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Innovative Materials Solutions for Electronics

Electroless Plating Tutorial

CMC Laboratories
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Why Use Electroless and Immersion Plating?

- **Uniform thickness distribution**
 - ✦ Less sensitive to surface features than electrolytic
 - ✦ Can plate inside tubes and occluded areas
- **Can plate electrically isolated features**

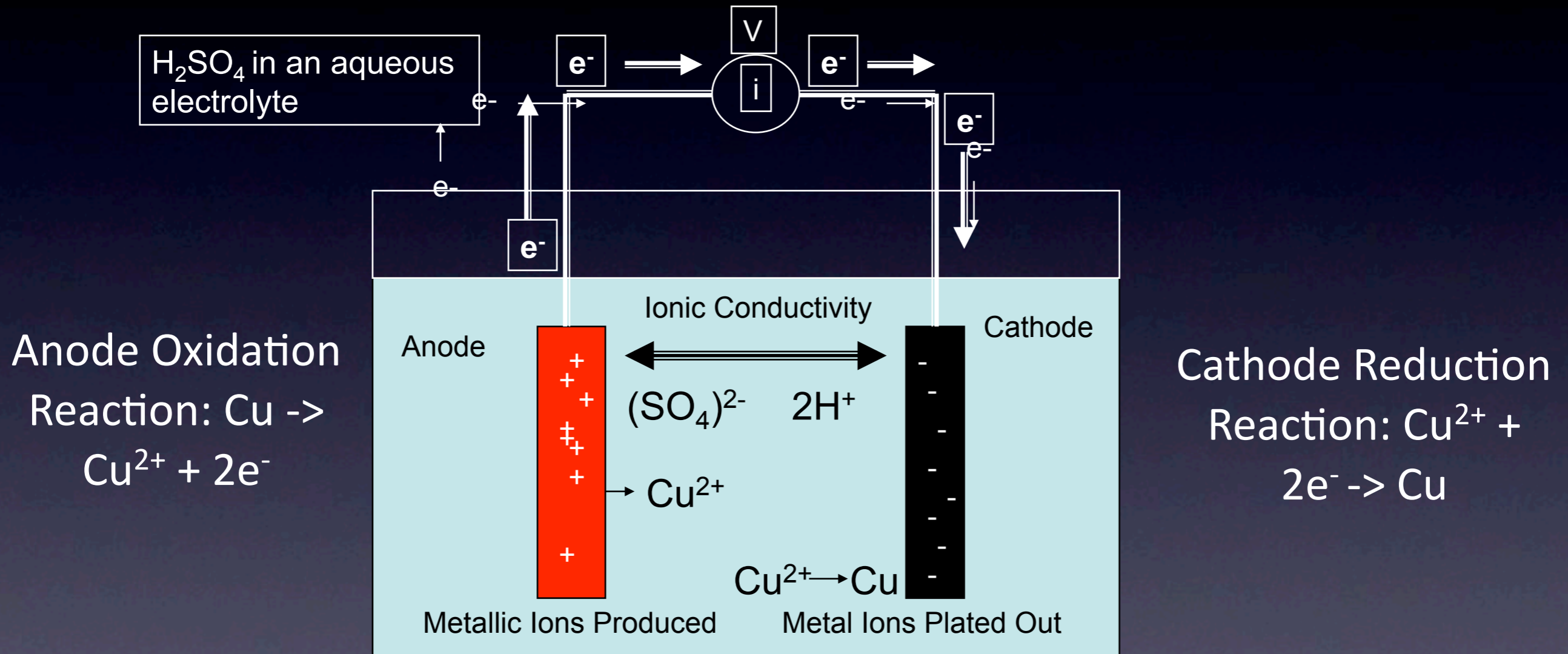


Red-Ox Reaction Concept

- Red- short for “Reduction”
- Ox- short for “Oxidation”
- Chemical “reduction” means to gain electrons in a chemical reaction
- Chemical “oxidation” means to give up electrons in a chemical reaction
- In a red-ox reaction, one species gives up electrons (electron donor) and another species takes up these electrons (electron acceptor)
- An “electronegative” material wants to give up electrons in a chemical reaction
- An “electropositive” material wants to gain electrons in a chemical reaction
- Redox behavior is used to understand all types of chemical reactions, including all types of plating



