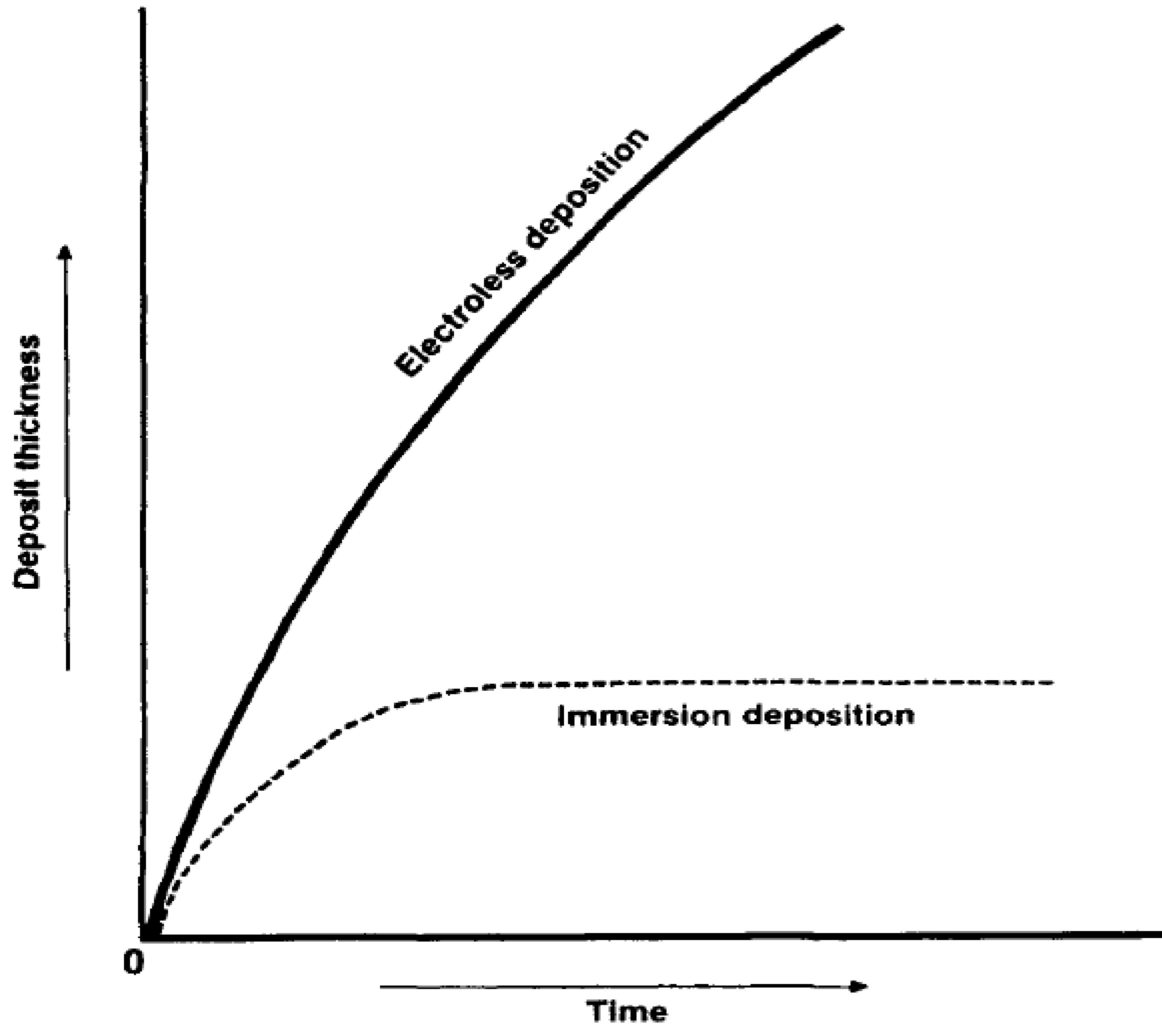

Plating Processes

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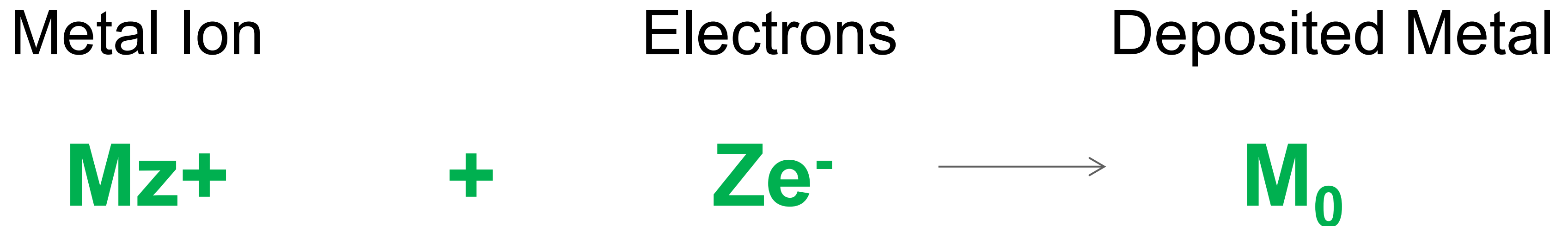
Reduction of metal ions from solution



Source for this reduction:

- Electrolytic plating- Applied current
- Electroless plating- chemical reaction in solution
- Displacement plating- dissolution of electrode metal

