Putting pieces together in the material space

Considerations for integrating Cobalt

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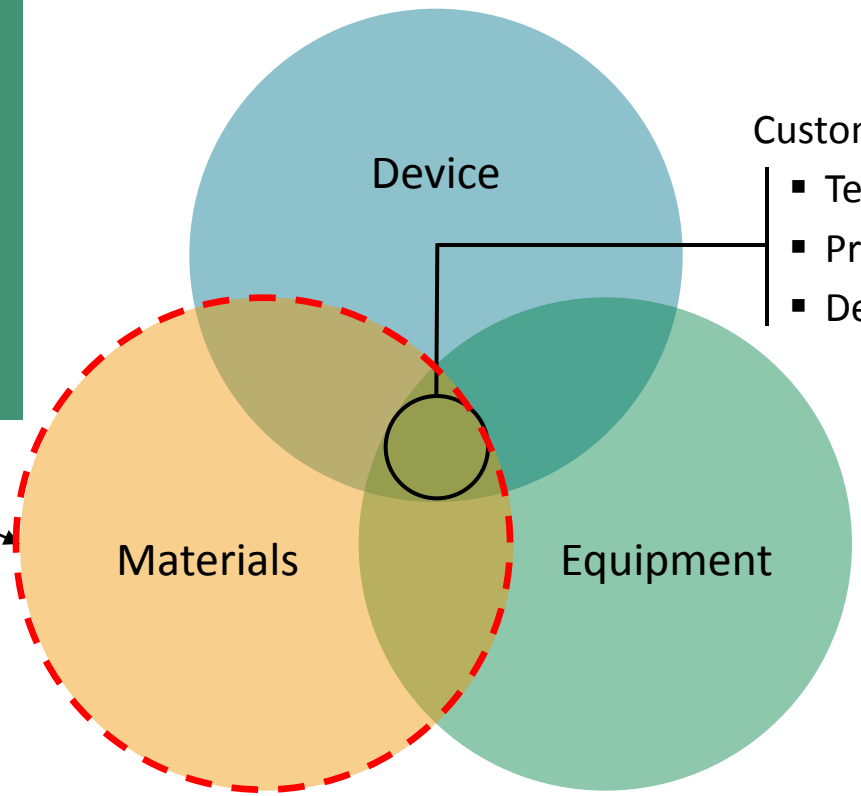
creating a material advantage

Increasing Interdependency within Semiconductor Ecosystem

Opportunity to "put the pieces together" in the materials space

- Materials, handling, sensing, and delivery components
- Enabling new paradigms



Customers Care About:

- Technology Performance
- Process Yield
- Device Cost

Significant overlap within the Semiconductor Ecosystem

- Increasing need to work together in this space
- Targeted collaborations are key to advanced node challenges

