University of Utah
Fundamentals of Microfabrication

Electro Chemical Deposition:
Principles, Methods and Applications

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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**

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 Setup
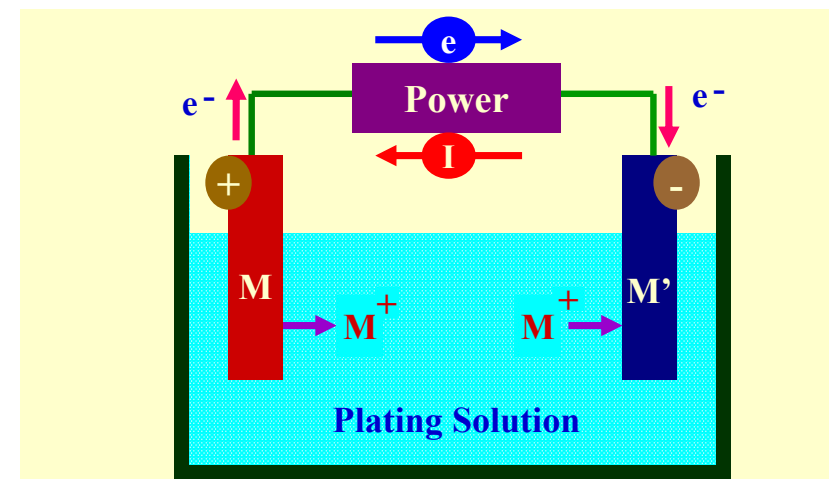
Electroplating Applications

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

Electroforming

Electroforming is a process used for making metallic articles with tight dimensional tolerance
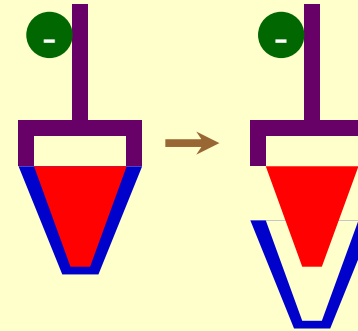
By depositing a metal into or on to a mold or mandrel, a free-standing metal object is made

Useful for the production of originals and making exact copies of originals

Need for Electroforming

• Accuracy of reproduction
• Production of foils and mesh-products
• Screen-printing cylinders
• Manufacture of complex shaped objects
• Manufacture of large or small products
• Manufacture of molds

Electroforming Applications

• Micro components and prostheses
• Complex wave guides
• Metal bellows
• Reflectors, Nose cones
• Heat exchangers, micro filters
• Decorative ware

When combined with lithography, electroforming is extremely useful for making micro parts, and overcomes the difficulty of traditional machining

LIGA Process

X-rays	
Mask	
Resist	Mold
Substrate	
Develop Resist	Embossing
Plating	μ-Structure
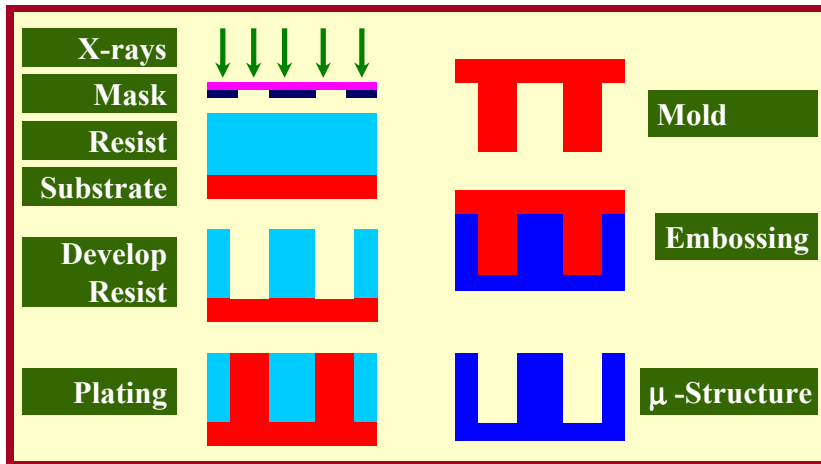
Electrochemical Deposition

Understanding the relationships between micro-structure and mechanical properties is one of the main goals of metallurgy and materials science.

This allowed the tailoring of materials properties by varying the composition and the structure.

The fascinating field of electro deposition allows one to tailor the surface properties of a material or to form the entire part by electroforming.

To explore new materials for a variety of applications.

Faraday's Law

The amount of electrochemical reaction that occurs at an electrode is proportional to the quantity of electric charge (Q) passed through the cell.