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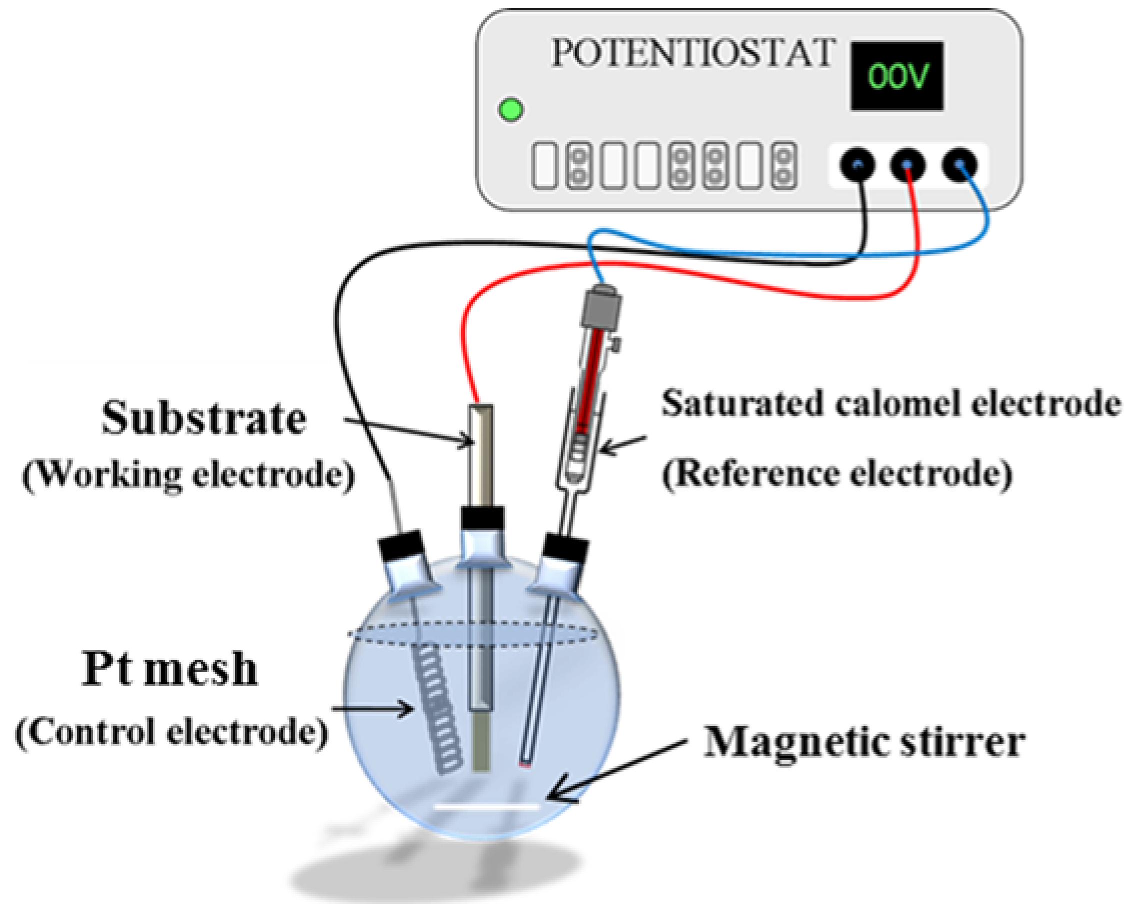
Electroplating-electrically driven REDOX reactions



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Electrochemical Potential E_0

- More positive Eo: stronger oxidation agent (electron acceptor)
- More positive Eo : more noble metal
- More negative Eo :stronger reducing agent (electron donor)

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The electromotive force E_0

Metal/Metal Ion Couple	Electrode Reaction	Standard Value (V)
Au/Au^{+}	$Au^{+} + e \Leftrightarrow Au$	1.692
Au/Au^{3+}	$Au^{3+} + 3e \Leftrightarrow Au$	1.498
Pd/Pd^{2+}	$Pd^{2+} + 2e \Leftrightarrow Pd$	0.951
Cu/Cu^{+}	$Cu^{+} + e \Leftrightarrow Cu$	0.521
Cu/Cu^{2+}	$Cu^{2+} + 2e \Leftrightarrow Cu$	0.3419
Fe/Fe^{3+}	$Fe^{3+} + 3e \Leftrightarrow Fe$	−0.037
Pb/Pb^{2+}	$Pb^{2+} + 2e \Leftrightarrow Pb$	−0.1262
Ni/Ni^{2+}	$Ni^{2+} + 2e \Leftrightarrow Ni$	−0.257
Co/Co^{2+}	$Co^{2+} + 2e \Leftrightarrow Co$	−0.28
Fe/Fe^{2+}	$Fe^{1+} + 2e \Leftrightarrow Fe$	−0.447
Zn/Zn^{2+}	$Zn^{2+} + 2e \Leftrightarrow Zn$	−0.7618
Al/Al^{3+}	$Al^{3+} + 3e \Leftrightarrow Al$	−1.662
Na/Na^{+}	$Na^{+} + e \Leftrightarrow Na$	−2.71

Source: G. Millazzo and S. Caroli, *Tables of Standard Electrode Potentials*, Wiley, New York, 1978.

Least tendency to corrode

Greatest tendency to corrode

Faraday's law

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$$W = \frac{A_{wt}}{nF} Q$$

$W \; is \; weight \; of \; product$
$A_{wt} \; atomic \; weight, n \; numbre \; of \; electrons \; involved \; in \; the \; reaction$
$F \; Faraday \; constant \;\; 96487 \; Cmol^{-1}$
$Q \; electric \; charge$

- Used to determine a relationship between plating conditions and amount of metal deposited
- Valid as long as no side reactions are occurring

Exercise1

The weight of a Co deposit is 0.00208 g on a substrate of surface (a) 7.5cm^2
What is the thickness h of the Co deposit? Density Co (d) 8.71gcm^{-3}

Exercise 2

Determine the time required to obtain a Cu deposit of thickness 1 micron when electrodeposition is done at 4A. The surface area (a) of the cathode is 314 cm^2.

Current efficiency

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Current efficiency

‘Current efficiency CE of an jth process is defined as the number of coulombs required for that reaction Qj divided by the total number of coulombs passed Qtotal’

$$CE = Q_j / Q_{total} = w_j / w_{total}$$

Side reactions

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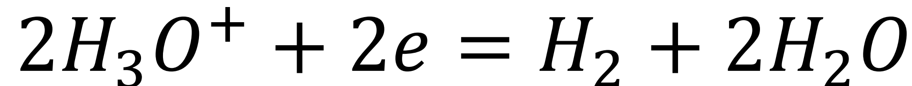
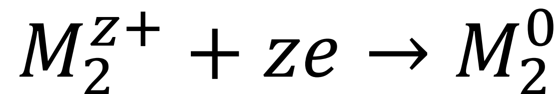
1) Hydrogen evolution

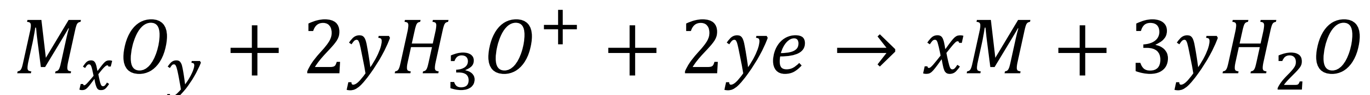


2) (co-deposition) other metal



3) Partial reduction of metal ions

4) Reduction of surface oxide layers



Exercice 3

When a current of 3A flows for 8 minutes through a cell composed of two Pt electrodes in a solution of Cu(NO3) in dilute HNO3 acid, 0.36g of Cu is deposited on the cathode.
Calculate the current efficiency for the deposition of copper
(Atomic weight 63.55).