Electroplating Example

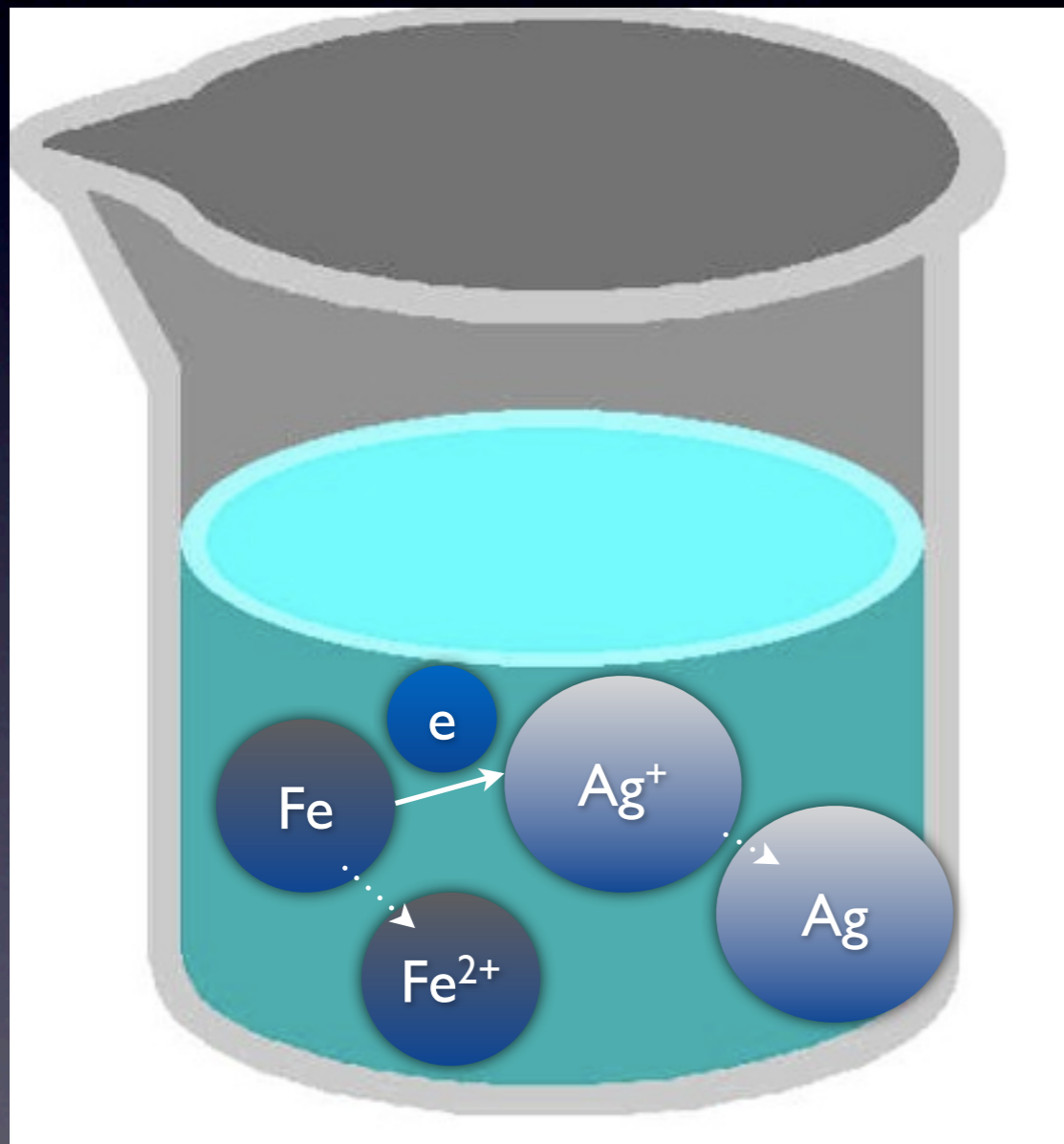


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For Electroplating, the external circuit transfers the electrons from the electron donor to the electron acceptor



Oxidation- Reduction Reactions in Solution



Example: Fe Metal in AgNO₃ Solution



When Fe is added, a redox reaction occurs:



Electrons are donated from the Fe and accepted by the Ag⁺ in solution

Electron transfer between the reactants occurs in solution

The Fe was oxidized and the Ag was reduced in this reaction.

