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3.9 Advances Wet Chemical and Cleaning Process

(A) Electrochemical Deposition (ECD)

also:electroplating (EP)* or *electrodeposition

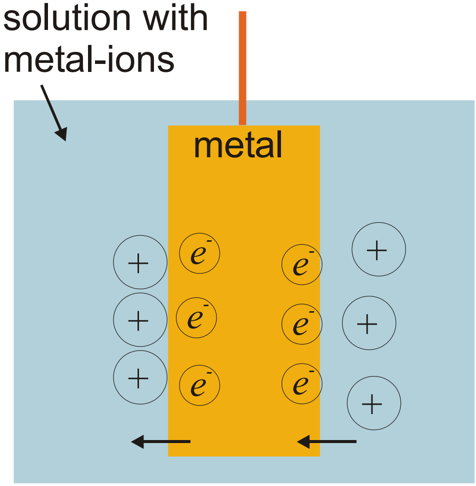
(B) Electroless Deposition (ELD)

3.9 Advances Wet Chemical and Cleaning Process

Basics

- If piece of metal immersed into solution containing its own ions a electrochemical double layer is formed: Helmholtz double layer
- Metal dissolves and ions from solution are deposited on metal
- Equilibrium potential E_{eq} is established – given by NERNST-Equation:

$$E_{eq} = E_0 + \frac{R \cdot T}{z \cdot F} \cdot \ln \frac{a_{Me^{z+}}}{a_{Me}}$$



E_0	Standard electrode potential	R	Molecular gas constant
T	Temperature	z	Valency of ions
F	Faraday constant	a	Activity of metal/ions resp.

Concept of electrochemical deposition

- Two electrodes immersed into electrolyte and external voltage is applied
- Disturbance of equilibrium conditions at double layer
- Reactions that takes place correspond to a redox reaction
- Anodic Reaction: oxidation of metal – dissolution into metal ions

$$Me \rightarrow Me^{z+} + z \cdot e^{-}$$

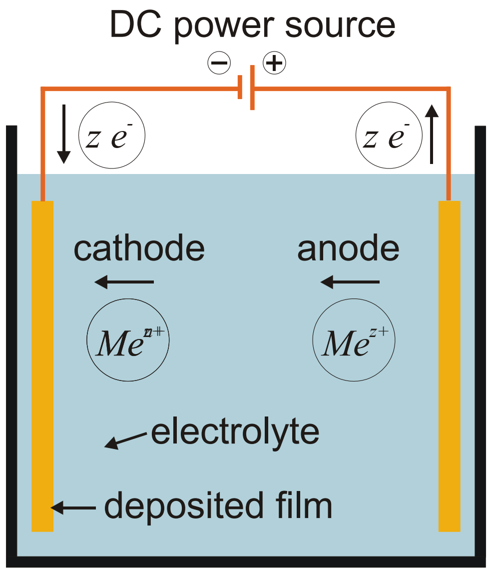
- Cathodic Reaction: reduction of metal ions – deposition of metal

$$Me^{z+} + z \cdot e^{-} \rightarrow Me$$

- Resulting potential:

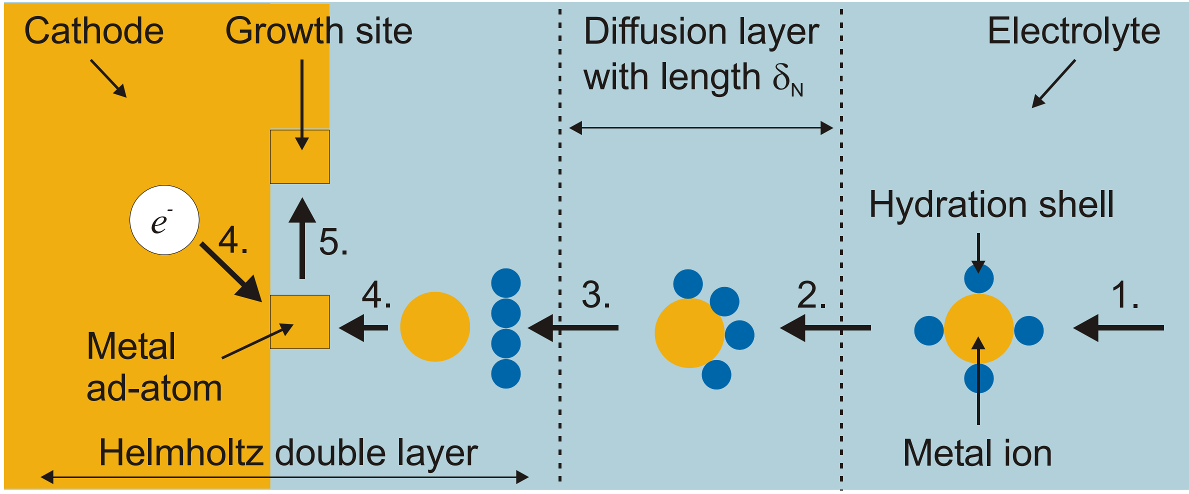
$$E = E_c - E_a + I \cdot R_S$$

I	Current
R_S	Resistance of electrolyte
E_c, E_a	Potential at anode and cathode resp., established different from E_{eq} due to overpotentials



Reaction mechanisms at cathode

1. Hydrated metal ions (ions with hydration shell) reach the cathode surface due to transportation mechanisms and enter the diffusion layer
2. Ions pass diffusion layer due to concentration gradient and hydration shell aligns with the field strength that increases towards the cathode surface
3. Ions enter Helmholtz double layer and hydration shell is stripped off due to high field strength in this layer
4. Reduction of ions with electrons from the cathode to form metal atoms that adsorb at the metal surface (ad-atoms)
5. Diffusion of ad-atoms to a energetic favorable growth sites and integration into the metal crystal lattice



Reaction mechanisms at cathode [1]

Overvoltage

- Potentials of electrodes E_a, E_c deviate from the equilibrium potential E_{eq} by a overvoltage η
- This overvoltage is caused by the inhibition of each single reaction step
- The overall overvoltage is:

$$\eta = \eta_{tr} + \eta_{diff} + \eta_{re} + \eta_{crys} + \eta_{res}$$

η_{tr}	charge transfer ov	η_{diff}	diffusion ov	η_{re}	reaction ov
η_{crys}	crystallization ov	η_{res}	resistance ov		

Deposition rate *r*

- Derived from 1. Faraday's law:

$$m = \frac{M \cdot I \cdot t}{z \cdot F} \Rightarrow t_f = \frac{M \cdot I \cdot t}{A \cdot \rho \cdot z \cdot F} \Rightarrow r = \frac{M \cdot J}{\rho \cdot z \cdot F}$$

m	Mass	M	Molar mass	I	Current
t	Deposition time	z	Valency	F	Faraday constant
t_f	Film thickness	A	Active area	ρ	Density
j	Current density	r	Deposition rate		

