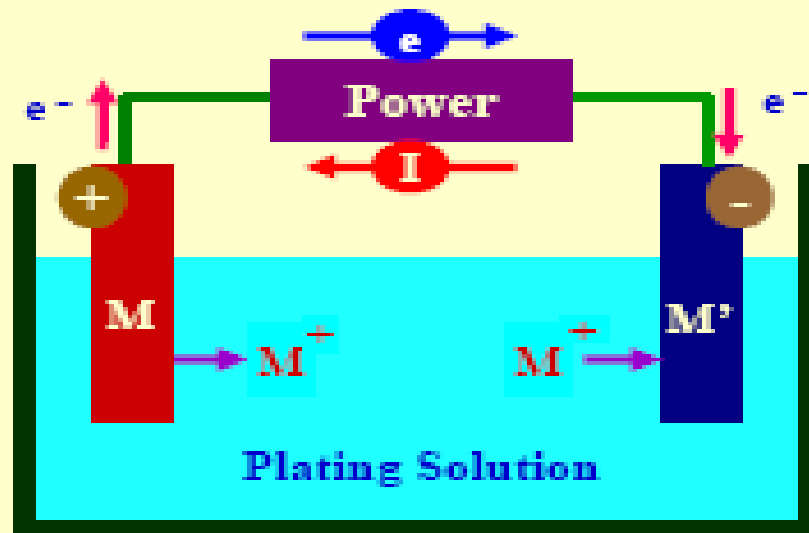**ELECTRODEPOSTION**

Lecture by: Dr. M. M. Karanjakar

05/02/2019

# Electrodeposition



Electroplating Setup
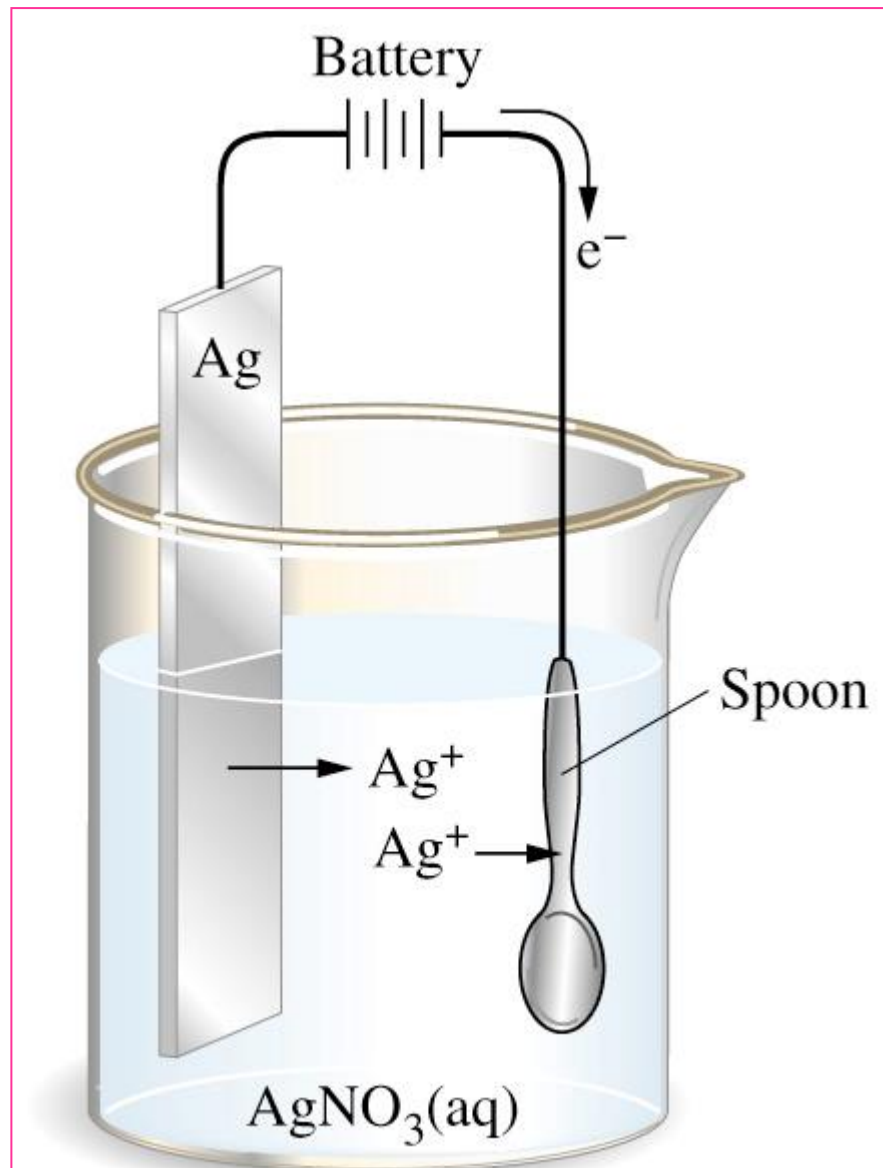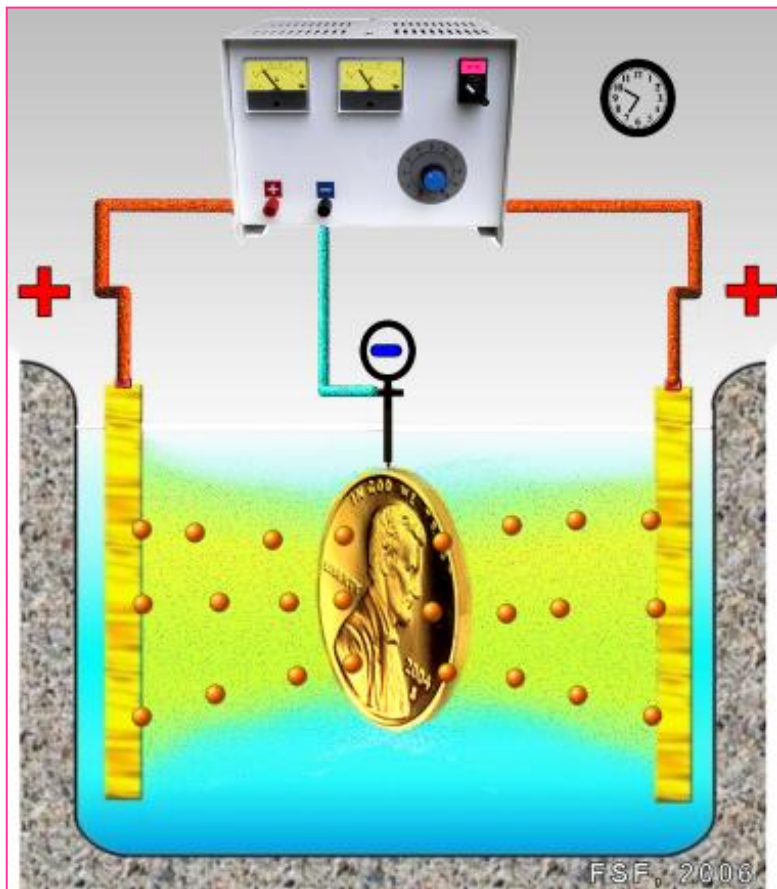
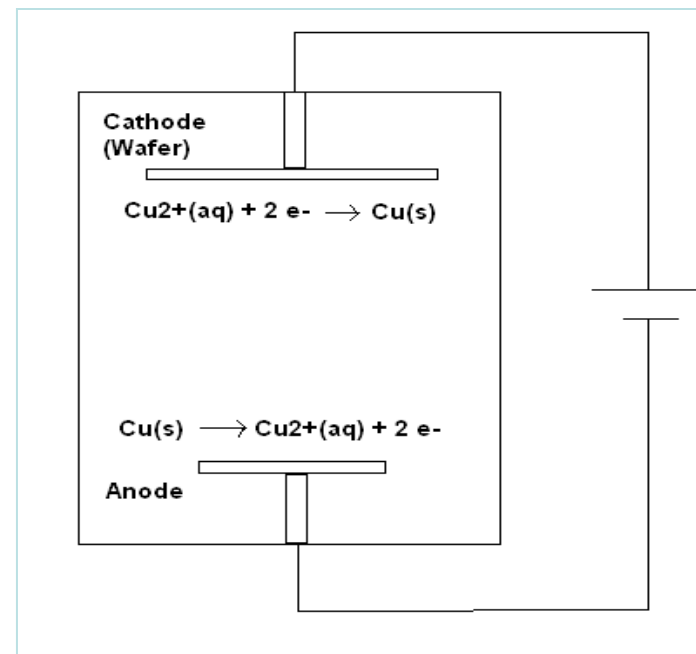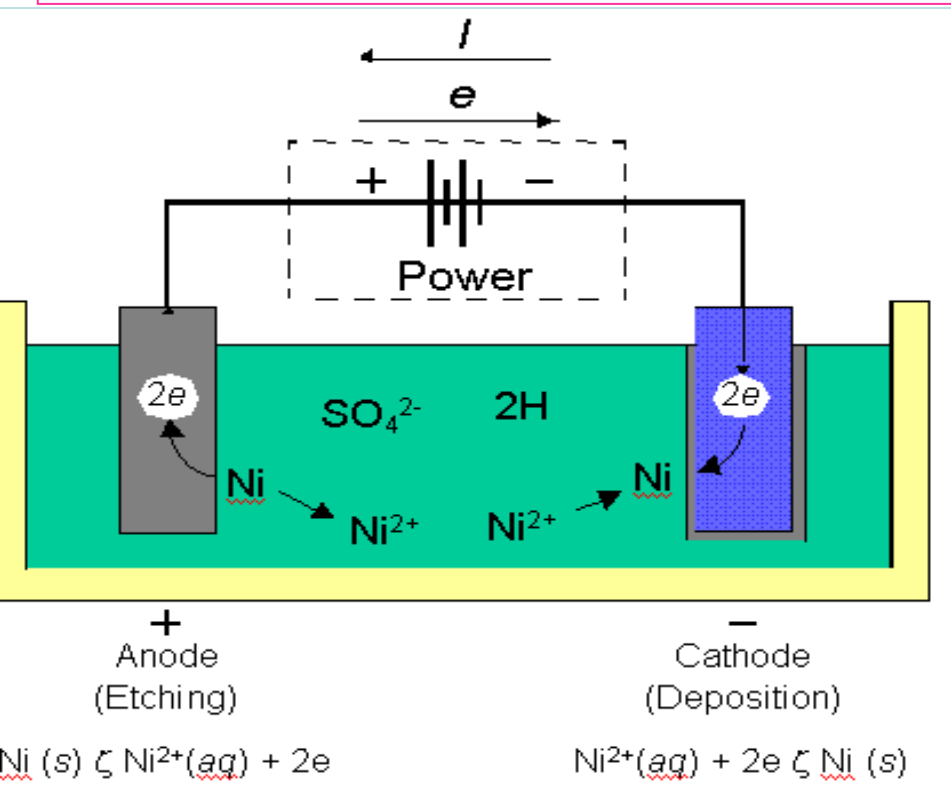# Electrochemical Processes
## Electro Deposition

- Introduction
- Experimental Setup
- Importance of Electro Deposition
- Bath Formulations
- Electroless and Displacement Depositions
- Equilibrium Electrode Potentials
- Factors Affecting the Electrodeposits
- Micro and Nano-scale Structures

Battery

Ag

Spoon

Ag$^+$

Ag$^+$

AgNO$_3$(aq)

e$^-$

Ag$^+$ + e- --→ Ag
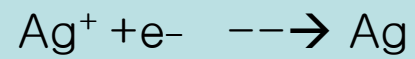
The process used in electroplating is called **electrodeposition** and is analogous to a galvanic cell acting in reverse. The item to be coated is placed into a container containing a solution of one or more metal salts. The item is connected to an electrical circuit, forming the cathode (negative) of the circuit while an electrode typically of the same metal to be plated forms the anode (positive). When an electrical current is passed through the circuit, metal ions in the solution take up excess electrons at the item. The result is a layer of metal on the item.