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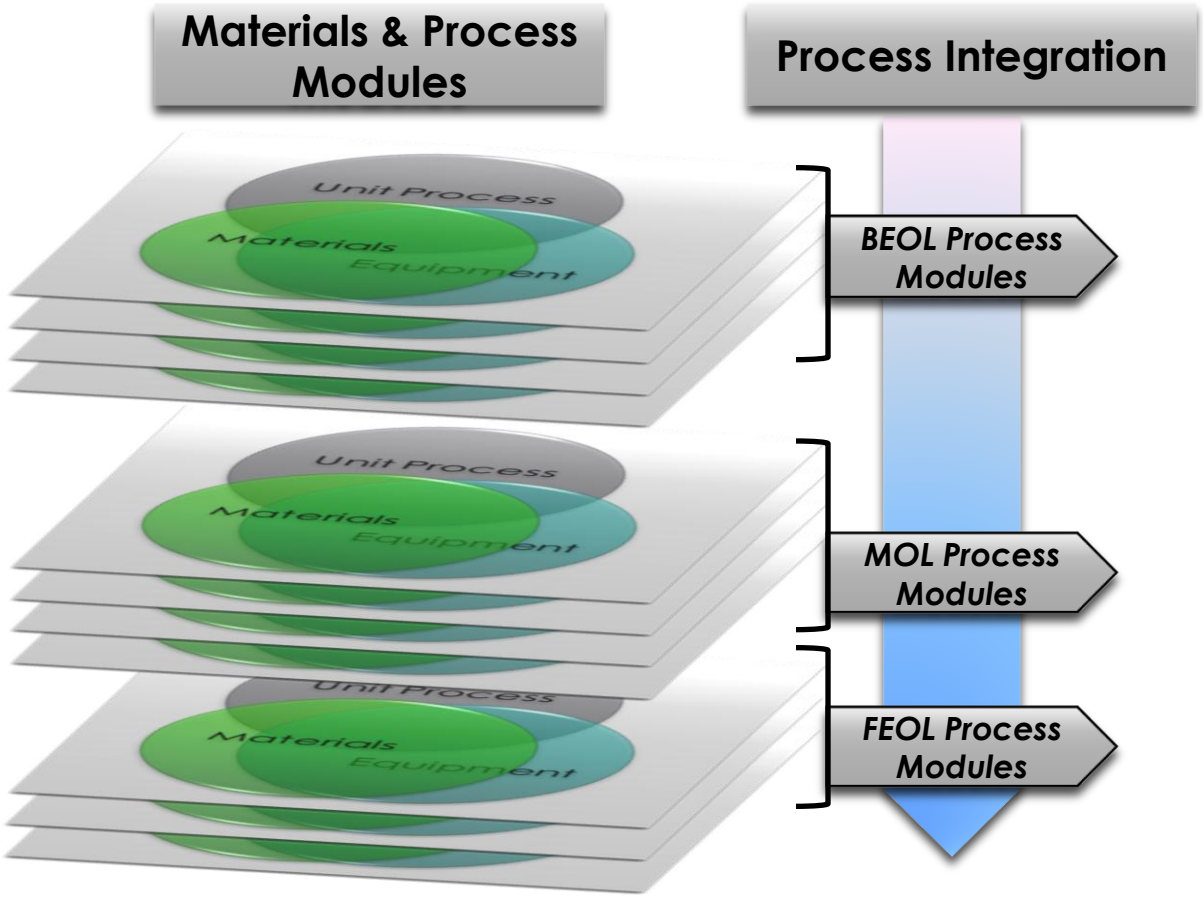
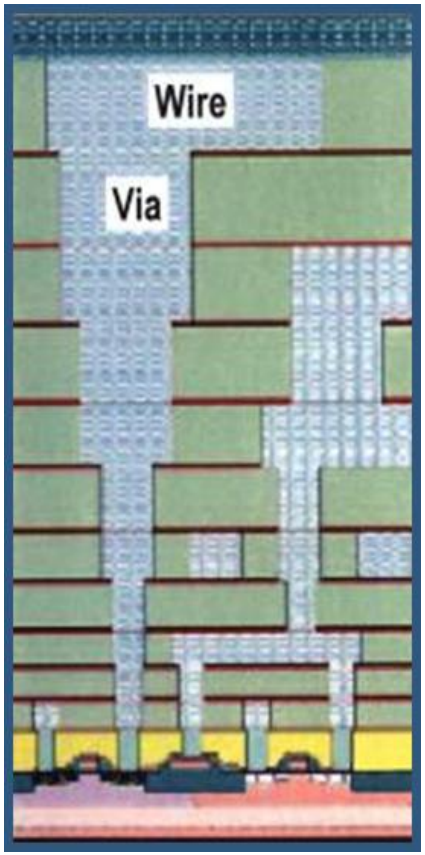
Integrated Stack: Putting Materials Together to Enable Performance





Understanding the integrated stack and material interactions enables tailored solutions that fit customer requirements