Current efficiency

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CE depends on:

- Metal
- Solution type
- Temperature
- CD
- convection
- pH

Metal	Type of the electrolyte	Average cathodic efficiency
Ag	Cyanide	0.98
Au	Citrate	0.60
Au	Phosphate	0.95
Cd	Cyanide	0.90
Cd	Sulf.-ammonia	0.90
Co	Sulfate	0.88
Cr	Chromate	0.18
Cu	Sulfate	1.00
Cu	Cyanide	0.75
Cu	Pyrohosphate	0.99
Fe	Chloride	0.90
Fe	Sulfate	0.92
Fe	Fluoroboric	0.95
Ni	Sulfate	0.96
Ni	Sulfamate	0.98
Pb	Fluoroboric	0.99
Pd	Amino-chloride	0.80
Re	Sulf.-ammonia	0.25
Rh	Sulfate	0.70
Sb	Citrate	0.94
Sn	Stannate	0.80
Sn	Pyrophosphate	0.90
Sn	Sulfate	0.95
Zn	Cyanide	0.80
Zn	Sulfate	0.97

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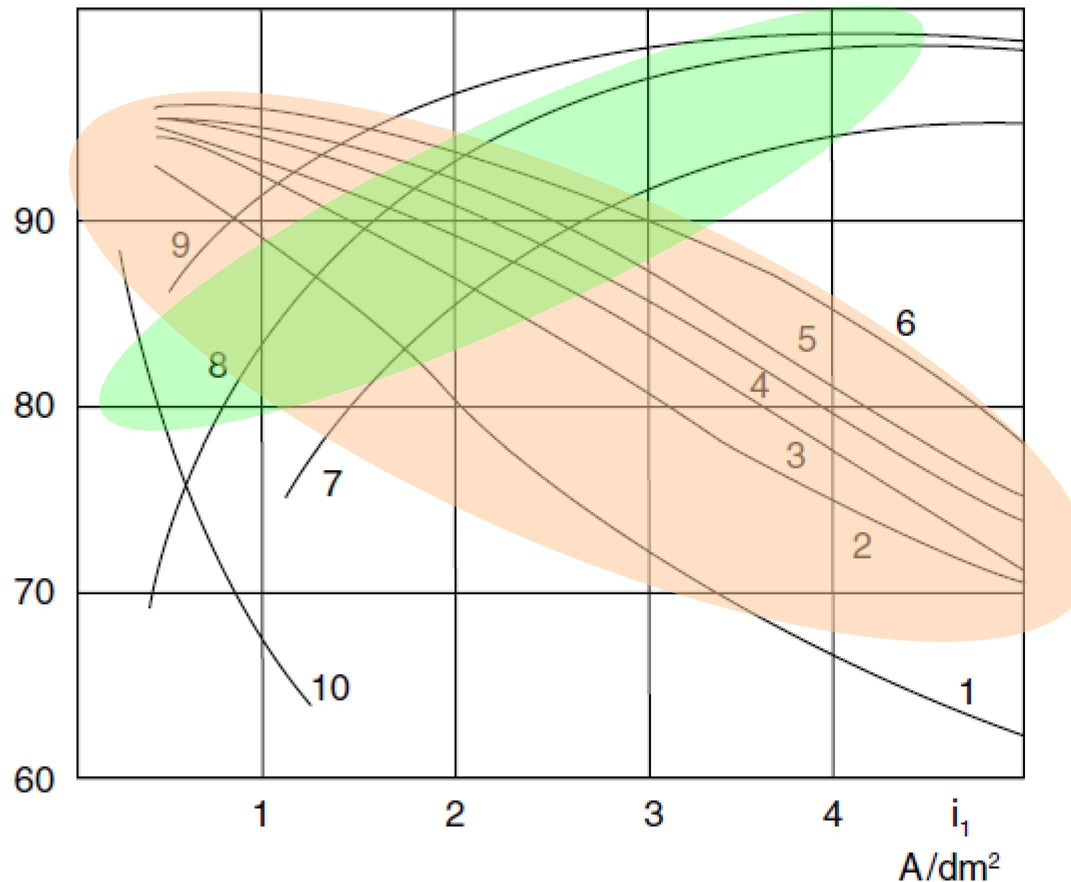

Au/Au^{+}	1.69
Cu/Cu^{2+}	0.34
Fe/Fe^{3+}	-0.04
Ni/Ni^{2+}	-0.26
Zn/Zn^{2+}	-0.76

Dependence of cathodic current efficiencies on current density for various metal deposition processes

1. *Copper cyanide solution, 2 cadmium cyanide, 3 copper pyrophosphate, 4 tin stanate, 5 antimony citrate, 6 zinc cyanide, 10 gold citrate*

7 iron sulfate, 8 nickel sulfate, 9 zinc sulfate

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What happens during deposition?

Electrolyte dynamics

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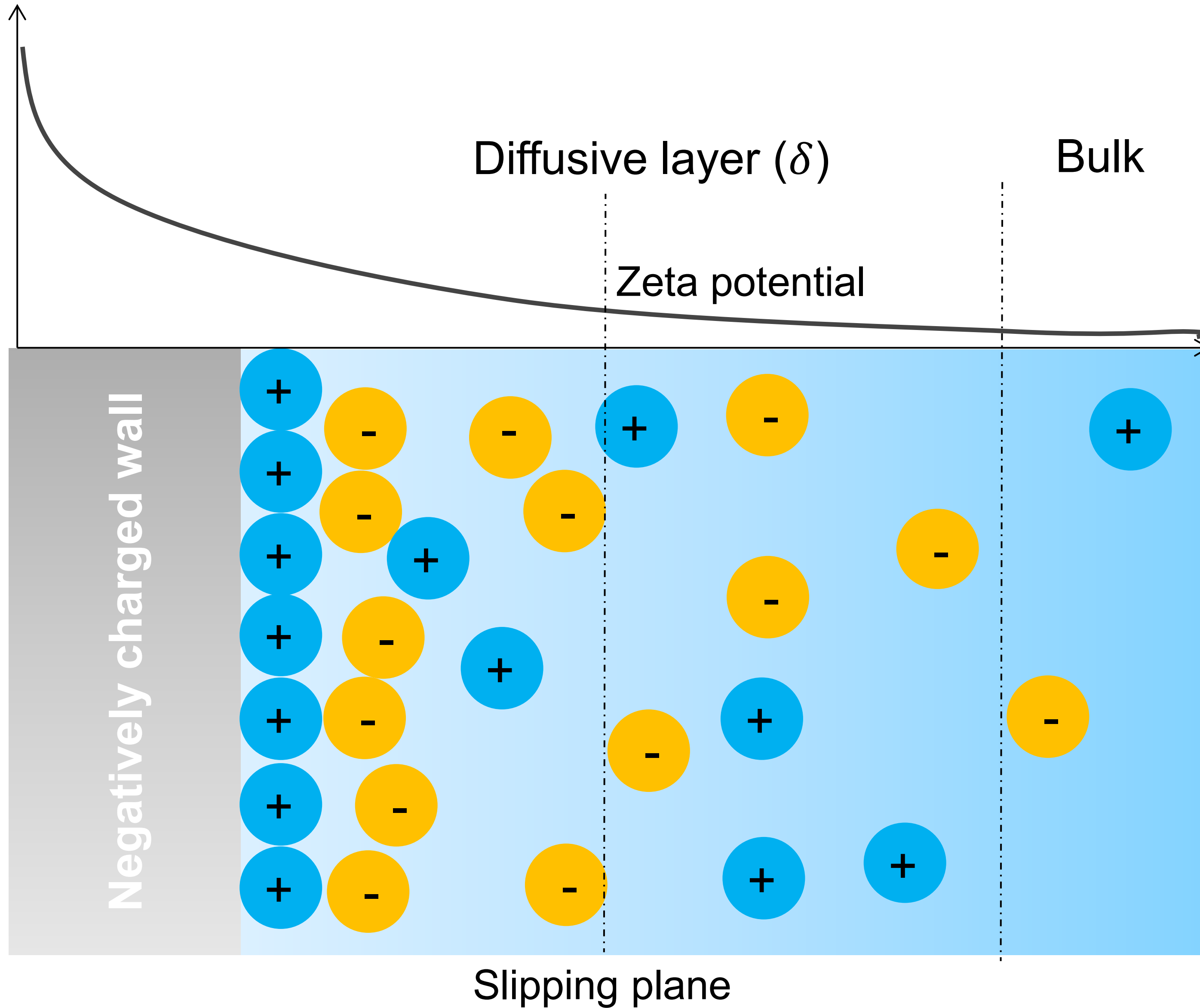