$I$

$e$

$+$  $-$

Power

$2e$

$SO_4^{2-}$  2H  $2e$

Ni  Ni

$Ni^{2+}$  $Ni^{2+}$

$+$
Anode
(Etching)

$-$
Cathode
(Deposition)

Ni (s) ⇌ Ni²⁺(aq) + 2e

Ni²⁺(aq) + 2e ⇌ Ni (s)



Cathode
(Wafer)

$Cu^{2+}(aq) + 2 e^- \longrightarrow Cu(s)$

$Cu(s) \longrightarrow Cu^{2+}(aq) + 2 e^-$

Anode

# Introduction

**What is Electro deposition?**

Electro deposition is the process of coating a thin layer of one metal on top of a different metal to modify its surface properties.

Done to achieve the desired electrical and corrosion resistance, reduce wear&friction, improve heat tolerance and for decoration.

E.D. is a surface coating method that forms an adherent layer of one metal on another.

# Electroplating Applications

Automotive parts

Printed circuitry and electrical contacts

General engineering components

Gold-Silver wares and Jewelry

Musical Instruments and Trophies

Soft metal gaskets

Anti-seize bearings

Decorative door, light & bathroom fittings

Production of micro parts for MEMS

# Electrodeposition Merits

- Very uniform coverage is obtainable, including the edges and corners.
-  Greater operating flexibility.
- Superior mechanical and corrosion performance properties.
- Greatly reduced solvent emissions and fire hazards.
- Highly automated and mechanized process.
- Low maintenance and manpower costs.
- Highly efficient with up to 95% of the coating material being utilized.
- New technology with great potential for future technological innovations and applications.

## Additional advantages of the cathodic electrodeposition

- Significant improvement (3-4 folds) in corrosion performance.
- Superior throwing power (penetration) performance.
- Improved resistance to saponification.
- Reduced conversion coating (zinc/iron phosphate) disruption.
- Inherent stability and chemical resistance

# Electrodeposition : merits

- It can be used to grow functional material through complex 3D masks.
- It can be performed near room temperature from water-based electrolytes.
- It can be scaled down to the deposition of a few atoms or up to large dimensions.

For microelectronics related applications, electrochemical deposition has the following advantages over vacuum techniques:
- room-temperature process, thus reducing problems with thermal stress;
- low cost of equipment, no vacuum required
- high rate of deposition
- artificial material structuring such as multilayers;
- conformal deposition or deposition through resist masks;
- great reliability for high aspect ratio structures and excellent shape fidelity.
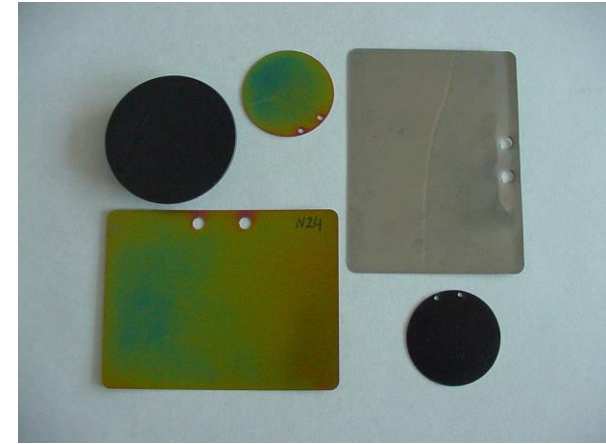
# Electrodeposition: Applications

*Alloys electroplating for anticorrosive coatings*
electrodeposition of Zn-X alloys for the automotive industry, particularly Zn-Ni and Zn-Mn alloys.



*Magnetic thin films and multilayers*
preparation of metallic coatings with possible application in the electronic industry.. Coatings preparation requires a previous choice of the adequate substrate for each application (modified silicon substrates, metals, carbon, conducting monolayers over glass, ...).

Fig. 1. Electrochemically fabricated flip-chip interconnects.[2]
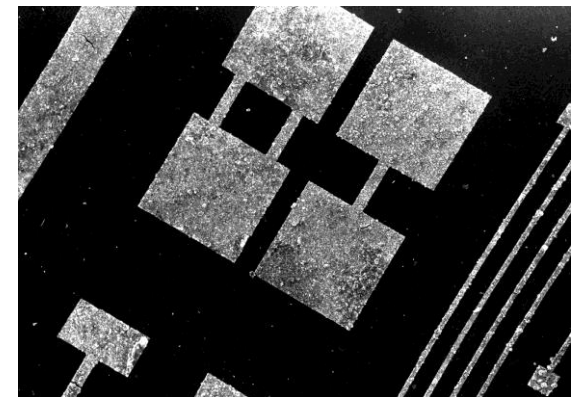
FIG. 1. Miniature copper mask from the site of Loma Negra on the far north coast of Peru, ca. 200 C.E. Removal of the green copper corrosion products reveals a bright gold surface. The extremely thin layer of gold was applied to the sheet copper by electrochemical replacement plating. [Figure reprinted with permission from Heather Lechtman, Sci. Amer., 250(6), 56 (1984).]
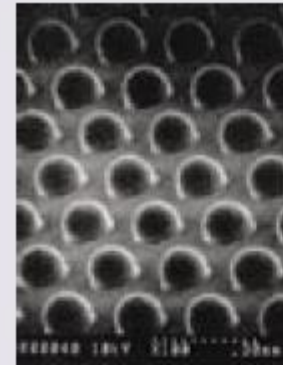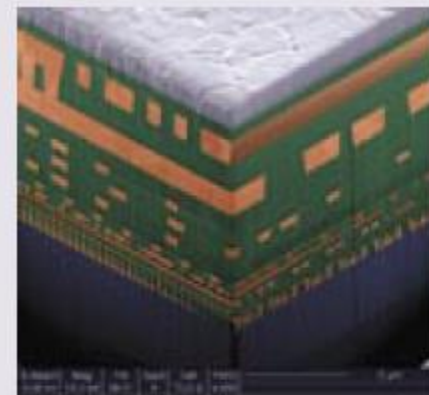
Courtesy of International Business Machines Corporation. Unauthorized use not permitted.

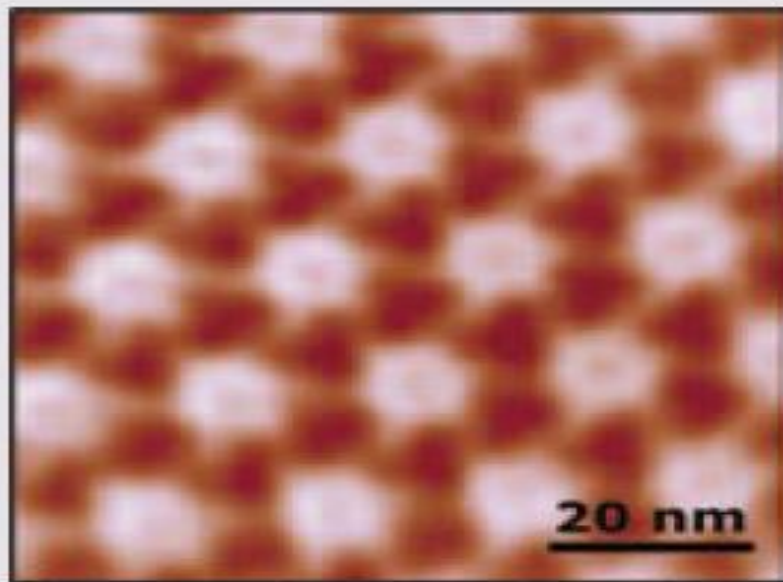FIG. 2. A ten level copper on-chip interconnect scheme of 90 nm CMOS node fabricated in low dielectric constant material.[7]

**Fig. 1.** Nanometer-scale cuprous oxide (colorized red) can be electrodeposited through the openings in the hexagonally packed intermediate layer protein (white regions) from the bacterium Deinococcus radiodurans. Purified crystalline protein sheets are first adsorbed to a conductive substrate, and then electrodeposition is carried out to fill the nanometer-scale pores in the protein (see scale bar). Details of the method are given in Ref. 4.
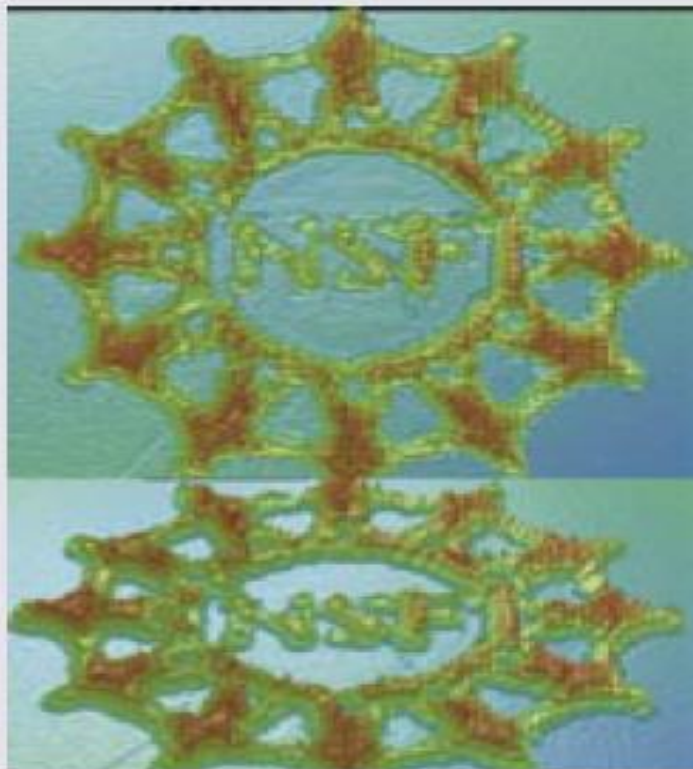