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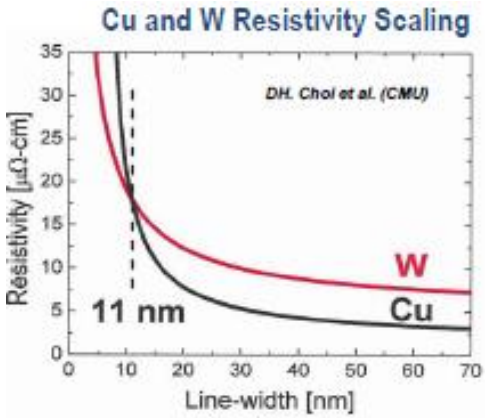
Changes in Metallization

Device Scaling causing interconnect challenges

- Line resistivity increasing due to Cu electron free mean path and film roughness
- Reliability issues due to Cu electro-migration below 20 nm
- High aspect ratio features causing yield issues

Alternative interconnect metals

- Al, Co and W are alternatives
  - display better rho vs. Cu <20 nm
- Al displays poor EM performance
- Co displays better EM performance
  - can be deposited by ALD, CVD
  - can be integrated into device?

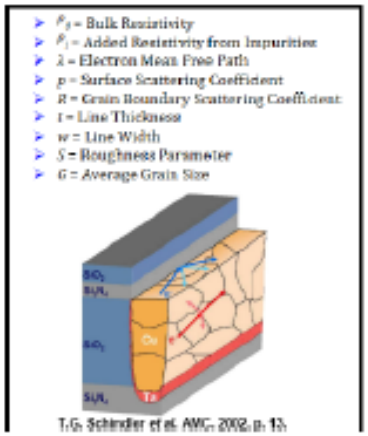


Mayadas-Shatzkes Model

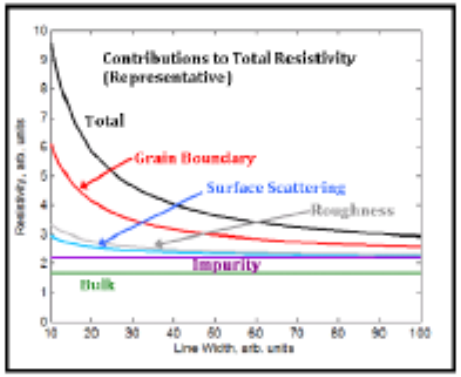
$$\rho = (\rho_0 + \rho_i)\left[1 + \frac{3}{8}(1-p)\lambda\left(\frac{1}{t}+\frac{1}{w}\right)\cdot S + \frac{3}{2}\left(\frac{R}{1-R}\right)\frac{\lambda}{G}\right]$$

Total, Bulk, Impurity, Surface, Roughness, Grain Boundary

Rossnagel & Kuan. J. Vac. Sci. Tech. B. 22 (2004) 240.



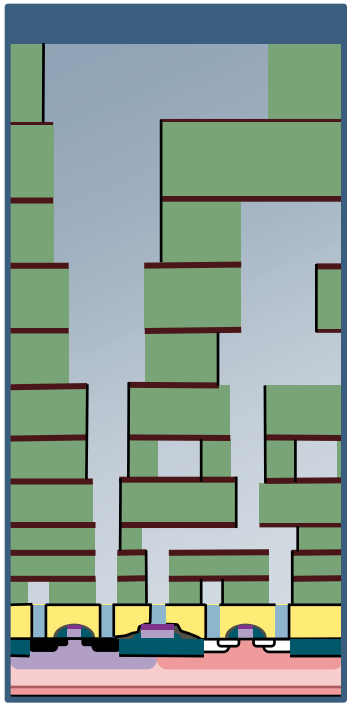
T.G. Schindler et al. AMC, 2002, p. 13.

