Copper Electroless Plating for On-Chip Metallization. An Overview

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Outline

- Fundamentals of Electrochemistry
- Electroless Plating Mechanism
- EL Cu Properties
- Catalytic/Activation Layers
  - Cu/Al
  - Cu contact displacement
  - Ru catalytic layer/liner
  - SAM
  - TiO_2/Pd^{2+}
- Applications of EL plating
  - Liner
  - Fill
  - EM cap
- Summary

Fundamentals of Electrochemistry – Part 1

Thermodynamics:

F = Faraday constant
(96 485.3415 C / mol)

As the electrons start to move, they produce current, whose magnitude depends on the number of electrons

The total charge carried by electrons:

$$Q = n \times F \qquad (1)$$

Since the electrons (charge) are moved through an electric potential, *work* is done

$$W = n \times F \times E \qquad (2)$$

The amount of work can be identified through the change in Gibbs Free Energy under conditions of reversibility, constant temperature (25 C) and pressure (1 atm)

$$\boxed{\Delta G^0 = -nF\Delta E^0} \qquad (3)$$

Thermodynamic property, which can be determined

Standard Electrochemical Potential

Fundamentals of Electrochemistry – Part 2

Gibbs Free Energy (ΔG^0) is the difference (ΔE^0) between two half cell potentials

If $\Delta G^0 > 0$, the reaction is non-spontaneous and endothermic

If $\Delta G^0 < 0$ the reaction is spontaneous and exothermic

In electrochemical reactions, all the electrons that are *used* must also be *released*.

EXAMPLE 1: Reaction between copper and zinc

$$Zn \longrightarrow Zn^{++} + 2\,e^- \quad = 0{,}663\ V$$

$$Cu^{++} + 2\,e^- \longrightarrow Cu \quad = 0{,}336\ V$$

$$Cu^{++} + Zn \longrightarrow Cu + Zn^{++} \quad = 1{,}100\ V$$

ΔE^0

RESULT: ΔG^0 **= 212,3 kJ**

Fundamentals of Electrochemistry – Part 3

TABLE 18.1 Standard Reduction Potentials at 25°C

	Reduction Half-Reaction		E° (V)	
Stronger oxidizing agent	$F_2(g) + 2e^-$	$\longrightarrow 2F^-(aq)$	2.87	Weaker reducing agent
	$H_2O_2(aq) + 2H^+(aq) + 2e^-$	$\longrightarrow 2H_2O(l)$	1.78	
	$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	1.51	
	$Cl_2(g) + 2e^-$	$\longrightarrow 2Cl^-(aq)$	1.36	
	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	$\longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.33	
	$O_2(g) + 4H^+(aq) + 4e^-$	$\longrightarrow 2H_2O(l)$	1.23	
	$Br_2(l) + 2e^-$	$\longrightarrow 2Br^-(aq)$	1.09	
	$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80	
	$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77	
	$O_2(g) + 2H^+(aq) + 2e^-$	$\longrightarrow H_2O_2(aq)$	0.70	
	$I_2(s) + 2e^-$	$\longrightarrow 2I^-(aq)$	0.54	
	$O_2(g) + 2H_2O(l) + 4e^-$	$\longrightarrow 4OH^-(aq)$	0.40	
	$Cu^{2+}(aq) + 2e^-$	$\longrightarrow Cu(s)$	0.34	
	$Sn^{4+}(aq) + 2e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15	
	$2H^+(aq) + 2e^-$	$\longrightarrow H_2(g)$	0	
	$Pb^{2+}(aq) + 2e^-$	$\longrightarrow Pb(s)$	−0.13	
	$Ni^{2+}(aq) + 2e^-$	$\longrightarrow Ni(s)$	−0.26	
	$Cd^{2+}(aq) + 2e^-$	$\longrightarrow Cd(s)$	−0.40	
	$Fe^{2+}(aq) + 2e^-$	$\longrightarrow Fe(s)$	−0.45	
	$Zn^{2+}(aq) + 2e^-$	$\longrightarrow Zn(s)$	−0.76	
	$2H_2O(l) + 2e^-$	$\longrightarrow H_2(g) + 2OH^-(aq)$	−0.83	
	$Al^{3+}(aq) + 3e^-$	$\longrightarrow Al(s)$	−1.66	
	$Mg^{2+}(aq) + 2e^-$	$\longrightarrow Mg(s)$	−2.37	
	$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.71	
Weaker oxidizing agent	$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.04	Stronger reducing agent

Fundamentals of Electrochemistry – Part 4

What if the conditions differ from unit activity and standard temperature conditions ??

R = Universal Gas Constant
(8,3144 J / mol K)

The Nernst Equation

$$E = E^0 - \frac{RT}{nF}\ln\left(\frac{C_{ox}}{C_{red}}\right)$$

concentration (oxidized side)

concentration (reduced side)

EXAMPLE 2: The dependence on the concentrations

$Cu^{++} + Zn \longrightarrow Cu + Zn^{++}$ = 1,100 V ΔE^0

Cu^{++} = 0,5 mol
Zn^{++} = 0,01 mol

$$E = 1{,}100\,V - 0{,}0591\log\left(\frac{0{,}01}{0{,}5}\right)V$$

$$E = 1{,}200\,V$$

Electroless Cu Plating - Mechanism

Background:

Electrochemical reaction to deposit Cu without the passage of current

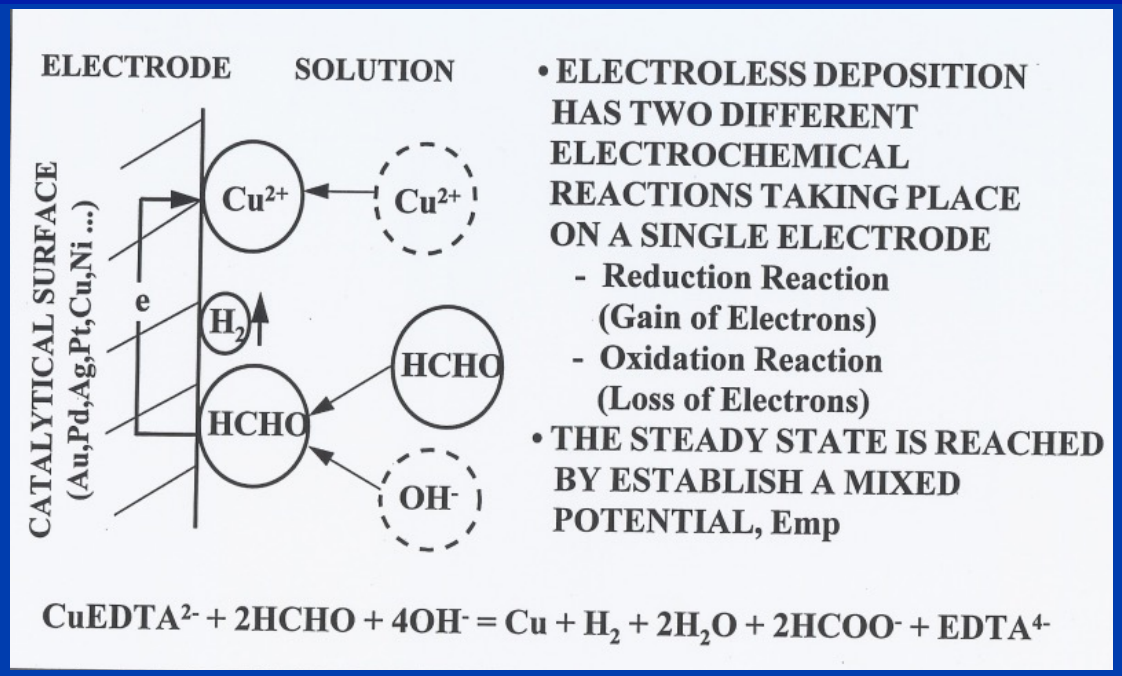
Oxidation: $CHO\text{-}COOH + 2OH^- \rightarrow (COOH)_2 + 1/2\ H_2 \uparrow + 2e^-$

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

Side reactions :

Cannizaro reaction (Temp dependent): $2RCHO + OH^- \rightarrow RCH_2OH + RCOO^-$

Cu_2O formation (pH dependant): $2Cu^{2+} + RCHO + 5OH^- \rightarrow Cu_2O + RCOO^- + 3H_2O$



Electroless Plating - Thermodynamics

Thermodynamically favorable reaction

$HCHO + 3\ OH^- = HCOO^- + 2H_2O + 2e$

$E^o ox = 1.14\ V$

$Cu^{2+} + 2\ e = Cu$

$E^o red = 0.337\ V$

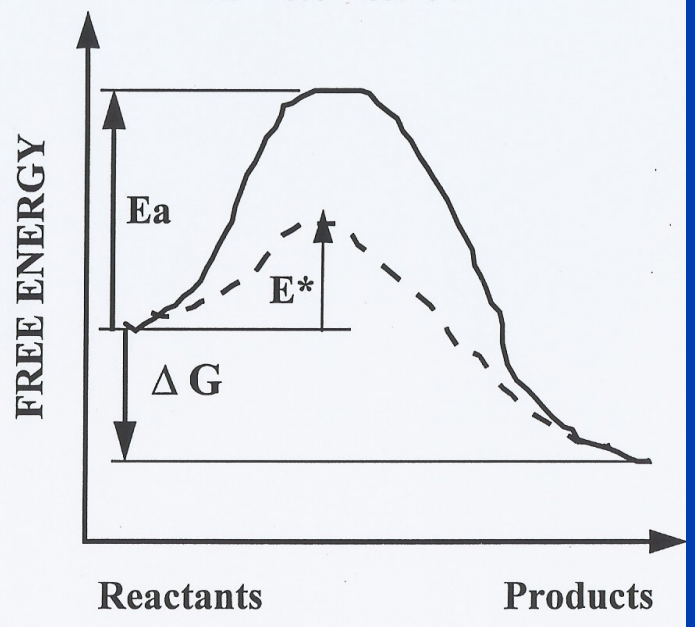
$\Delta G^o = -\ nFE^o;\ E^o = E^o ox + E^o red;$

$Eo = 1.477\ V;$

$\Delta G^o < 0$ (spontaneous reaction)

Kinetically inhibited reaction

Ea = 0.6 - 0.7 eV



Elecroless Cu deposition is thermodynamically favorable (ΔG<0) and Kinetically inhibited reaction (potential barrier exist – need for catalytic surface and temperature activation)

Electroless Cu Deposition

Electroless Cu System

- Wafer
- Catalytic seed
- Plating Solution
  - Copper ions
  - Reducing agent
  - Complexing agent
  - pH adjuster
  - additives

Issues to Address

- Catalytic activity of seed layer
- Hydrogen evolution
- Stability of plating solution
- Control of plating solution
  - pH
  - Concentrations
  - Deposition rate

Electroless Plating – Key requirements

- Deposition is carried out at basic pH (usually, pH>11)
- Deposition Temperature > 30C
- Slow rate of deposition – 10 – 150 nm/min depends on solution temperature (30 – 90C)
- Need a catalytic/activation substrate/layer (e.g.: Ru, Pt, Pd, Cu, Ni, Co etc)
- If surface is not catalytic, then need Pd acitivation
  - Pd-Sn
  - Contact displacement
  - TiO_2/Pd^{2+}
  - SAM of Pd

Reducing Agents for Cu and Ni/Co Electroless Deposition

Metals	Reducing Agents	pH	Temperature, C
Cu	Formaldehyde (HCHO)	Basic	20-70
	Borohydride $(BH_4)^-$	Basic	20-30
	Hypophisphite $(H_2PO_2)^-$	Basic/Acidic	50-90
	DMAB $(CH_3)_2HN\ BH_3$	Neutral/Acidic	60-80
	Glyoxylic Acid OHCCOOH	Basic	40-70
	Hydrazine Borane $N_2H_4\ BH_3$	Acidic, neutral	30-50
	Fe(II)/Fe(III)	Acidic	25
	Ti(II)/Ti(IV)	Acidic	25
	Cr(II)/Cr(III)	Acidic	25
	V(II)/V(III)	Acidic	25
Ni/Co	$(H_2PO_2)^-$	Acidic, basic	25-90
	$(BH_4)^-$	Basic	50-90
	$(CH_3)_2HN\ BH_3$	Acidic, neutral	50-80
	$(C_2H_5)_2HN\ BH_3$	Acidic, neutral	50-80
	$N_2H_4\ BH_3$	Basic	20-50
	$C_5H_5N\ BH_3$	Basic	70-90