**Fig. 2.** Electrochemical printing (EcP) involves localized electrodeposition beneath a rastering print head; no masking step is needed. Two different viewing angles show the topography of a complex EcP pattern that is 1.8 mm across and 700 nm high. In this case, copper was EcP patterned with a 1000 dots per inch lateral resolution. This single image shows the multiscale nature of electrodeposition, where the thin film is easily controlled at the nanoscale while lateral dimensions can be macroscopic. Details of EcP can be found in Ref. 6.
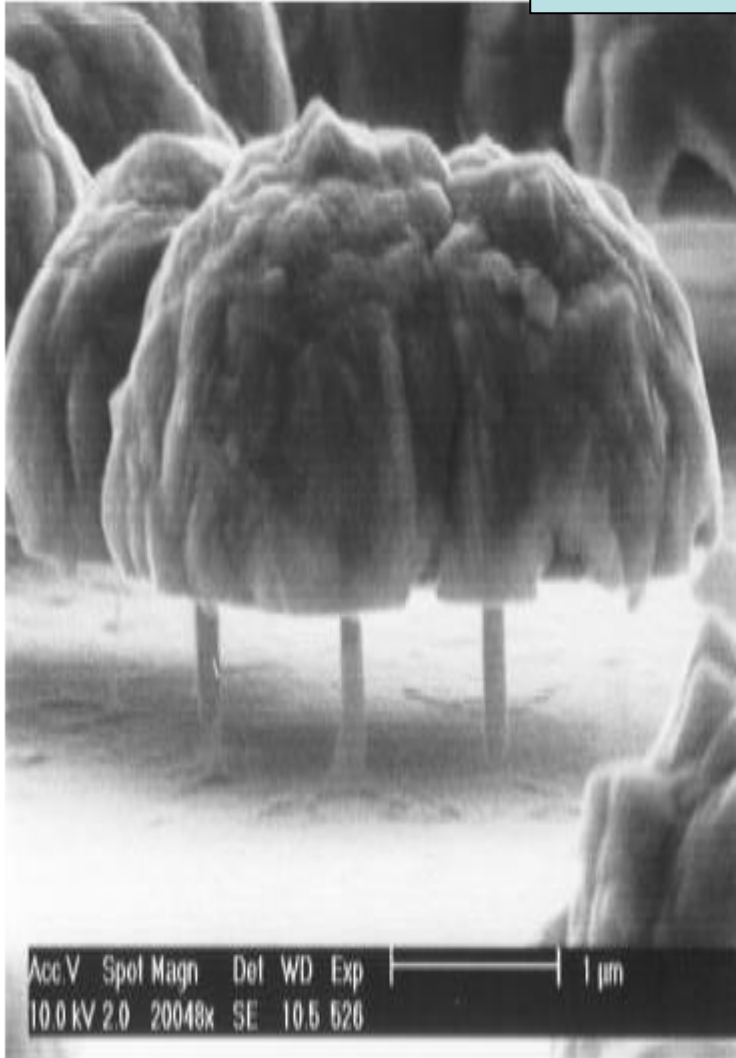
**Figure 5.** SEM picture of copper mushroom structures grown on top of nanowires (height 700 nm, diameter 130 nm).
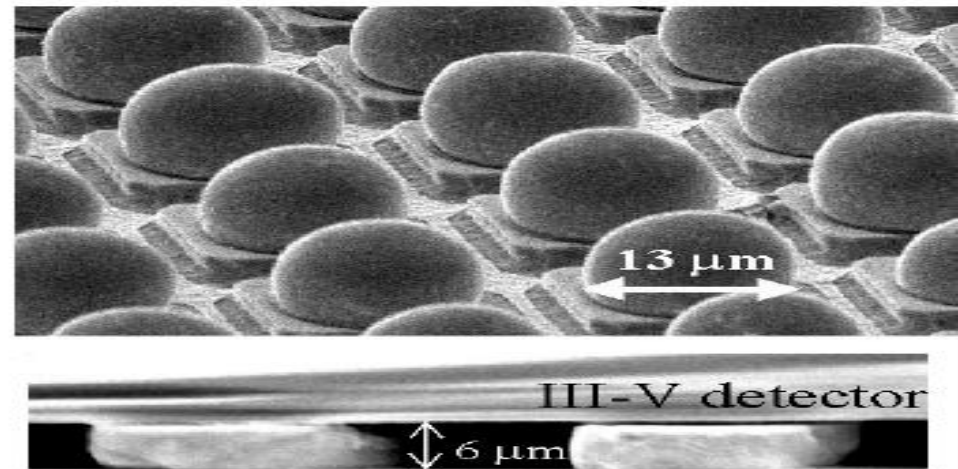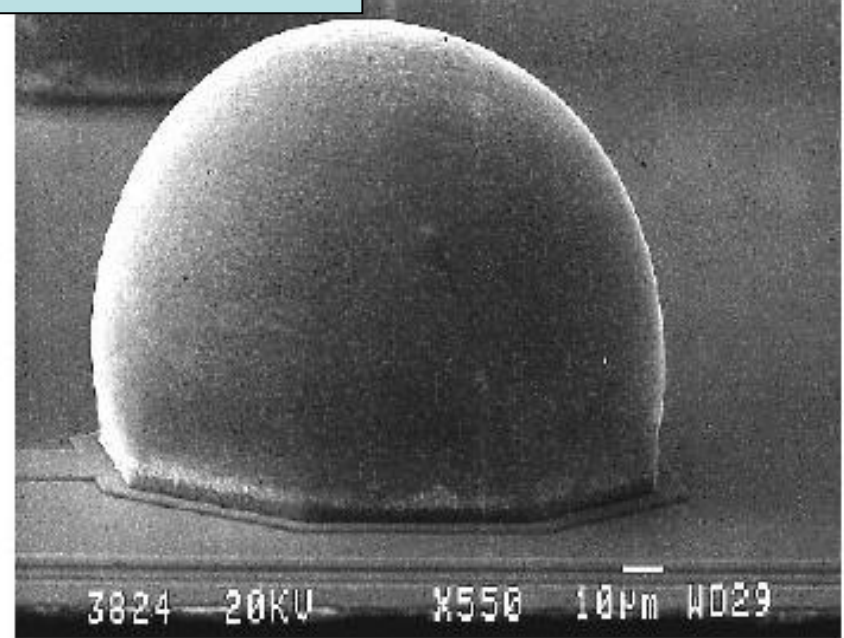


`3824  20KU      X550    10µm  W029`



13 µm

III–V detector

6 µm

Si–Readout IC

**Figure 8.** Indium solder bumps after reflow (top) and after flip-chip bonding (bottom).

## Electrodeposition Paint Recovery



In the electrodeposition paint industry, the most important part of the process is the one that allows unused paint to be recycled. This allows electrodeposition to be cost-effective, and in the long run, possible. The process of electrodeposition of paint requires that paint solids be concentrated from a rinse water bath and returned to a paint tank that will have parts submerged into it. The more effective the removal of the paint solids from the water, the more effective the system. The water removed from the paint bath is then used in rinsing the parts after they have been coated.

# Synthesis of Nanostructured Materials Using Template-Assisted Electrodeposition

High quality silver contacts on ceramic superconductors obtained by electrodeposition from non-aqueous solvents

*Electrodeposition of metallic multilayers:* (*ca*. 10 – 100 Å) layers of magnetic (*e.g*. Co, Ni and Fe–Ni) and non-magnetic (*e.g*. Ag, Pt and Cu) metallic multilayers. This approach has the advantage over MBE and sputtering that the capital coast of the equipment is much lower, and that it can be used to prepare multilayers in geometries inaccessible to other fabrication methods.

*Electrodeposition of shape-memory alloys:* Certain alloys of titanium, gold, and copper exhibit shape-memory behavior, and this property can be exploited to manufacture microvalves, actuators and other devices. A number of shape-memory materials (*e.g*. Cu-Zn, Au-Cd and Mn-Cu) can be prepared electrodeposition,

*Electrodeposition of gold on to semiconductor wafers:* the electrodeposition of gold on to patterned lithium niobate wafers for use in integrated optical devices..

# Basics of Electrodeposition

- The simplest form is :
  - a bath consisting of an electrolyte containing metal-ion (ex: $CuSO_4$ solution for the deposition of Copper),
  - an electrode or substrate on which the deposition is desired,
  - a counter electrode.

- When a current flows through the electrolyte,
  - cations move toward the cathode,
  - anions move towards the anode
  - they may deposit on the electrodes after undergoing a charge transfer reaction.
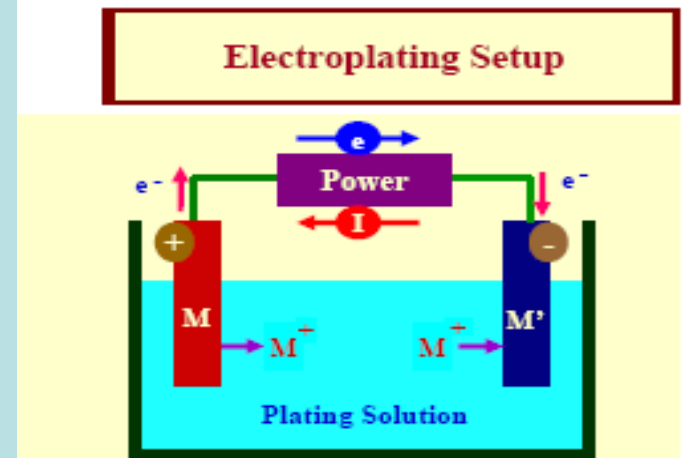
# Faraday's law

- The total amount of chemical change produced by an electric current is proportional to the total charge passing through the electrolyte

- 

- 

- The ratio of the mass electrodeposited to its gram-equivalent weight is constant equal to 1 faraday or 96500 (C) or 26.8 (Ah)

## Electrochemical Equivalence

The electrochemical equivalent of a metal Z(M) is the weight in grams produced or consumed by one coulomb of charge

$W_{eq} = A / n$

When $Q = 1$, $W_{(Q=1)} = Z$

$W_{eq} = 96487 \, Z$

$Z = W_{eq} / 96487 = W_{eq} / F$

$Z = A / nF$

$W = ZQ = AQ / nF$

# Influencing factors in Electro deposition

The morphology and composition of electrodeposits vary significantly, and depend on:
- Current density
- The nature of the anions or cations in the solution
- Bath composition and temperature
- Solution concentration
- Power supply current waveform
- The presence of impurities
- Physical & chemical nature of substrate surface

## Current Efficiency

Current efficiency is the ratio between the actual amount of metal depositing (or dissolved) $M_a$ to that calculated theoretically from Faraday's law $M_t$ in %.

$$C.E. = (M_a / M_t) \times 100$$

C.E. indicates the faction of total current that generates desired products.

The overall amount of chemical change produced by a given quantity of electricity can be determined.

Cathode & anode efficiencies - In an ideal situation, cathode efficiency will be equal to anode efficiency.

## Cathode Efficiency

The ratio of the weight of metal actually deposited to the weight that would have resulted if all the current had been used for depositing it is called the cathode efficiency.

Cathode efficiency in plating depends on:
- Electrolyte or bath
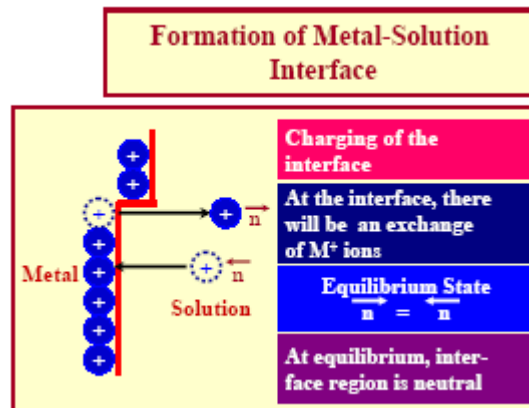- Concentration of chemical component
- pH and agitation
- Current density

The current efficiency in Ni plating is close to 100%, and in Cr plating it is approximately 20%
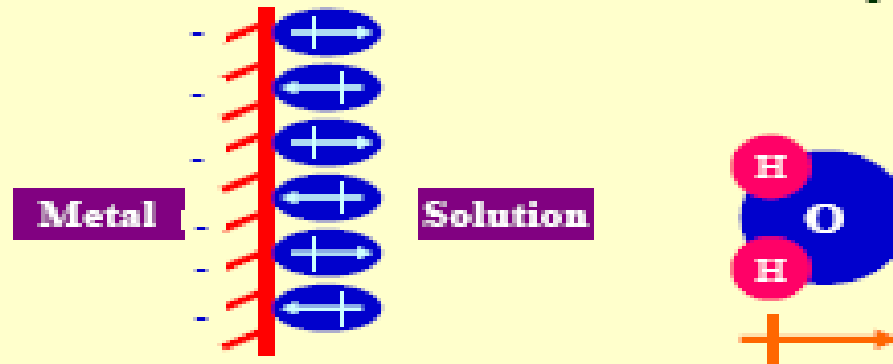
# Metal electrolyte Interface

- Deep in the bulk of the two phases (solid and liquid), the charge carriers are under the influence of isotropic forces:
  - The net force on a carrier is thus zero, when averaged over a large volume
- When a metal electrode is immersed:
  - the anisotropic nature of the forces at the interfacial region results in a new arrangement of solvent dipoles and ions of the electrolyte

- 

- A compact double layer known as the Helmholtz double layer adjacent to the electrode is formed with:
  - Completely oriented water dipoles and contact adsorbed ions.
  - The electrode-electrolyte interface has the decisive role in the electrodeposition process
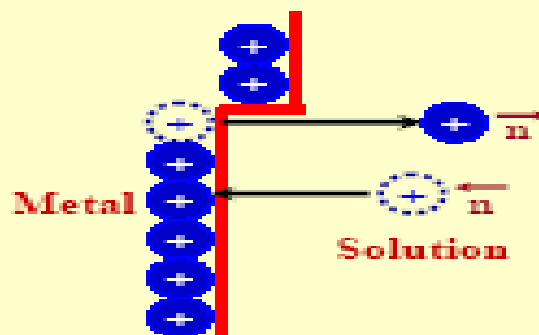
- 



**Formation of Metal-Solution Interface**

Metal / Solution

Charging of the interface

At the interface, there will be an exchange of $M^+$ ions

Equilibrium State
$\overrightarrow{n} = \overleftarrow{n}$

At equilibrium, interface region is neutral

S. Soukane (1999)

# Water Structure At The Interface

The presence of excess charge on metal causes ion redistribution and reorientation of water dipoles.