Transport mechanisms

- Convection
  - Forced convection induced by agitating the bath (stirring, air bubbling)
  - Natural convection due to density gradients caused by depletion at cathode surface and due to gravitation (minor impact)
- Diffusion
  - By concentration gradient in diffusion layer caused by depletion of copper ions at the cathode surface because of the reduction reaction
  - Flux through diffusion follows Fick‘s law
- Migration
  - Movement of copper ions within the electrical field between the electrodes
  - Can be neglected, since conc. of copper ions < conc. sulfur ions
- Overall flux is sum of flux of each mechanism:

$$j = \underbrace{(c \cdot v)}_{convection} + \underbrace{\left(-\frac{D}{\delta_N} \cdot \nabla c\right)}_{diffusion} + \underbrace{(-z \cdot \mu \cdot F \cdot c \cdot \nabla \varphi)}_{migration}$$

c	Ion concentration	v	Flow velocity	D	Diff. Coefficient
δ_N	Length of Diff.-layer	z	Valency	μ	Ion mobility
F	Faraday constant	φ	Potential		

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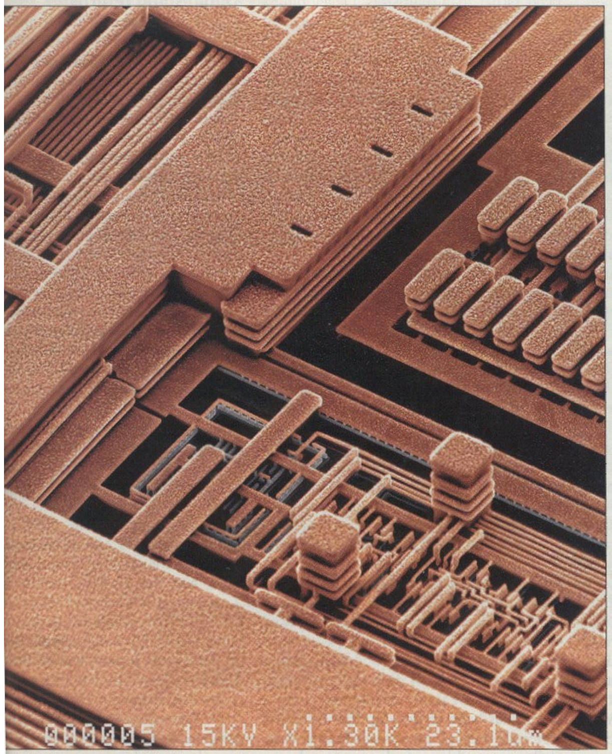
Application of Copper ECD in Damascene Interconnects

Background

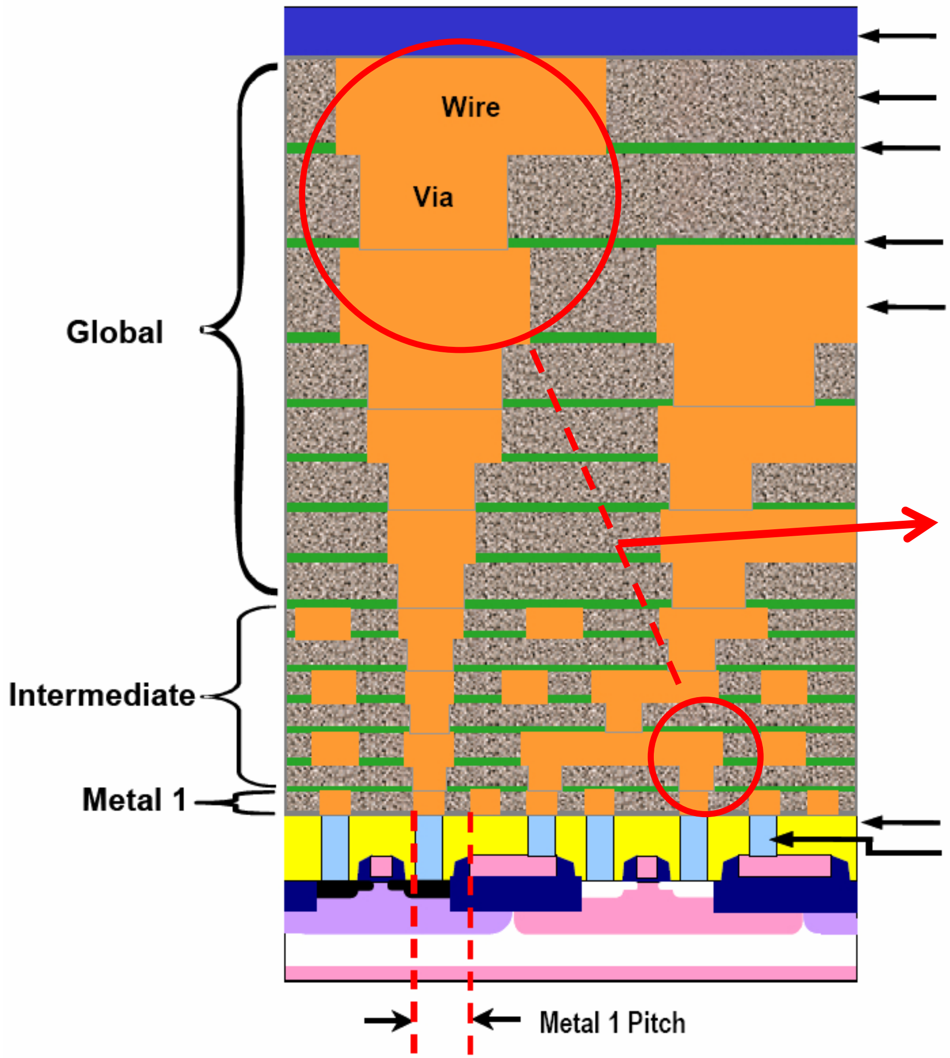
- Copper has replaced Aluminum in recent years because of higher conductivity and better electromigration resistance
- Copper ECD has better ability to fill high aspect ratio trenches compared to PVD and CVD and moreover its less expansive
- Filling of multilayer structures in one step can be done (Dual Damascene)

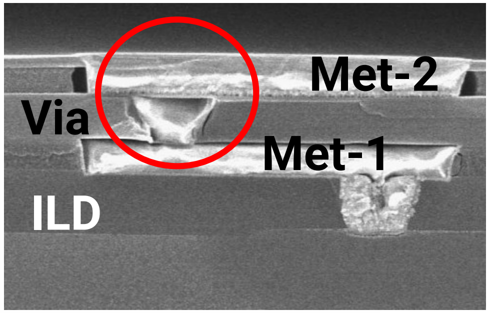


[1] IBM Corp.'s new CMOS 7S process for manufacturing ICs uses copper for its six levels of interconnections, and has effective transistor channel-lengths of only 0.12 μm. It is the first commercial fabrication process to use copper wires [see "The Damascus connection," p. 25].