Diffusion to the electrode

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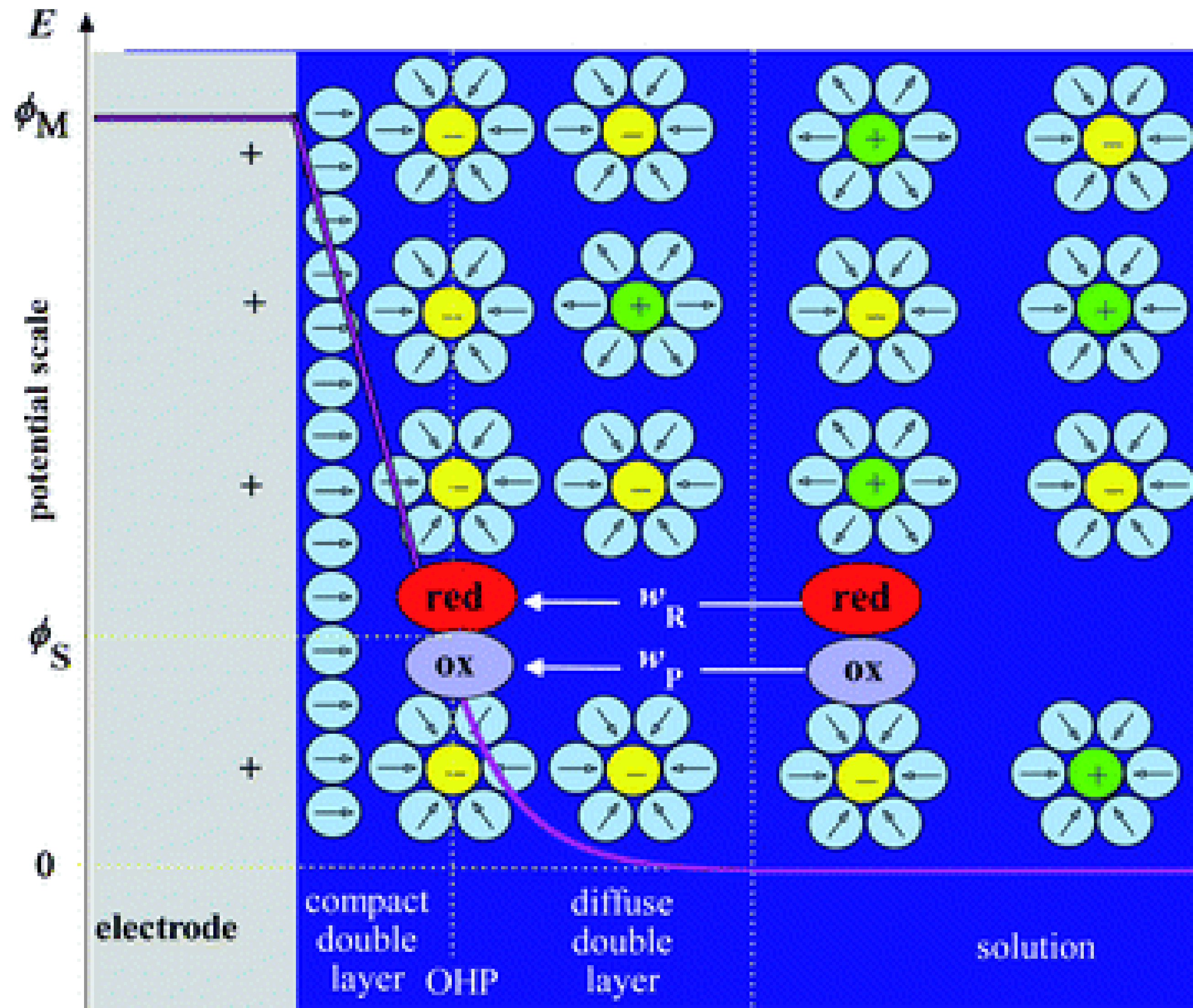

Summary of process

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Applied voltage to an electrode results in alignment of ions in solution (to screen out the applied field)

Produces an electrochemical potential near the electrode surface

Ions in solution form complexes with polar species (water) or other ligands

These complexes (ion and ligands) must diffuse through the double layer to react at the electrode surface

Critical Parameters in Solution

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Ligands slow the diffusion of ions through solution