Metal | Solution

H O H

# Formation of Metal-Solution Interface
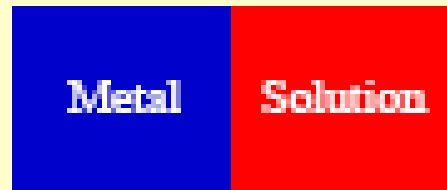


Metal

Solution

**Charging of the interface**

At the interface, there will be an exchange of $M^+$ ions

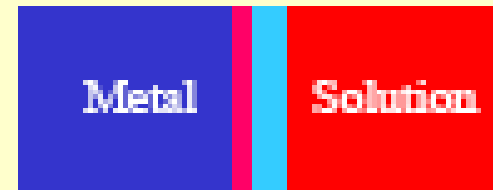**Equilibrium State**
$$\overrightarrow{n} = \overleftarrow{n}$$

At equilibrium, interface region is neutral
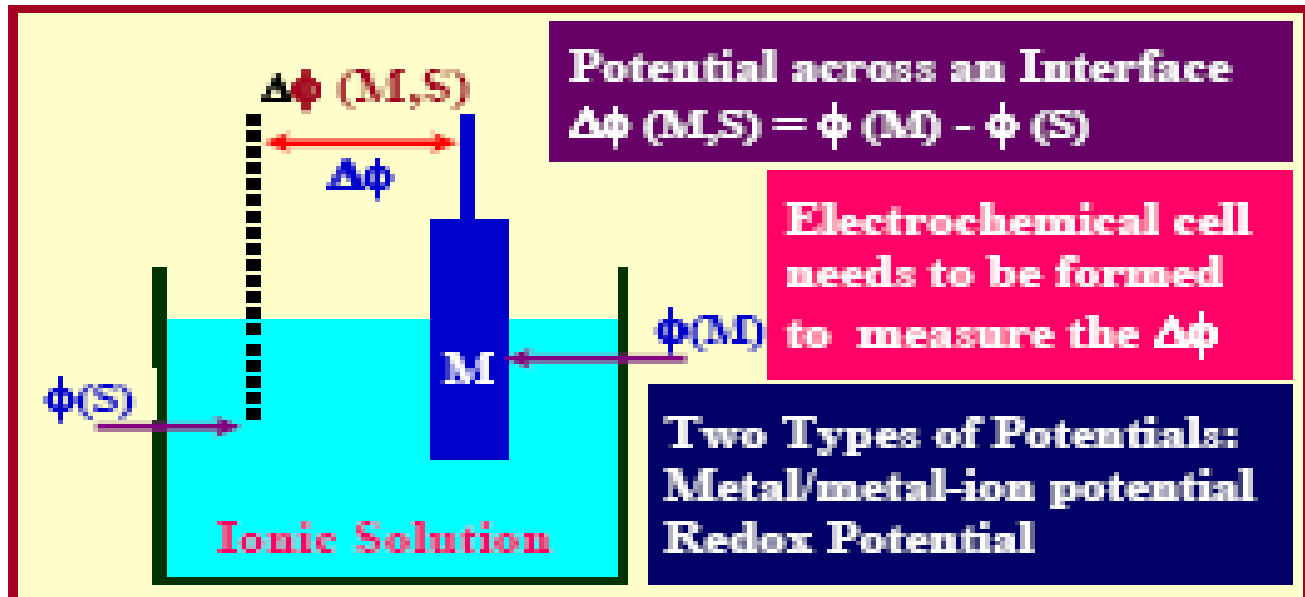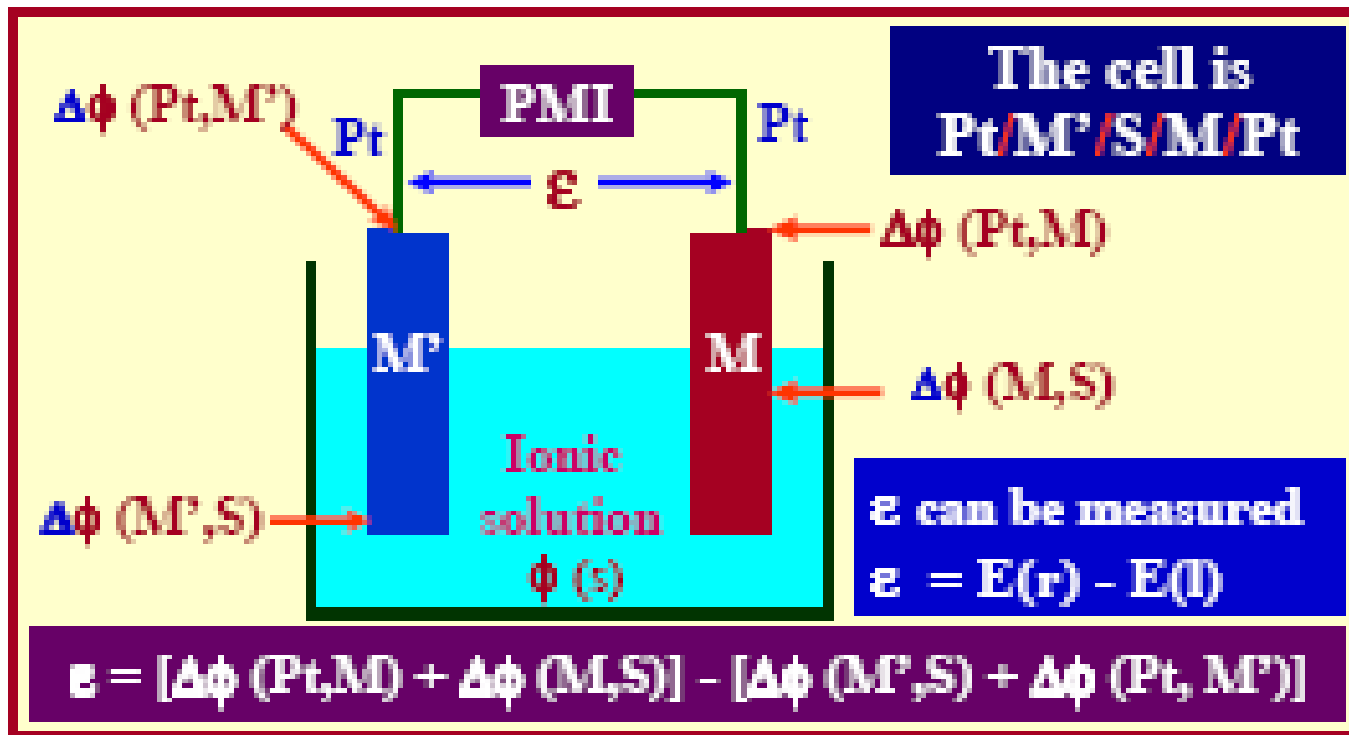
# Inter Phase Formation

## Two Phases in Contact

| Metal | Solution |
|-------|----------|

| Metal | | | Solution |
|-------|--|--|----------|

**At the Moment of contact, $t = 0$**

**At equilibrium condition, $t = x$**

# Steps Involved in the Electrodeposition process

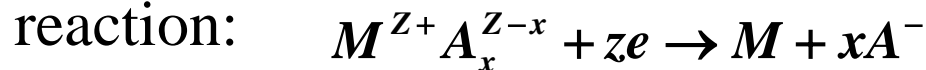- Example of a cathodic electrodeposition involving $M^{Z+}$ ions:

- The ions can be:

  - In a hydrated form, depositing with the overall cell reaction:
  $$M^{Z+} \cdot nH_2O + ze \rightarrow M + nH_2O$$

  - Complexed form electrodepositing with the overall cell reaction:
  $$M^{Z+}A_x^{Z-x} + ze \rightarrow M + xA^-$$

- This occur in the following successive steps:

  - ionic transport

  - discharge

  - incorporation of adatoms onto the substrate followed by nucleation and growth

# Process that occur in the electrolyte bulk

- Ions that are sufficiently removed from the electrode can move toward it under the influence of:
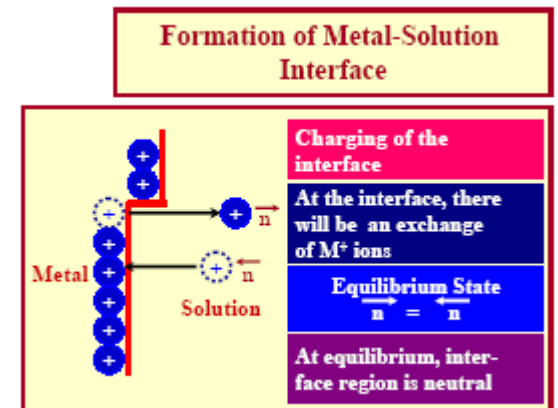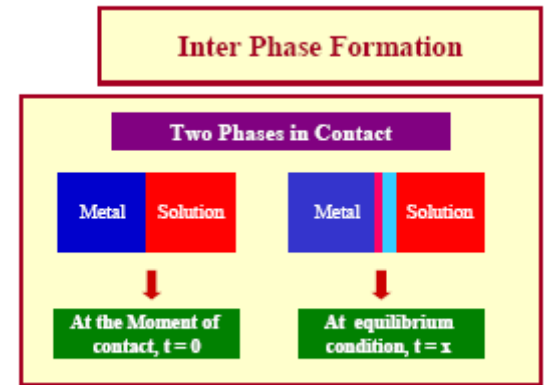
- •

  – the potential gradient

  –
  $$\nabla \Phi$$

  –

  – a concentration gradient

  –
  $$\nabla C_i$$

  –

  – a convective current

  –
  $$C\vec{U}$$

  –



Inter Phase Formation

Two Phases in Contact

Metal | Solution    Metal | Solution

At the Moment of contact, t = 0 | At equilibrium condition, t = x



Formation of Metal-Solution Interface

Charging of the interface

At the interface, there will be an exchange of M+ ions

Equilibrium State

At equilibrium, interface region is neutral

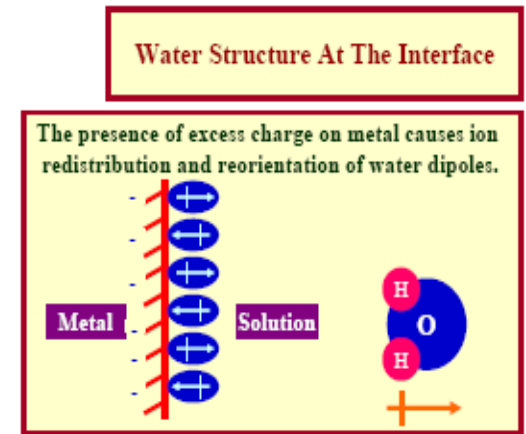S. Soukane (1999)

# Processes that occur near the electrode but within the electrolyte

- Ions species are normally surrounded by a hydration sheath
- They move together as one entity
- They accept electrons from the cathode or donate electrons to the anode This ion discharge reaction occurs in the electrolyte between 10 and 1000 A from the electrode



**Water Structure At The Interface**

The presence of excess charge on metal causes ion redistribution and reorientation of water dipoles.