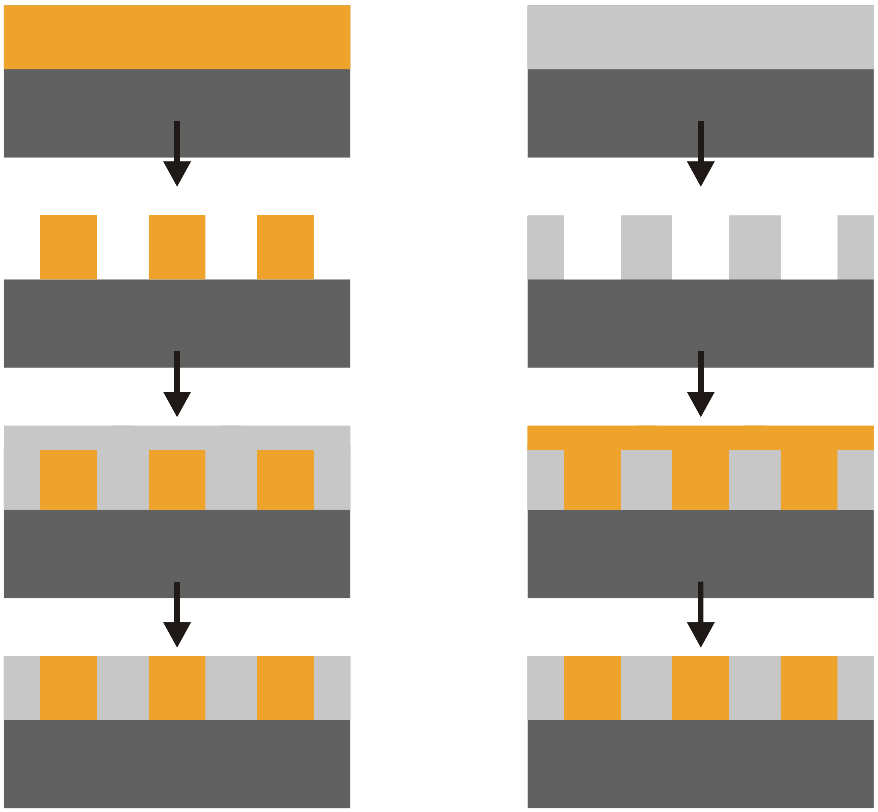
CMOS interconnects [IBM]

Application of Copper ECD in Damascene Interconnects



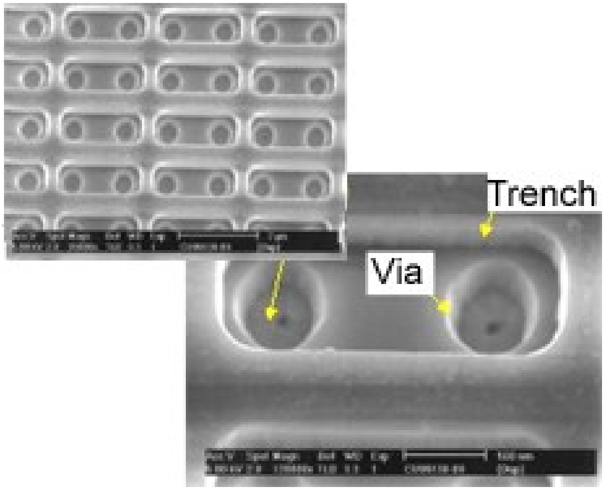


Basic Principle

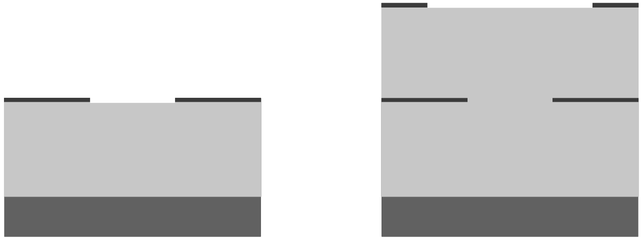


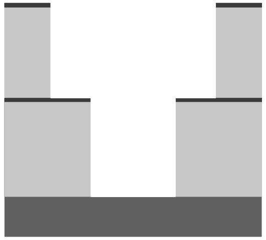
Dual Damascene Technology

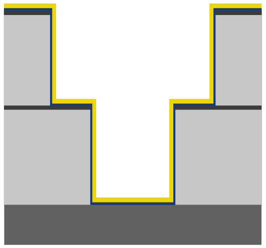
- Vias and trenches filled in single step ECD
- Barrier (Ta/TaN, Ti/TiN) and Cu-seed deposition e.g. by ionized PVD
- CMP for planarization

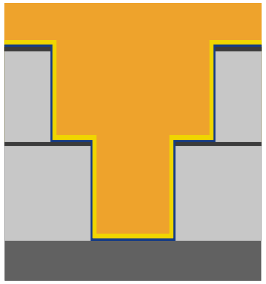


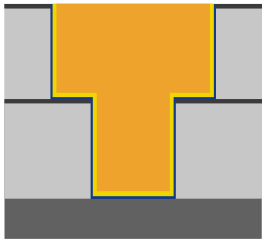
Trench and Vias [IMEC]

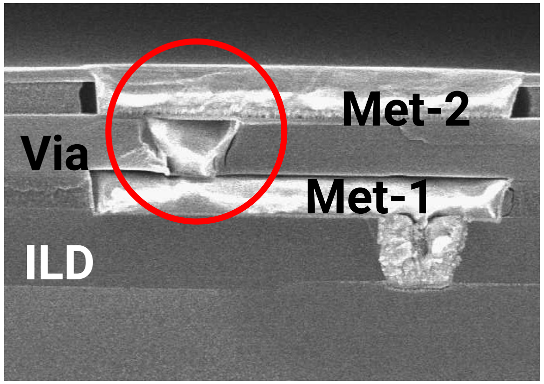

Isolator deposition and Hardmask deposition / Structuring (Layer 1+2)


Isolator structuring


Barrier and Seed layer deposition


Cu deposition


CMP



Basic requirements for Copper electroplating

- Plating Cell
  - Simplest form: Beaker (research, initial tests)
  - Advanced semiconductor plating tool (Fountain Plater)
  - Rack Plater for PCB-industry
- Electrolyte
  - copper sulfate, conducting salt
  - Additives
- Convection: Stirrer or circulation Pump
  - Electrolyte movement
  - Wafer rotation or lateral movement
- Anode
  - soluble copper anode
  - inert anode (Ti+Pt)
- Cathode (piece to be deposited => i.e. Wafer)
  - Seed Layer (e.g. Cu) + barrier (e.g. TiN) + adhesion layer (e.g. Ti)
  - Wafer holder
- Power Supply (DC or Pulsed)

Principle of acid copper plating

- Electrolyte is a dissociated copper sulfate salt:

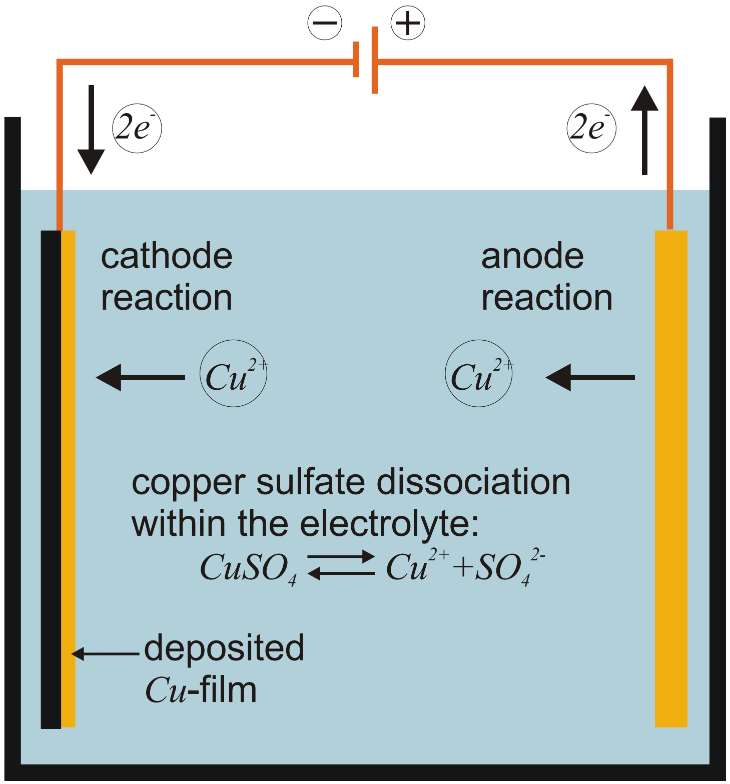
$$CuSO_4 \rightleftarrows Cu^{2+} + SO_4^{2-}$$