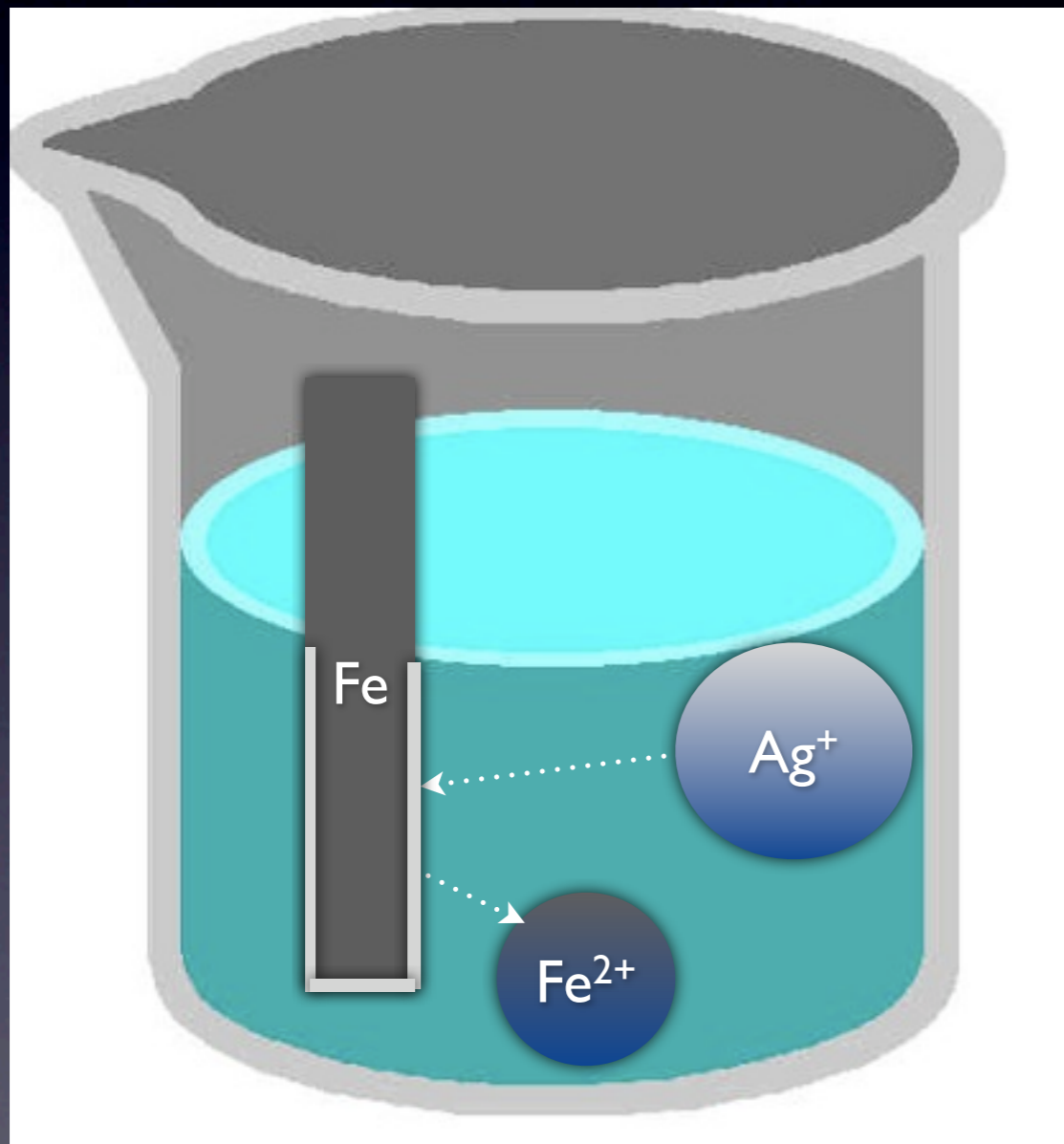


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Immersion Plating



Immersion Plating

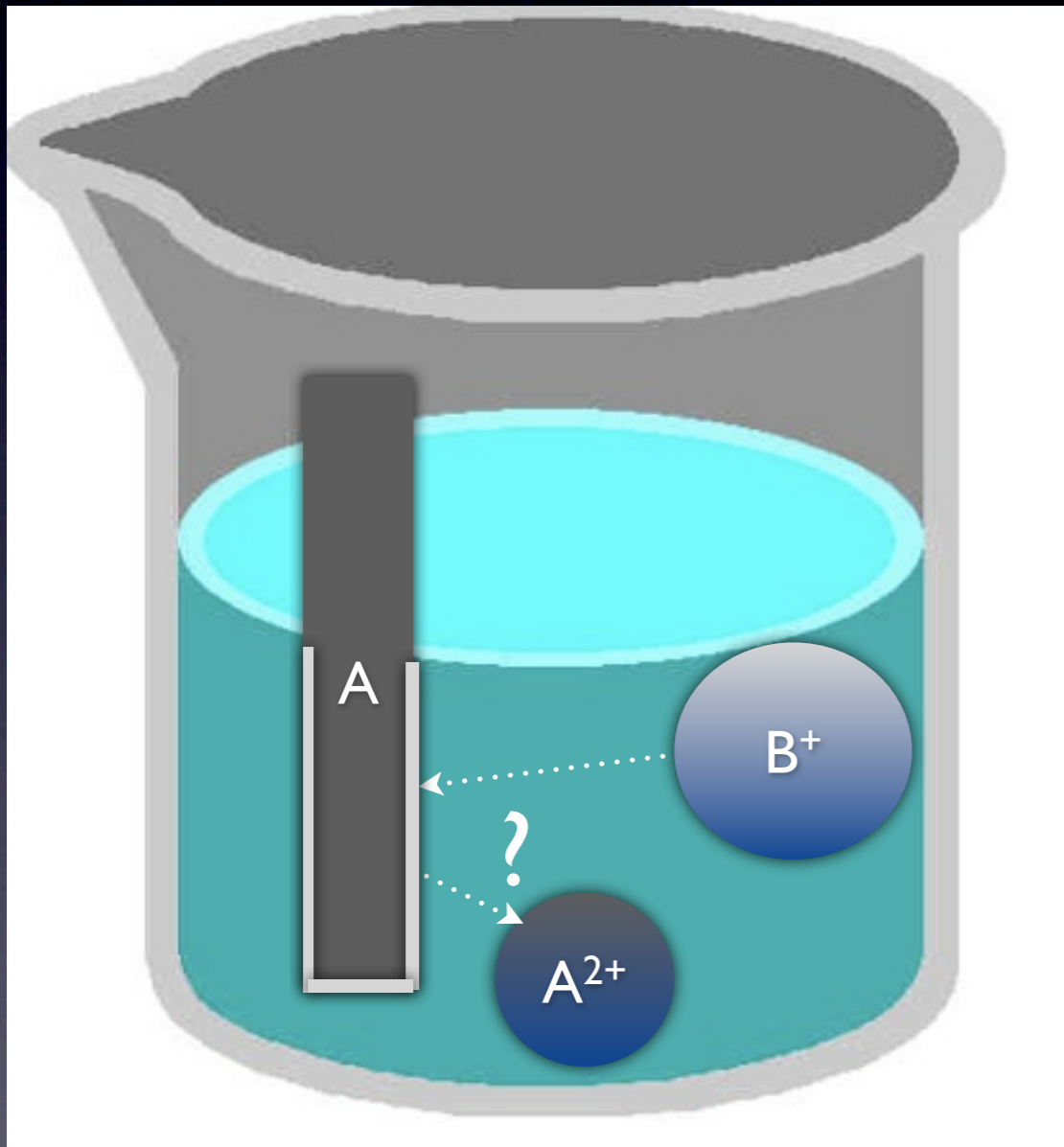


Example: Fe Metal Rod in AgNO_3 Solution

Same chemical Reaction as solution case
Fe metal oxidizes (corrodes) and is dissolved in solution
Ag ions are reduced and plate out on the Fe rod as Ag metal coating
Electrons are donated from the Fe to the Ag
Once the surface is coated with Ag, the reaction stops (no more Fe reactant)
Ag layer is about 5 microinches thick



What Determines Whether Immersion Plating Will Occur?



Reactivity is based on order in electrochemical series

- ◆ Materials near the top of the series want to oxidize
- ◆ Materials near the bottom want to reduce
- ◆ If A is higher on the chart than B, then B will immersion plate on A
- ◆ Pt will plate on everything except Pt

Groups	Metal	
Group A Group B Group C Group D	Potassium	K
	Calcium	Ca
	Sodium	Na
	Magnesium	Mg
	Aluminium	Al
	Zinc	Zn
	Iron	Fe
	Tin	Sn
	Lead	Pb
	Hydrogen	H
	Copper	Cu
	Mercury	Hg
	Silver	Ag
	Gold	Au



Immersion Plating Characteristics

- Very simple solution chemistry
- Extremely thin deposit (5-10 μ inches)-
advantageous for coating expensive noble metals
(Au, Pd, Pt, Ag)
- Uniform surface coverage- used for plating the
inside of tubes, for example

