What is Electroplating?

- An electrochemical process where metal ions are transferred from a solution and are deposited as a thin layer onto the surface of a cathode.

- The setup is composed of a DC circuit with an anode and a cathode sitting in a bath of solution that has the metal ions necessary for coating or plating.

- Electroplating can enhance:
  - Chemical properties---increase corrosion resistance
  - Physical properties---increase thickness of part
  - Mechanical properties---increase tensile strength & hardness
Electroplating and Electrolysis

Electroplating is a procedure that uses electrolysis to apply a thin layer of a metal over the surface of another metal.

Electrolysis is the process of making a non-spontaneous chemical redox reaction occur by passing electricity through a substance. (electrolytic cell)
Plating Definitions

- **Electroplating**: Deposition of a metal film by means of an electrical current flow which provides electrons to convert metal ions to metal atoms at an interface.

- **Immersion Plating**: Deposition of a metal film at an interface driven by oxidation of surface metals which supply electrons to convert metal ions in solution to metal atoms.

- **Electroless Plating**: Deposition of a metal film at an interface driven by oxidation of a reducing agent which supplies electrons to convert metal ions to metal atoms.
In 1800 Alessandro Volta created the “voltaic pile”

Was the first galvanic cell able to produce a steady flow of electrical current

Stack of copper and zinc discs separated by cloth soaked in saline solution (electrolyte)
Scientists now able to apply constant current electricity to their experiments

In 1805, Italian chemist Luigi Brugnatelli, successfully electroplated silver medals with gold.

Brugnatelli's inventions were kept secret by the French Academy of Sciences and did not become used in general industry until English and Russian scientists independently discovered technique 35 years later.

1940 first patent for electroplating awarded, and soon factories in England were mass producing silver plated items, including teapots, brushes and utensils (see Engr45 “Spooning” presentation for more info…).
An **electrolytic cell** is a device in which an external source of electrons (electrical circuit) is used to make a non-spontaneous redox reaction take place.

Molten (liquid) state of a pure substance is the medium which the cell is made. Ex: molten NaCl
Oxidation at anode

\[ 2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^- \]

Reduction at cathode

\[ \text{Na}^+ + \text{e}^- \rightarrow \text{Na} \]

\[ E_{net}^0 = E_{ox}^0 + E_{red}^0 \]
\[ = (-1.36 \text{ V}) + (-2.71 \text{ V}) \]
\[ = -4.07 \text{ V} \]

The net cell voltage of -4.07 V

Because it is a non-spontaneous reaction the \( E_{net}^0 \) is always less than zero.
NOTE:
The cathode is still under going reduction, but now is negative.
The anode is still under going oxidation, but now is positive.

REASON:

4 The electrodes are connected to a power source that pump e- from negative to positive.
4 The electrode that is connected to the power source is the cathode.
4 Since electrons are being forced into the cathode it becomes negative.
Examples of electroplating

- Coating jewelry with thin layer of expensive metal.
- Coating chromium over steel to make rust resistant.
Metal
wood
plastic
Nickel Electroplating
Nickel Electroplating

- The goal was to electroplate nickel onto a copper leaf for a decorative design.

- We covered our sample in wax leaving certain areas uncovered by the wax and exposed to be electroplated.

- Being an electrochemical process, the wax would not be removed during electroplating and would control where the metal would be plated.

- The plating solution used was a mixture of:
  - Nickel Sulfate Hexahydrate (300 g/L),
  - Boric Acid (45 g/L)
  - Nickel Chloride Hexahydrate (45 g/L)
How it works

Copper Cathode is reduced (accepts electrons)

Nickel Anode is oxidized (gives us electrons)

Ni^{2+} ions within solution become attracted to Copper cathode
How it works
Auxiliary anodes – example showing location of auxiliary anode to increase thickness deposited into recessed area of work.
Figure 16
Plating rack specifically designed for automotive wheels
Step 1: Prepare Samples

Clean off the sample using acid solution
(we used weak acetic acid in the form of vinegar for 10 min)

Tape off area that you intend to plate, this will prevent wax from coating surface
Step 2: Melt Wax

- Melt wax in well-ventilated space
  - (use caution, Safety is NOT an accident!)
  - Note: Reduce heat once all the wax has melted
  - If you add too much heat and do not allow proper cooling, you could melt the tape on your sample during the next step.
Step 3: Cover in Wax

Dunk the prepared leafs with tape on them into the hot wax.