- Redox reaction for acid copper plating is:

$$Cu \underset{\text{Red.}}{\overset{\text{Ox.}}{\rightleftarrows}} Cu^{2+} + 2 \cdot e^{-}$$

- Anode types:
  - Soluble copper anode (provides cupric ions)
  - non soluble inert anode (ions are added from external source)
- Seed layer: mostly Cu
- Additives to control film properties

  (grain size, ductility, stress, brightness)



Copper deposition with soluble anode

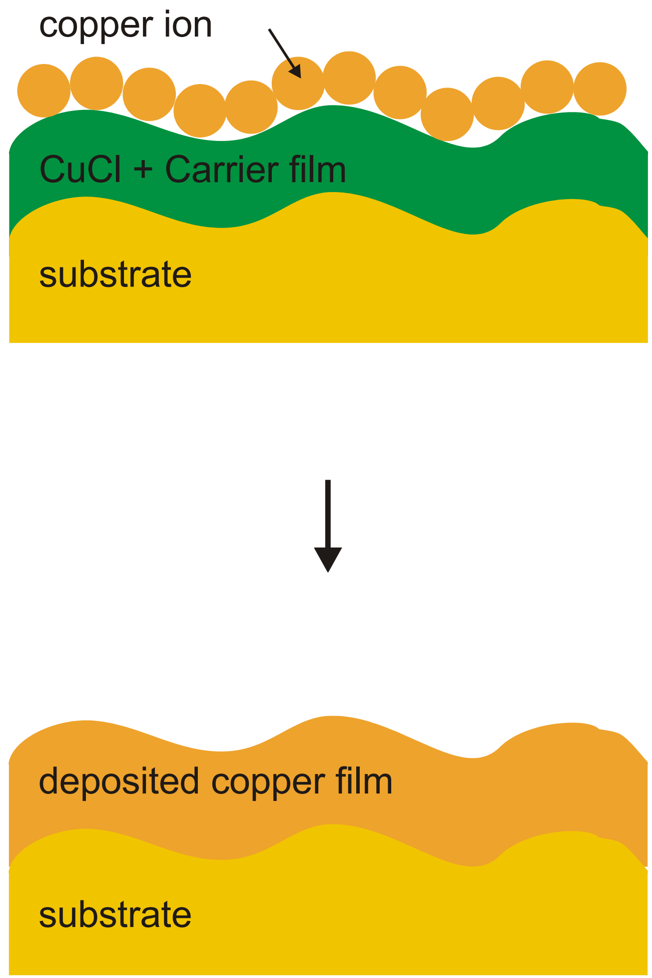
Composition of a acid copper plating bath

	Component	Chemical basis	meaning
Basic	Copper sulfate	Metal salt	-Provision of cupric ions
Basic	Sulfuric acid	Acid	-Increase in conductivity
Additives	Chlorine	Halogen	-Weak inhibition of deposition -Necessary for operation of other additives
Additives	Carrier (suppressor)	Polyether (PEG, PAG)	-Inhibition of deposition -Uniformity of deposit
Additives	Brightener (accelerator)	Organic Sulfur compound (SPS, MPS)	-Acceleration of deposition -Bright deposits -Incorporation in deposit -Weak grain refiner
Additives	Leveler	Organic Nitrogen compound (JGB)	-Strong inhibition of deposition -Smooth surfaces (leveling) -Strong grain refiner

Effect of plating additives

- Chlorine (CL)
  - CL is a surface active complexing agent
  - CuCl-film is formed at the surface
  - Film slightly inhibits reaction
  - Required for action of other additives

- Suppressor or Carrier (C)
  - Adsorption of C promoted by CL
  - Inhibition of Cu deposition (suppresses current density)
  - Deposited film has even thickness (uniformity)

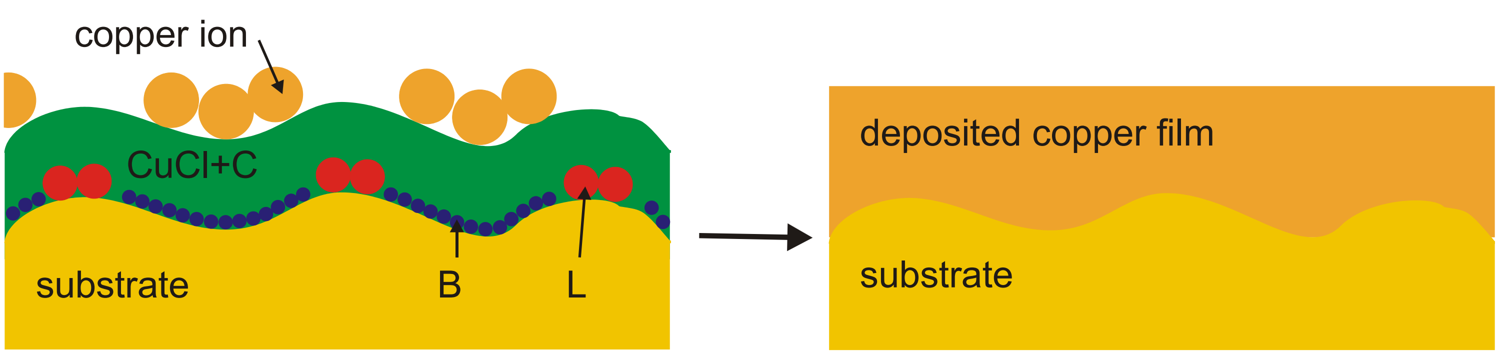


Deposition with CL and Carrier

3.7 - 16

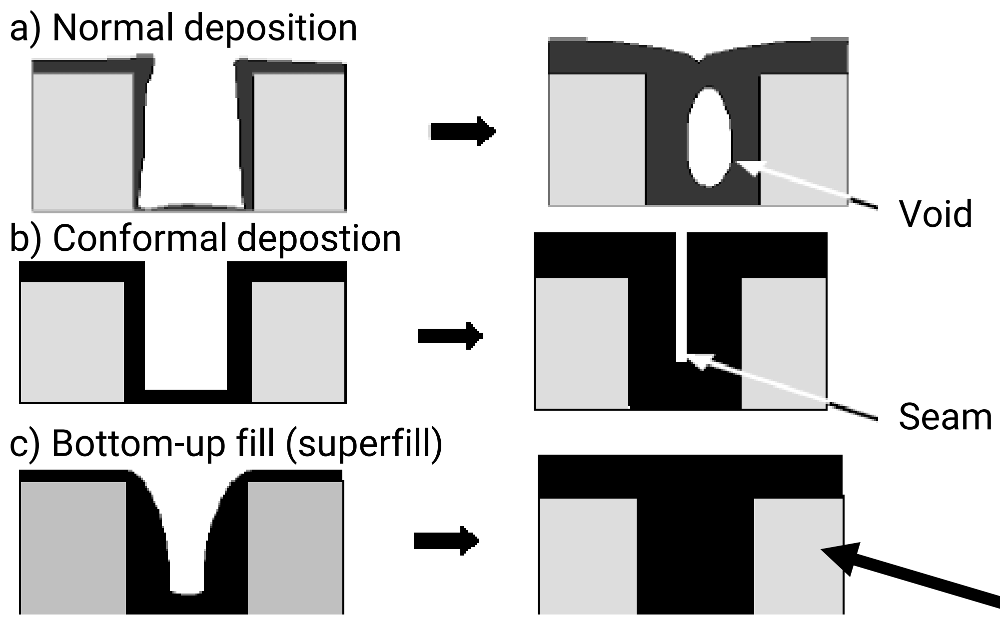
- Accelerator or Brightener (B)
  - Copper and B form Cu-thiolate film
  - Film interacts with CL to accelerate copper ion reduction (C^{2+} → Cu)
  - Grain refinement → bright deposit (mirror like films)