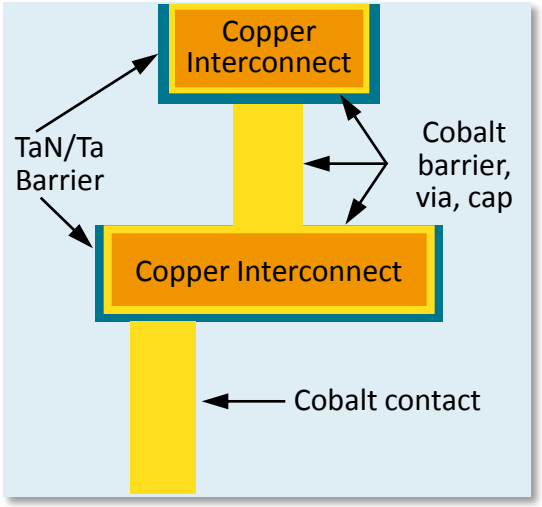


Introduction of Cobalt Drives a New Product Cycle

Copper interconnect resistivity and reliability degrades as linewidth decreases – new metallurgy needed

IC Cross Section





Broad Process Implications
ALD/CVD precursors
Precursor delivery systems
Advanced gas filters
Post CMP clean formulations
Post Etch Clean formulations
Cu and Co plating formulations
Advanced filtration
Advanced fluid handling

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Process Implications of Inflection Point Innovations

Cobalt

Lithography	Etch	Deposition	Clean	CMP	Implant	Fab Facility
Advanced Photoresist Packaging	Formulated Cleans	Copper Plating	Formulated Cleans	Formulated Cleans	Safe Gas Delivery Systems	Advanced FOUPs
Filtration and Dispense	Gas Filters and Diffusers	CVD and ALD Deposition Materials	Filtration	Filtration	Electrostatic Chucks	AMC Filtration
Gas/Liquid Purification	Gas Purification	Gas Filtration and Purification	Fluid Handling	CMP Cleaning Brushes	Gas Purification	Bulk Chemical Delivery
Reticle Pods	Specialty Materials	Specialty Materials	Containers	Pad Conditioners	Specialty Materials	Wafer Shippers

Entegris solutions enable technology inflection points in semiconductor processes

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Cobalt Deposition Overview

- Cobalt CVD has been demonstrated with:
  - Cp_2Co
  - $CpCo(CO)_2$
  - $Co(CO)_3NO$
  - $Co_2(CO)_8$
  - dicobalt hexacarbonyl tert-butylacetylene: "**CCTBA**" a Co(0) compound
- Very few examples of Cobalt ALD
  - Organometallic reagents and reducing agents (H, Hydrazine, Ammonia)
  - Unclear whether these are true ALD or just pulsed CVD
  - Customer experience has been that it is difficult to get C, O & N free films with published precursors

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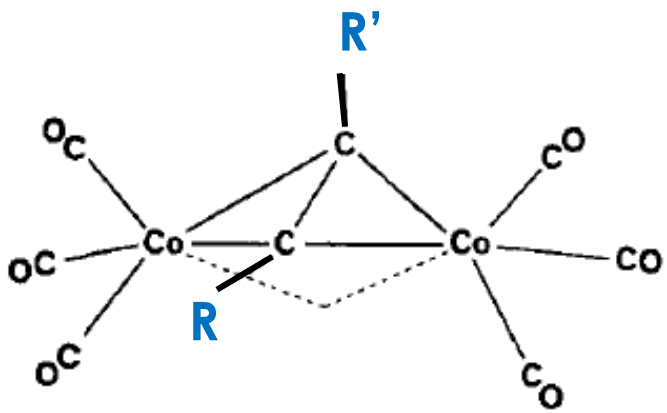
DiCobalt HexaCarbonyl-η^2-μ^2-acetylenes



Ability to enhance Co complexes

- Impact of terminal 'H' towards stability?
- Structure - stability relationship?
- Electronic effects towards stability?