Keep in wax for five seconds and remove.

Allow to cool, and dip into wax two more times until wax builds up on surface.

When completely cool peel off tape to reveal copper metal for plating.
Step 4: Electroplating
Step 4: Electroplating

- Anode
- Cathode
- Nickel ion solution
- Spacers
Step 5: Clean off sample

- Remove sample from electroplating
- Clean with soap and water and pat dry
- Use an open flame to melt off wax
- Sample may require a light polishing, be gentle
Results

<table>
<thead>
<tr>
<th>Trial 1</th>
<th>Trial 2</th>
<th>Trial 3</th>
<th>Trial 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time: 2 min</td>
<td>Time: 30 min</td>
<td>Time: 15 min</td>
<td>Time: 10 min</td>
</tr>
<tr>
<td>700 mA</td>
<td>350-380 mA</td>
<td>120-200 mA</td>
<td>180-220 mA</td>
</tr>
</tbody>
</table>
Surface of Copper after Plating
Surface of Nickel after Plating
What went wrong?

- Cathode and electrode too close [all Trials]
- Chemical plating solution was not removed before cleaning wax off surface, reacted with flame [Trial 1]
- Too much time, resulting in a buildup of weak deposits and dark colors [Trial 2]
- Surface not clean (tape residue melted to surface) [Trial 3]
Multi-station counterflow rinse tank
Electroless Plating

Plating driven entirely by chemical reactions - no external source of electric current is required

- Deposition of metal onto a part surface occurs in an aqueous solution containing ions of the desired plating metal - the workpart surface acts as a catalyst for the reaction in the presence of a reducing agent

- Electroless platable metals are limited: nickel and certain of its alloys, copper, and gold

- Notable application: copper for plating through-holes of printed circuit boards
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.
Electroless Deposition

\[ M^{2+}_{\text{Soln}} + \text{RED}_{\text{Soln}} \rightarrow M_{\text{lattice}} + \text{OX}_{\text{Soln}} \]

This \( X_n \) requires a catalytic surface. The Reductant is the source of electrons.

Common Reducing Agents:
- Formaldehyde
- Hypophosphorous acid
- Alkali borohydrides
- Alkali diboranes
How can we electroplate one metal onto another metal surface?

\[ \text{Zn(s)} + \text{CuSO}_4 \rightarrow \text{ZnSO}_4(aq) + \text{Cu(s)} \]
Electroless Bumping

- NiAu bump
- Pd bump

- Hard bumps
- Cost-effective bumping process (no photolithography)
Module 4

Copper Electroplating for IC Applications

- Electrochemical fundamentals
- Process/hardware impacts
- Additives and feature fill capability
- Plated film properties
ELECTROCHEMICAL DEPOSITION OF THIN METAL FILMS

Electroless Metal Plating:

Oxidation (Anodic):
\[
\text{HCHO} + \text{H}_2\text{O} \rightarrow \text{HCOOH} + 2\text{H}^+ + 2\text{e}^- 
\]

Reduction (Cathodic):
\[
\text{M}^{n+} + \text{n e}^- \rightarrow \text{M}^0 
\]

Non-conducting

Electroless plating

Activation

Conducting

Thickness limit \(\approx 1 \mu\text{m}\)
Common Coating Metals

- **Zinc** - plated on steel products such as fasteners, wire goods, electric switch boxes, and sheetmetal parts as a sacrificial barrier to corrosion
- **Nickel** - for corrosion resistance and decorative purposes on steel, brass, zinc die castings, and other metals; also used as a base coat for chrome plate
- **Tin** - widely used for corrosion protection in "tin cans" and other food containers
- **Copper** - decorative coating on steel and zinc, either alone or alloyed as brass; also, applications in printed circuit boards
- **Chromium** - decorative coating widely used in automotive, office furniture, and kitchen appliance and one of the hardest electroplated coatings for wear resistance applications
- Precious metals (**gold, silver, platinum**) - plated on jewelry; gold is also used for electrical contacts
Electroforming

Electrolytic deposition of metal onto a pattern until the required thickness is achieved, after which the pattern is removed to leave the formed part.