- Leveler (L)
  - Inhibition of copper deposition
  - Adsorbs preferentially ad peaks and valleys thus levels the deposit
  - Refines grain structure

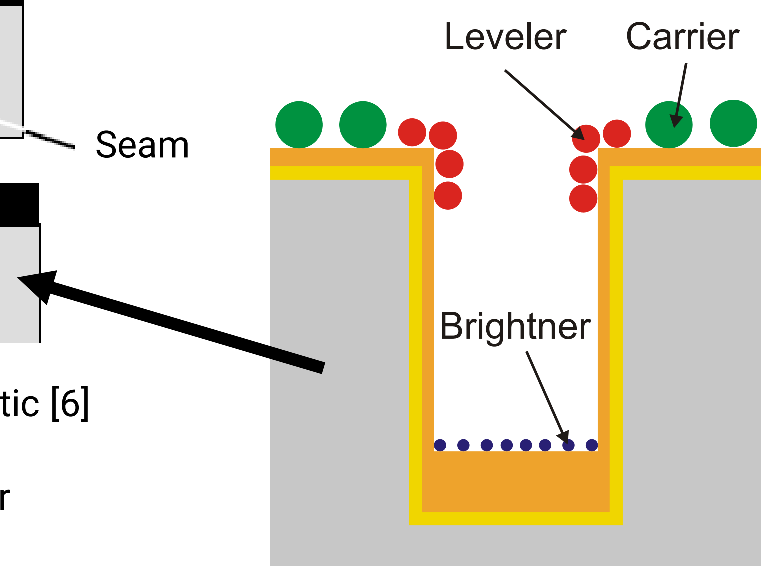


Deposition with optimized additive composition

Fill characteristics – effect of plating additives



Effect of additive composition on fill characteristic [6]



Bottom-up fill with optimized additive composition

a) High current density at trench edges leads to faster deposition at those sites

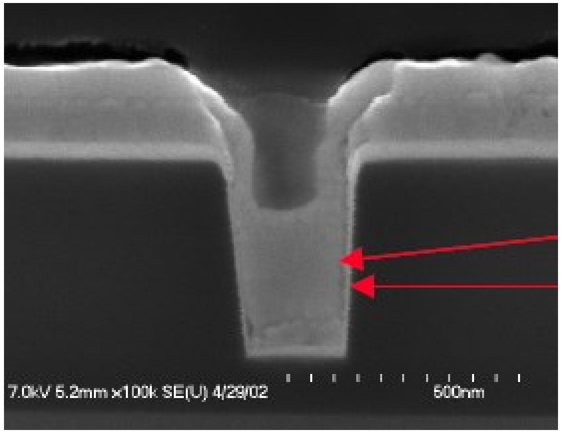
b) Excess suppressor concentration leads to conformal deposition

b) Optimized composition of additives leads to perfect trench-fill characteristic

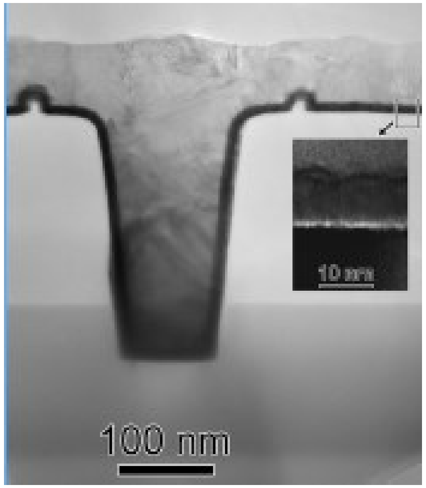
Seedless Plating onto barrier layers

- Background of Seedless plating
  - Defect free seed layers in high aspect ratio trenches are difficult to fabricate
  - Corrosion of thin seed layers in electrolyte
  - Decrease in conductivity in narrow trenches due to higher fraction of resistive barrier layers

  -> Need for new barrier materials
- Requirements
  - Barrier behavior: Cu immiscible with barrier material
  - High conductivity
  - Good wetting of barrier layer with electrolyte
- Methods and Materials
  - Research is done on: Ru, Pt, Pd, Rh, Ir, Ag
  - Methods: ionized PVD, CVD, ALD



Seed layer in small trenches [7]



Seedless superfill on 15nm Ir (ALD) [7]