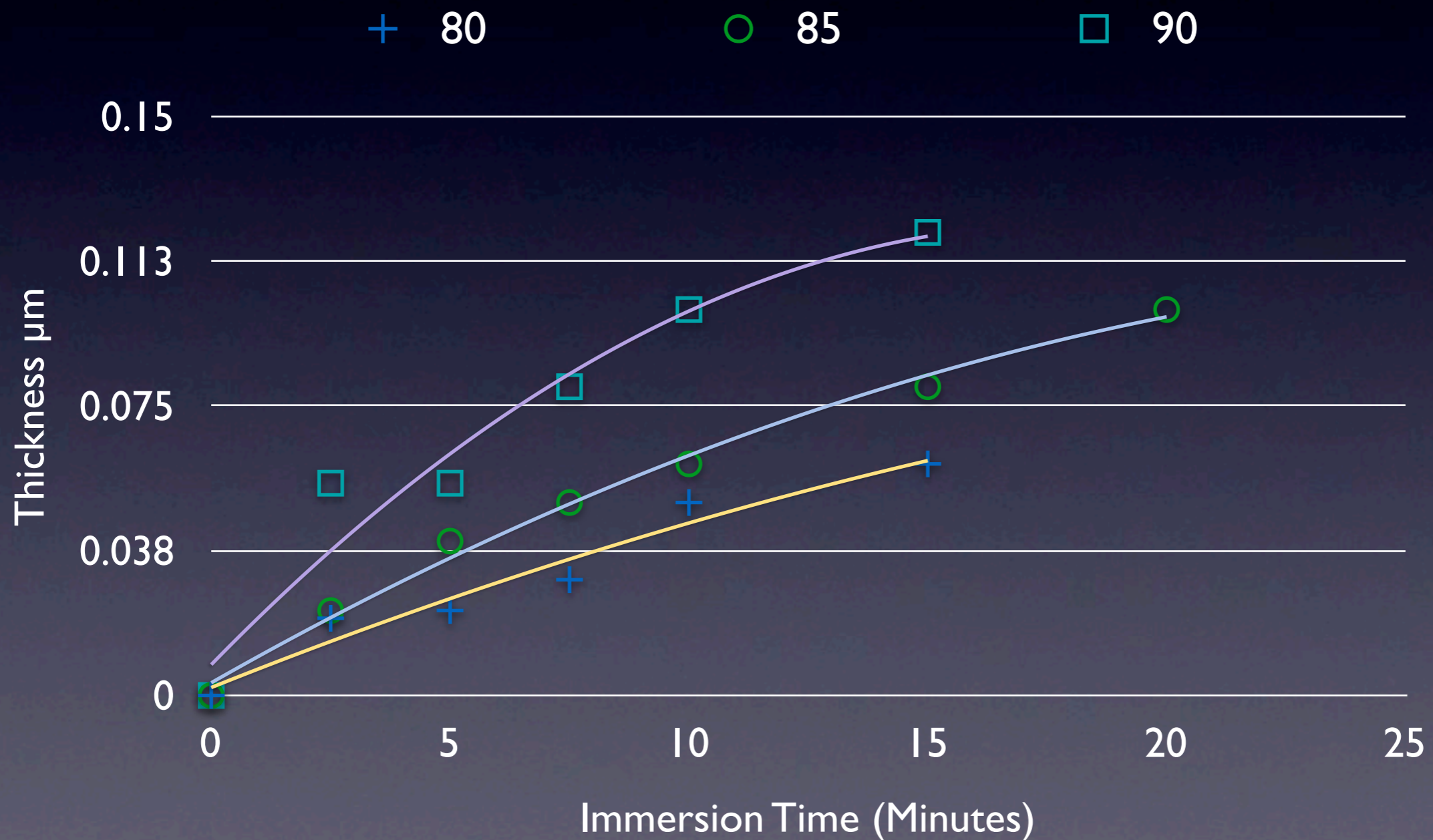


Immersion Plating Formulations

Deposit	Base Metal	Bath Components
Gold	Copper	Potassium Au cyanide, Potassium cyanide.
Copper	Aluminum	Copper sulphate, Ethylenediamine
Nickel	Copper	Nickel sulfate, ammonium nickel sulfate, sodium thiosulfate
Palladium	Copper, Nickel	Palladium Chloride, HCL
Platinum	Copper, Nickel, Gold or Palladium	Chloroplatinic Acid, HCL
Silver	Copper	Silver Cyanide, Sodium Cyanide Silver Nitrate, Ammonia



Immersion Au Plating Rate





Ni-Pd-Au Example

- Developed at Texas Instruments in 1989
- Standard plating for lead-frames and other components
- Highly solderable
- Electroplated Nickel layer (160 - 200 μ inches)
- Thin electroplated Pd layer (10 μ inches)
- Ultrathin immersion Au layer (2 μ inches)
- Au layer reduces oxidation of Pd and improves solder wetting



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Electroless Plating



Electroless Plating Overview

- Immersion plating is driven by oxidation of the base metal - plating stops when base metal surface is completely covered
- Electroless plating is driven by oxidation reactions of plating bath constituents
- Electroless plating is “autocatalytic” or continuous
- Plating continues even when the surface of the base metal is covered



Basic Components of an Electroless Plating Bath

- Electroless bath chemistry is highly complex (compared to immersion or electrolytic plating)
- Aqueous solution of metal ions (electron acceptors)
- Reducing agents (electron donors)
- Complexing agents
- Bath stabilizers



Basic Electroless RedOx Reaction

- Chemical reducing agents in solution oxidize and the metal ions in solution are reduced to form metal atoms
 - * $(\text{Chemical Reducing Agent}) \rightarrow (\text{Chemical Reducing Agent})^+ + e^-$
 - * $(\text{Metal Ion in Solution})^+ + e^- \rightarrow \text{Metal atom}$
- The surface of the base metal to be plated acts as a “catalyst” for this reaction



What is a Catalyst?

- “Catalyst” is a material that increases the rate of a chemical reaction without directly participating in the reaction
- Catalyst is not one of the reactants
- Metals, and particularly noble metals, are good catalysts for many reactions. Electrical insulators are not good catalysts

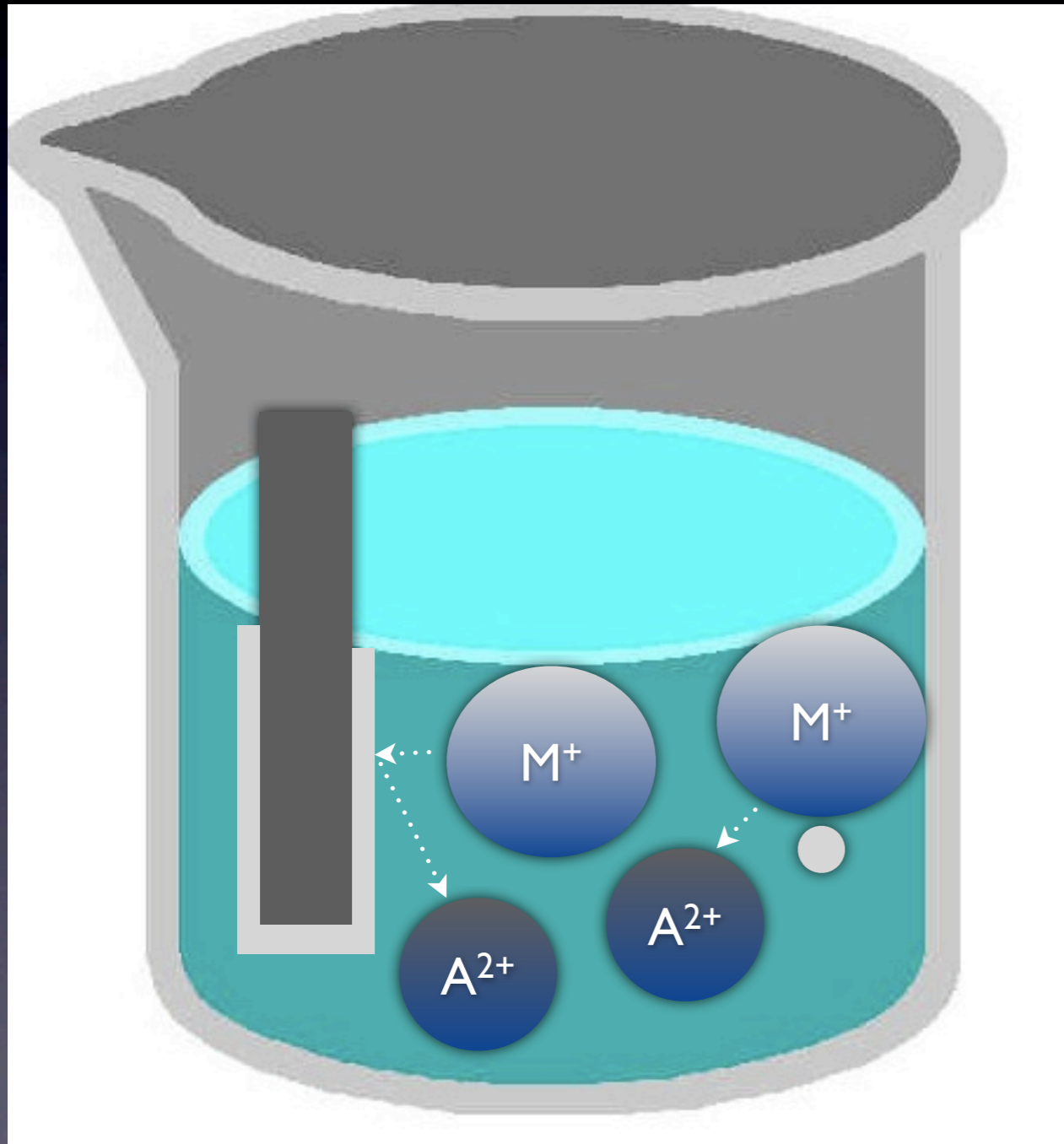


Catalytic Role of the Substrate Surface

- The electroless plating RedOx reaction occurs faster on the substrate surface than in the plating solution away from the surface
- This results in electroless plating on the substrate compared to metal precipitation in solution