The weight of a product of electrolysis is W, then

$W = ZQ$ (Z is the electrochemical equivalent)

Since $Q = It$, it follows that $W = ZIt$

Production of one gram equivalent of a product at the electrode (Weq) in a cell needs 96487 Coulombs

Electrochemical Equivalence

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

$$W_{eq} = A / n$$

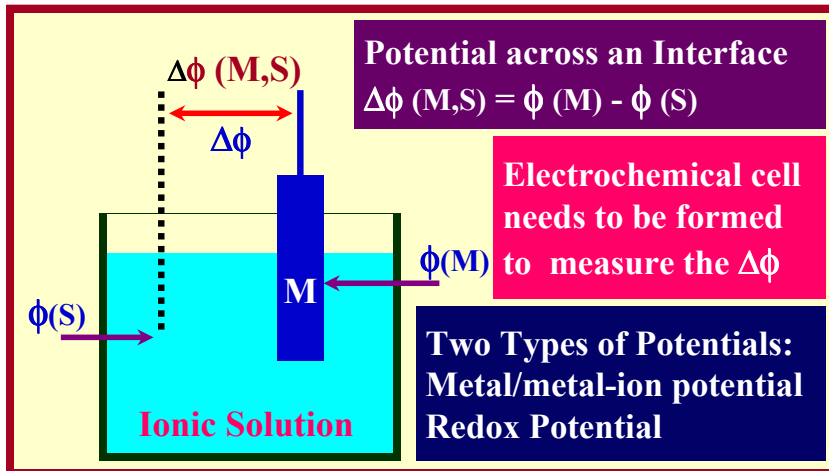When $Q = 1$, $W_{(Q=1)} = Z$

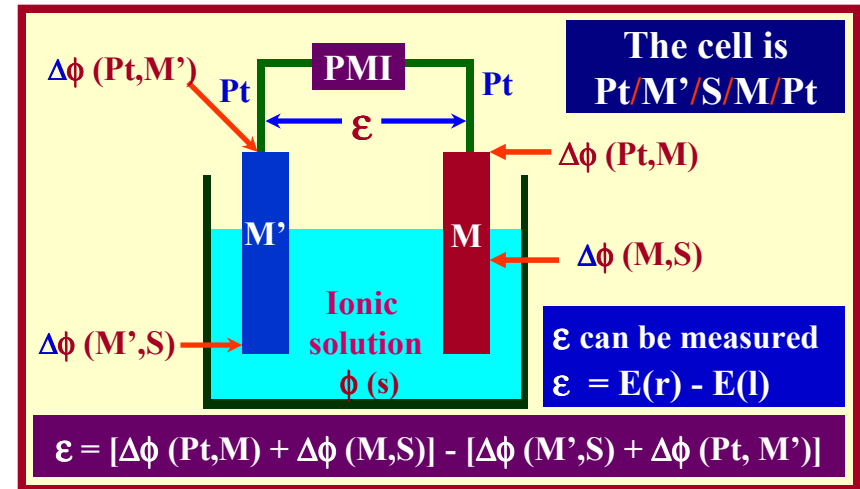$$W_{eq} = 96487\, Z$$

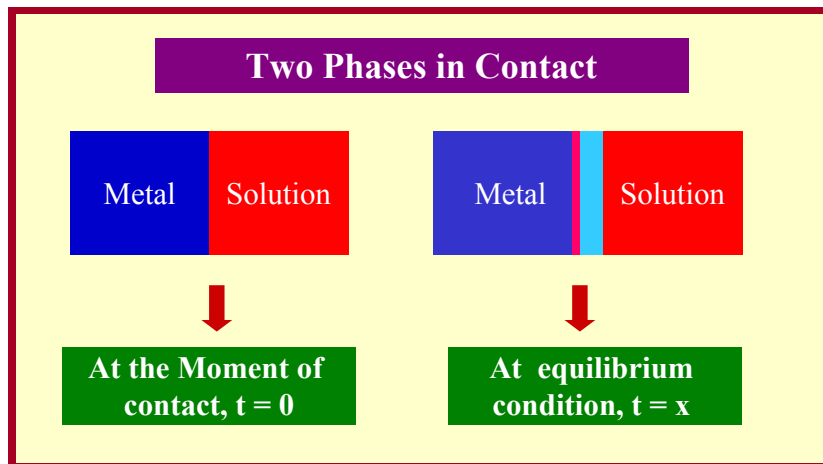$$Z = W_{eq} / 96487 = W_{eq} / F$$

$$Z = A / nF$$

$$W = ZQ = AQ / nF$$

Equilibrium Electrode Potential

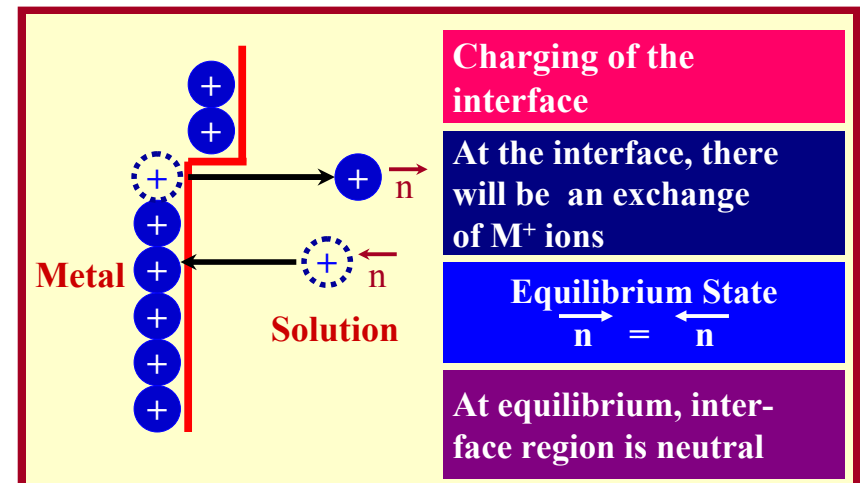**Potential across an Interface**
$\Delta\phi (M,S) = \phi (M) - \phi (S)$

Electrochemical cell needs to be formed to measure the $\Delta\phi$

Two Types of Potentials:
Metal/metal-ion potential
Redox Potential

$\Delta\phi (M,S)$
$\Delta\phi$
$\phi(M)$
$\phi(S)$
M
Ionic Solution

Cell Voltage and Electrode Potential

The cell is Pt/M'/S/M/Pt

$\Delta\phi (Pt,M')$ Pt   PMI   Pt
ε
$\Delta\phi (Pt,M)$
M'
M
$\Delta\phi (M,S)$
Ionic solution
$\phi (s)$
$\Delta\phi (M',S)$

ε can be measured
$\varepsilon = E(r) - E(l)$

$\varepsilon = [\Delta\phi (Pt,M) + \Delta\phi (M,S)] - [\Delta\phi (M',S) + \Delta\phi (Pt, M')]$

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
$\overrightarrow{n} = \overleftarrow{n}$