Metal | Solution

H O H

# Processes that occur on the electrode surface

- The atoms deposited have a tendency to form either an ordered conglomerate of crystalline phase or a disordered amorphous phase.

# Mechanism of ion discharge at the electrode: The Butler-Volmer equation

- The total free energy change required for the electronation is the sum of two free energies:
  - the free energy change required for the cathodic reaction when the interfacial potential drop is zero
  - the free energy change due to the electrical work done by the ion in crossing the potential across the double layer
  - $$j_0 = zFk_c a_{M^+} \exp\left(-\frac{zF\alpha_c \Delta\Phi_e}{RT}\right) = -zFk_a a_M \exp\left(-\frac{zF\alpha_a \Delta\Phi_e}{RT}\right)$$

- The interface is made to depart from equilibrium by application of an electric field.
- The potential drop to a new value $\Delta\Phi = \Delta\Phi_e + \eta_a$
- The net current density is therefore
- 
$$j = j_0\left[\exp\left(-\frac{zF\alpha_c \eta_a}{RT}\right) - \exp\left(\frac{zF\alpha_a \eta_a}{RT}\right)\right] \quad \text{Butler-Volmer equation}$$

# Compound Semiconductor Electrodeposition

- Special considerations:
  - Semiconductor films are relatively resistive (in comparison to metals). Interfacial potential and charge distribution may drastically change once the first few layers have been formed.
  - Resistivity of a semiconductor is highly sensitive to defects, and it may continue to vary during deposition. In an extreme situation a non-degenerate semiconductor may even become a degenerate semiconductor

- Apart from a few elemental semiconductors, most of the semiconductors of interest are compound semiconductors

- Most of the compound semiconductors have at least one metallic (Ga, In, Cd, Cu, Zn,…) and one non-metallic (S, Se, P, As,…) component as in GaAs, GaP, InP,… The reduction potential of the nonmetals are widely different from those of metal ions
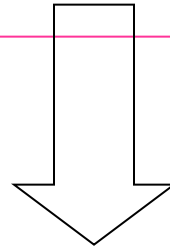
Thermodynamic factors influencing the electrodeposition of semiconductors

# Thermodynamic factors influencing the electrodeposition of semiconductors

- Simple electrodeposition of a compound $A_rB_s$

- $$rA + sB \rightarrow A_rB_s$$

-
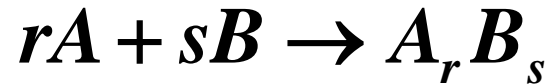
- According to Nernst equation, the electrode potentials for A and B can be written

- $$E_A = E_A^0 + \frac{RT}{mF}\ln\left(\frac{a_{A^{m+}}}{a_A}\right) + \eta_A$$

-

- $$E_B = E_B^0 + \frac{RT}{mF}\ln\left(\frac{a_{B^{m+}}}{a_B}\right) + \eta_B$$

-

- For deposition of either A or B the respective deposition potential should be kept more negative than $E_A$ or $E_B$

-

- If $E_A$ is not markedly different from $E_B$:
  - $E_A$ can be made equal to $E_B$ by simply adjusting the ionic activities of the constituents.

- $E_A$ is widely different from $E_B$;
  - Even in this case deposition is possible by the use of a complexing agent

S. Soukane (1999)

- Role of complexant:
  - A complexant that forms a complex ion with one of the discharging ions is known to change the deposition potential.

$$M^{l+} + qX^{p-} \rightarrow MX_q^{l-pq}$$
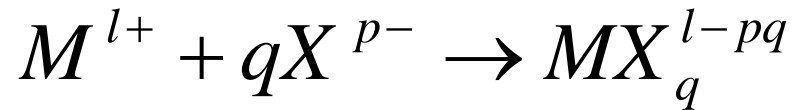
- Suppose a complex ion $X^{p-}$ present in the bath complexes with an ionic species $M^{l+}$ as: q is the coordination number (number of coordinate bonds to the complexing ion) The Nernst equation for the complex ion can be written as:

- 
- 
- 

$$E = E^0_{M^{l+}} - \frac{RT}{lF}k^* + \frac{RT}{lF}\ln\left(\frac{a_{MX_q^{l-pq}}}{a_{X^{p-q}}}\right)$$

$k^*$ stability constant of the complex

- Copper plating example:
- The standard equilibrium potential of Copper(II) is 0.34V. If the electrolyte contains 1 M $Cu^{2+}$ and the activity coefficient of these ions is 0.5, then $E_{cu(II)}$=0.257V In the presence of sodium or potassium cyanide, a complex ion is formed that reduces the activity of the ions to $10^{-18}$. Simultaneously $Cu^{2+}$ is reduced to $Cu^+$ for which the standard potential is 0.55V.

$$Cu(CN)_3^{2-}$$

- The copper deposition potential is now

$$E_{Cu^+} = 0.55 + 0.59 \log 10^{-18} = -0.5V$$

)

## Typical Composition of Nickel Baths

| Material | Watts Quantity | Sulfamate Quantity |
|---|---|---|
| Nickel Sulfate | 250 g/L | -- |
| Nickel Sulfamate | -- | 350 g/L |
| Nickel Chloride | 5 g/L | 25 g/L |
| Boric Acid | 25 g/L | 80 g/L |
| Ferrous Sulfate | 8 g/L | -- |
| Additives | 3 g/L | 15 ml/L |

nential region, the species

AB

B — $I_{B.lim}$

A — $I_{A.lim}$

$E_A^{eq}$     $E_B^{eq}$

Current

Cathodic Potential ——→ (−)
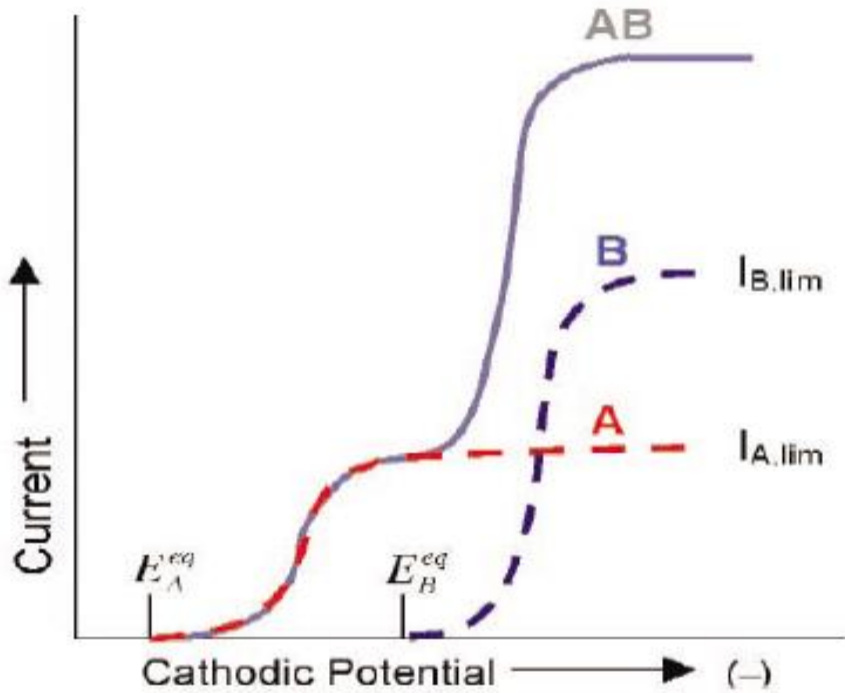
FIG. 1. An ideal polarization curve for the electrodeposition of the binary alloy AB results from the sum of pure metal (A and B) polarization curves.

Alloy deposition

An+ + $n$e−→ A
and
Bm+ + $m$e− → B
where the constants $n$ and $m$ are the number of electrons transferred.

The cathodic electrodeposition of binary compound (e.g. CdSe) depends on the simultaneous electrodeposition of two ion species ($Cd^{2+}$ and $HSeO_2^+$). Obviously it is different from the electrodeposition of a single ion species. One difficulty comes from the widely differing values of equilibrium potentials. According to the Nernst equation, the potential of the electrode is given by:

$$E_M = E^o_{M^{n+}/M} + \frac{RT}{nF} \ln \left( \frac{a_{M^{n+}}}{a_M} \right)$$

where $a_{M^{n+}}$, $a_M$ the activities of the ions in the solution and of the atoms in the electrodeposits respectively and $E^o_{M^{n+}/M}$ is the standard electrode potential. The cathodic deposition involves cadmium ions and selenium compounds which are reduced at the cathode, precipitating a semiconductor film on the substrate.

$$H_2SeO_3 + Cd^{2+} + 4H^+ + 6e \xrightarrow{\longleftarrow} CdSe + 3H_2O$$

Let $\eta_M$ stand for the overpotential during discharge of the $M^{n+}$ ion. The cathodic electrodeposition of CdSe can be achieved if $E = E_{Cd} + \eta_{Cd^{2+}} = E_{Se} + \eta_{HSeO_2^+}$. However, the electrolysis might involve codeposition of elementary Cd and Se, a process that must be avoided. The elementary reactions are:
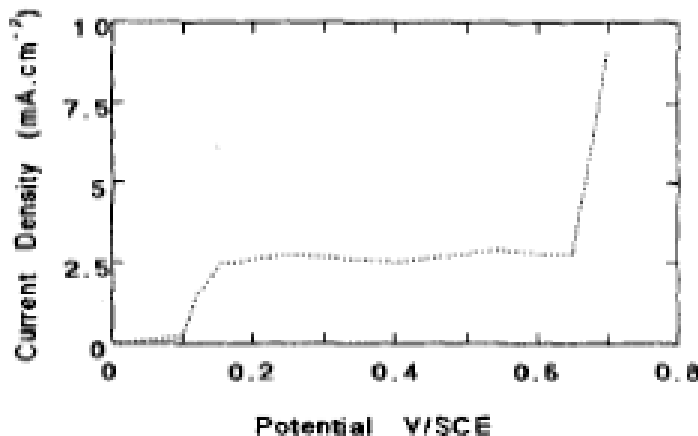
$$Cd^{2+} + 2e^- \xrightarrow{\longleftarrow} Cd \quad (E^o = -0.64 \text{ V/SCE})$$

$$H_2SeO_3 + 4H^+ + 4e^- \xrightarrow{\longleftarrow} Se + 3H_2O \quad (E^o = +0.5 \text{ V/SCE})$$