Removing ligands slows diffusion through the EDL

The more strongly complexed an ion, the harder it is to reduce the ion

pH control is critical to reduce the level of ligands attachment to ions

Temperature and agitation improve ion diffusion rates

Atomistic aspects of electrodeposition

Metal lattice

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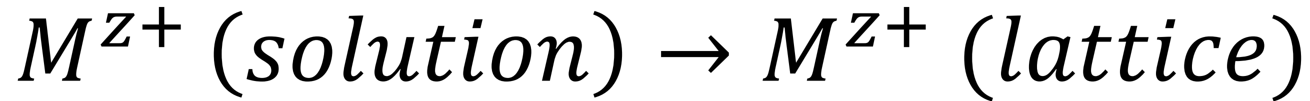
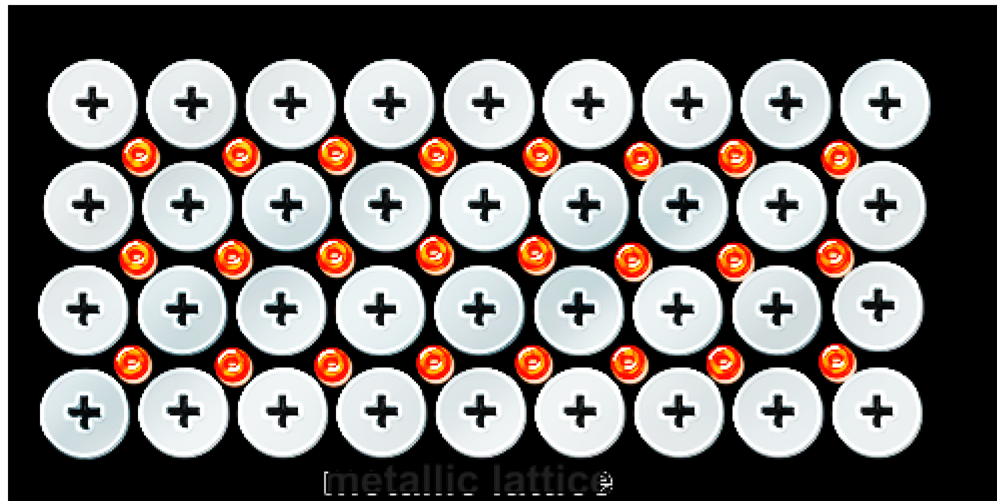
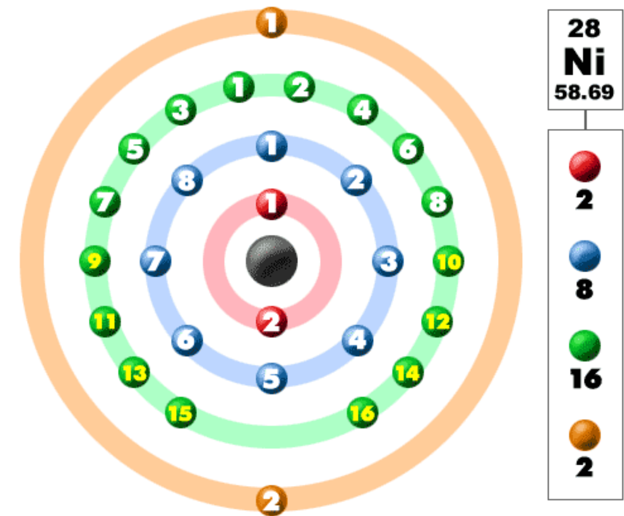
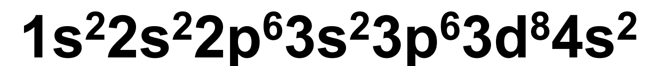
Metal ion M^{z+} is transferred from solution into metal lattice







Metal lattice



Surface of the metal lattice

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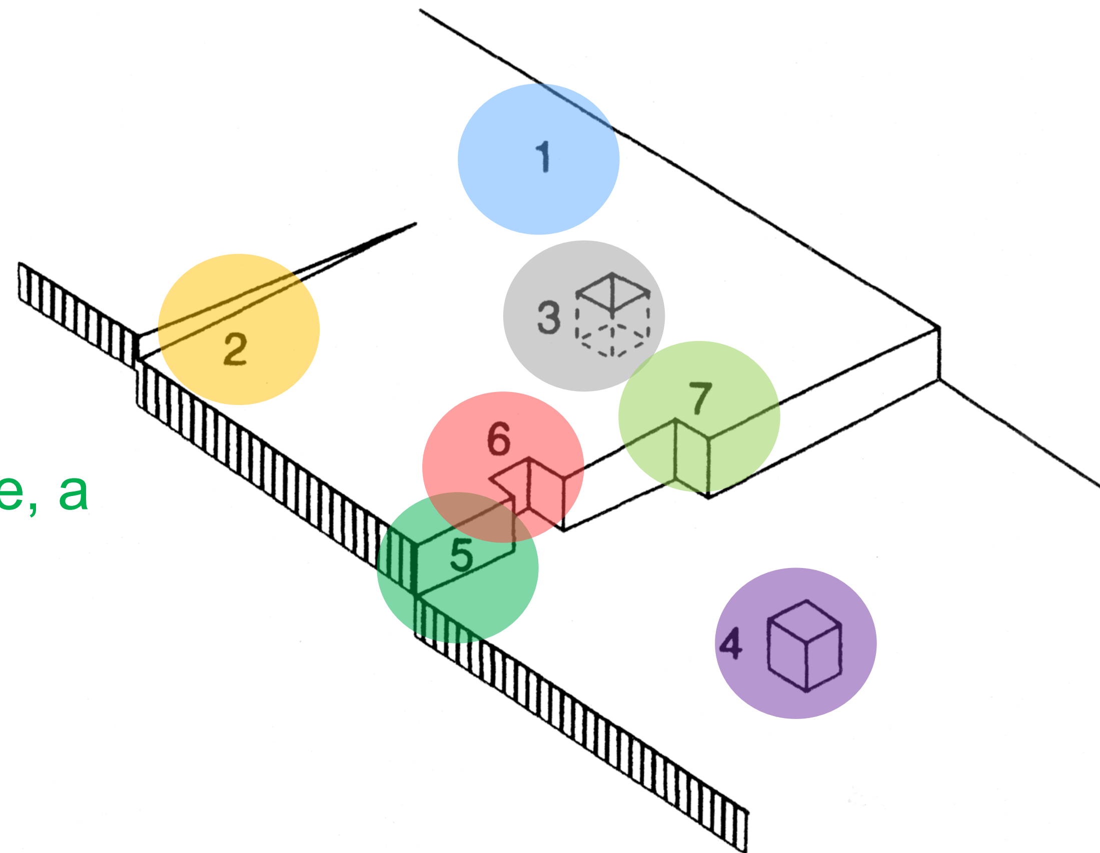
The structure of real surfaces differs from those of ideal surfaces by surface roughness!