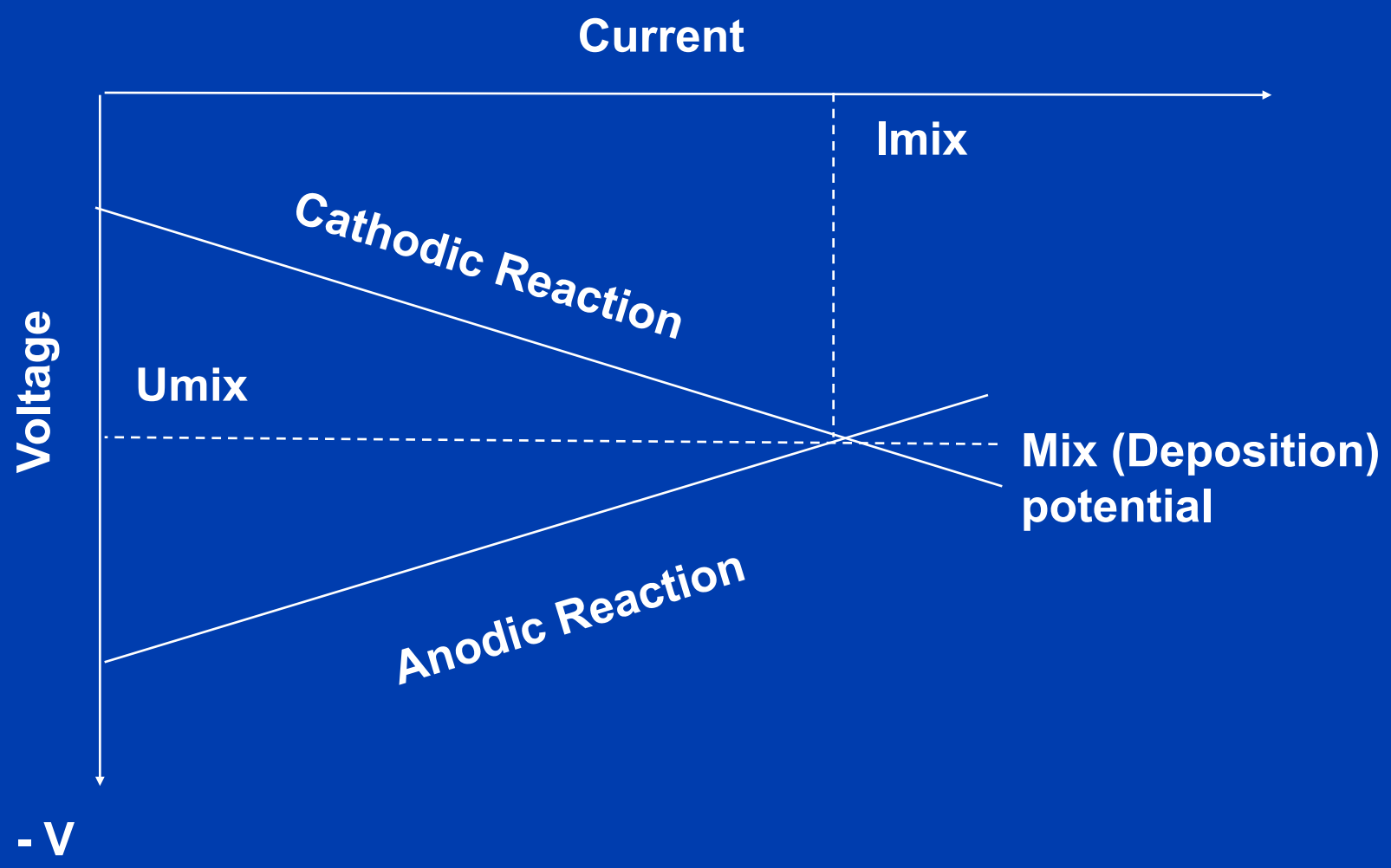
Catalytical Materials for EL

Reducing Agents	Catalytic Materials	Non-catalytic Materials
HCHO	Cu, Ag, Pd, Pt, Au, Pd_2Si, PtSi	Cd, Ni, Co, Pb, Sn, Bi, Sb, Zn, Ti, Ta
$H_2PO_2^-$	Ni, Co, Fe, Rh, Pd, Au, $CoSi_2$, $NiSi_2$	W,Re,Zn,Cd,Hg,V, Cr,Ag,Sn,Mn,Mo,Tl
$(BH_4)^-$	Ni, Co, Fe, Rh, Pd, Pt, Cu, Au, Ag, Ru	W, Re, Zn, Cd, Hg, V, Cr, Sn, Mn, Mo, Tl
N_2H_4 H_2O	Ni, Co, Fe, Rh, Pd, Pt, Ag, Au, Ru	W, Re, Zn, Hg, Sn, Cr, V, Mn, Mo

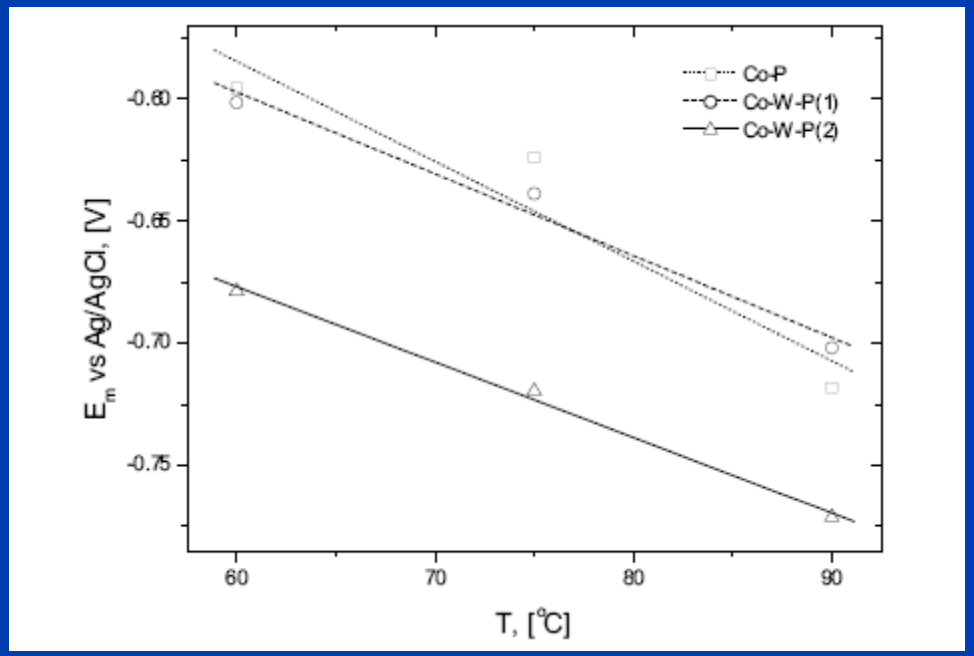
Redox Potentials and Stability Constant

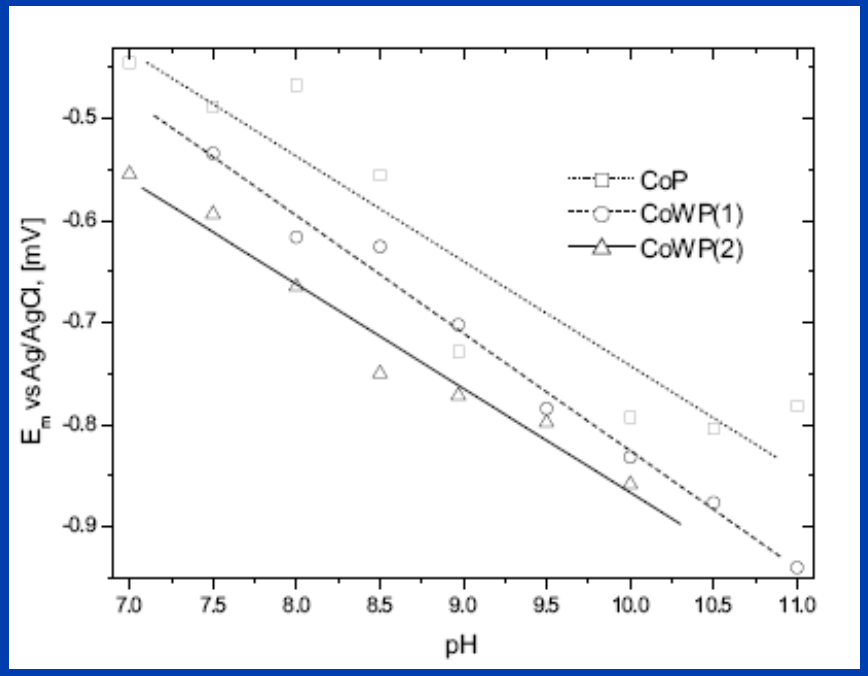
Reaction	Potential, V	pK
$HCHO + 3OH^- = HCOO^- + 2H_2O + 2e$	0.19–0.09pH	
HCHO + H2O = HCOOH + 2H+ + 2e	0.056–0.06pH	
$2HCHO + 4OH^- = 2HCOO^- + H_2 + 2H_2O + 2e$	0.32 – 0.12 pH	
$HCOO^- + 3OH^- = CO^{2-}{}_3 + 2H_2O + 2e$	0.25 – 0.09 pH	
$Cu^{2+} + 2e = Cu$	0.345	
$(CuCOOH)^+ + 2e = Cu + HCOO^-$	0.285	
$(CuCH_3COO) + e = Cu + CH_3COO^-$	0.276	
$(CuSuc) + 2e = Cu + Suc^{2-}$	0.243	2.6
$(CuMal) + 2e = Cu + Mal^{2-}$	0.203	3.42
$(CuTart_3)^{4-} + 2e = Cu + 3Tart^{2-}$	0.154	5.76
$(CuCit)^- + 2e = Cu + Cit^{3-}$		5.9
$[Cu(NH_3)_2]^+ + e = Cu + 2NH_3$	- 0.11	7.64
$(CuEn)^{2+} + 2e = Cu + En$		10.54
$(CuEDTA)^{2-} + 2e = Cu + EDTA^{4-}$	-- 0.216	18.8

EL Galvanic Cell



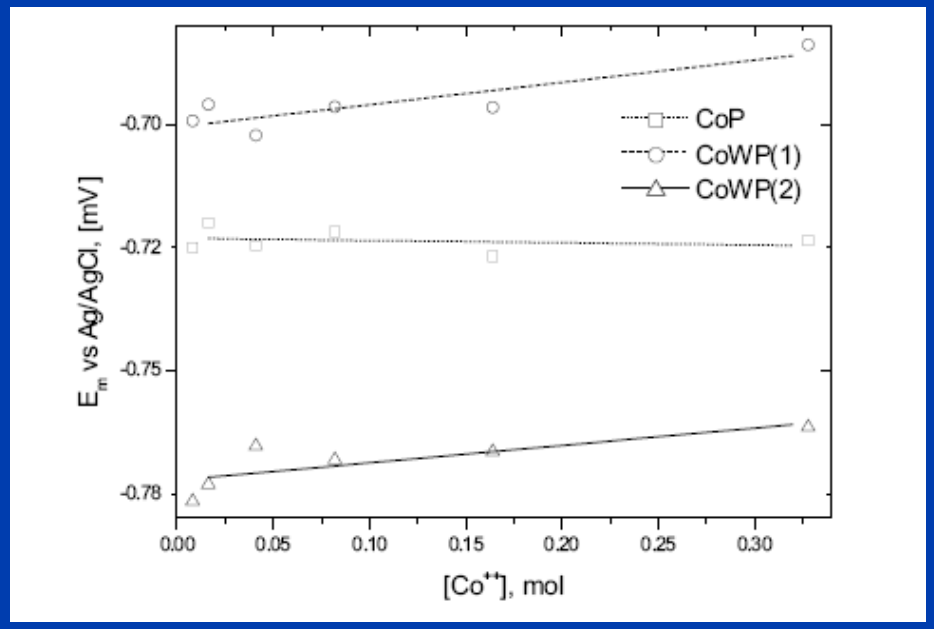
Mix Potential vs Temperature and pH

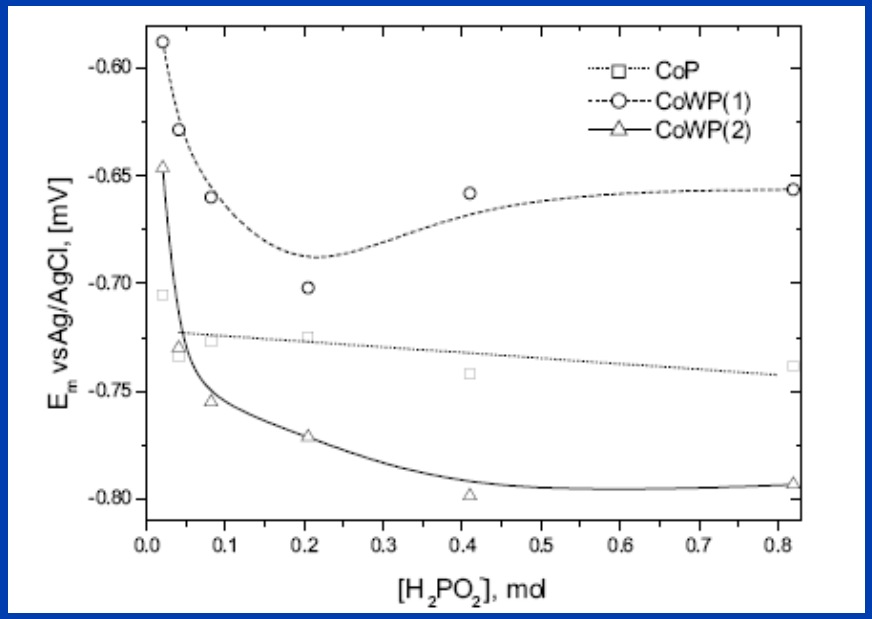




Mixed potential increases with temperature and pH increase (i.e. Cu deposition rate increases)

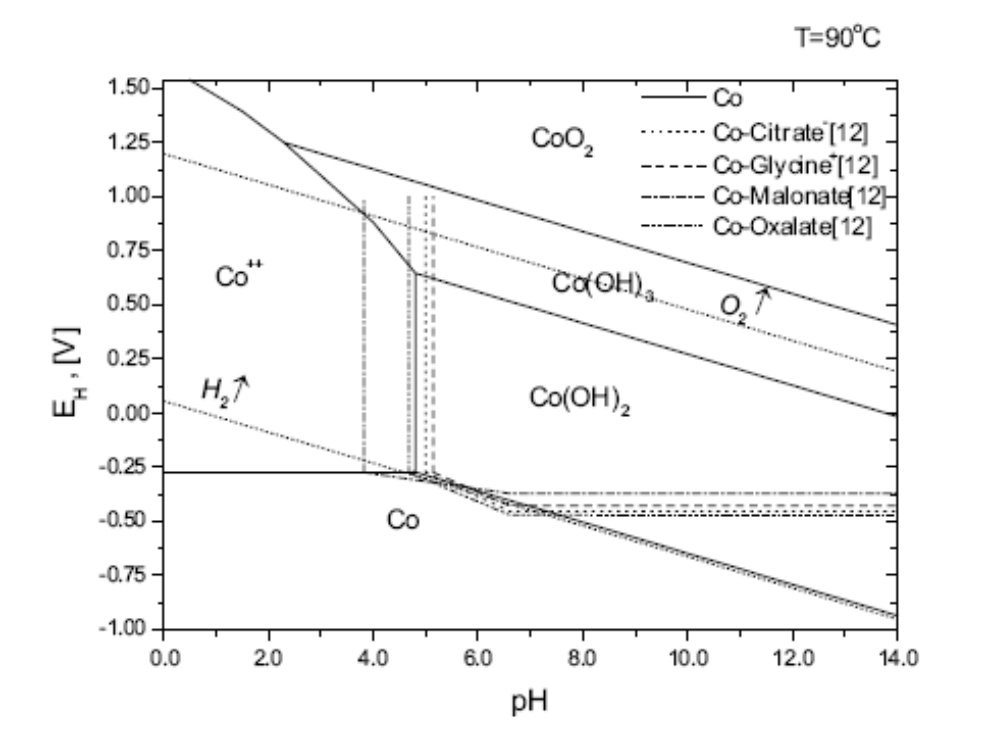
Mix Potential vs Concentrations

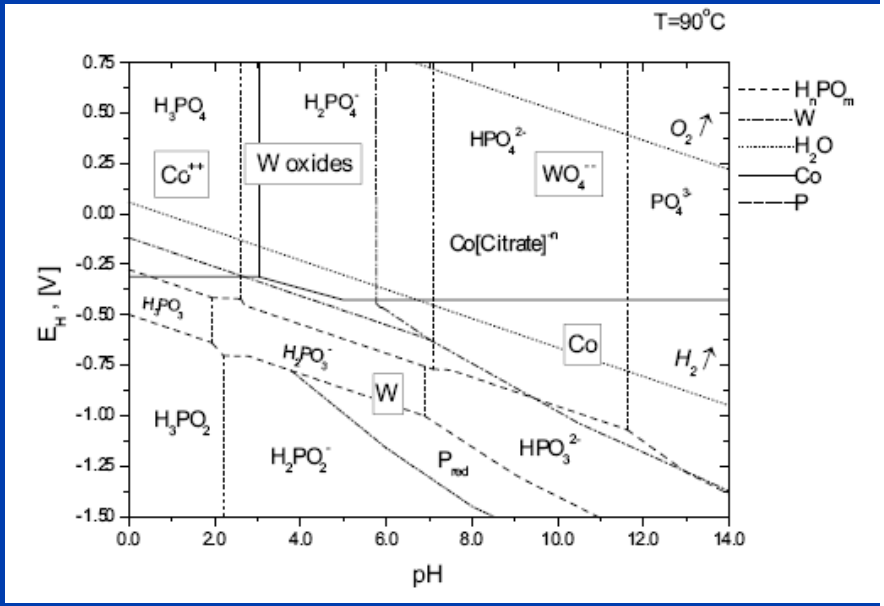




Mixed potential (Cu deposition rate) increases with increasing pH to certain concentration and has small dependence on metal ion concentration