FIG. 1 Voltammogram for deposition of CdSe from a solution of 0.2M $CdSO_4$ and $7 \times 10^{-4}$ M $H_2SeO_3$, pH 2 and T= 18°C. Sweep rate 20 mV/S.
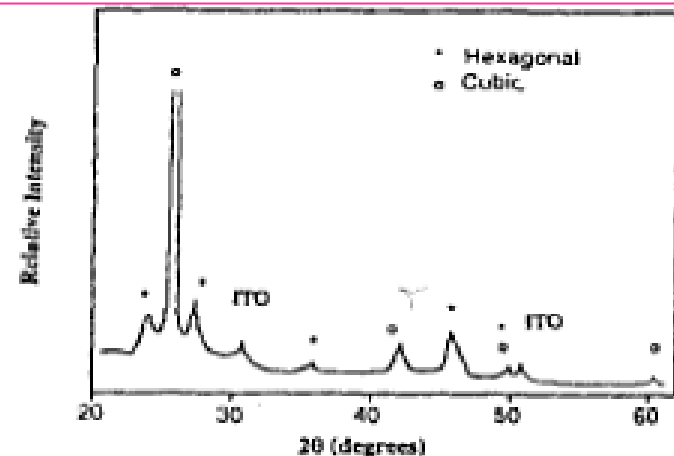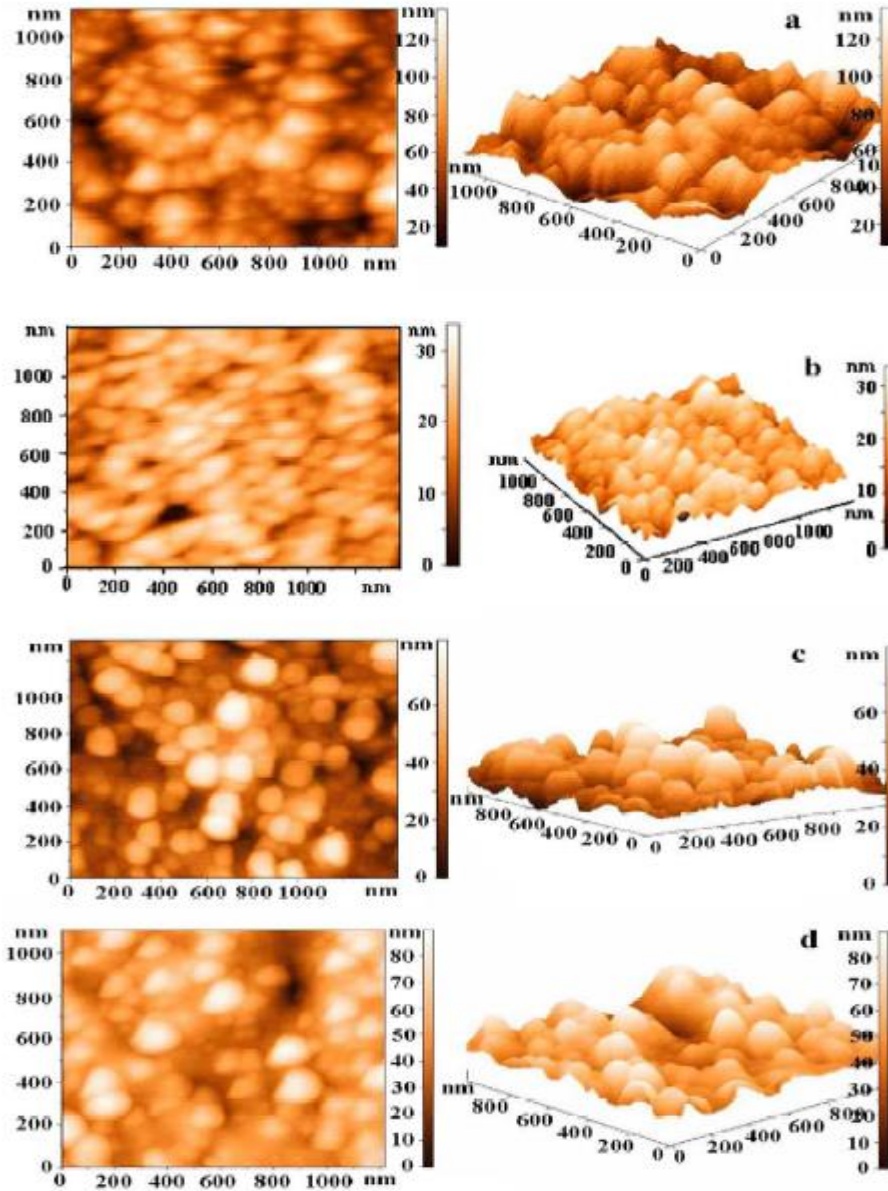
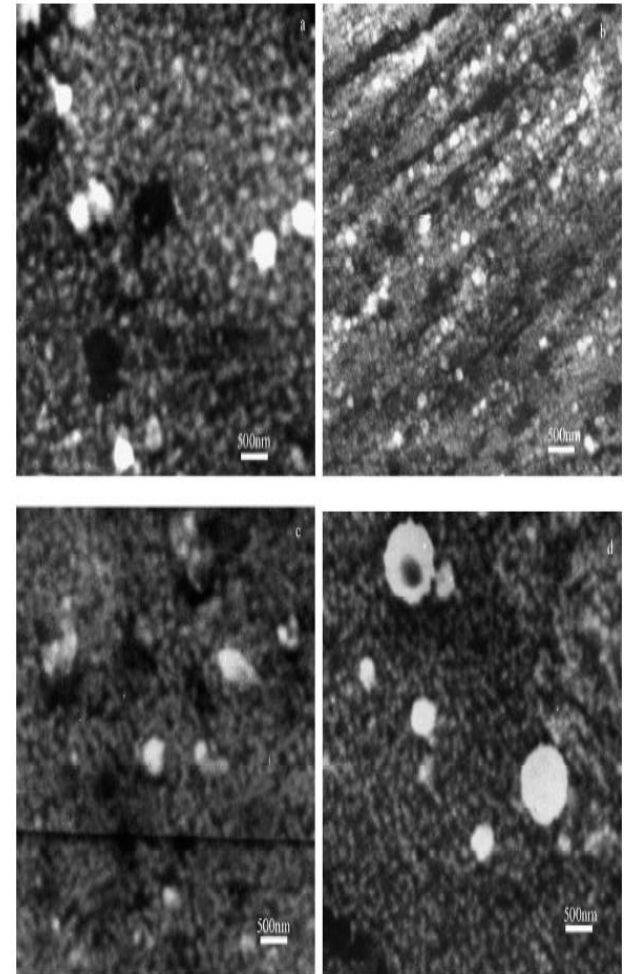FIG. 2 XRD patterns of CdSe deposited from an electrolyte containing $CdCl_2$ at E= - 0.5 V vs. SCE and T= 75°C.

AFM images of CdSe films electrodeposited at different potentials for 30 min: (a) −0.65 V; (b) −0.70 V; (c) −0.71 V; (d) −0.72 V.

Fig. 5. SCM images of CdSe films electrodeposited at different potentials for 30 min: (a) −0.65 V; (b) −0.70 V; (c) −0.71 V; (d) −0.72 V.
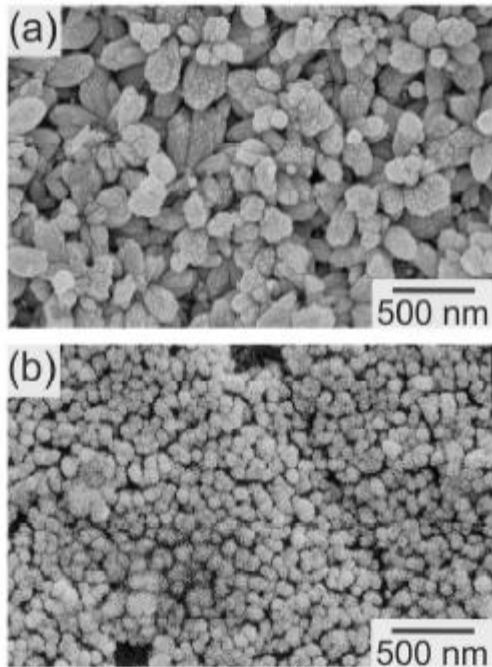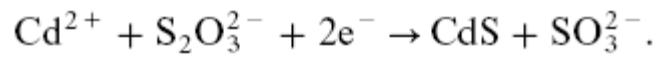
$$Cd^{2+} + S_2O_3^{2-} + 2e^- \rightarrow CdS + SO_3^{2-}.$$



Fig. 5. SEM photographs of CdS thin films electrodeposited on ITO (a) and Ni (b), same as those in (a) and (b) in Fig. 4.
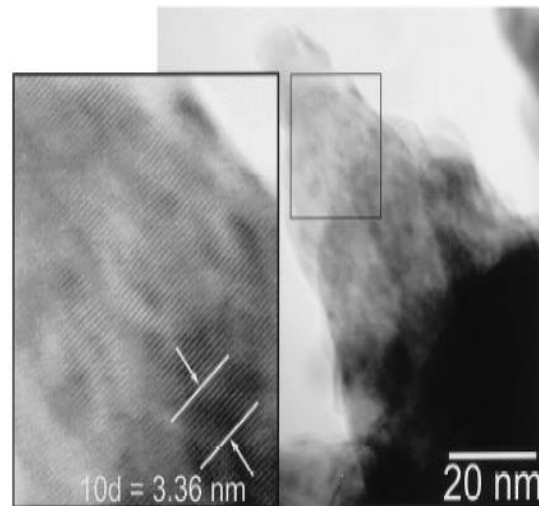


Fig. 6. TEM photograph of CdS crystallite electrodeposited on a Ni mesh in a 0.08 M CdCl₂ + 1 M NH₄SCN (pH 4.2) aqueous solution at − 0.7 V vs. SCE. The left-hand picture is a close up of the deposit showing the lattice fringe corresponding to the (002) planes of hexagonal CdS.
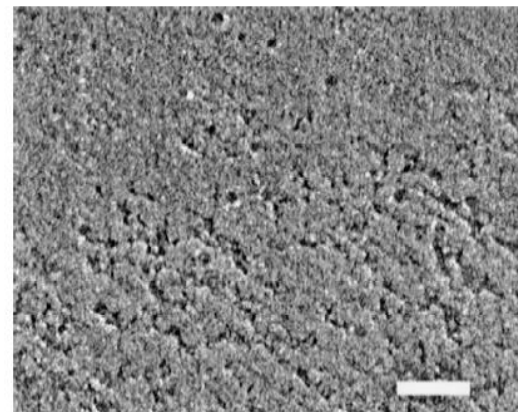
Fig. 2. SEM micrograph of CdS electrodeposited at − 0.85 V vs. SCE on mechanically polished Mo. The white length scale bar corresponds to 1.0 μm.

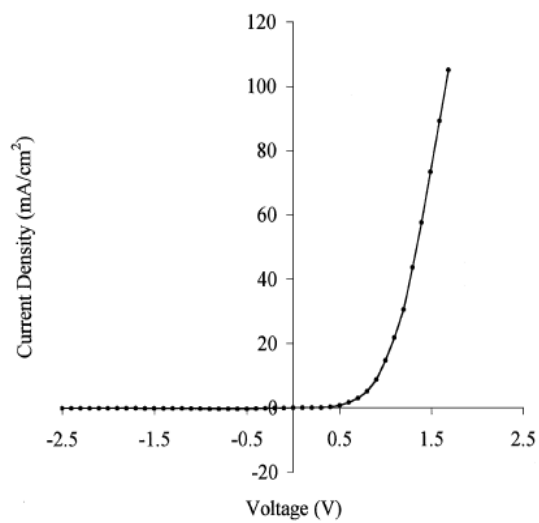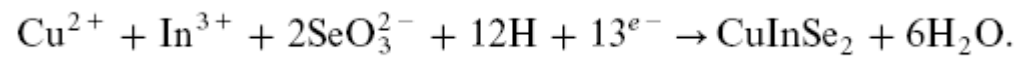$$Cu^{2+} + In^{3+} + 2SeO_3^{2-} + 12H + 13^{e-} \rightarrow CuInSe_2 + 6H_2O.$$



Fig. 9. Current density vs. voltage behavior of an electrodeposited CdS on CIS pn junction.
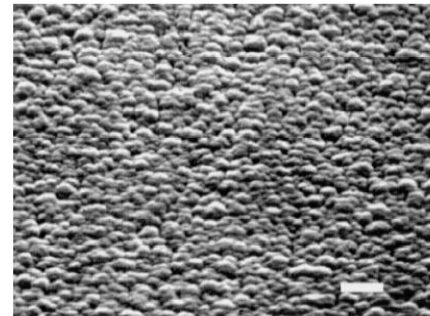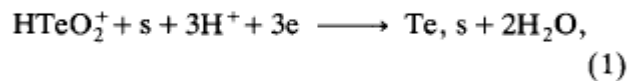


Fig. 1. SEM micrograph of CIS electrodeposited at $-1.1$ V vs. SCE on mechanically polished Mo. The white length scale bar corresponds to 1.0 μm.