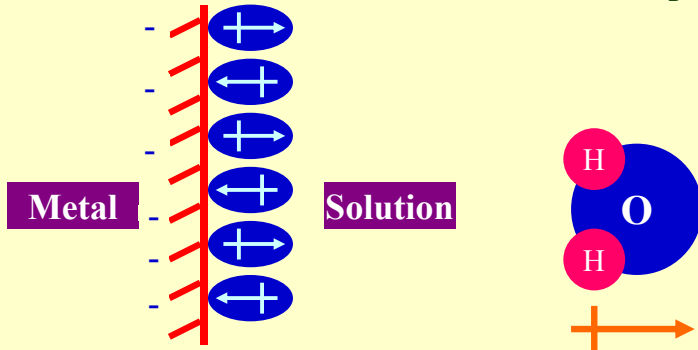
At equilibrium, interface region is neutral

Metal
Solution
$+$ n
$+$ n

Water Structure At The Interface

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

Requisites for Electroplating MEMS Applications

A conducting surface as a seed layer is required.

Clean substrates, solutions, and containers, etc.
  Even low impurity levels would result in poor-quality films.

Good resist adhesion on the substrate is required.

The plating solution must have easy access to recesses, and be compatible with the resist and substrate materials.

Uniform current distribution on the substrate surface.

Typical Composition of Nickel Baths

	Watts	Sulfamate
Material	Quantity	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

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

Pulse and Pulse-Reverse Plating

In dc-plating, constant current is used, and the rate
of arrival of metal ions depends on their diffusion
coefficient (electrode-to-part spacing and agitation).

In PC and PRC, a modulated current waveforms
are used to get a better leveling of the deposit, and
to minimize the porosity, contamination, etc.

The morphology of some metal and alloy deposits
were found to be superior to the dc-plated deposits.

Complex current wave forms can be generated by
using pulse rectifier: unipolar and bipolar pulses.