Pourbaix Diagram for EL Systems





Electroless Nucleation

$$r^* = 2\,\sigma\,V / [n\,F\,(E_{Me} - E_{Red})]$$

For Cu-CH_2O system $E_{Me} - E_{Red} = 0.3 - 0.4$ V

Critical radius of nuclei (r^*) is about 0.3 nm

When r in the solution is > than r^*, the solution is decomposed

Stability of the solution can be increased by decreasing the difference between E_{Me} and E_{Red} with

- stronger complexing agent
- decreasing pH

and addition of additives to block nuclei growth

Additives in EL Solution

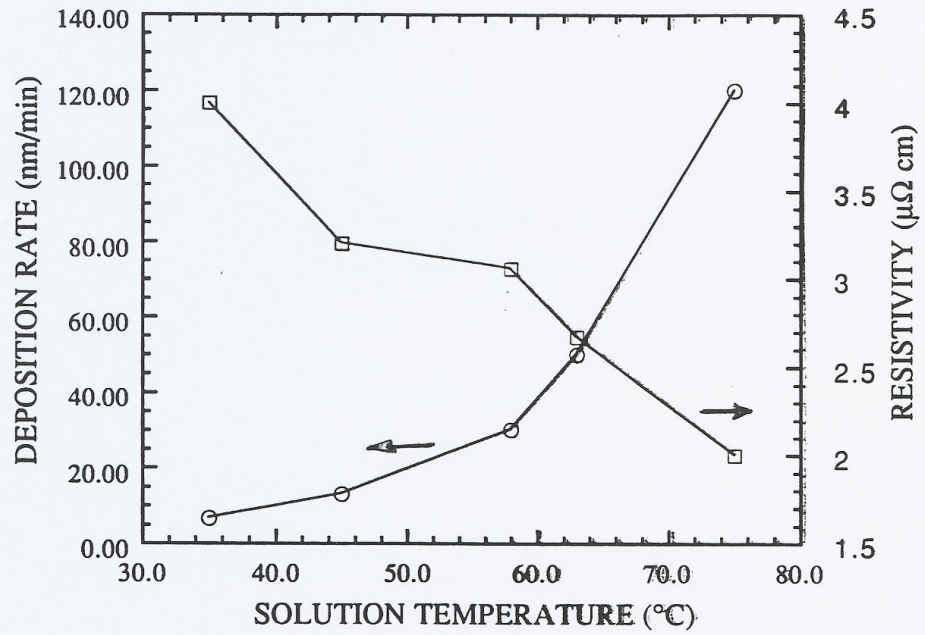
- Metal Containing compounds:
  - V. Mo, Nb, W, Re, Tl, Sb, Bi, Ce, Hg, Ag, As
- Sulfur-Containing compounds
  - Sulfites, thiosulfates, sulfates
- Nitrogen-Containing compounds
  - Tetracyanoethylene, cyanides, pyridines, 2,2' – Dipyridyl
- Sulfur and Nitrogen Containing compounds
  - Cysteines, cystines, diethylditiocarbamates, thiosemicarbazide

Deposition Condition Study

Parameters	Parameter Change	Deposition Rate Change	Resistivity Change
$CuSO_4$ 5 H_2O concentration	↑	↑	↔
HCOH concentration	↑	↑	↑
RE610 concentration	↑	↓	↓
2-2' Dipyridyl or CN^- concent	↓	↓	↑
pH (11.8-12.2)	↑	↑	↓
pH (12.2-12.8)	↑	↔	↔
pH (>12.8)	↑	Unstable Sol	Unstable Sol
Temperature	↑	↑	↓

↔ - no strong effect; ↑ - increases; ↓ - decreases

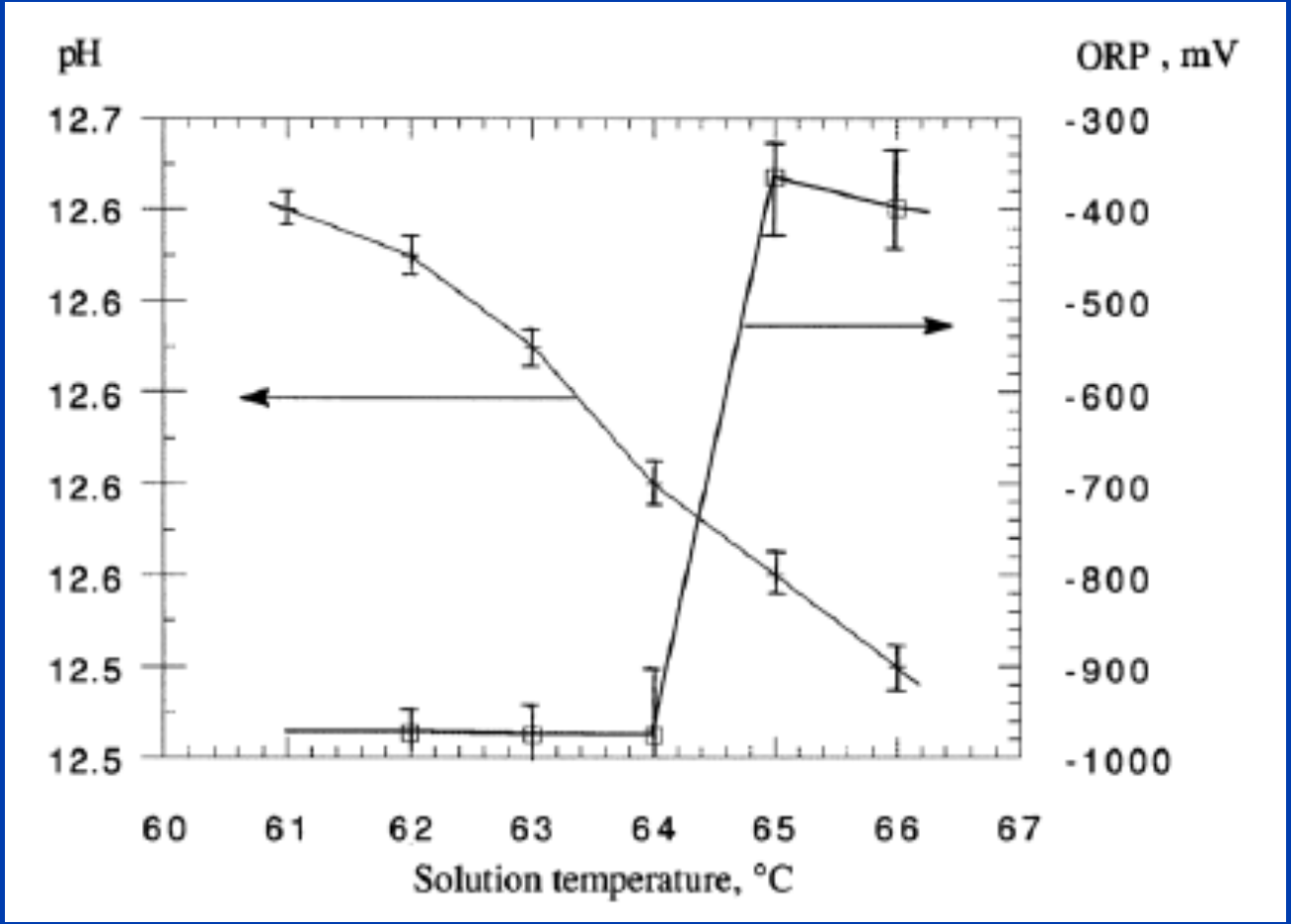
EL Cu Plating Rate and Resistivity



Electroless Cu deposition rate and resistivity vs solution temperature

Increase of solution temperature increases deposition rate for EL Cu (about 150 nm/min at 80C) and decreases Cu resistivity (down to about 2 μOhm cm)

EL Cu ORP and pH vs Temperature



Kinetics of EL Cu Plating

$$R = K[C_{Cu^{2+}}]^a[C_{HCHO}]^b[C_{OH^-}]^c[C_{EDTA^{4-}}]^d$$

$[C_{Cu^{2+}}]$ is between 0.015 and 0.1 mol l^{-1}, $0.05 \leq C_{HCHO} \leq 0.5$, $0.07 \leq C_{OH^-} \leq 0.3$ mol l^{-1}, $0.03 \leq C_{EDTA^{4-}} \leq 0.4$ mol l^{-1} and the temperature is 50°C, the values of the reaction orders (a, b, c, d) are 0.78, 0.13, 0.02, and 0.02, respectively. However, for other ranges of chemical conditions, for example, $0.003 \leq C_{Cu^{2+}} \leq 0.03$, $0.03 \leq C_{HCHO} \leq 0.4$, $0.5 \leq C_{OH^-} \leq 2.0$ mol l^{-1}, and at 21°C solution temperature, the values of the reaction order (a, b, c) are 0.37, 0.0, 0.37, respectively.

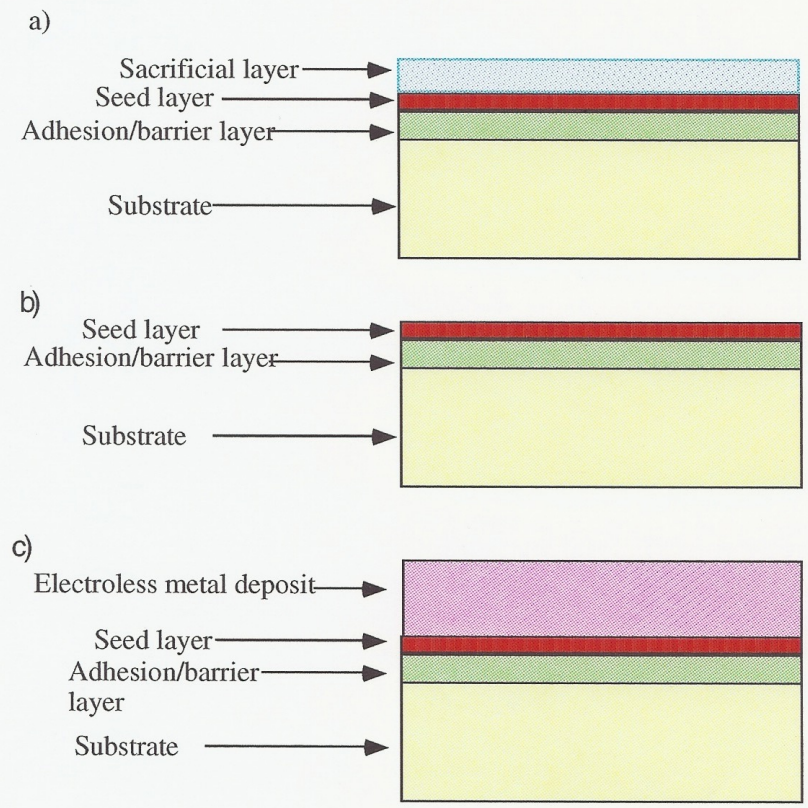
Properties of EL Cu Films

Properties	Electroless Cu Films	Al Films
Resistivity, μΩ cm	1.7 – 2	Al – 2.655
Grain Size, μm	0.1 – 1	Bamboo, line width
Texture	(111) or (100)	(111)
Melting Temp, C	1085	660
Density, g/cm^3	8.56 – 8.76	2.699
Internal Stress, N/mm^2	+/- 20 to +/- 60	
Tensile Strength, N/mm^2	350 – 450	
Microhardness, N/mm^2	610 – 660	PVD – poor, CVD – good
Conformality, %	Up to 90%	~ 10
EM MTF, h	~ 1000	

Composition of EL Cu

Element	ppm, Weight	ppm, Atomic
H	30 - 200	1900 – 12700
H after anneal	Few ppm	Few ppm
C	90 – 800	480 – 4230
O	70 – 250	280 – 990
N	20 – 110	90 – 500
Na (with NaOH)	20 – 70	55 – 190
Na (with TMAH)	Few ppm	Few ppm

Protected Cu Activation Layer for EL Cu



a) Al is deposited on Cu seed layer to protect its catalytic properties.

b) The Al layer is dissolved in the basic bath.

c) Cu is electrolessly deposited onto catalytic seed layer.

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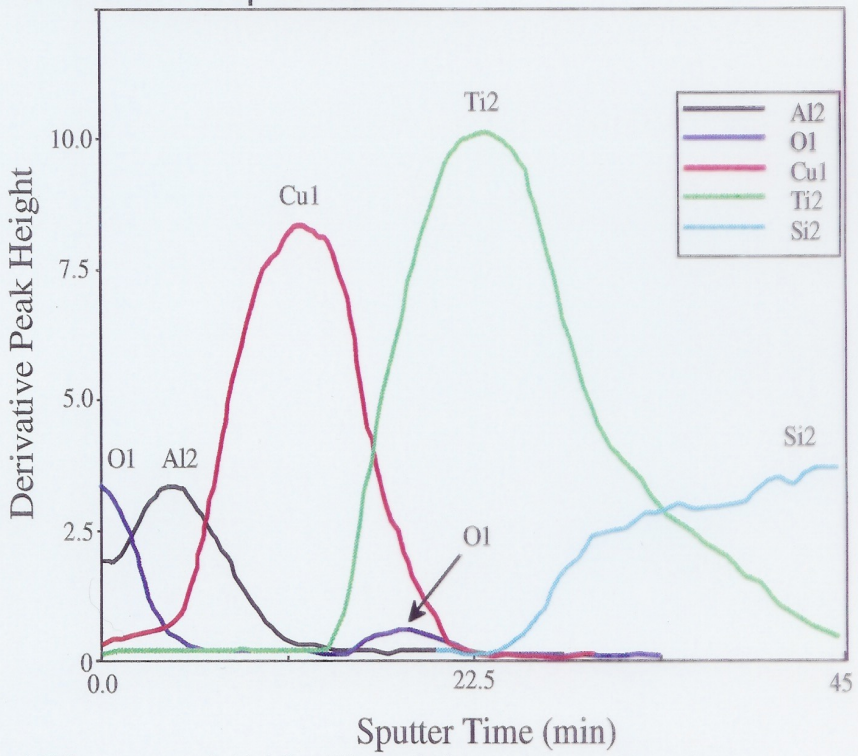
Protected Cu Activation Layer - Cont

a. before deposition.