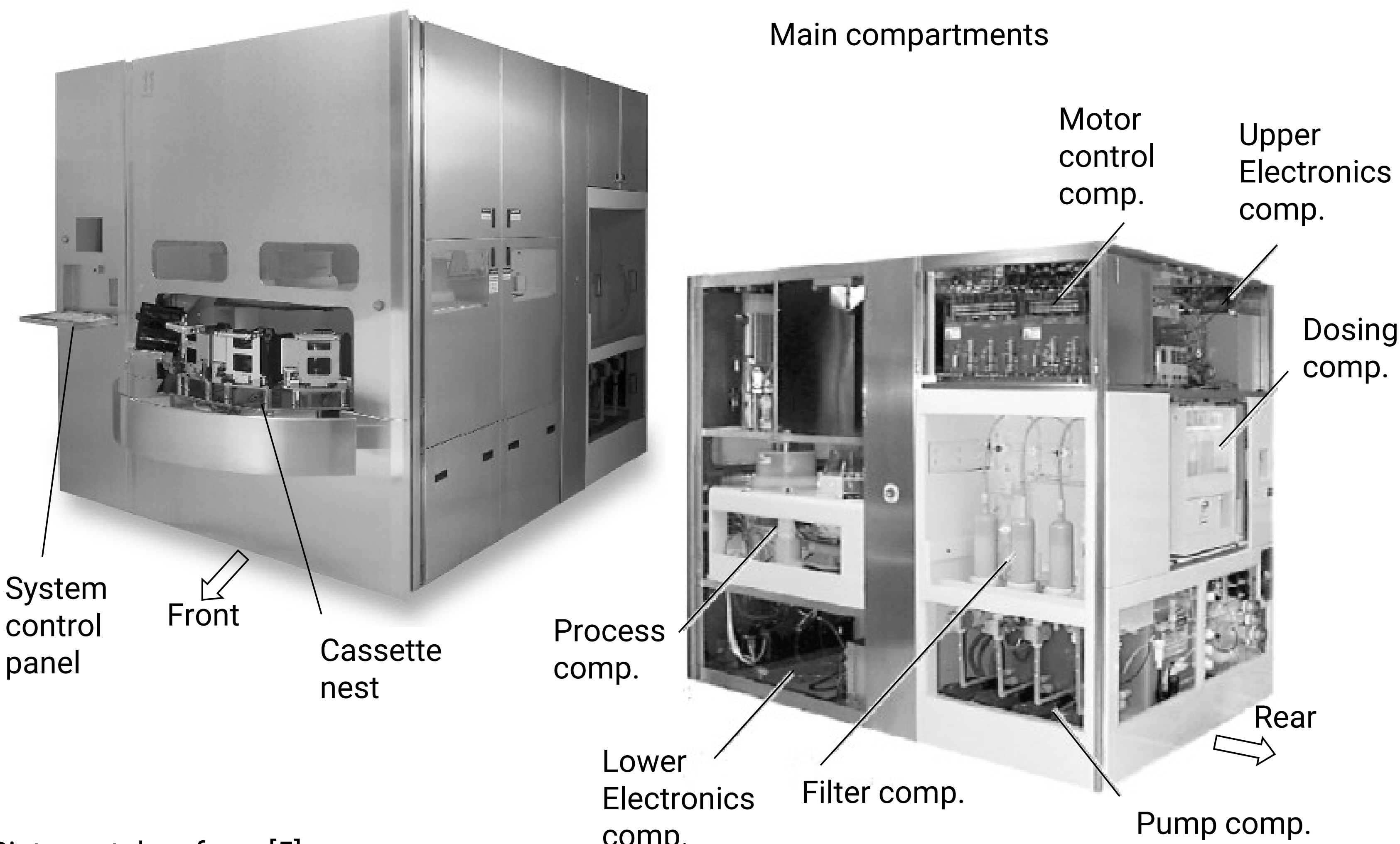
3.9 Advances Wet Chemical and Cleaning Process

Equipment for Copper ECD

Basic facts

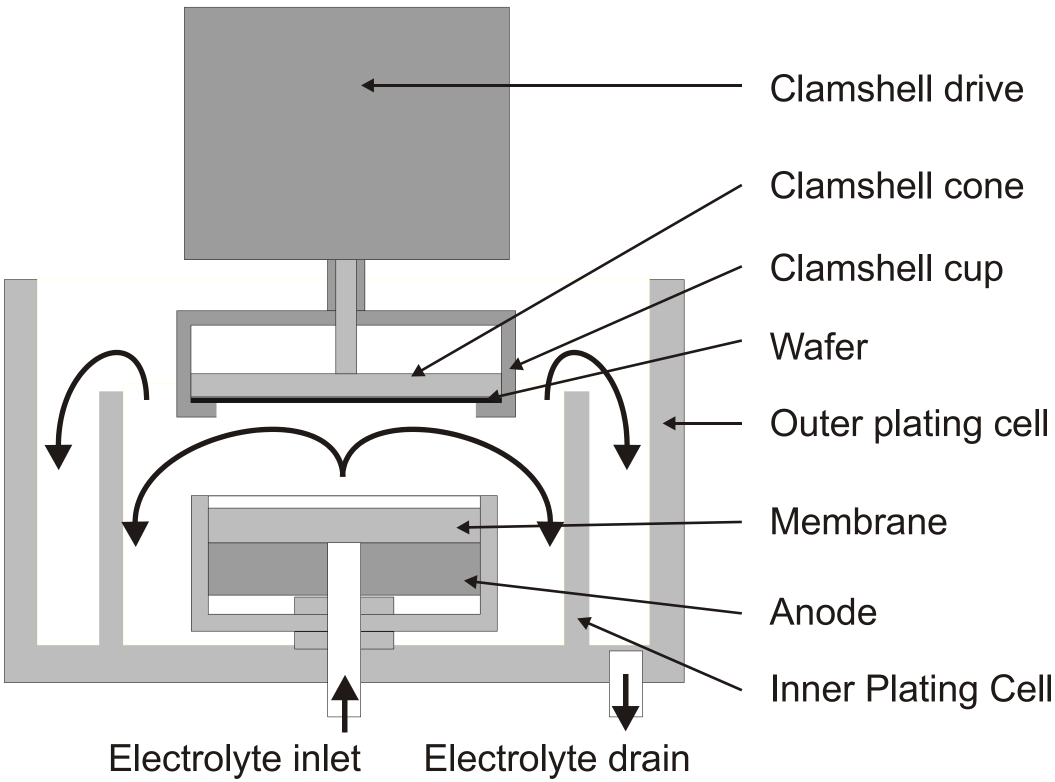
- Pre/post treatment cells for cleaning, rinsing and drying
- Plating cells:
  - Contain plating solution (cupric ion solution)
  - (Soluble) Anode
  - Cathode i.e. workpiece (Wafer) in a holder
- Two basic concepts of plating cells:
  - Vertical cathode-anode-arrangement used in older PCB-plating tools for high troughput
  - Horizontal cathode-anode-arrangement in new PCB tools and in Semiconductor fabrication for more precise deposition processes
- Main manufacturers of electroplating tools:
  - Lam Research (former Novellus), AMAT (former Semitool)
  - Semsysco, Classone (spin off from Semitool); Tel Nexx (f. Nexx Systems)
- Bath chemistry suppliers:
  - Enthone (Cubath Viaform), Atotech, BASF

Semiconductor Copper ECD tool (Novellus Sabre Concept II)



Pictures taken from [5]

Fountain Plating Cell



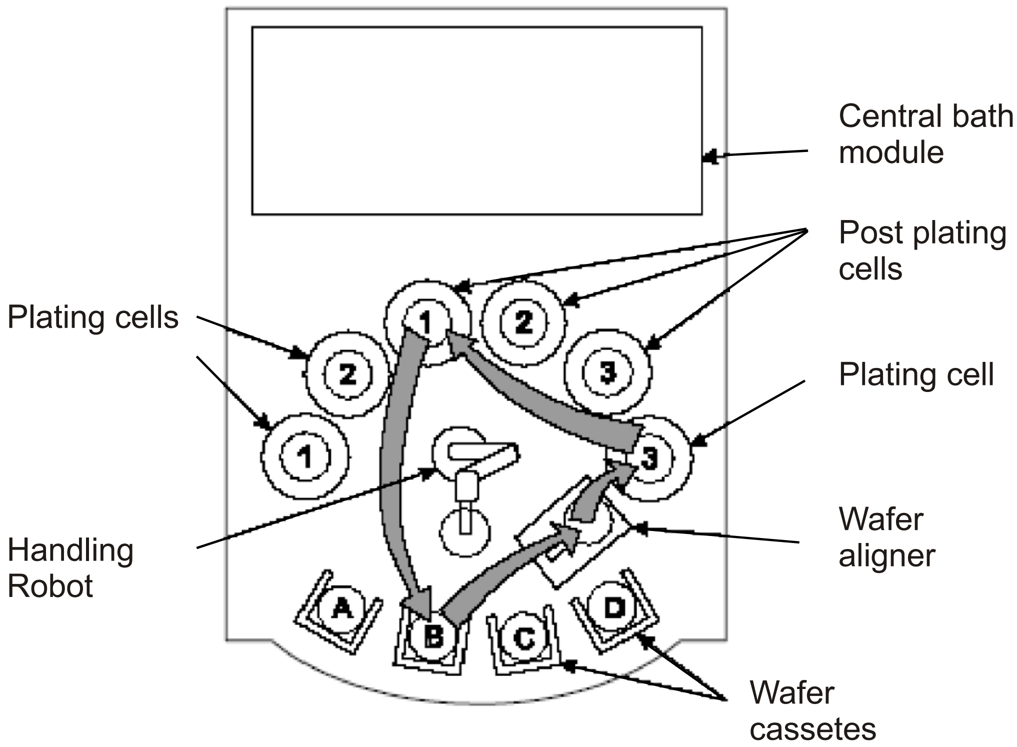
Principle of fountain plating cell

Plating cells and post plating cells in the process compartment [5]