Cobalt Precursor - Abbreviation	R'	R	synthesized	m.p.	b.p.	STA T_{50}	STA % NVR	Film Growth	NMR	Conducting Films	Deposition Rate
CCTBA	H	t-Butyl	yes	13		138.4	6.8	yes	yes	yes	1
CCTMSA	H	TMSi	yes	31		138.3	5.8	yes	yes	yes	0.95
CCBTMSA	TMSi	TMSi	yes	81		175.6	1.8	yes	yes	yes	<0.75
CCTMSP	Me	TMSi	yes	-		149.6	1.98	yes	yes	yes	0.90
CCTBP	Me	t-Butyl	yes	-		151.4	1.52	yes	yes	yes	1.0

- Terminal 'H' on alkyne reduces thermal stability
- Di-substituted alkynes enhance stability

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Selectivity Testing

30 Torr, 50 μmole/min, 0.5 lpm H_2

Temperature (°C)	Substrate	Position	Deposition Rate (A/min)
290	SiO_2	C	7.6
	Cu	BL	15.4
250	SiO_2	C	0.24
	Cu	CL	8.1
200	ULK	C	0
		L	0
	Cu	C	11.7
		L	11.3
150	ULK	CB	0
		L	0
	Cu	C	3.6
		B	4.9

Excellent selectivity at ≤ 200 °C

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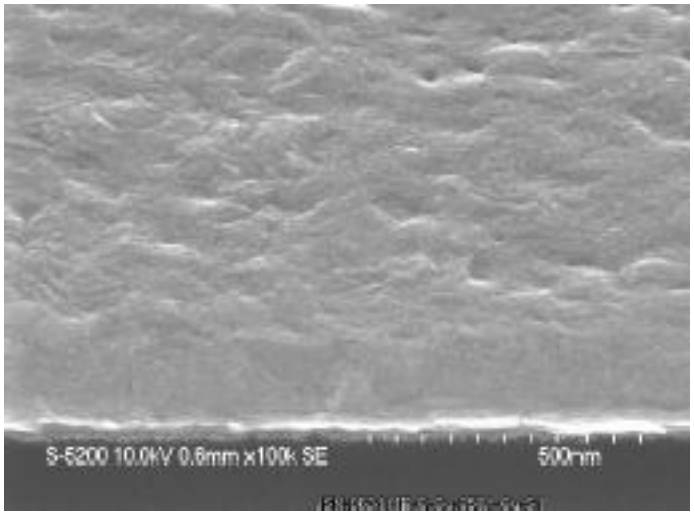
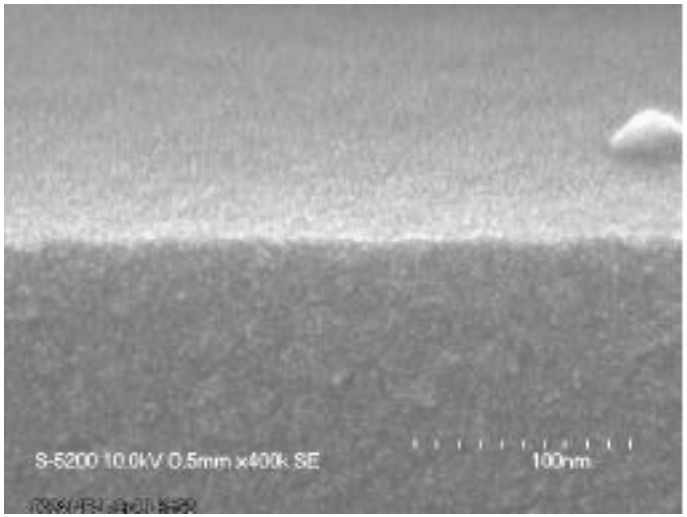
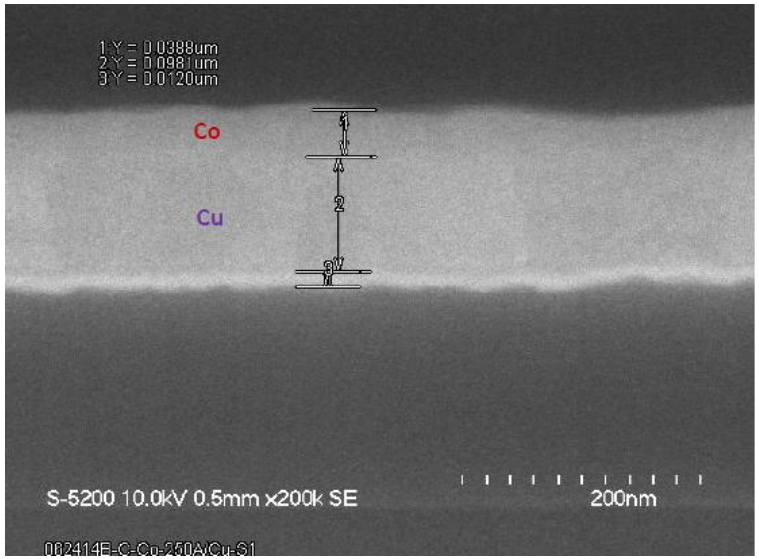
Excellent Selectivity: Cu *vs* ULK