Autocatalytic Reaction in Solution or On a Catalytic Surface



- ◆ Metal ion in solution M^+
- ◆ Reducing agent in solution A
- ◆ Plating reaction:
 - $A \rightarrow A^+ + e$
 - $M^+ + e \rightarrow M$
- ◆ This reaction can occur in solution or on the substrate surface
- ◆ If substrate surface is a catalyst, the reaction will occur faster on the substrate than in solution
- ◆ If the substrate is not a catalyst, metal will precipitate out in solution
- ◆ Plating rate is a function of the specific Red/Ox reaction, catalytic surface, pH, temperature, metal ion/reducer concentration

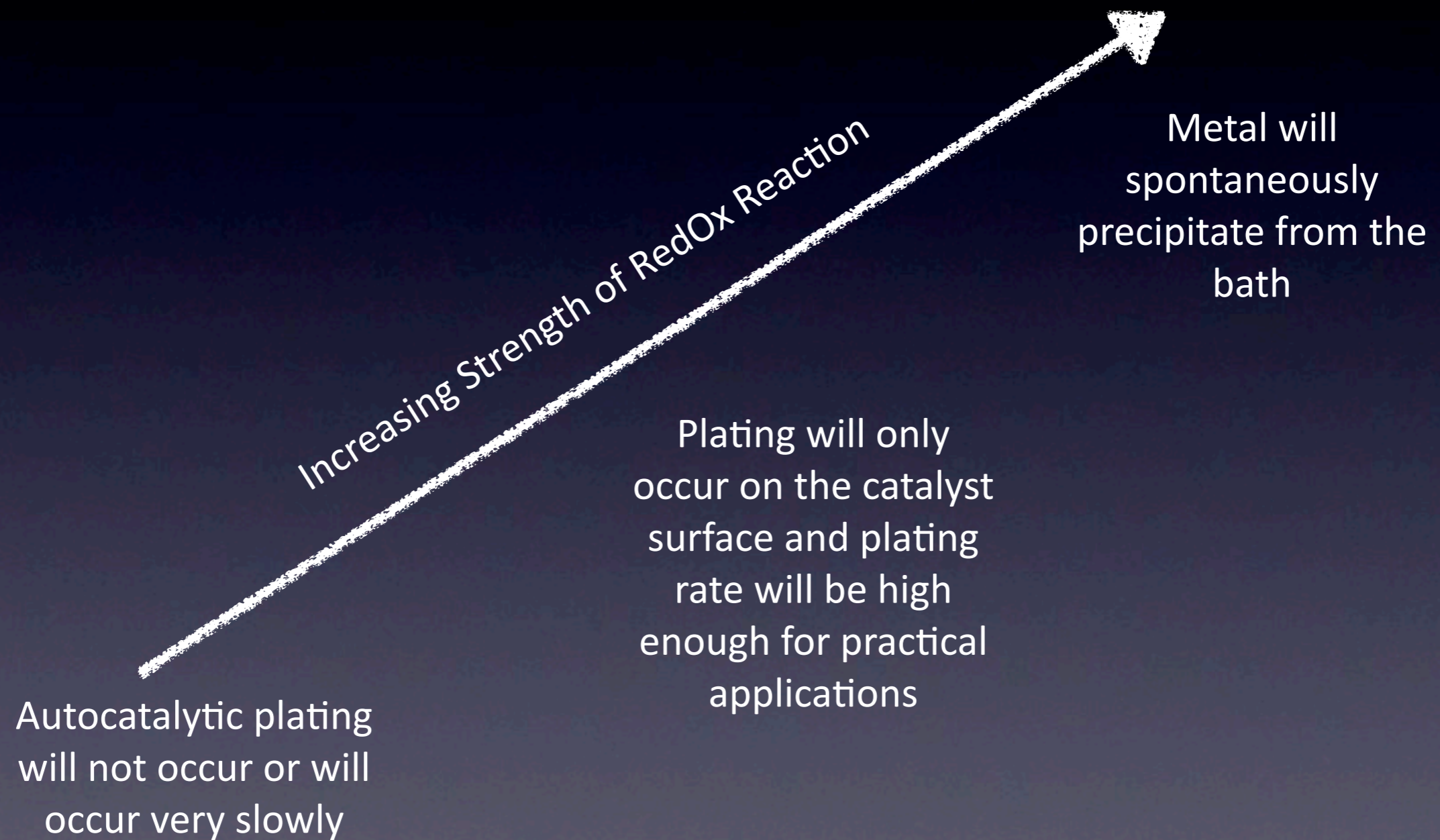


Substrate Catalytic Requirements

- Base substrate metal must be a catalyst for the autocatalytic RedOx reaction in order for plating to initiate
- Base metal surface preparation is critical. Oxide and other contamination must be removed before plating.
- If base metal catalytic properties are poor, a Pd or Pt seed metal can be deposited in some cases (done on Ag)
- Plated surface must be a catalyst for the autocatalytic RedOx reaction in order for plating to continue once the surface is covered



Chemistry Balance in Electroless Baths





How can this type of balance be
achieved?