Density of metal surface atoms 10^{15}cm^{-2} vs. Density of dislocations 10^{8}cm^{-2}

1. Perfect flat face,terrace
2. Emerging screw dislocation
3. Vacancy in the terrace
4. Adatom in the terrace
5. Monoatomic step in the surface, a ledge
6. Vacancy in the ledge
7. Kink: a ledge in the ledge



Simple defects

Atomistic view of electrodeposition

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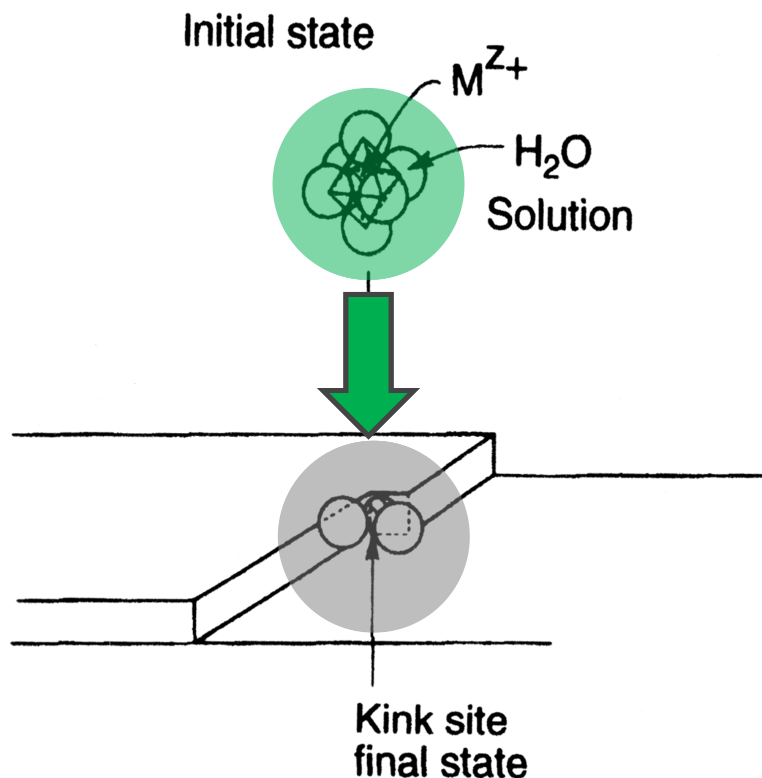
$$[M(H_2O_x)]^{z+}\ (solution) \rightarrow M^{z+}(kink)$$



- Initial state are hydrated structure $[M(H_2O_x)]^{z+}$
- Final state is an M adion (adatom, adsorbed ion, atom)
- Adion are attached to the crystal via a kink site

Process is done via (1) Step-edge site ion-transfer
(2) Terrace site ion-transfer

Step-edge Ion-transfer Mechanism

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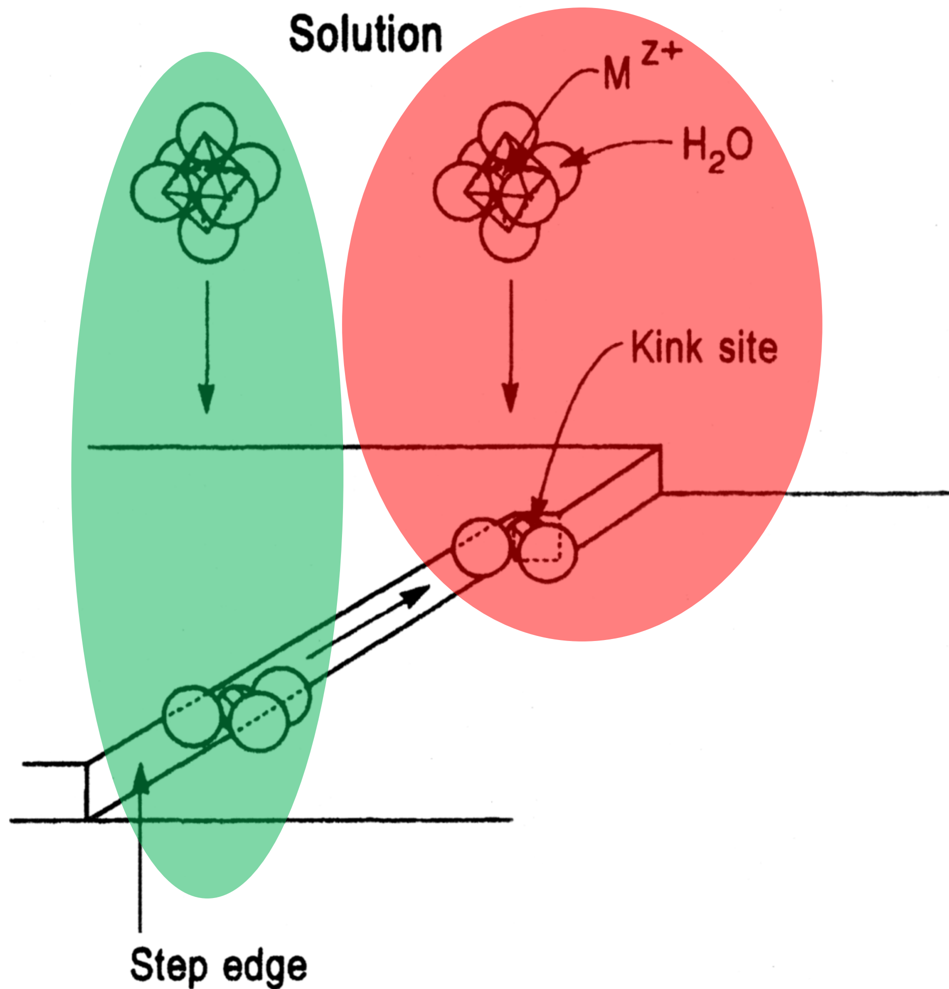

Direct transfer to the kink

Indirect transfer to the step-edge site other than a kink, the transfered metal ion diffuses along the step edge until it finds a kink

Terrace Ion-Transfer Mechanism

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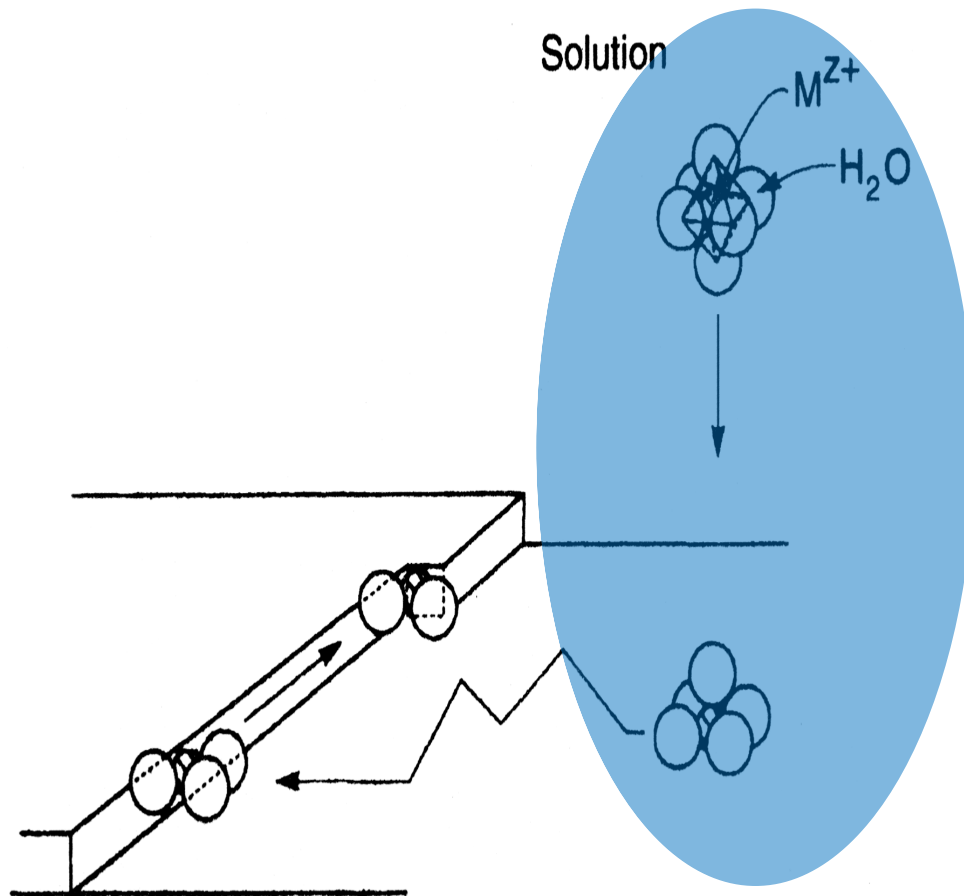