Characteristics of Unipolar Currents

To characterize a train of current pulses, three
parameters need to be known
- The cathodic peak pulse current density (J_c)
- The cathodic pulse length (t_c)
- The interval between pulses (t_p)

The average current density J_{av} is measured,
and it is expressed for PC as: $J_{av} = (J_c \times t_c)/(t_c + t_p)$

The duty cycle (T) which represents the portion of
the time in each cycle when the current is ON.
It is defined by $T = t_c/(t_c + t_p)$; $J_{av} = J_c \times T$

Characteristics of Bipolar Currents

To characterize a train of pulse-reverse current
waveform, four parameters need to be known.
- The cathodic peak pulse current density (J_c)
- The cathodic pulse length (t_c)
- The anodic pulse time (t_a)
- The anodic current density (J_a)

$$J_{av} = (J_c \times t_c + J_a t_a) / (t_c + t_a)$$
$$T_{prc} = (J_c \times t_c - J_a t_a) / (J_c t_c)$$

Effects of Pulsed Current on the Deposit Properties

PC affects the mechanism of electro-crystallization,
which in turn, controls the physical and mechanical
properties of the deposit.

Nucleation rate of the deposit $\propto$ current density.

Use of high J_{av} pulses can produce deposits with
reduced porosity, and finer grains through the
desorption of impurities and renucleation of deposits
with the formation of new, smaller crystal grains.

Grain size depends on the duty cycle and the bath.

Low C and N content, deposits with low stress,
increased ductility and electrical conductivity.

Structure and Properties of Deposits

The crystalline structure formed as a result of E.D. depends on a competition between rates of new crystalline formation and existing crystal growth.

Several factors in plating process influence the crystal structure and grain size of the deposits.

Plating Bath Control Using Ampere -Time Instruments

Plating is done by following a quantity called amperage which indicates the total amount of current that has passed through a plating bath.

A change in bath's resistance will change amperage.

The amount of metal deposited depends on three factors:

Amperage, Plating time, Current efficiency of the bath

-Ampere-time x C.E. = mg of metal deposited

-Thickness (μ") = mg of metal x Factor plated area (in^2)

-Ampere-time x C.E. = Thickness Area factor

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) x 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%

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.

Strike Baths

- Strike bath is made by an extremely high current density for a very short time or in a specially formulated bath.
- In some cases, the required potential for metal deposition may not be reached in recesses and vias.
- Other processes such as hydrogen evolution or reduction of ions such as Fe3+ to Fe2+ may occur.

In such cases, a preliminary strike bath deposit may be the solution.

Electroless Deposition

$$M^{z+}_{Soln} + RED_{soln} \longrightarrow M_{lattice} + OX_{soln}$$
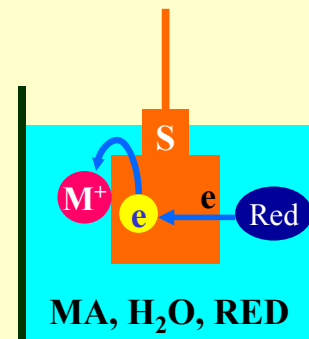
This X_n requires a catalytic surface. The Reductant is the source of electrons.

S

M+   e   e   Red

MA, H$_2$O, RED

Common Reducing Agents:
- Formaldehyde
- Hypophosphorous acid
- Alkali borohydrides
- Alkali diboranes

Advantages of Electroless Deposition

No electrical contact is needed
It is possible to plate both conductive and
   insulating surfaces, provided the surfaces are
   first sensitized.
It is readily adaptable for three-dimensional
   coverage.
No field lines are present, and this enhances deposit
   uniformity

Mixed Potential Theory

The catalytic reaction must be conducted in such a way that a homogeneous reaction between Mz+ and RED in the bulk of the solution is suppressed.

The equilibrium potential of the RED (Eeq, Red) must be more negative than that of the metal electrode (Eeq,M), so that the reducing agent can function as electron donor and Metal ion as electron acceptor.

Metallizing Nonconductors

Certain parts or components whose functions are
   fully utilized only when the properties of both a
   metal and non-metal are combined.
Generally a part is made of plastic or ceramic, and
   the metal added to its significant surfaces to impart
   specific metallic properties.
1. For electrical conductivity, as in PCB.
2. For metallic appearance, as in the buttons,
   door knobs, wheels in toys, etc.
3. For strength, as in woman's high heel shoes.

Developing Good Adhesion
Metal Deposition on Polymers

For metallizing nonconductors, their surfaces need
   to be mechanically roughened, or etched, or made
   hydrophilic. Nonconductors need pre-conditioning
   of their surfaces.
Polymers: ABS, Polyimides, Polysulfones, etc.
   Cr_2O_3/H_2SO_4 (0.5:1.0); Neutralize in $NaHSO_3$
Fluorocarbons: Na metal in anhydrous NH_3 or THF
Need to be treated further in sensitizing, nucleating
   (catalytic), accelerator solutions prior to plating in
   electroless solution.

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 Embrittlement

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.

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.