The electrodeposition mechanism of CdTe implies several steps, whereby surface sites, s, are involved [1,2]. The first step is the reduction of $HTeO_2^+$ at a site s:

$$HTeO_2^+ + s + 3H^+ + 3e \longrightarrow Te, s + 2H_2O, \qquad (1)$$

and Te, s is reduced into Te(-II) forming CdTe with $Cd^{2+}$ cations:

$$Te, s + Cd^{2+} + 2e \longrightarrow CdTe + s. \qquad (2)$$
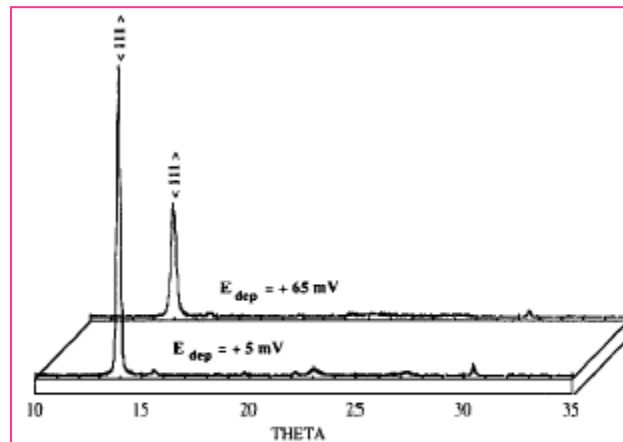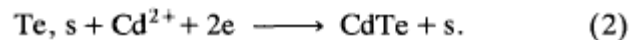


Fig. 1. XRD spectra of 1 $\mu$m CdTe films deposited on CdS on tin oxide. Deposition potential: +5 and +65 mV versus the $Cd/Cd^{2+}$ potential in the same solution.
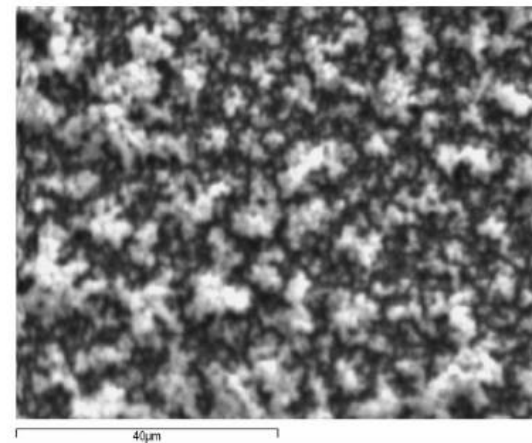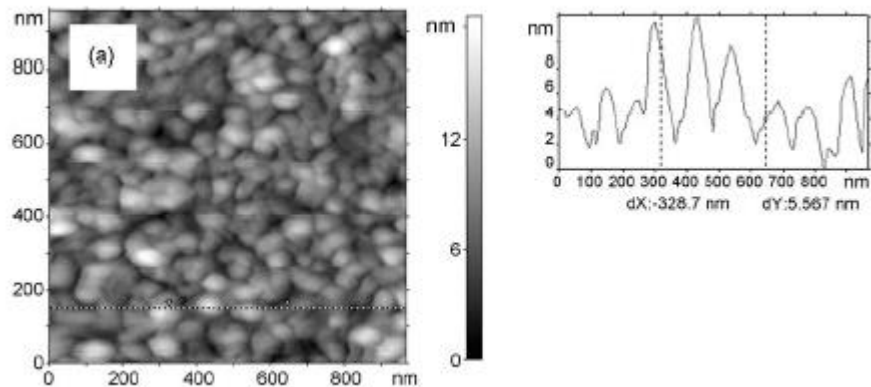
Fig. 8. SEM-micrograph of CdTe-film deposited for condition of Fig. 6.

# Electrodeposition of Silicon

- The electrodeposition of Silicon in aqueous electrolytes is not possible for one major reason;
  - The standard potential of Silicon at the cathode is more negative than that of hydrogen. One always obtains hydrogen evolution at the cost of silicon deposition.

- Nonaqueous baths have been used for silicon electrodeposition:
  - leads to amorphous silicon and the main application is for solar cells

S. Soukane (1999)

# FUSED-SALT ELECTRODEPOSITION OF THIN-LAYER SILICON
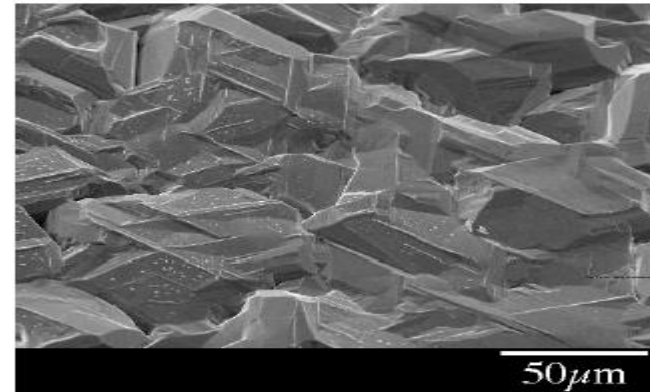


Fig. 4. Top view of epitaxial silicon deposited onto c-Si at a rate of 45 μm/hr. The high growth rate of the film resulted in faceting.



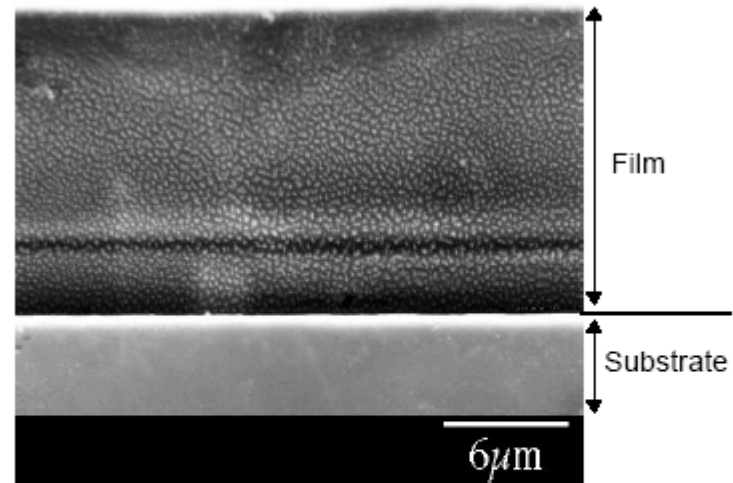1. Schematic of the Electrodeposition Cell



Fig. 2. SEM side view of a stain-etched silicon film deposited on c-Si. The etch was used to enhance the contrast between deposit and substrate. The striation in the deposit is due to an unintended change in temperature during deposition.
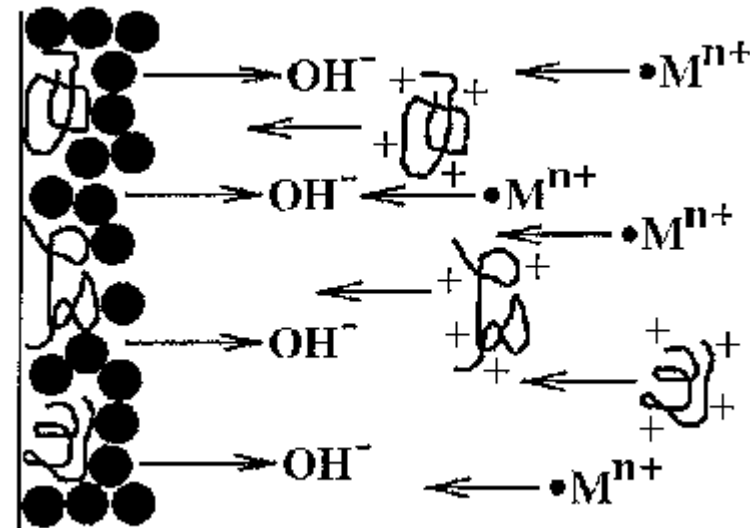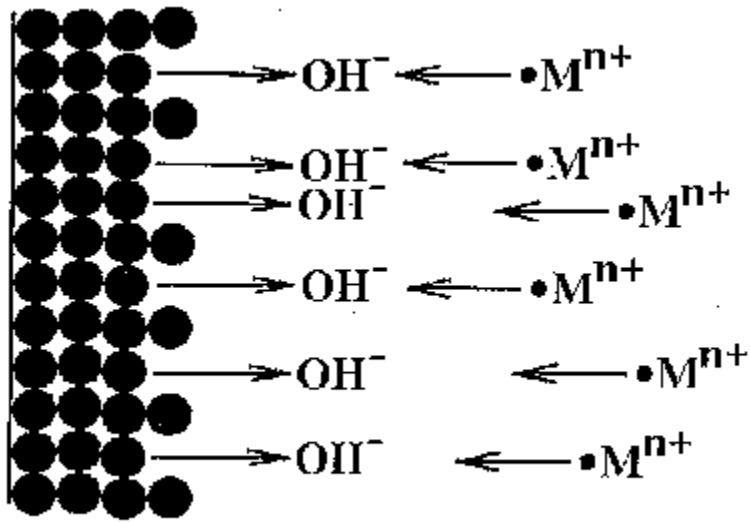
Electrolytic deposition produces ceramic materials and provides their deposition. In the cathodic electrodeposition method,[4] the following reactions are used to generate base at an electrode surface:

$$2H_2O + 2e^- <==> H_2 + 2OH^- \quad (1)$$

$$NO_3^- + H_2O + 2e^- <==> NO_2^- + 2OH^- \quad (2)$$

$$O_2 + 2H_2O + 4e^- <==> 4OH^-$$
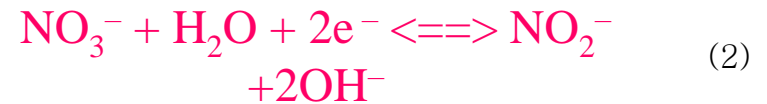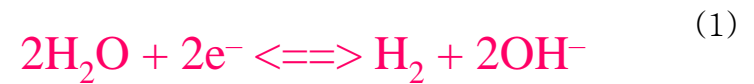
The (a−top) electrolytic deposition of ceramic particles and (b−bottom) intercalation of cationic polyelectrolytes into electrolytic deposits.

## Macro Throwing Power

The ability of a bath to produce deposits of more or less uniform thickness on cathodes having macroscopic irregularities is termed Macro-throwing power.

Ni plating (also other acidic Cu and Zn baths) show poor throwing power. If the C.E. values are close to 100% at low and high current density values, then the macroscopic irregularities on the cathode will lead to non-uniform deposits.

Alkaline baths have better macro throwing power, since the metal ions are present as complex ions.

## Uniform Electrodeposit Through The Use of Complex Baths

- In most complex baths, the deposition potentials are amenable to hydrogen evolution which competes with metal deposition such that C.E. falls as current density is increased. This results in a more uniform deposit on cathodic macro irregularities.