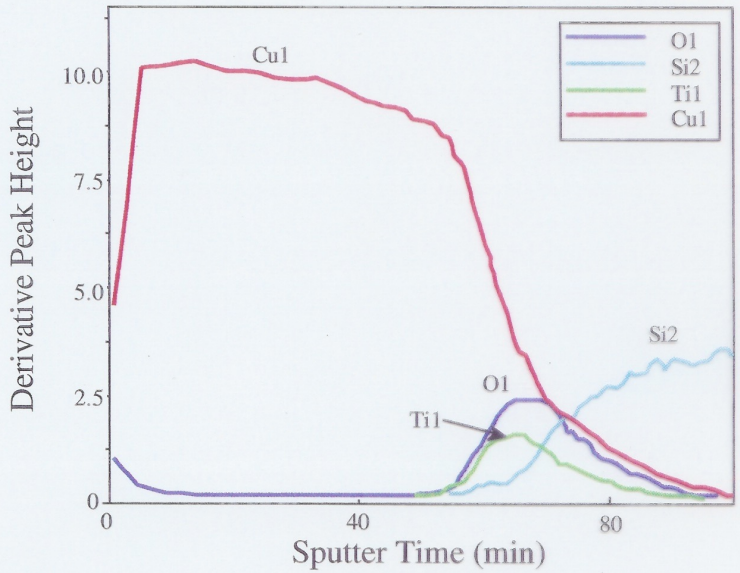


AES spectra of Al/Cu/Ti multilayer film on Si substrate.

- No surface oxide on Cu seed layer,

b. After deposition.

AES of Electroless Copper Deposited on a Al/Cu/Ti Film

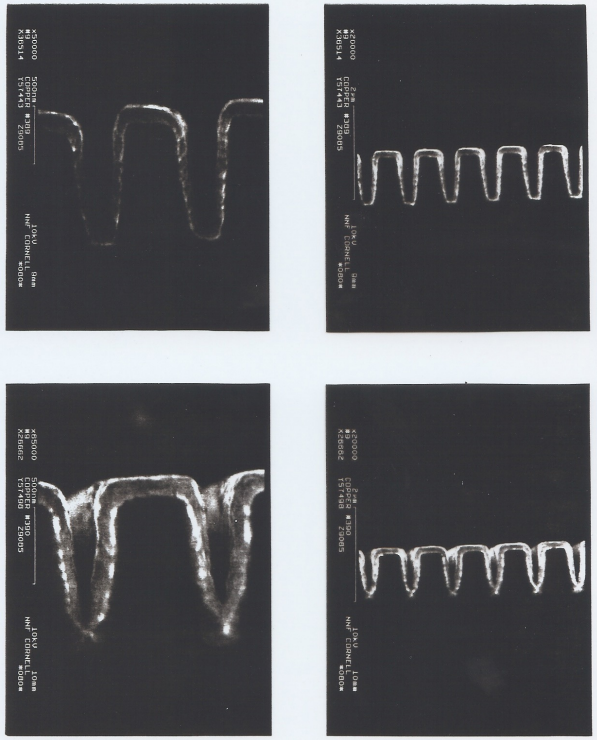


* No surface oxide on Cu seed layer,
* Complete Al dissolution

- Complete dissolution.

EL Cu Plating On Cu/Al Catalytic layer – Trench Fill

PROCESS INTEGRATION. CONFORMAL COPPER ELECTROLESS PLATING ON SPUTTERED Cu SEED



CLEAVED SEM CS OF ~ 0.3 μm TRENCHES OF HIGH A.R. (~ 3) PLATED WITH ~ 0.14 μm ELECTROLESS Cu ON SPUTTERED Ti/Cu/Al

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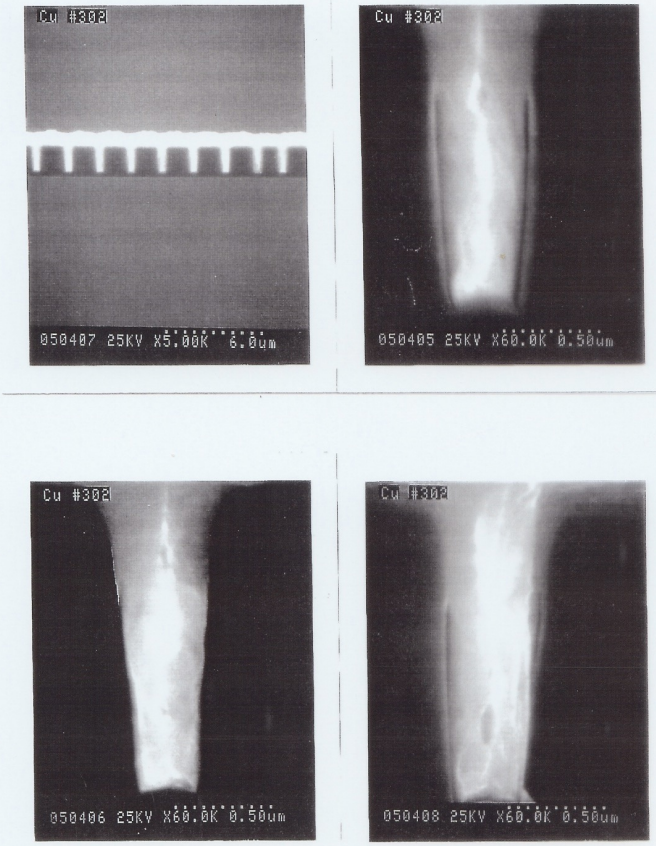
Electroless Cu-filled 0.3 μm wide trenches with aspect ratio of 5.5



0.3 μm Cu-filled trenches - No voids/seams

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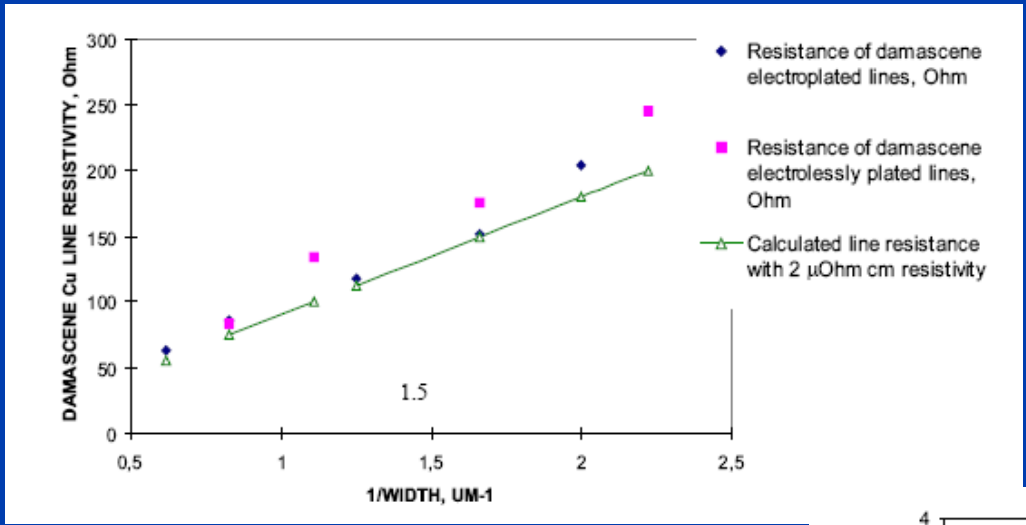
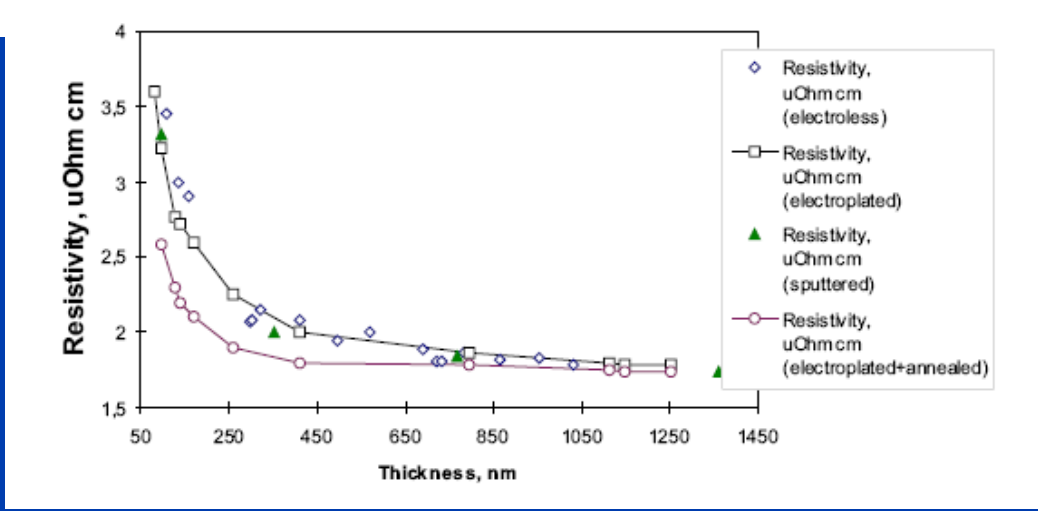
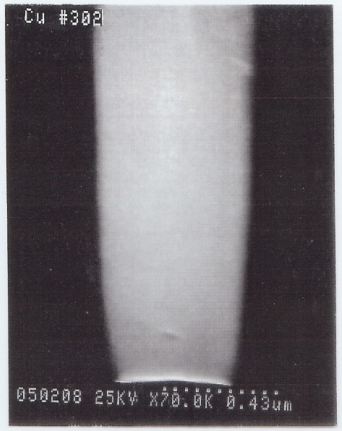
EL Cu Resistivity

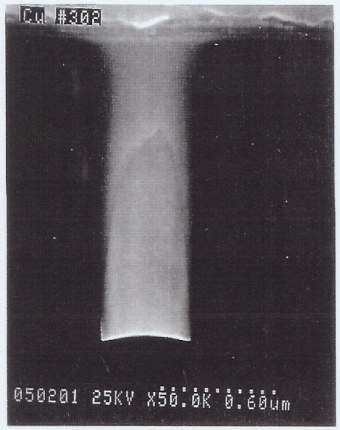


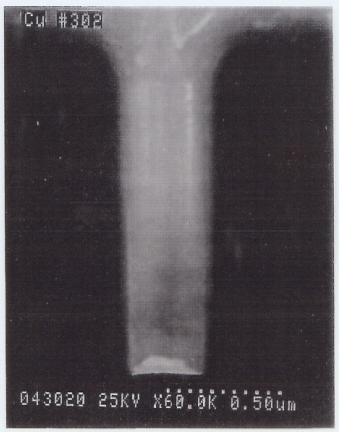


EL Cu Plating On Cu/Al Catalytic layer – Via Fill



0.55 µm via - no voids/seams





0.35 µm via - no voids/seams

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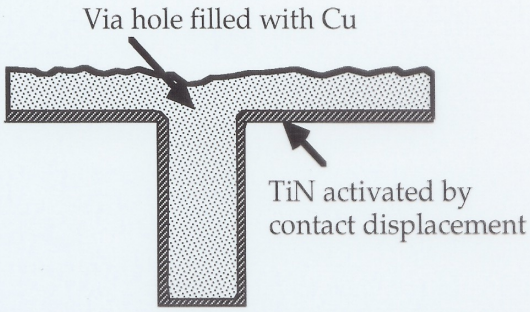
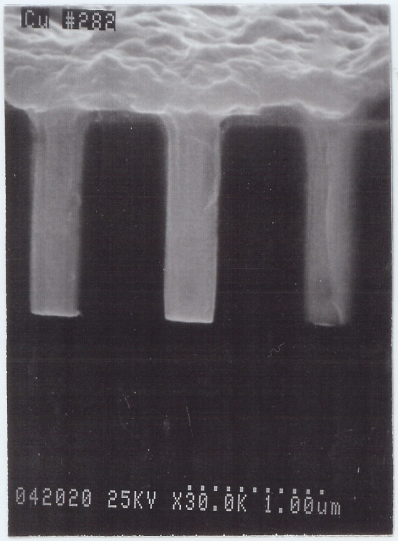
Solution for Contact Displacement Cu Deposition on TiN

Components	Concentration
Cu^{2+}	0.001 – 1 mol/l
F^-	0.001 – 5 mol/l
Surfactant	0.01 – 0.1 g/l
Temperature	18-20 C
Time	10 – 15 sec

Contact Displacement Catalytic Layer for EL Cu Plating

Blanket Electroless Cu deposition using contact displacement seeding





0.35 µm Cu plugs (aspect ratio 4.3) deposited on contact displacement seeding

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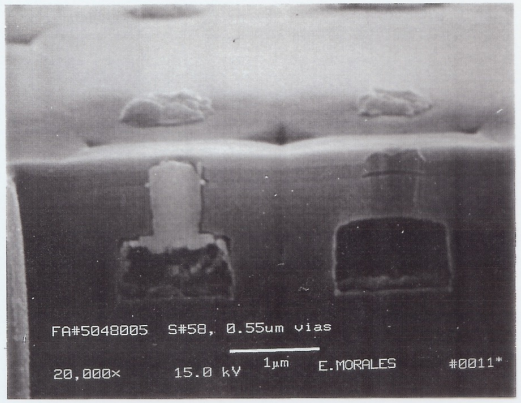
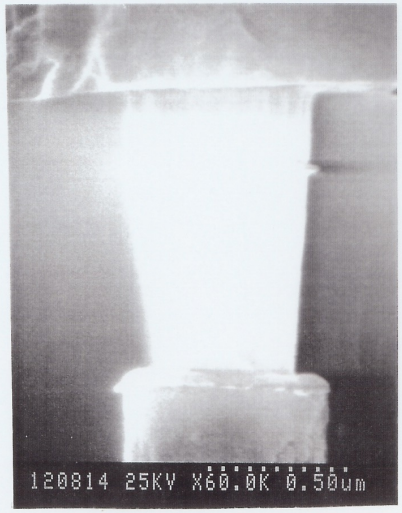
Selective Cu using contact displacement seeding