Role of Stabilizers

- Additives that inhibit the rate of the RedOx Reaction
- Used to prevent spontaneous metal precipitation from the bath
- Heavy metal salts or organic compounds
- “Steric” inhibitors- physically prevent the reactants from coming in contact with each other



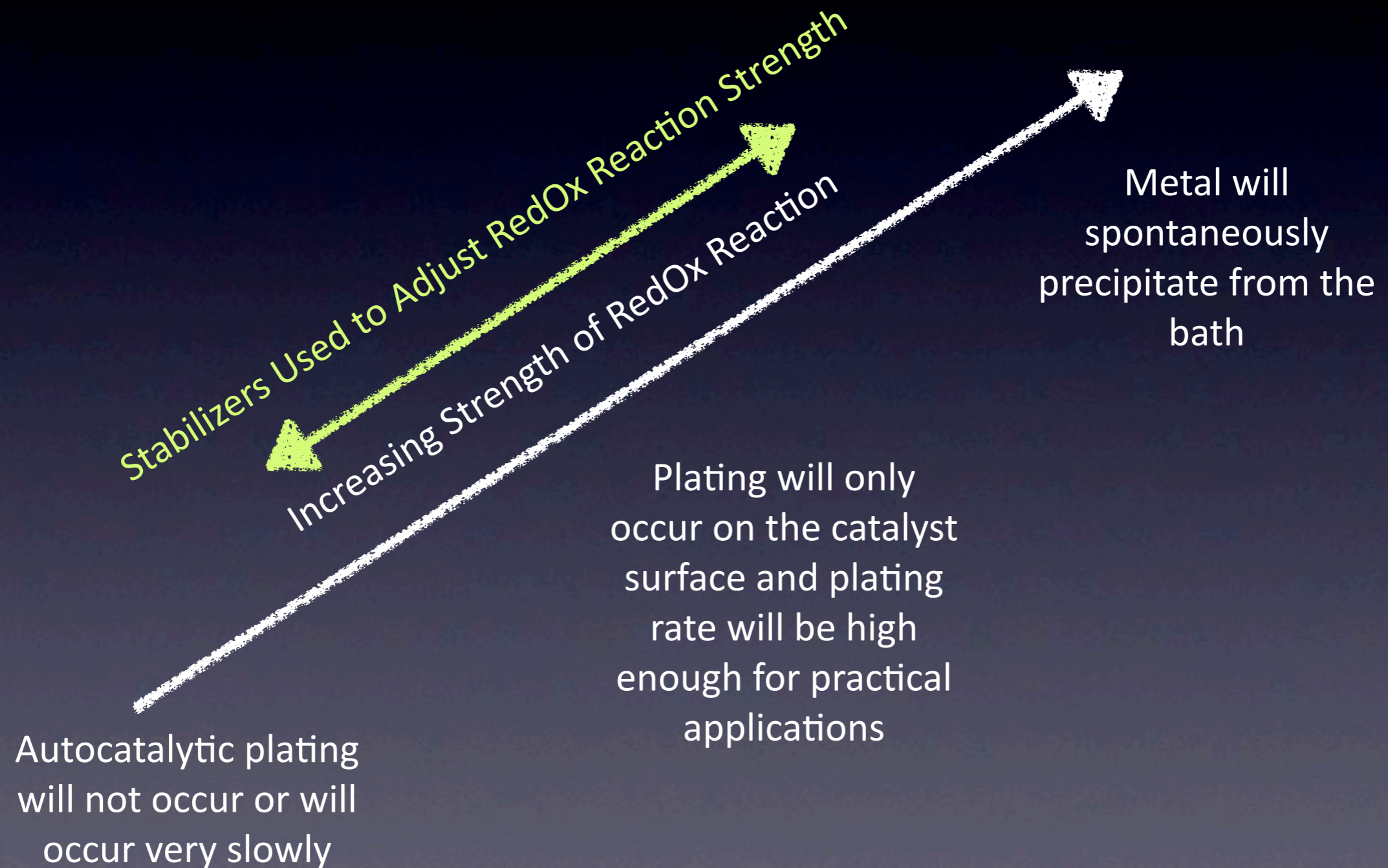
How Steric Inhibitors Work



Steric inhibition: the rate that these 2 people can find each other is inhibited by the other people surrounding them



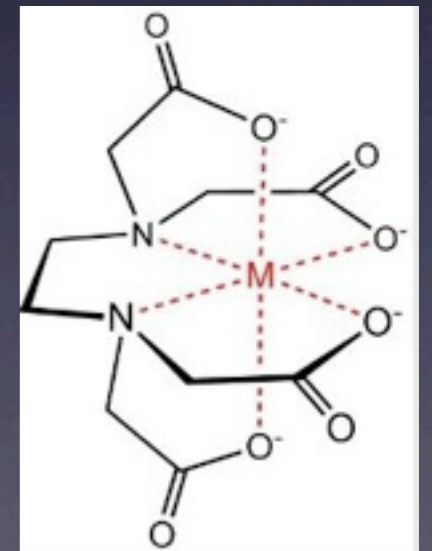
Role of Stabilizers





Role of Complexers

- Complexers play a similar role to stabilizers
- Compounds that surround and bond to the free metal ions in solution (“Chelator”)
- Can be used to adjust the concentration of available free metal ions
- Adjusts the RedOx reaction rate





Build Up of Reaction Products

- Electroless plating tank is a closed chemical system
- By products from the reduction reaction build up in the tank [electroless Ni, orthophosphite ions accumulate (HPO_3^{2-})]
- Dissolved metal from the substrate builds up
- Decrease the plating rate
- Eventually, the bath spontaneously precipitates
- New bath must be built
- Typical bath lifetimes for rigorously maintained electroless baths are months (5 metal turns) compared to years for electrolytic baths



Bath Management Requirements

- Reducer and metal ion concentration must be replenished and controlled
- pH and temperature must be carefully monitored to balance plating rate with bath stability. Temperature control for some baths must be very tight ($\pm 2\text{C}$). It is very important that the temperature never exceed the bath vendor guideline.
- Stabilizer and complexer concentration must be controlled. Stabilizer concentrations are very low, similar to grain refiners < 10 ppm
- Since plating rates vary with bath lifetime, coupons should be periodically plated and evaluated to determine the current plating rate
- pH should be maintained ± 0.2 of bath vendor guidelines
- During continuous use, analyze for metal every 2 hours and reducer every 4 hours



Key Practices to Enhance Bath Lifetime

- Continuously filter all baths. This will filter out any small metal precipitates which can initiate bath instability
- Carefully inspect all polypropylene tanks for wear including scratches or other damage. Scratches can become nucleation sites for metal precipitation. Use disposable tank liners if possible which can be discarded if scratched.
- Uniform solution agitation is critical to avoid local overheating which results in plate out on tank heaters or other tank components.
- During periods of non-use, turn off heat but continue filtration.
- At any sign of metal precipitation, bath should be filtered out into a clean holding tank, allowed to cool and then analyzed.
- Inspect racks carefully for cracks in protective coating. If rack stripping agents are dragged into the electroless tank, it will cause instability.
- Frequently change the filter bags and filter chambers.



Key Attributes of Electroless Plating Compared to Electrolytic Plating

- Electroless deposit has a more uniform thickness and is less dependent on surface features than electrolytic
- Plating rate is controlled by chemical reaction in solution
- Effected by concentration of reactants, temperature, pH, steric inhibitors and chelating agents
- Electrically isolated features can be plated



Key Attributes of Electroless Plating Compared to Electrolytic Plating

- Electroless baths must be tightly controlled so that the reaction rate is not too slow or too fast
- Bath lifetime is limited due to build up of reaction products and impurities. Chemical costs are higher than electrolytic baths
- Catalytic surface of substrate is key to initiating plating. Elaborate surface preparation is sometimes required.