- When the ions are complexed, they encounter high concentration polarization (CP). If the CP is high, the micro throwing power is rather poor.

- The ability to produce a deposit over a surface including recesses is called covering power.

# Electroplating Modeling

- Express the flux of species to the electrode:
  - Does the potential has an effect on the concentration distribution?

- 

- Nernst-Planck equation for dilute solutions

- 

- $$N_i = -z_i u_i F C_i \nabla \Phi - D_i \nabla C_i + Cv$$

- 

- Stephan-Maxwell approach need to be used for concentrated solutions.

S. Soukane (1999)

- The material balance for each minor component (no homogeneous reactions):

- $$\frac{\partial C_i}{\partial t} = -\nabla.N_i + R_i$$

-

- Multiplying z$^i$F and summing over all species leads to the charge balance;

- $$\frac{\partial}{\partial t} F \sum_i z_i C_i = -\nabla.F \sum_i z_i N_i$$

-

- Electroneutrality is assumed in all solutions, except in the double layer that is usually taken as part of the boundaries and is expressed by:

- $$\sum_i z_i C_i = 0$$

-

- This leads to: $$\nabla.F \sum_i z_i N_i = 0$$

-

- Introducing the flux density gives:

- 

$$\nabla . F \sum_i z_i \left( -z_i u_i F C_i \nabla \Phi - D_i \nabla C_i \right) = 0$$

- 

- Introducing conductivity, which is defined as

- 

$$\kappa = F^2 \sum_i \left( z_i \right)^2 u_i C_i$$

- 

- we arrive at

- 

$$\nabla . \left( \kappa \nabla \Phi \right) + F \sum_i z_i \nabla . \left( D_i \nabla C_i \right) = 0$$

- 

- The current i is given by

$$i = -\kappa \nabla \Phi - F \sum_i z_i D_i \nabla C_i$$

S. Soukane (1999)

- the flow of current is entirely due to electrochemical reactions of the metal ions. Therefore, the normal derivatives of the potential and the metal ion concentration at the electrode surface are related by

- 
$$\nabla\Phi.n = nFD_M \nabla C_M.n$$

- 

- The potential of the electrolyte is related to the total overpotential

- 
$$\Phi = \Phi_E - \eta_{tot}$$

- 

- Which can be split into a concentration overpotential and a surface overpotential related to the current density i, by the Butler-Volmer equation for electrode kinetics

S. Soukane (1999)

- 
- The activation overpotential $\quad i = i_0 \left( e^{\alpha_a \frac{\eta_S F}{RT}} - e^{-\alpha_c \frac{\eta_S F}{RT}} \right)$
- 

- 
- The concentration overpotential $\quad \eta_C = \dfrac{RT}{nF} \ln \dfrac{C_M}{C_M^\infty}$
- 
- 
- 

- For the metal-ion species, since the flow of current is entirely due to the electrochemical reactions we can write

$$nFD_M \nabla C_M . n = i.n$$

S. Soukane (1999)

## Hydrogen Embrittlement

Hydrogen embrittlement is a generic term used to describe a variety of fracture phenomena having a common relationship to the presence of hydrogen in the metal as a solute or in the atmosphere as a gas.

In general any process producing atomic H at a metal surface will induce considerable hydrogen absorption in that metal (ED, ELD, Acid Pickling, E-cleaning). A large fraction combines to form bubbles of gaseous or molecular hydrogen which is not soluble in metals.

## Effects of Hydrogen Embritllement

Corrosion reactions can generate $H_2$, and choosing proper coating to prevent corrosion is important.

Permeation of H through various protective coatings is considered to show the effectiveness of various barrier layers on minimizing the H egress.

Problems as a result of H embrittlement/hydriding:
- Leakage from gas filled pressure vessels
- Breakage of aircraft components
- Blisters or fisheyes in Cu, Al, and Steel components
- Reductions in mechanical propeties of materials

## Mechanism of Hydrogen Embrittlement

The mechanism of may change depending on the source of H and the nature of applied stress.

1. The non-hydride forming systems such as Fe&Ni alloys fail because H-decreases the atomic bonding. The fracture seems to be associated with H-induced plasticity in the vicinity of the crack tip.
2. Metals which form stable hydrides (Nb, Zr, or Ti ) appear to fracture by a stress-induced hydride formation and cleavage mechanism.
3. Adsorption-decreased surface energy and high-pressure hydrogen gas bubble formations.

## Leveling of Deposit

Leveling is the progressive reduction of the surface roughness during deposition.

S.R. may be due to coarse mechanical polishing. Cathodic leveling results in a smooth deposit or a deposit of reduced roughness. Leveling occurs when metal is deposited in recessed areas than on peaks.

Leveling is important in metal finishing industry and in electronic industry for deposition through masks. In electroforming of MEMS devices leveling means uniform deposition in micro profiles.

# Leveling

- Additives are used to provide:
  - Smoother surfaces
  - Completely filled trenches

Same processing time (675s)
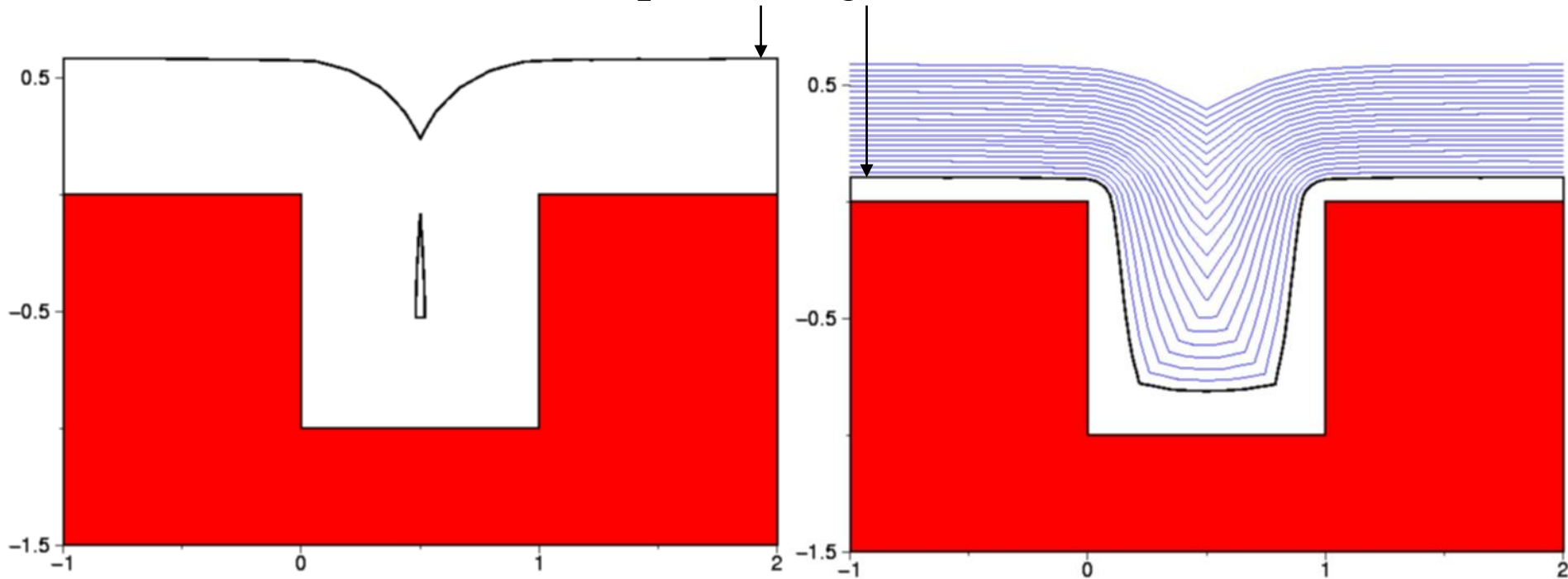


Subconformal plating                    Superfilling

# Types of Leveling

Leveling can be achieved in solutions either in the absence or presence of leveling agents.

There are two types of leveling:

1. Geometric leveling in the absence of additives.
2. True or electrochemical leveling in the presence of additives.

# Dealing with additives

- How are the additives being consumed.

- 

- Mass transfer limited regime
  - Use of inhibition models.

- 
$$\Psi^a = \frac{1}{1 + K_{lev} \dfrac{N_A^*}{N_M^*}} \qquad\qquad \Psi = \frac{1}{1 + bN_A^{*\,p}}$$
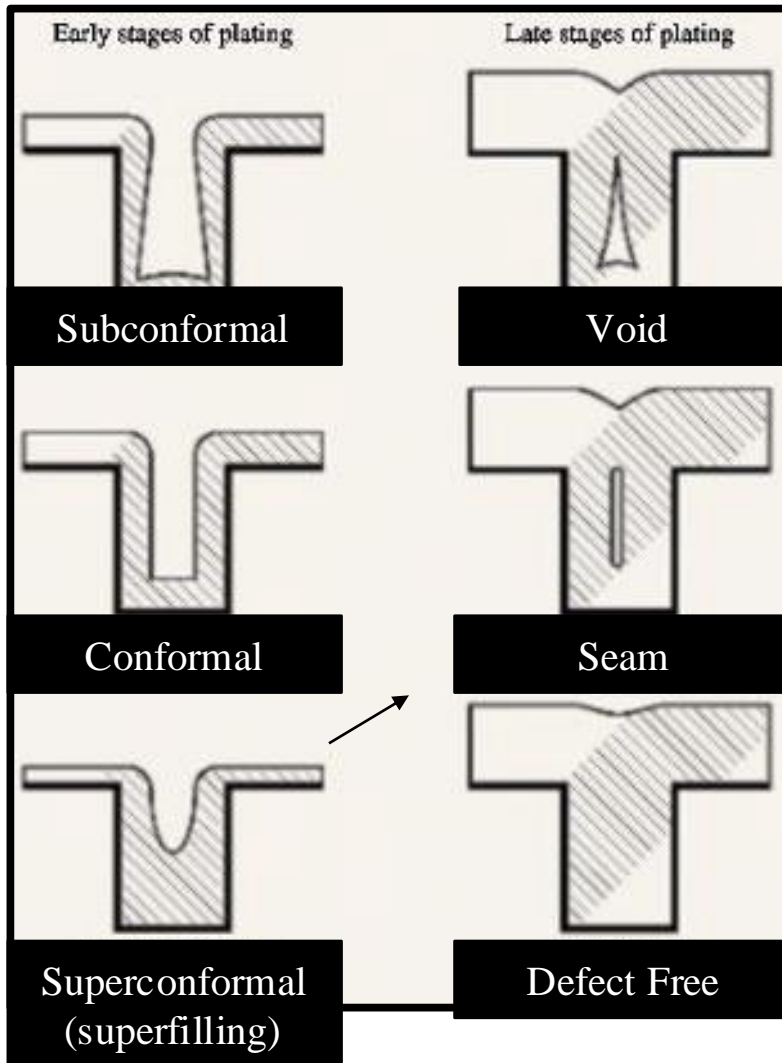- 

- 

- kinetic regime
  - Chemical mechanism using an adsorption model for the species involved

- 
  a: Andricacos et al

-

# Leveling Agents In Cu ECD



- Simple Cu plating often results in deposits with voids or seams. Deposits with such defects, lead to early failure of ICs.

- Void-free profile, can be obtained using leveling agent.

Taken from, P. C. Andricacos *et al.*, *IBM J. of Res. and Dev.*42(5),567 (1998).

# Leveling Action

•We focus on additives that are polymer molecules, which can occupy vacant surface sites, introducing competition for surface sites·[‡]

•Diffusion generated concentration gradients of additive, and depletion of additives in the interior of features (by consumption) can yield higher Cu deposition rates at feature bottoms than at their tops, resulting in superfilling.[†]