- The same process as electroplating with different purpose.
  - Typical plating thickness is only about 0.05 mm or less, electroformed parts are often substantially thicker, so the production cycle is proportionally longer.
- Metals: copper, nickel, and nickel cobalt alloys.
- Typical applications: fine molds and dies (e.g., for lenses) and plates for embossing and printing.
- Notable application: molds for CDs and DVDs.
  - Surface details imprinted onto a CD are measured in μm or μ-in (1 μm = 39.4 μ-in).
  - These details are readily obtained in the mold by 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 is a three stage process which can be used for the manufacture of high aspect ratio, 3-D microstructures in a wide variety of materials (e.g. metals, polymers, ceramics and glasses). The name is derived from the German acronym Lithographie, Galvanof ormung und Abformung, i.e. lithography, electroplating and moulding.

Irradiating a resist (polymer) is the first step in the process. This can be achieved using laser light, electron or ion beams or X-rays from a synchrotron radiation source, the latter being essential for deep structures.

All the methods use a shadow printing process. In the deep X-ray lithographic process a 2-D absorber pattern from a mask is transferred into the depth of a thick resist by the chemical changes induced by a highly collimated beam of X-rays. Development of the irradiated areas of the resist results in a 3-D replication of the pattern and a metallic master mould can then be produced by electroplating into the 'free' areas.
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.
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.
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.
Hot Dipping

Metal substrate (part) is immersed in a molten bath of a second metal to coated the part.

- Common substrate metals: steel and iron
- Coating metals: zinc, aluminum, tin, and lead
- Primary purpose is corrosion protection

Processes

- **Galvanizing** - zinc (Zn) coated onto steel or iron
  - By far the most important hot dipping process
- **Aluminizing** - coating of aluminum (Al) onto a substrate
  - Excellent corrosion protection, in some cases five times more effective than galvanizing
- **Tinning** - coating of tin (Sn) onto steel for food containers, dairy equipment, and soldering applications
- **Temeplate** - plating of lead-tin alloy onto steel
Conversion Coating

A family of coating processes in which a thin film of oxide, phosphate, or chromate is formed on a metallic surface by electro/chemical reaction.

- Immersion and spraying are the two common methods of exposing the metal surface to the reacting chemicals.
- Reasons:
  - Corrosion, preparation for painting, wear, lubricity, electrical resistance, appearance, and part identification.
- Two categories:
  - Chemical treatments – phosphate coating (Zn and steels) and chromate coating (Al, Cd, Cu, Mg and Zn).
  - Anodizing – An electrolytic treatment producing a stable oxide layer on Al and Mg.
- Common metals treated: steel (including galvanized steel), zinc, and aluminum.
Chemical Conversion Coatings

Base metal is exposed to chemicals that form thin nonmetallic surface films

1. *Phosphate coating* - transforms base metal surface (e.g., steel, zinc) into phosphate film by exposure to phosphate salts and dilute phosphoric acid
   - Useful preparation for painting of automobiles

2. *Chromate coating* - transforms base metal (e.g., aluminum, copper, magnesium, zinc) into various forms of chromate films (sometimes colorful) using solutions of chromic acid, chromate salts, etc.
Anodizing

Electrolytic treatment that produces a stable oxide layer on a metallic surface

- Applications: aluminum and magnesium most common; also zinc, titanium, and other metals
- Dyes can be incorporated into the anodizing process to create a wide variety of colors
  - Especially common in aluminum anodizing
- Functions: primarily decorative; also corrosion protection