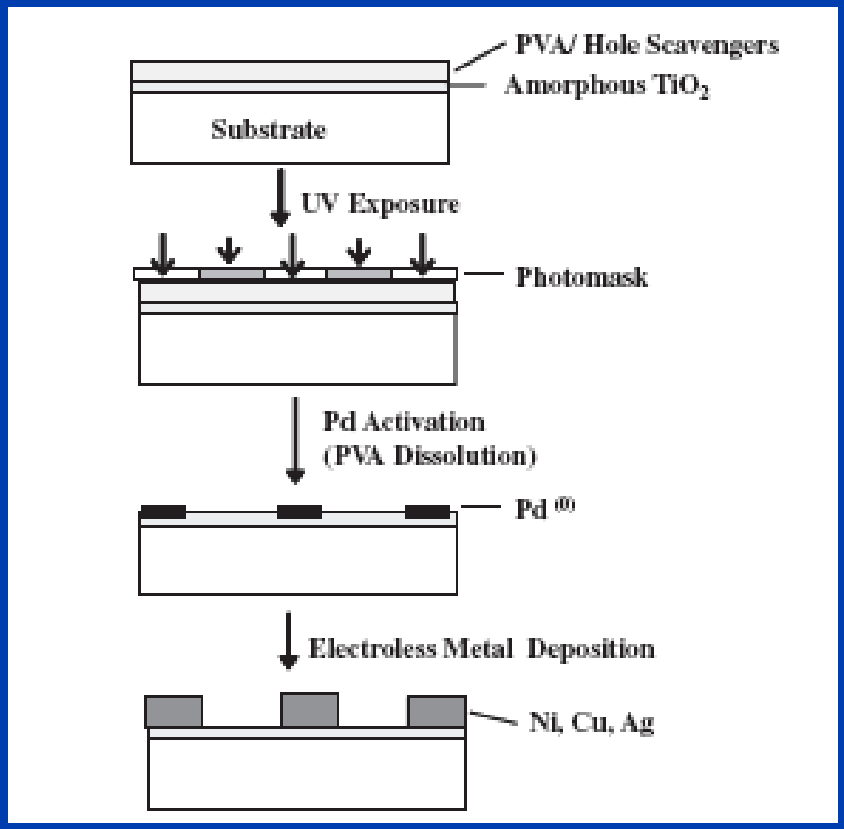
Demonstration of good selectivity of Cu plating

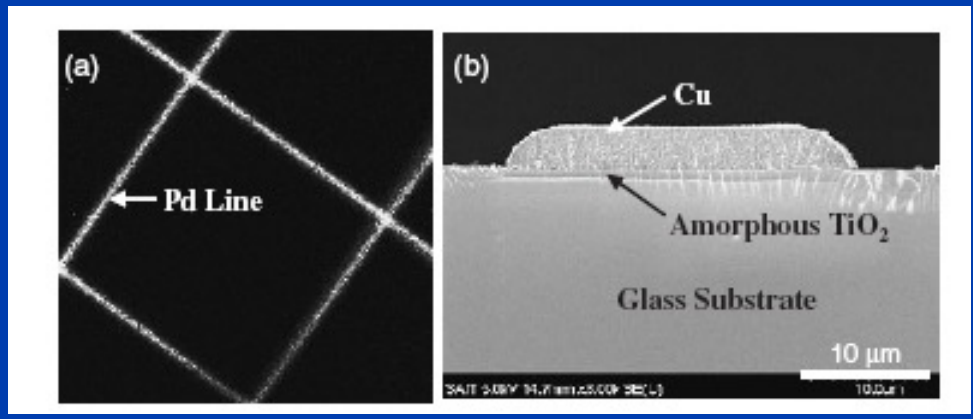


0.55 µm via hole filled with Electroless Cu

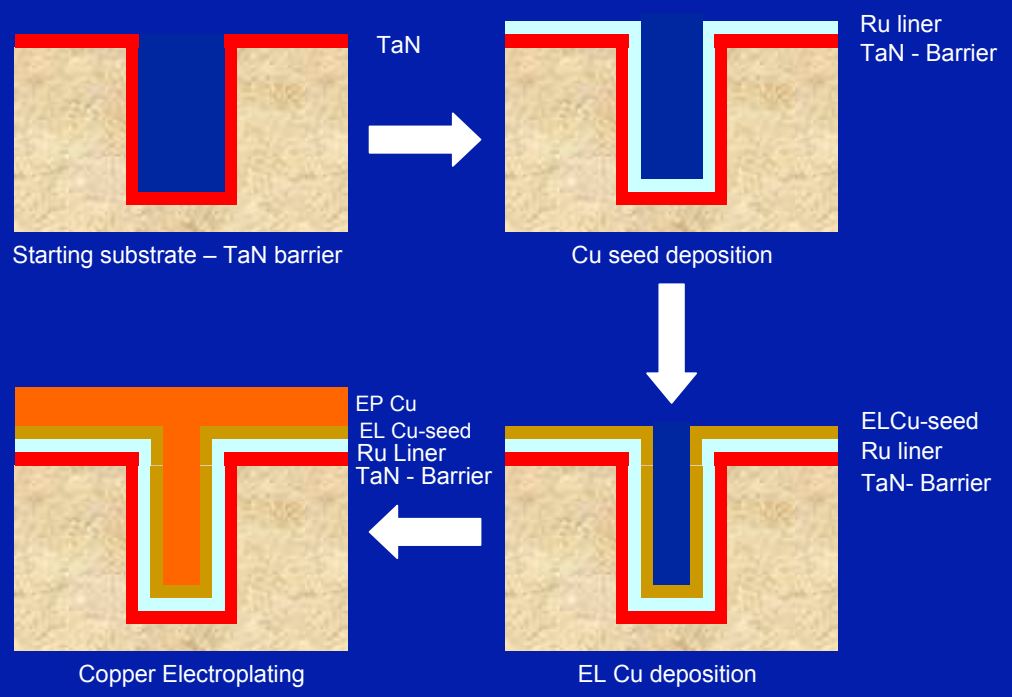
Y. Shacham-Diamand & V. Dubin SEMATECH/CU May 1995

Selective Photosensitive EL Plating





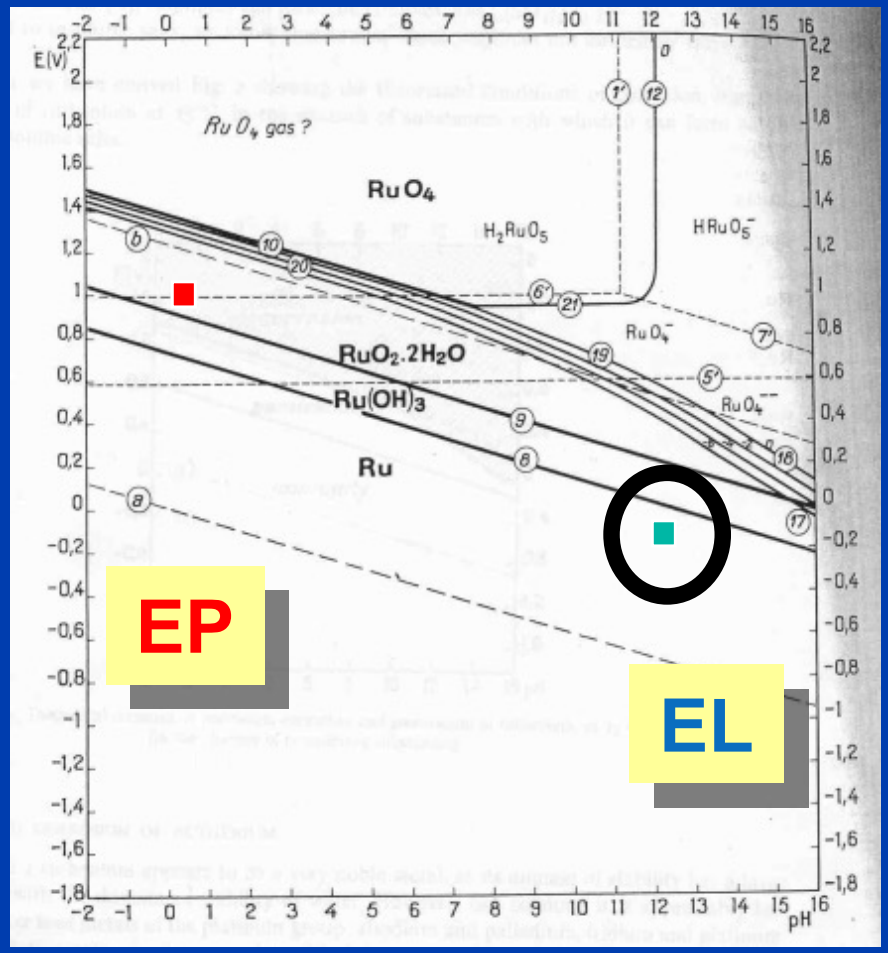
EL Cu seed on Ru Liner



Advantages:

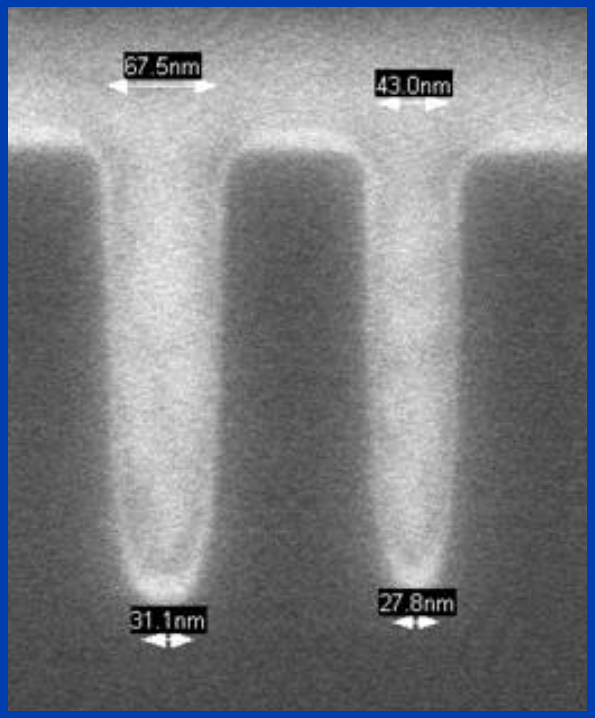
1. Ru are directly platable
2. EL Cu on Ru liner improves nucleation and reduces side wall voiding
3. EL Cu on liners will reduce the effective across wafer resistance

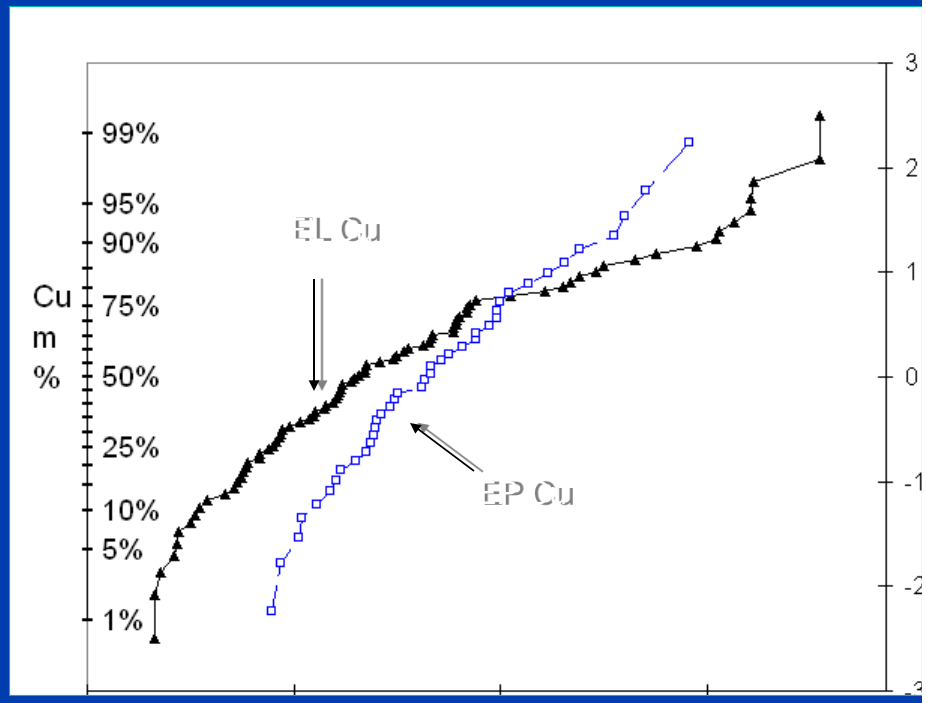
EL Cu Plating on Ru



EL Cu is nucleated on Ru at high pH >12

Gap Fill with EL Cu DP on Barrier





Line Resistance, a.u.