- Metal ion transferred from solution to the flat face of terrace region
- From this position, diffuses on the surface, seeking a position of lower energy
- Final position is a kink site

$$i = i_{se} + i_{tr}$$

Growth modes

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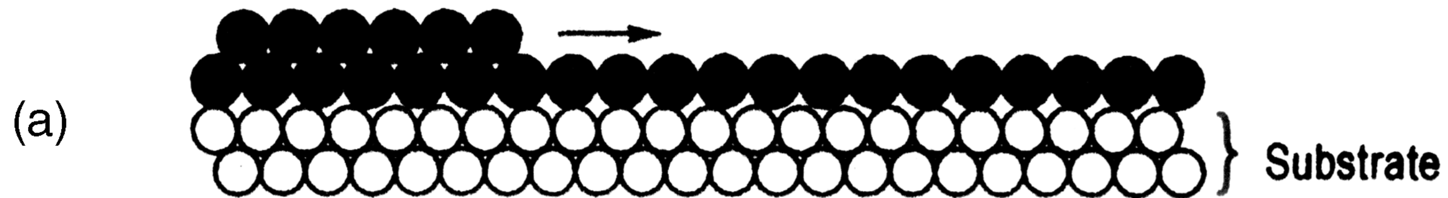
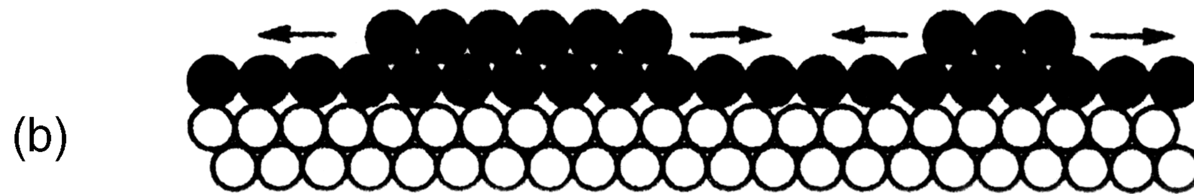
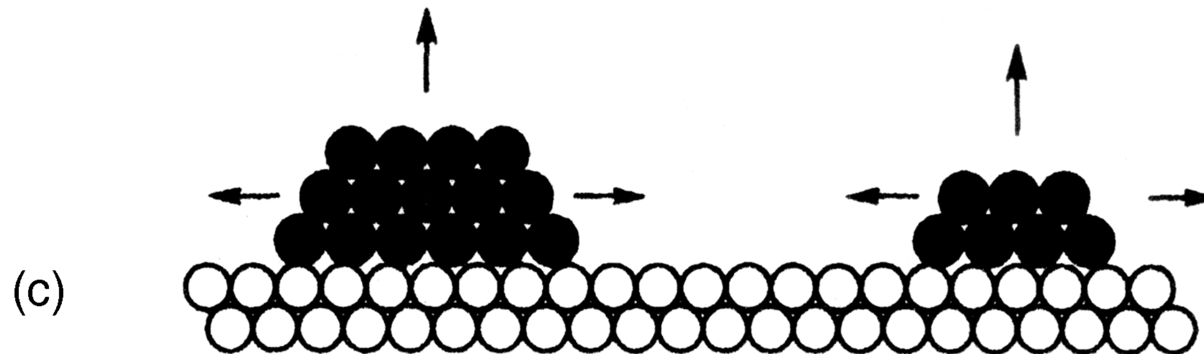
(a)



(b)



(c)



(a,b) Layer growth, © Nucleation coalescence

Columnar microstructure

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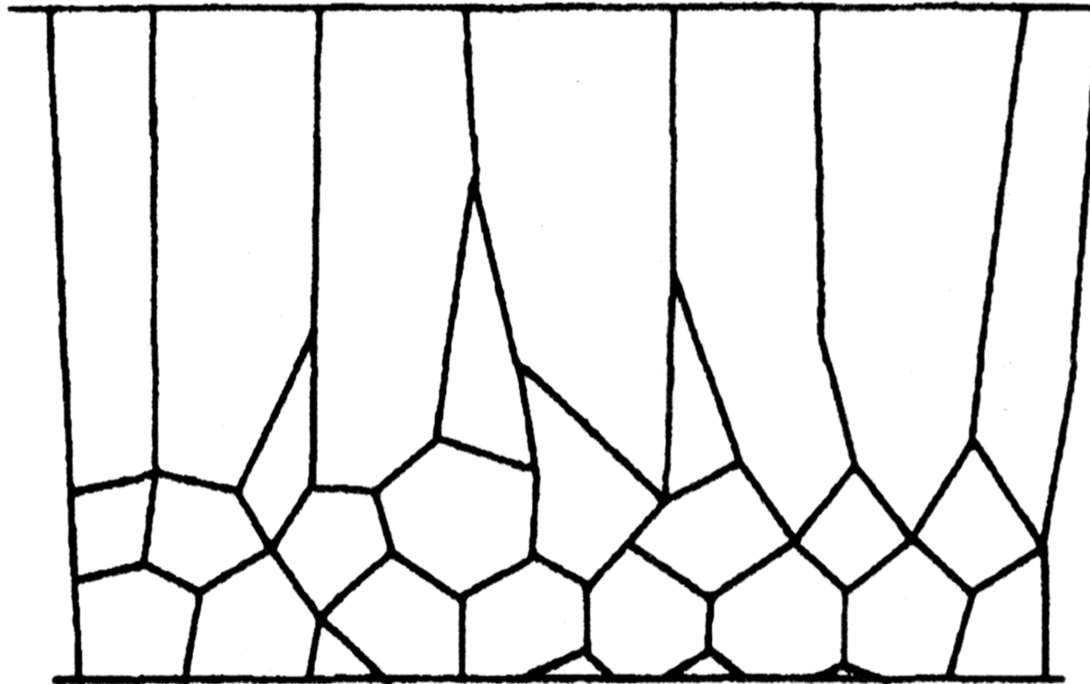

Competition between nucleation and growth processes is strongly influenced by the potential of the cathode

Bath composition

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Who does what?