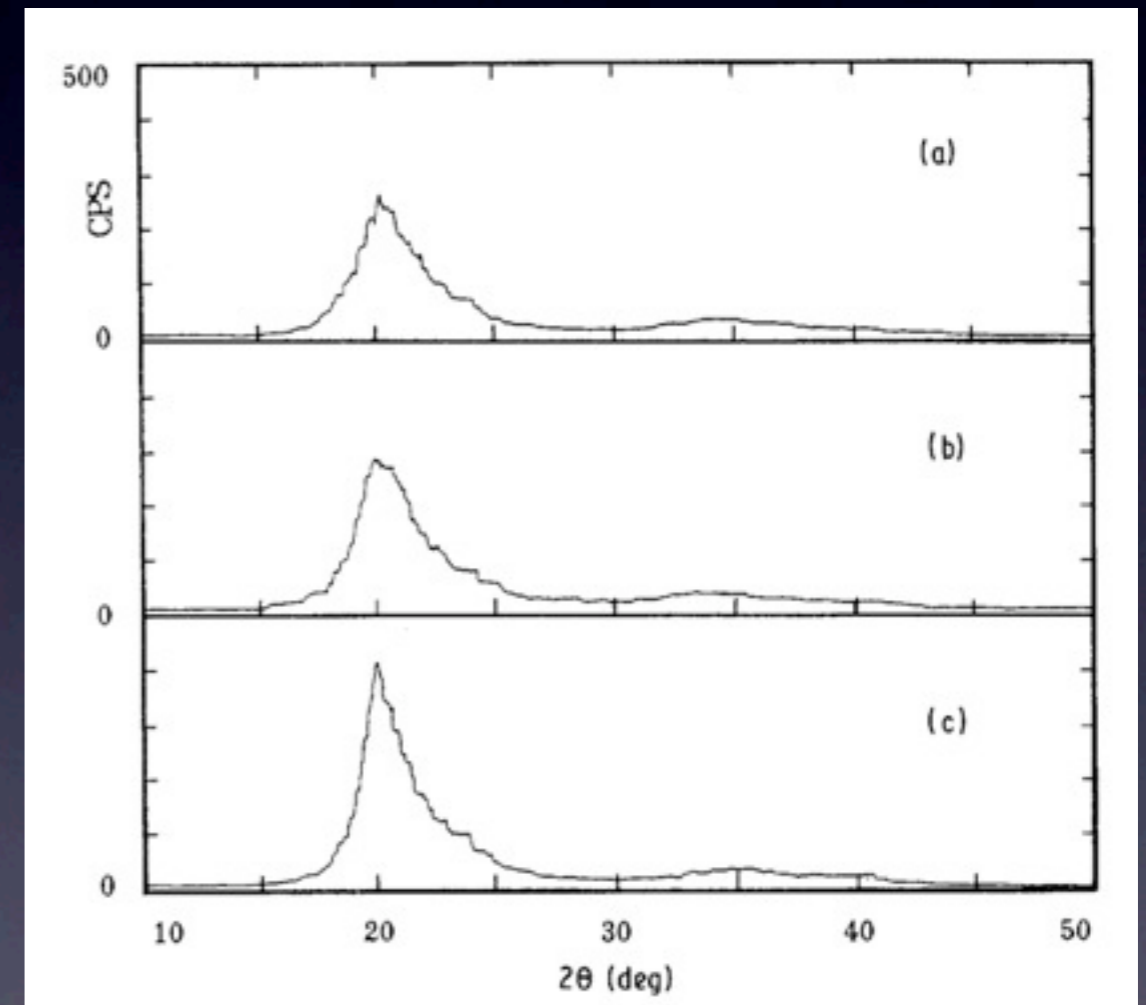
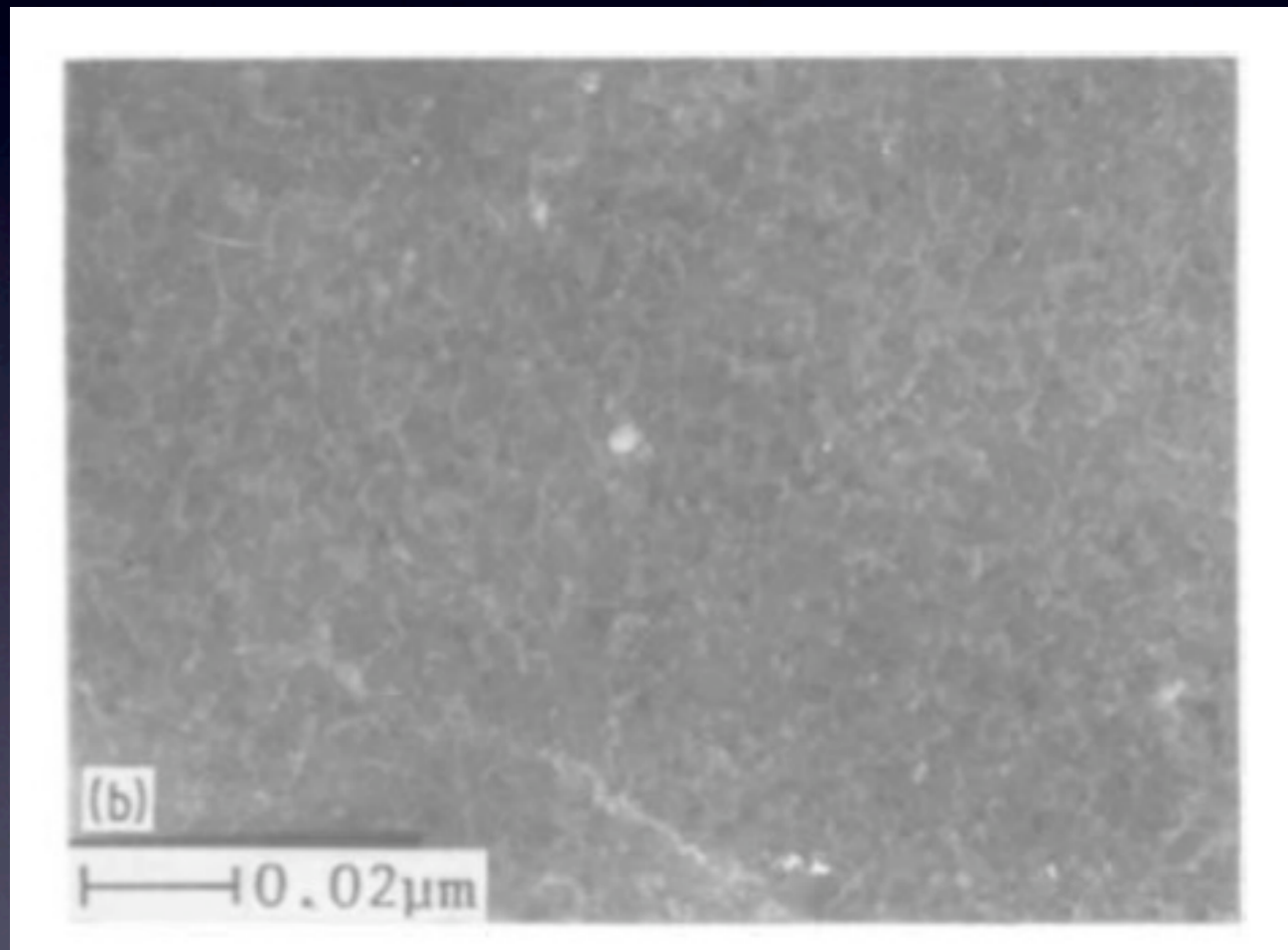