350 A Co on Cu (200 °C)



Negligible Co on ULK



	C	N	O	F	Si	Co
ULK, 061414B-L, OACo; TOA = 25	24.7	0.2	48.1	0.6	26.3	0.1
ULK, 061414B-L, OACo; TOA = 45	24.0	0.1	49.1	0.6	26.1	0.1
ULK, 061414B-L, OACo; TOA = 75	23.9	0.2	48.8	0.7	26.2	0.2

Confirmed by angle-resolved XPS

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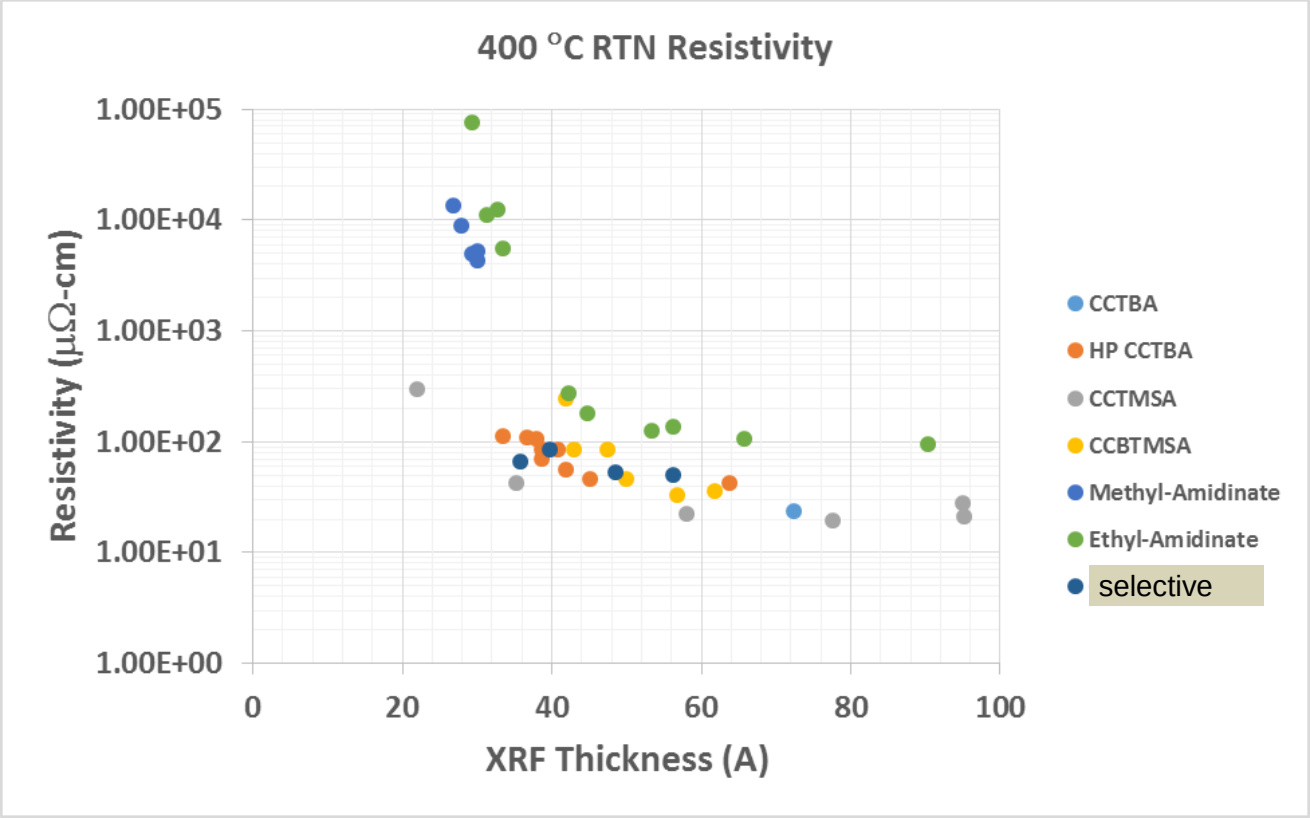
Film Resistivity – Rapid Thermal Anneal at 400°C