- Sub 50 nm EL Cu metallization was fabricated with EL Cu plating directly on Ta-based barrier
- EL Cu is capable of filling damascene features down to 10 nm
- EL Cu Line Resistance is comparable to EP Cu

Fabrication of EL Metal Layer on SiO_2 - SAM

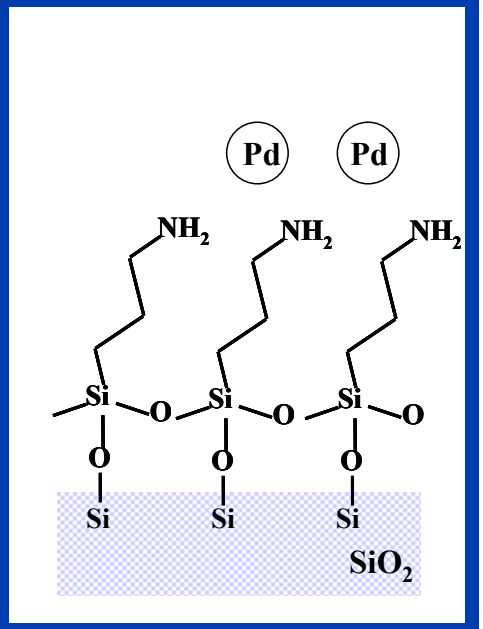
Substrate SiO_2(500 nm)/Si Wafer

SAM Formation Immersion into Organosilane Solution

spontaneous formation of Si-O bonds

Catalyzation Immersion into Aqueous $PdCl_2$ Solution

entrapment of Pd catalyst at amino group(s)



Plating Bath Composition

Substrate CVD-SiO_2 (500 nm)/Si

SAM Formation

	(g)
toluene	39.6
Aminopropyl-triethoxy silane (APS)	0.4

Catalysts

	(g dm^{-3})
HCl	0.43
$PdCl_2$	0.10
bath temperature	25 ^oC

Electroless deposition

	(mol dm^{-3})
Sodium citrate	0.2
$NiSO_4$	0.1
DMAB	0.05
pH	9.0
bath temperature	70 ^oC

Electroless NiB Deposition on SAM

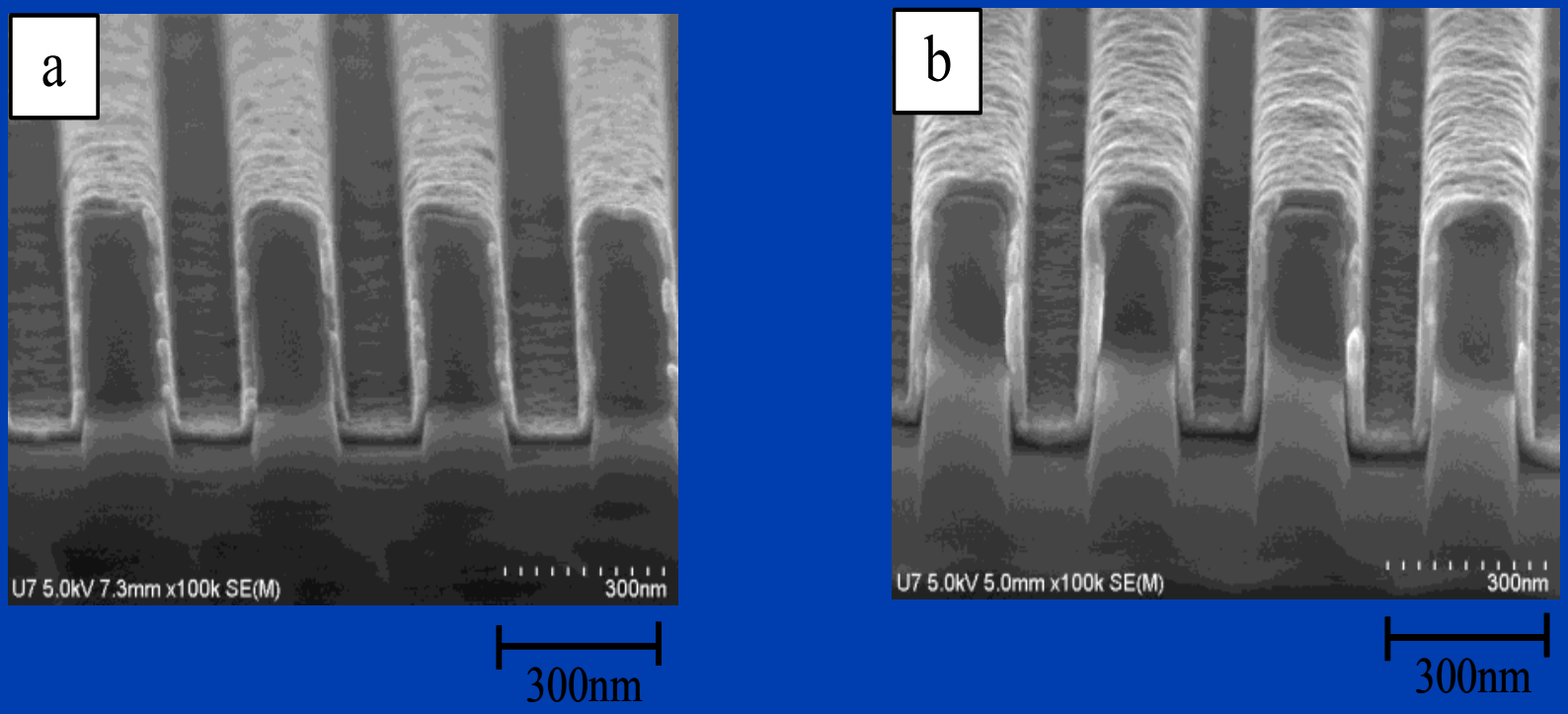
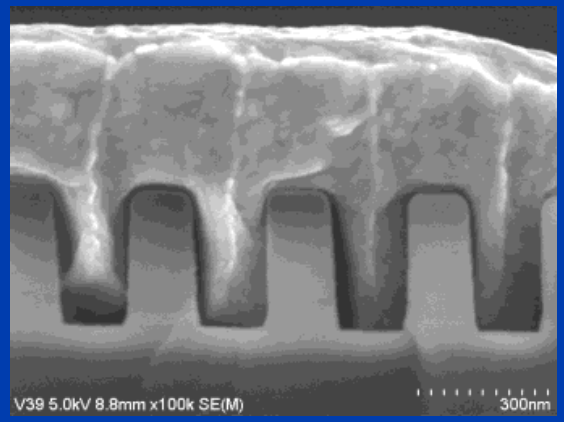


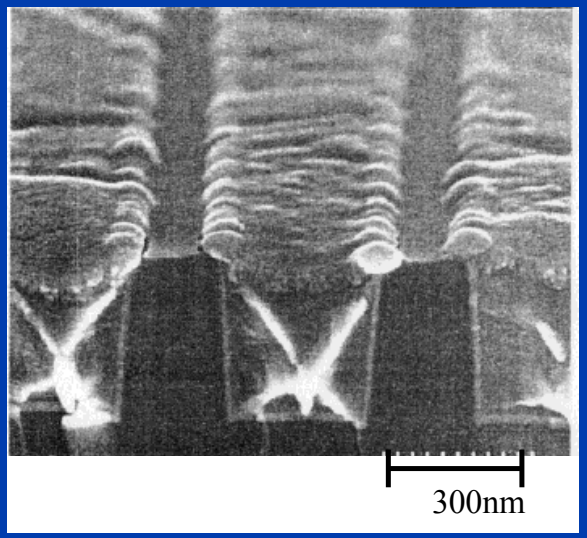
Figure 6. Cross-sectional SEM images of barrier layer deposited on the trench pattern substrate. The thicknesses of NiB film were a) 20nm and b) 30nm. The SiO_2/Si substrate with submicron trenches modified by Pd-activated SAM was used.

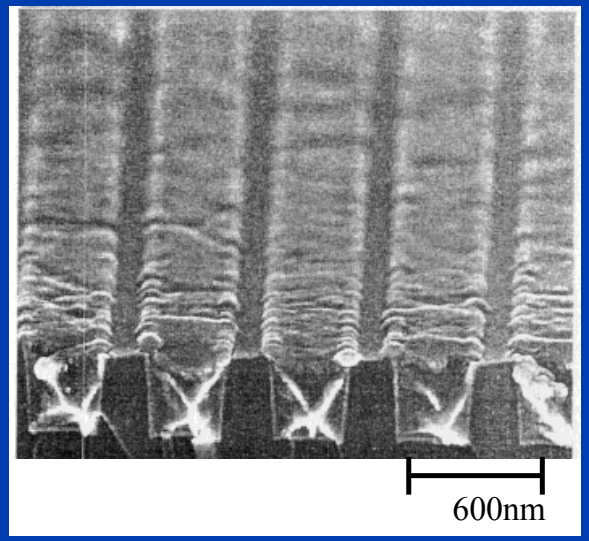
Barrier/Seed and Capping EL NiB Layers



Potential Application in Packaging and 3D

Cross-sectional SEM image of trench pattern after Cu electrodeposition. The NiB (40nm)/ SAM /SiO_2/Si substrate was used.



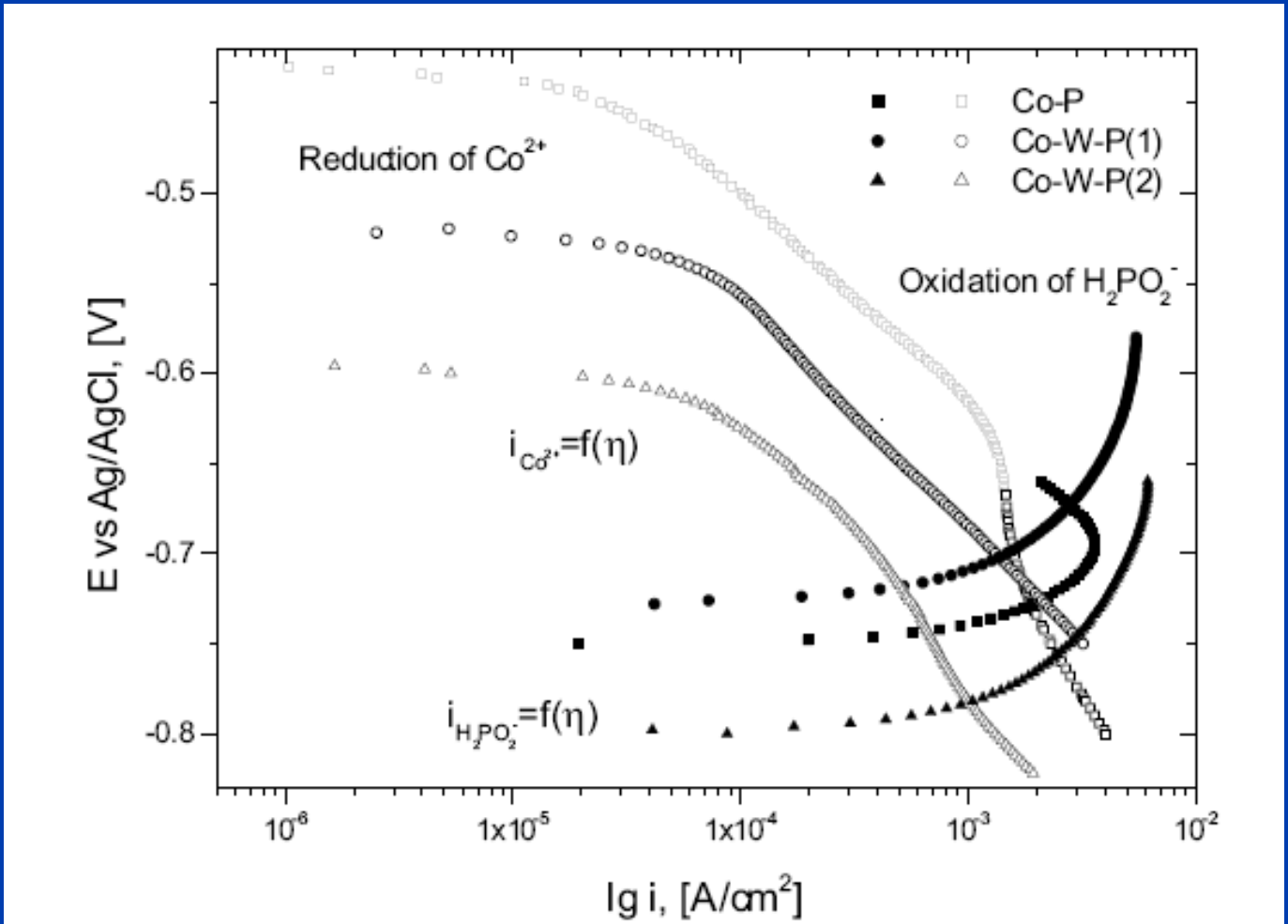


Surface and cross-sectional SEM images of NiB capping layer on Cu wiring pattern on Ta/SiO_2/Si Substrates.

EL CoWP Baths

Component	*Concentration, M*	*Co-P*	*Co–W–P(1)*	*Co–W–P(2)*
$CoSO_4 \cdot 7H_2O$	0.0082–0.33	×	×	×
$Na_3C_5H_5O_7 \cdot H_2O$	0.492	×	×	×
H_3BO_3	0.502	×	×	×
$NaH_2PO_2 \cdot 2H_2O$	0.02–0.82	×	×	×
$Na_2WO_4 \cdot 2H_2O$	0.0082–0.33		×	
$H_3[P(W_3O_{10})_4]$	0.005–0.02			×
KOH		To adjust pH		
Temperature 90±5°C				

I-V Curves for EL CoWP



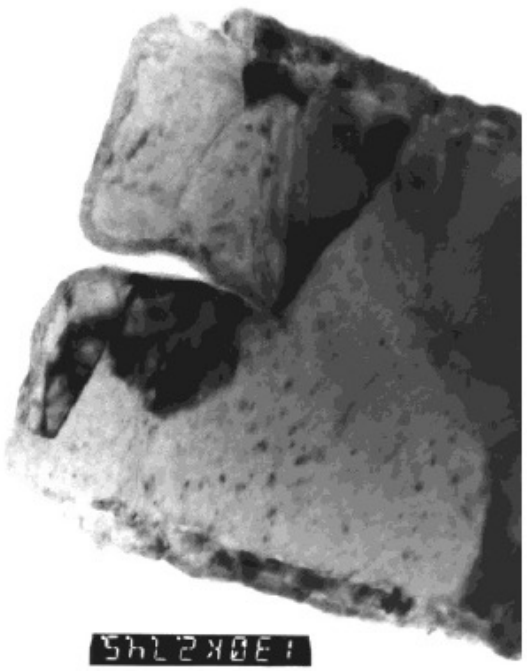
Kinetics of EL CoWP

Cobalt alloy	*Mixed potential (V vs. Ag/AgCl)*	*Deposition current* i_{dep} *(mA cm*$^{-2}$*)*	*Calculated deposition rate, w (mg h*$^{-1}$ *cm*$^{-2}$*)*
Co–P	–0.728	1.9	2.09
Co–W–P(1)	–0.702	1.374	1.51
Co–W–P(2)	–0.782	1.05	1.15

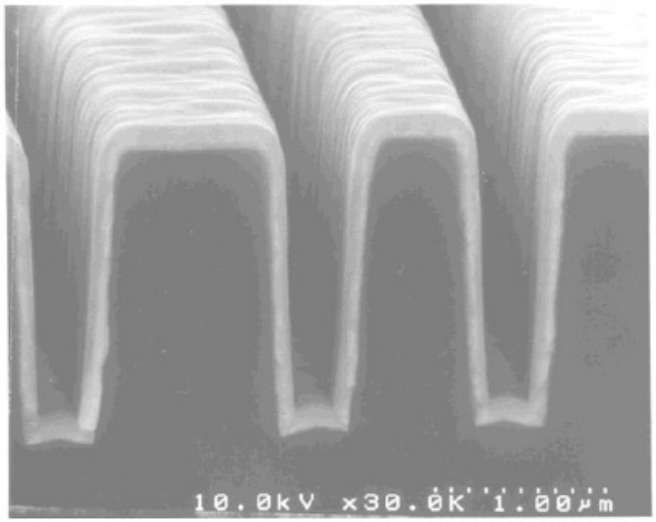
Composition of EL CoWP Films

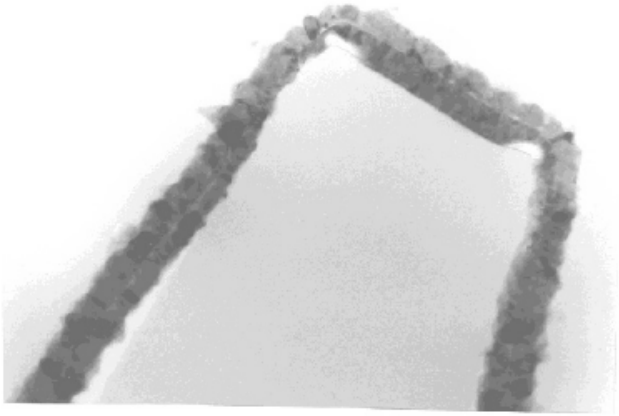
Component	*Content, atom. %*		
	Co–P	*Co–W–P(1)*	*Co–W–P(2)*
Co	94–95	92–95	85
W	–	2.5–4.5	12–13
P	5–6	2–4	2–3