Clamshell [5]

Process flow

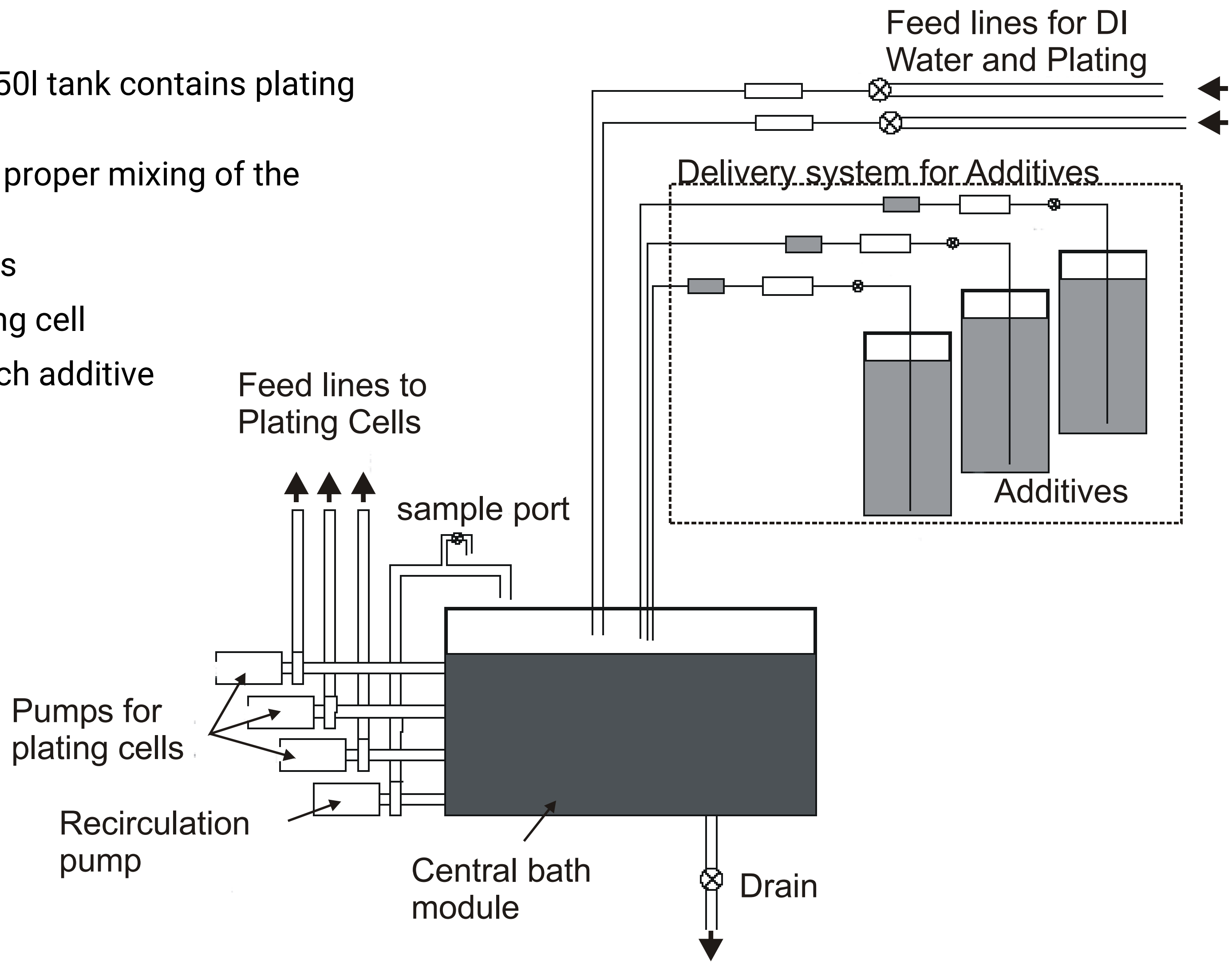
- Wafer cassettes are placed in the cassette Load port
- Wafer picked by handling robot out of cassette and placed into wafer aligner
- Centering and alignment of wafer for processing
- Handling robot places wafer into clamshell of plating cell
- Wafer is submerged into the plating solution and DC current is applied
- After processing the wafer is transported to a post plating cell for cleaning, rinsing and drying
- Return of wafer to cassette



Schematic of process flow [5]

Dosing System

- Central bath module: 150l tank contains plating solution
- Recirculation pump for proper mixing of the electrolyte
- Sample port for analysis
- 3 pumps for each plating cell
- Separate delivery of each additive



Schematic of dosing system [5]

3.9 Advances Wet Chemical and Cleaning Process

Electroless Deposition

Fundamentals

- Deposition process without any external power supply
- Two types of electroless deposition processes:

1. Reduction process
   - Reducing agent contained in the electrolyte
   - Electrons provided by oxidation of the reducing agent

$$\underset{\textit{Metal ion}}{Me^{z+}} + \underset{\textit{Reducing agent}}{Red} \rightarrow \underset{\textit{Metal}}{Me} + \underset{\textit{Oxidized form of Reducing agent}}{Ox}$$

2. Ion exchange process
   - Substrate surface has more negative standard potential
   - Electrons from exchange reaction with substrate

Oxidation:

$$Me_1 \rightarrow Me_1^{z+} + z \cdot e^-$$

Reduction:

$$Me_2^{z+} + z \cdot e^- \rightarrow Me_2$$

- Mostly for protection of bare metals: e.g. Zn, Sn on steel; Au on brass
- Only thin films because of self-inhibiting effect

Typical chemistry for the reduction process type

Chemistry	Meaning
Metal salt	- Provision of metal ions (e.g. sulfate based)
Complexing agent	- Prevents precipitation of metal salt
Reducing agent	- Supplies electrons for metal ion reduction (e.g. formaldehyde HCHO or hypophosphite $H_2PO_2^-$)
Activator	- Supports/activates oxidation of red. Agent (e.g. Pd)
Buffer	- pH maintenance (e.g. NaOH)
Stabilizers	- Retards homogeneous reactions (e.g. thiourea)
Accelerators	- Increase in deposition rate
Surfactants	- Wetting agent - Removal of evolved gases

Application in Damascene Technology

- Alternative method for seed layer deposition (conformal deposition)
- Deposition of cap layers on Cu lines
- Also alternative method for trench superfill