Component	Role	Example
Metal salt	Souce of plating metal	Copper sulfate
Acid, base additive	Provides ionic conductivity in the bath	Sulphuric acid
Organic additives	Affect deposition and crystal building process	Saccharin

Organic Additives

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Affect crystal growth as adsorbates on surface of cathode

-chemisorption (covalent bonds): electrons are shared or transfered (adsorption energy 20-100 $kcalmol^{-1}$)

-physisorption: van der Waals or electrostatic forces: no electrons transfer nor sharing (adsorption energy 5 $kcalmol^{-1}$)

Levelers	Improve plating thickness uniformity	Amines, amide, nitrogen
Brighteners	Control deposit brightness and hardness	Sulphur containing compounds

Leveling

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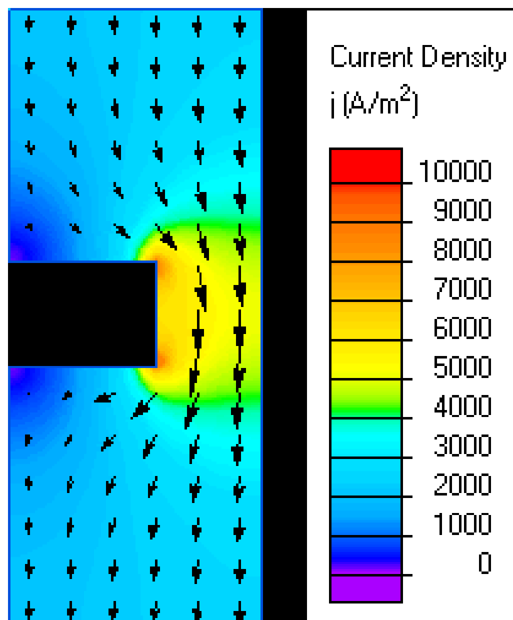
Progressive reduction of surface roughness during deposition

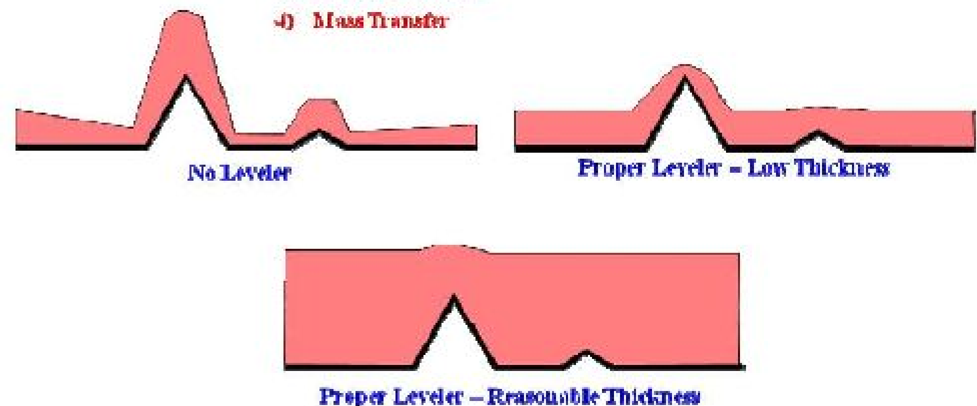
Leveling without additives

(current distribution uniformisation)
Pulse plating, geometrical configuration anode/cathode

Leveling with additives

Adsorb strongly to the surface at high current density regions. This lowers the plating rate at corners or protrusions and levels the deposit





Brightening

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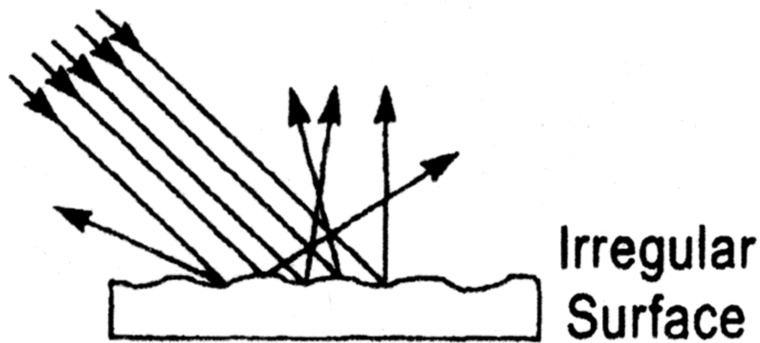
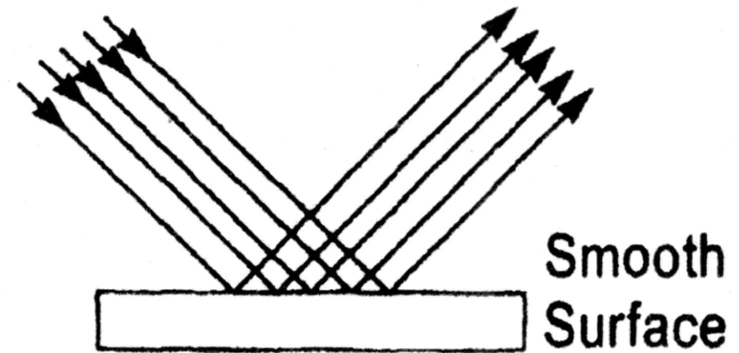
Optical reflecting power of the surface





Attach to metal ions during plating and facilitate charge transfer at the electrode:
1) diffusion controlled , 2) grain refining, 3) randomization of crystal growth

Conclusion

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Goals for the inorganic additives

– Acid, base concentration optimized for good solution conductivity
– Metal ion concentration sufficient to support plating current requirements

Goals for the organic additives

– Levelers attached to high current density surface features
– High concentration of brighteners in occluded features such as vias
– Result is higher plating rates in vias & lower plating rates on high current density features

Voltage effect on the plating process

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Goals for the plating cycle

For complex surfaces (vias, dense metal), facilitate the optimum organic distributions

Control the deposit grain structure (with grain refining additives)

Optimize the plating cycles is essential (Chapter 3)
- DC Plating
- Pulse Plating
- Pulse Reverse Plating