Conformal EL CoWP Plating



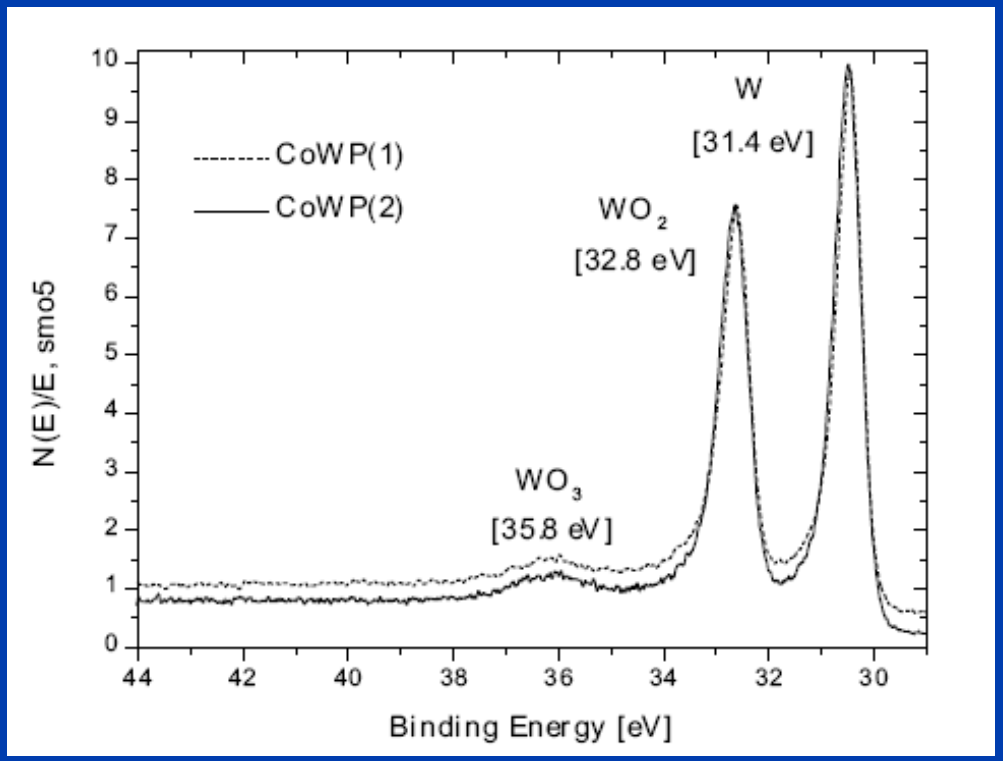
TEM cross section of the thin conformal CoWP film inside of 30–40 nm wide seam on the top of 0.4 μm wide in-laid Cu line.

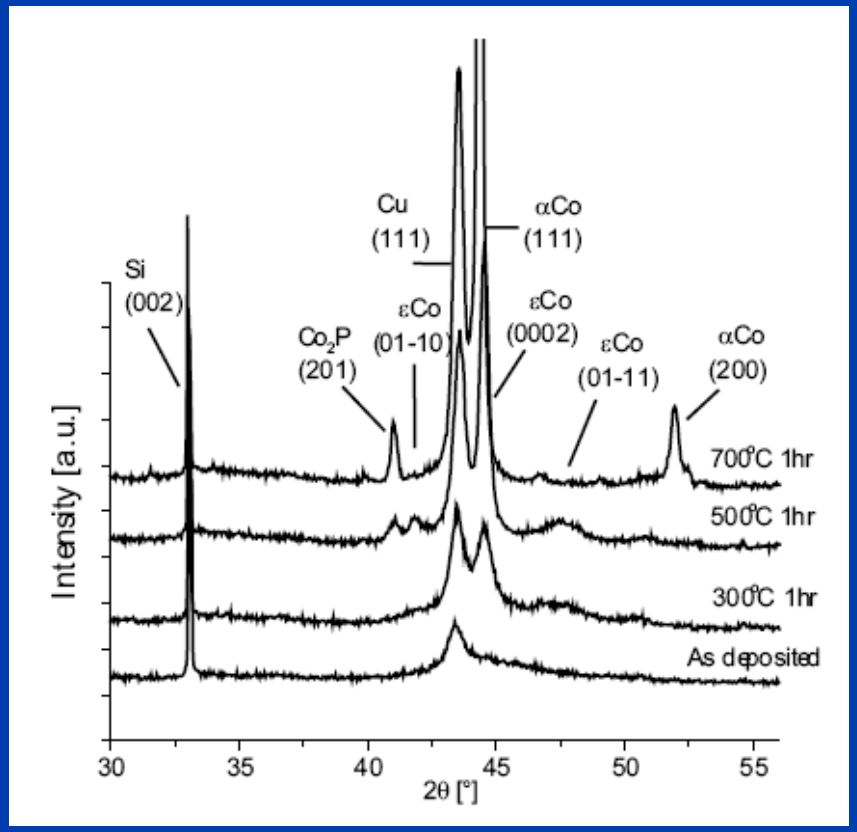




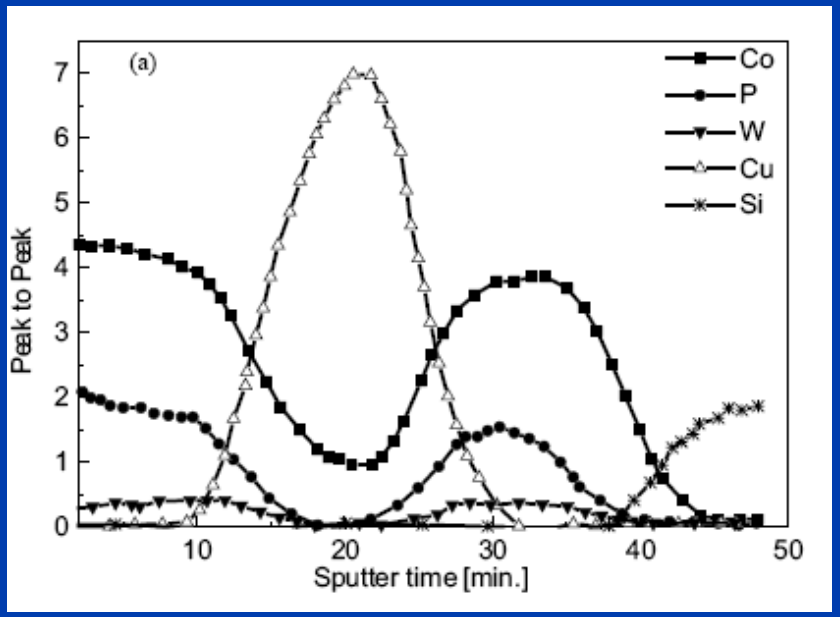
TEM cross-section of the thin electroless CoWP film on sputtered Co at the top of the trench.

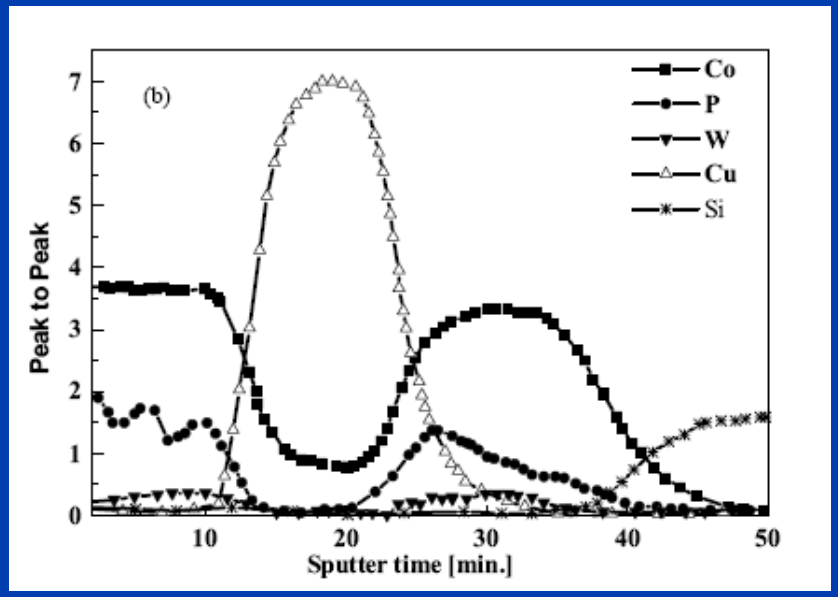
XPS and XRD of EL CoWP Films





CoWP Barrier Properties



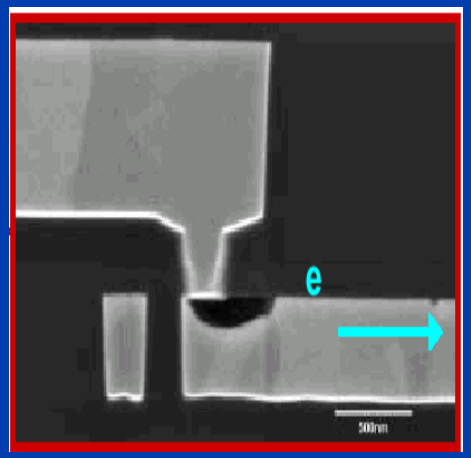


Before Anneal

After Anneal at 500C for 1h

Electromigration with EL Co Cap

- Cu is susceptible to electromigration (EM) failures under current stress. Diffusion paths of Cu:
  - Interfacial diffusion (FASTEST)
  - Grain boundary diffusion
  - Bulk diffusion



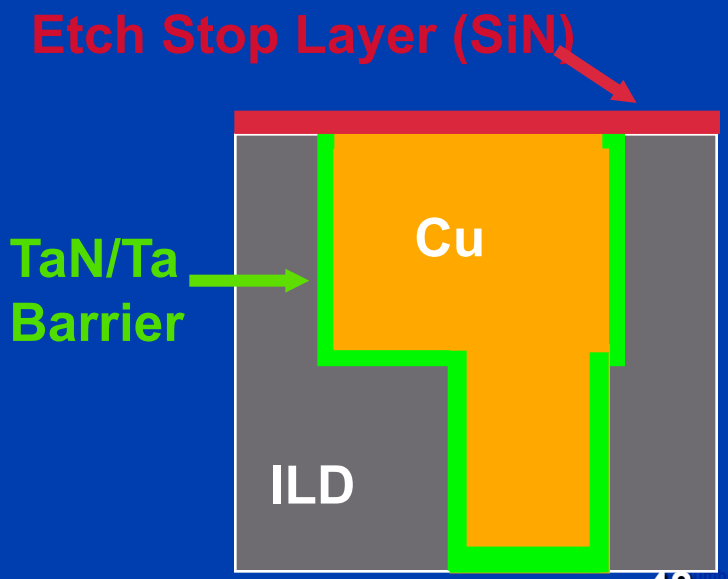
EM Failure

EL Co CAN PLUG UP THE FASTEST DIFFUSION PATHWAY (INTERFACIAL DIFFUSION)

- Etch Stop layer (SiN) protects ILD from Cu Diffusion and Cu from oxidation

→ however, the ES layer increases overall K_{eff}

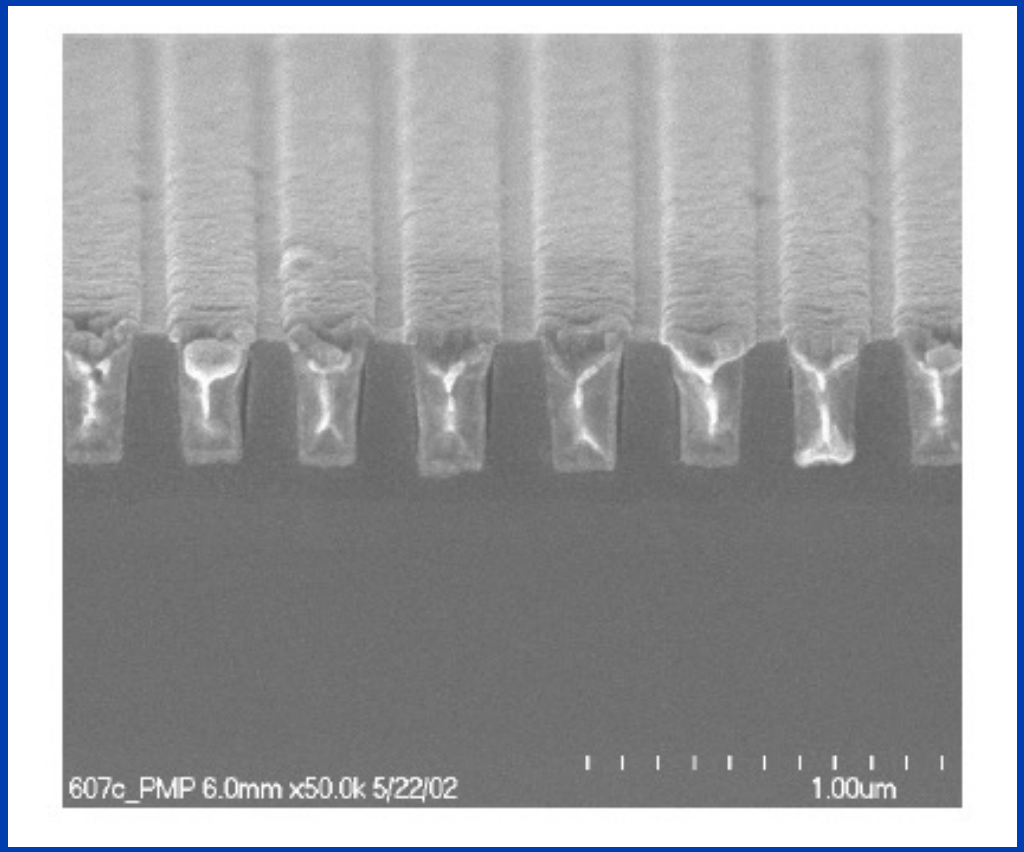
EL Co CAN BE USED IN LIEU OF SiN ES



Solution for Contact Displacement Pd Deposition on Cu lines

Components	Concentration
Pd^{2+}	0.2 g
HCl	1 ml
Glacial Acetic Acid	500 ml
HF (50:1)	250 ml
H_2O	245 ml