Examples for the reduction process type

- Nickel deposition
    - Deposition in alkaline or acidic solution with nickel provided from $NiSO_4$-salt
    - Complexing agents: organic acid or amine (ethylene diamine, citrate acid)
    - Reducing agent: hypophosphite (e.g. Sodium-hypophosphite: NaH_2PO_2)
    - Buffer for pH-maintenance is e.g. NaOH
    - Basic reaction steps

Oxidation of red. agent: $$H_2PO_2^- + H_2O \rightarrow H_2PO_3^- + 2 \cdot H^+ + 2 \cdot e^-$$

Reduction of Ni ions: $$Ni^{2+} + 2 \cdot e^- \rightarrow Ni$$

- Copper deposition
    - Mostly alkaline solutions with $CuSO_4$ as metal salt
    - Complexing agents
    - Reducing agents mostly formaldehyde (HCHO)
    - Reaction steps:

Oxidation of red. agent: $$HCHO + 3OH^- \rightarrow HCOO^- + 2 \cdot H_2O + 2 \cdot e^-$$

Reduction of Cu ions: $$Cu^{2+} + 2 \cdot e^- \rightarrow Cu$$

3.9 Advances Wet Chemical and Cleaning Process

Electroless deposition of copper diffusion barriers

Background

- Conventional barrier deposition shows several drawbacks for depositions in narrow trenches (non defect free, pinches off at trench top)
- Several process steps (blanket deposition, patterning)

Advantages of electroless deposition to ECD

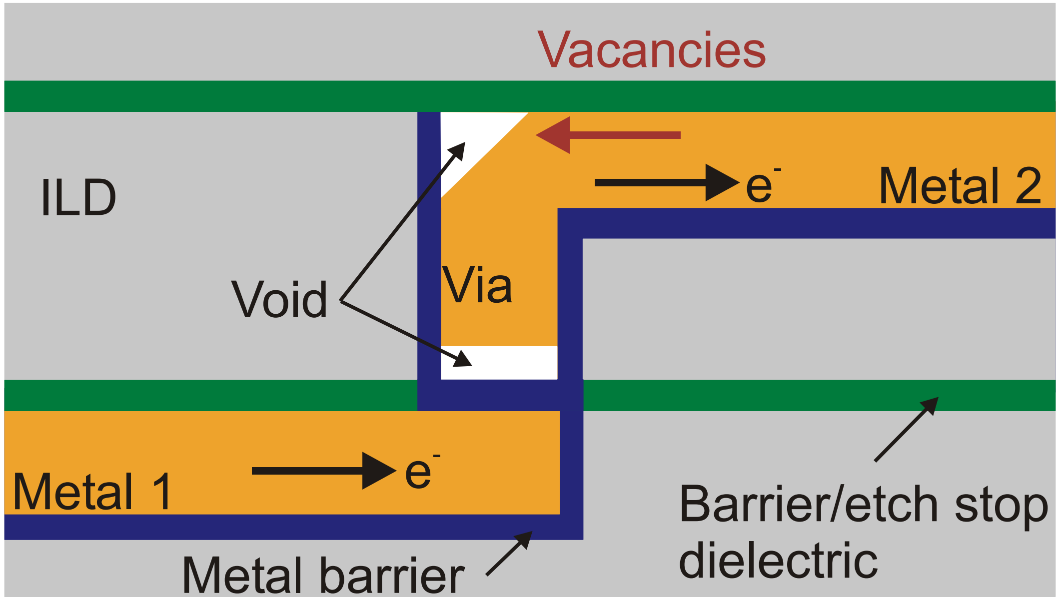
- Conformal deposition even within complex structures (narrow trenches)
- Deposition on non conductive materials
- Possibility of local selective plating - reduced process steps

Possible materials

- Ni alloys (NiMoP)
- Co alloys (CoWP, CoWB)

Electroless CoWP

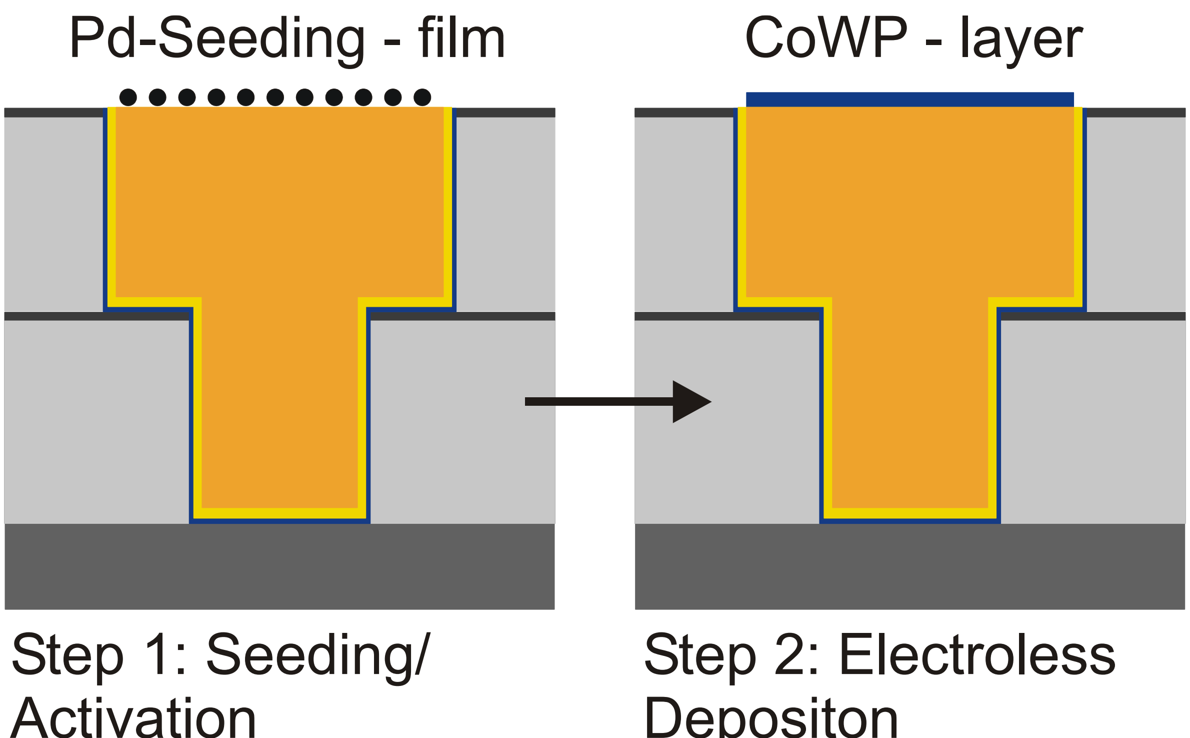
- Used as barrier metal and capping barrier layer
- Co forms metal-metal bonds with Cu while W and P stuff grain boundaries to inhibit Cu-diffusion
- CoWP has strong adhesion to copper and prevents Cu-diffusion/vacancy-movement and thus prevents void formation
- Copper reliability improvements through CoWP capping layers
- Device performance improvement due to lower k_{eff} compared to previous capping layers (SiN, SiC, SiCN)



Void formation through weak Cu-barrier/etch stop layer adhesion [10]

Electroless CoWP - Process

- Usually 90% Co, 2% W and 8% P
- Selective deposition onto Cu-lines after Pd-Activation (seeding) – Capping layer deposition with fewer process steps



Electroless CoWP as capping layer – Process steps

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