Electroless Nickel

- Plate a NiP or NiB Alloy
- Nickel Phosphorus- Amorphous Metal
 - * 1-4% P (low phosphorus)
 - * 5-9% P (mid phosphorus)
 - * 10-13% P (high phosphorus)
- NiP has many outstanding properties
 - * Excellent diffusion barrier (no grain boundary diffusion due to amorphous structure)
 - * Good solder and braze wetting
 - * Very hard but also ductile (unique combination of properties only found in amorphous metals)
 - * Excellent coverage in deep recesses and blind holes



NiP 10% Plated Film Structure



Hoon et. al., Journal of Materials Science 23 (1988) 1643

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Plating Tutorial for Tong Hsing, March 2009



NiP Bath Composition

Bath Component	Chemical	Formula	Concentration
Ni ion source	nickel sulphate	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	20 kg/m ³
reducing agent	sodium hypophosphite	$\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$	26 kg/m ³
complexing agents	succinic acid, aminoacetic acid, malic acid, citric acid		300 ppm
inhibitor	thiourea		0.5 ppm
pH adjustments	sodium hydroxide	NaOH	pH from 4.6 to 5.3



NiP Plating Reaction and Conditions

- $\text{NiSO}_4 + \text{NaH}_2\text{PO}_2 + \text{H}_2\text{O} \xrightarrow[\text{Catalyst}]{\text{Heat}} \text{Ni Plating} + \text{NaHPO}_3 + \text{H}_2\text{SO}_4$
- Temperature 87C +/- 1C
- pH will control phosphorus content (range 4.6 to 5.3 for 8-10%)
- Plating rate 5-15 $\mu\text{m}/\text{hour}$



Comparison of NiP and NiB

Parameter	N-B	N-P
pH	6.0-6.5 (neutral)	4.5 - 5.3 (acidic)
Bath temperature C	65	90
Cost factor	3-8 x	1
Typical thickness μm	1-2	3-20
Composition	Ni 99% B 1%	Ni 90-92% P 8-10%
Structure	Fine Crystals	Amorphous
Melt Point C	1400C	890C
Stress	tensile	compressive
Resistivity ($\mu\Omega\text{cm}$)	17	60
Solderability	excellent	good



Electroless Ni Bath Maintenance Procedures

- See general bath maintenance procedures in slide 29
- Air or solution agitation should be directed toward the work from below
- Air agitation is OK for NIP but should not be used with NiB



Electroless Au

- Very low plating rates (1.5 - 2 $\mu\text{m}/\text{hour}$)
- Very Expensive
 - ✦ High bath cost
 - ✦ High Au loss factor when baths precipitate metal and need to be replaced
- Can be difficult to initiate plating
- Typically only used to plate isolated features



Electroless Gold

- **High pH Electroless Au**

- * Used for HTCC and LTCC
- * Highly alkaline with pH 13-14
- * Very low plating rate: 2 μ m / hour
- * 99.9% Au purity- wire bondable

- **Neutral pH Electroless Au**

- * Used for AlN and other materials not stable in alkaline solutions
- * pH = 7.5
- * Very low plating rate: 1.5 μ m/ hour
- * 99.9% Au purity- wire bondable
- * Difficult to keep autocatalytic reaction from slowing down during plating cycle



Electroless Au Formulation- High pH Bath

Bath Component	Chemical
Au ion source	Gold hydrochloride trihydrate
complexing agent	Sodium potassium tartrate
reducing agent	Dimethylamine borane
stabilizer	Sodium cyanide
pH adjuster	NaOH
pH value	13.0
temperature	60C



Electroless Au Bath Maintenance Procedures

- Maintaining a Au bath as long as possible is very key because of the high cost of Au
- Very important to avoid localized heating. This involves tank design, agitation and heater placement
- A double walled tank is recommended for uniform heating
- Rinse very thoroughly before Au plating to avoid metal contamination dragged in from other tanks.
- Filtration of Au is extremely important.



Electroless Copper

- Used for plating PCB, EMF Shielding, and as a component in UBM
- Can be used to plate electrical insulators such as PCB or plastics if pretreated with SnCl_2 and PdCl_2 activators to form catalytic sites for plating initiation
- Most common bath has $\text{pH} = 12$ (alkaline) and uses formaldehyde as a reducer
- Plating rates typically $1\text{-}5 \mu\text{m/ hour}$
- Newer baths use alkanol amines (quadrol) as reducers and have plating rates $10 \mu\text{m/ hour}$



Electroless Copper Bath Composition

Bath Component	Chemical
Cu ion source	Cu^{2+} salt is used
complexing agent	$\text{KNaC}_4\text{H}_4\text{O}_6$ (Rochelle salt)
reducing agent	H_2CO (Formaldehyde)
stabilizer	2-Mercaptobenzothiazole (MBT)
pH adjuster	NaOH
pH value	12
temperature	25C



Electroless Summary

- Electroless plating requires chemical oxidation and reduction agents in the plating solution. This chemical reaction drives plating
- This is very different from electrolytic plating where reactions are driven by an external electrical circuit
- Electroless baths are more complex than immersion or electrolytic baths and much less stable
- When instability occurs in the bath, the metal plates out of solution and the bath must be reconstituted



Electroless Summary

- Bath instability can occur from build up of reaction by-products or from a bath control deviations in pH, temperature or chemical composition
- In general, electroless plating rates are much slower than electrolytic rates
- Plating cost are also higher
- Electroless plating is generally only used for plating isolated metallization pads where electrolytic plating is not practical or for plating difficult to reach features
- The lowest cost, most efficient and most used electroless bath is NiP



Immersion Plating Summary

- Immersion plating is driven by the oxidation of the base metal (corrosion)
- More noble metals plate onto less noble base surfaces
- Immersion Au is often used. It allows a very thin layer of Au to be plated on a base metal such as Ni. This prevents the Ni from oxidation and improves solder wetting.