Selective EL CoWP Plating on Cu lines



Disadvantage of EL CoWP with Pd activation:

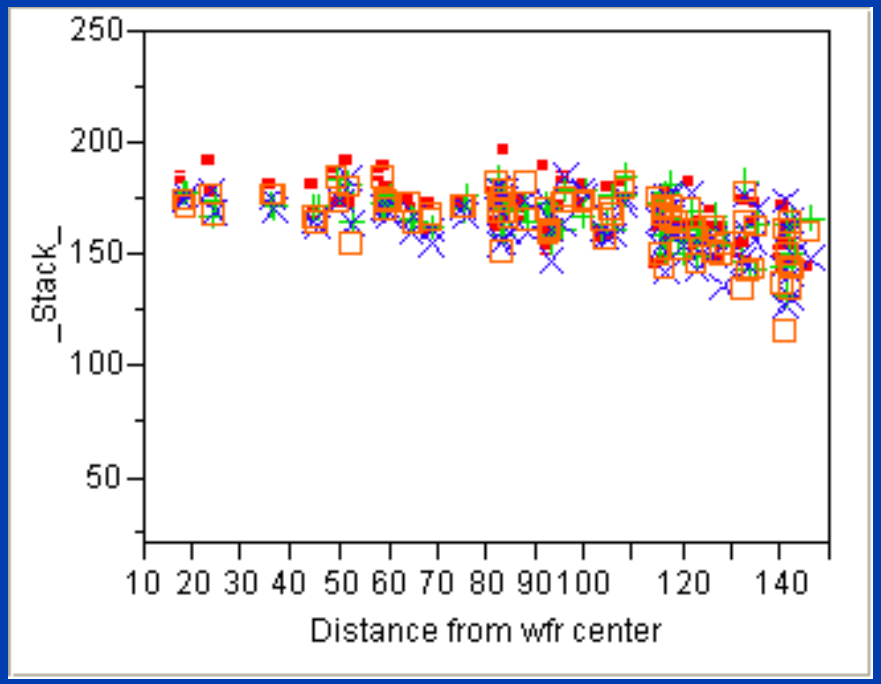
- additional activation step
- increase of Cu resistivity

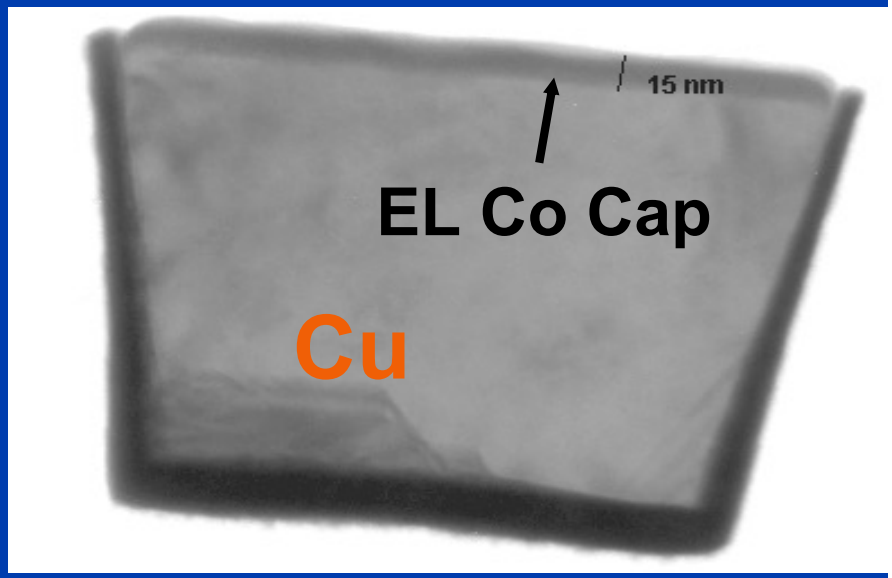
Solution for EL CoWB(P) Deposition

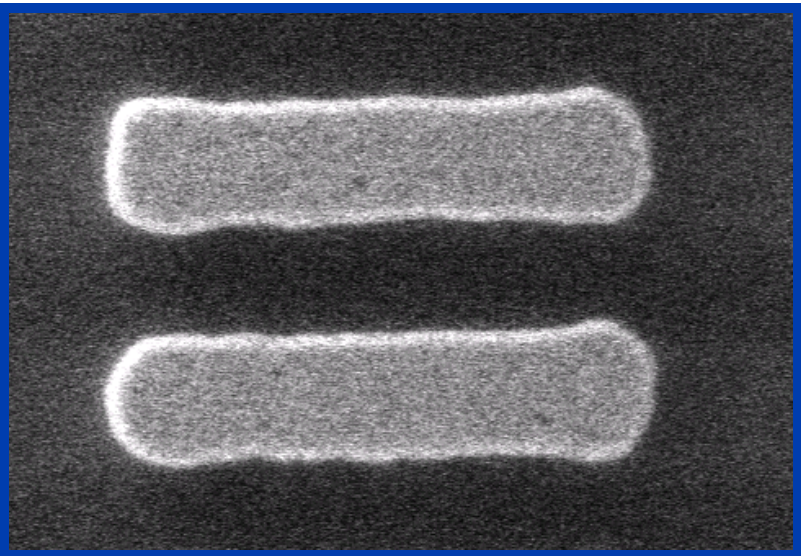
$CoSO_4$ $6H_2O$	-	30 g/l
Na_2WO_4 $2\ H_2O$	-	10 g/l
NH_4 hypophosphite	-	20 g/l
$(NH_4)_2H$ citrate	-	50 g/l

DMAB addition at 5 – 10 g/l allow direct plating on Cu

Selective EL Co EM cap

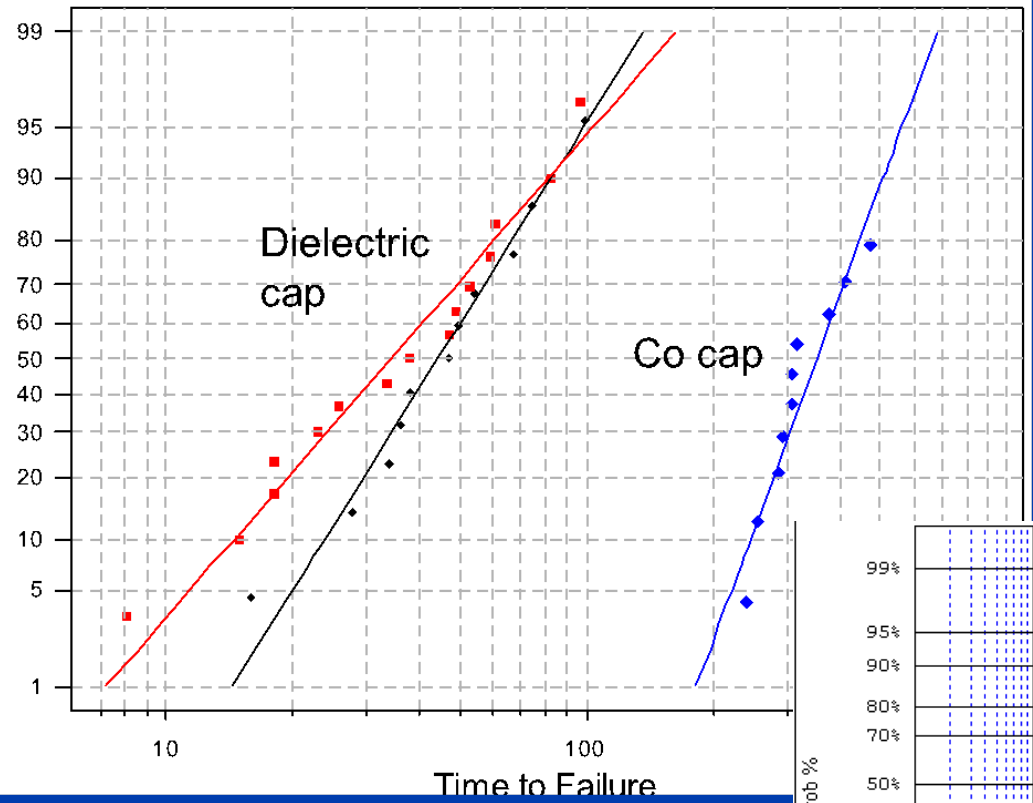




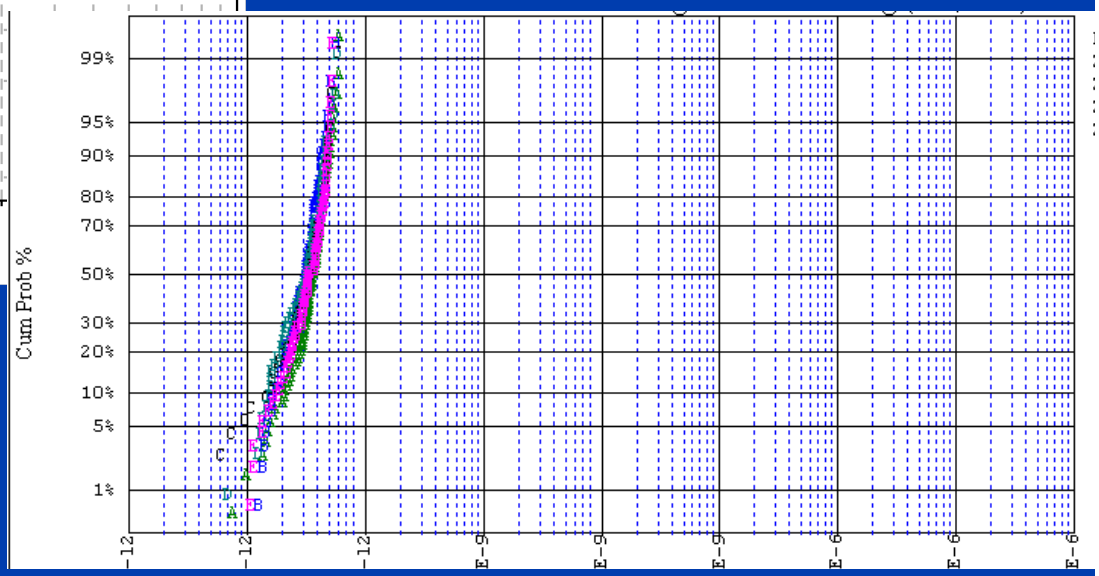


Selective, self-aligned, self-initiated and uniform EL Co cap was developed

Electromigration with EL Co

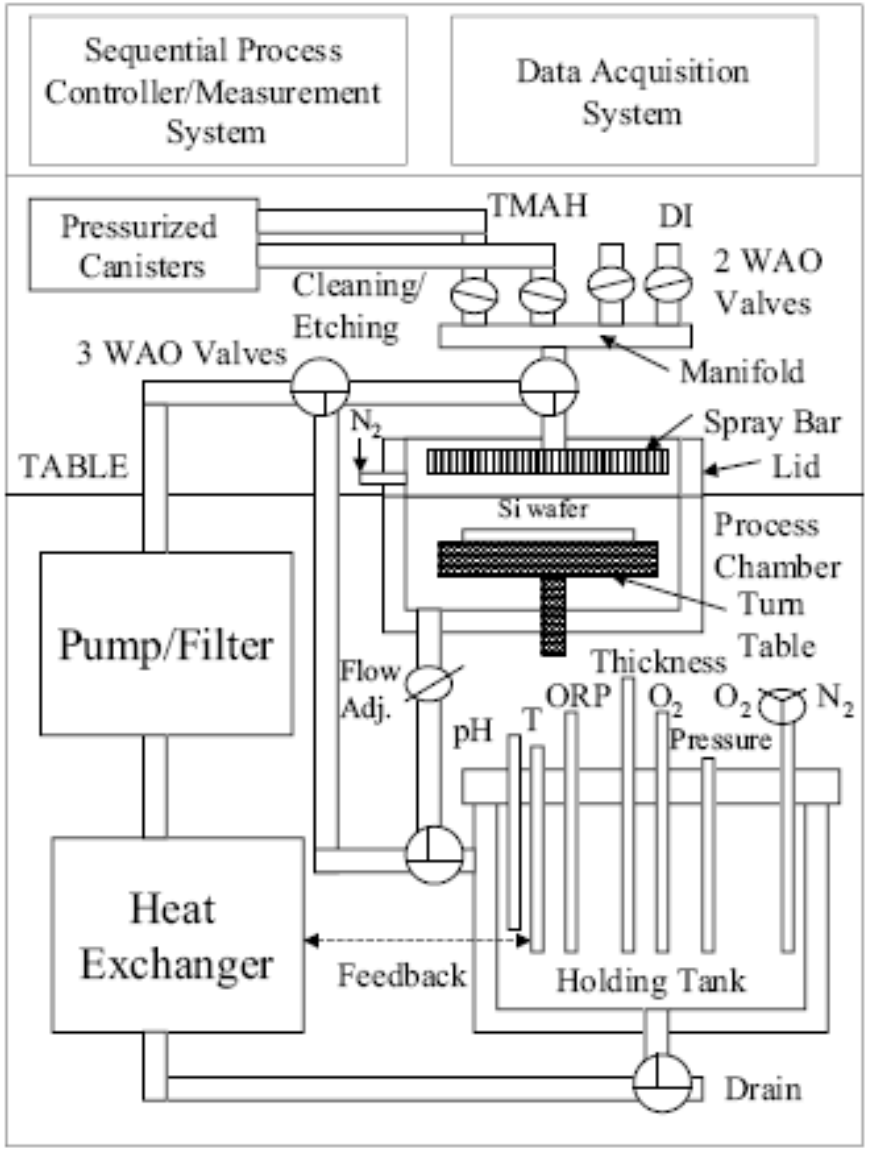


Selective, self-aligned and self-initiated EL Co cap improved Cu EM MTF by about 10x without Cu lines resistance increase



LTL leakage for EL Co cap is matched to No Co cap control

EL Cu Plating Tool Schematics



Summary

- EL Cu is catalytical process and requires activation if substrate is not catalytic for reducing agent
- EL Cu is slower process and more appealing for sub 50 nm (EP fill time is <1 sec which is difficult to control)
- EL Cu is conformal process. Novel additives or selective seed need to be used to fill sub 50 nm features
- EL requires anneal to remove H and TMAH as a pH adjuster to decrease alkaline metals in films
- EL Co is selective process and it can be used as an EM cap