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Selective Co Growth on Cu

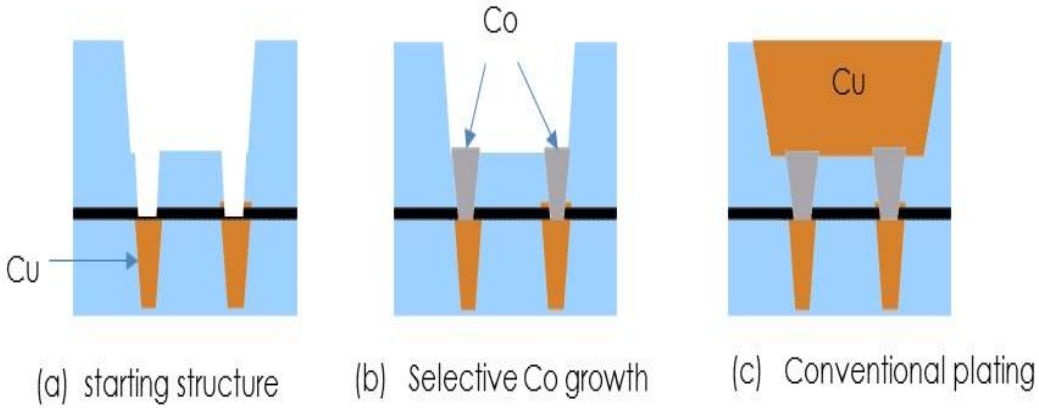
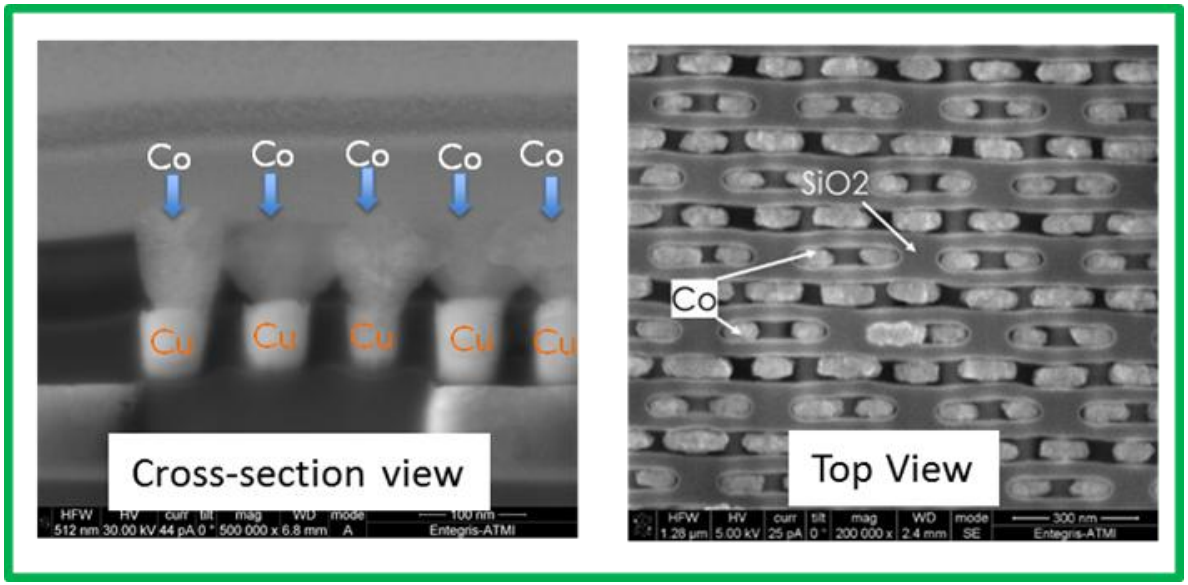
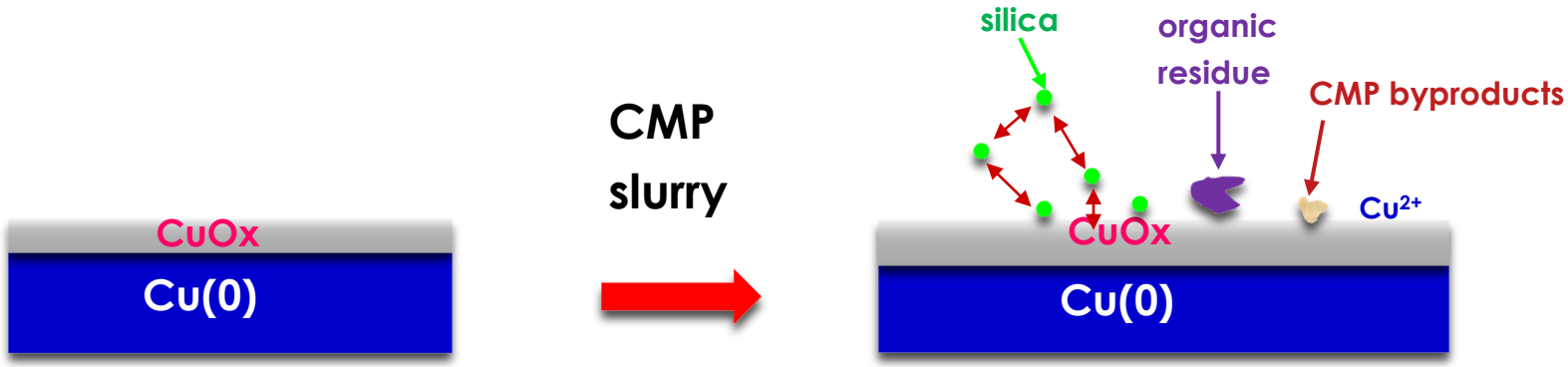


Fig. 2 Co selective growth integration



Traditional pCMP clean for copper



contaminated wafer

- Abrasive particles (e.g. silica)
- RR Promoters (aminoacids)
- Corrosion inhibitors (BTA, SHA)
- Oxidizers
- CMP pad and brush debris

Particles adhesion mechanisms

- **Physisorption** (van der Waals attraction – increases with PS)
- **Electrostatic** attraction or repulsion (zeta potential)
- **Chemisorption** (chemical reaction particle-surface, e.g ceria/TEOS)
- **Capillary condensation**

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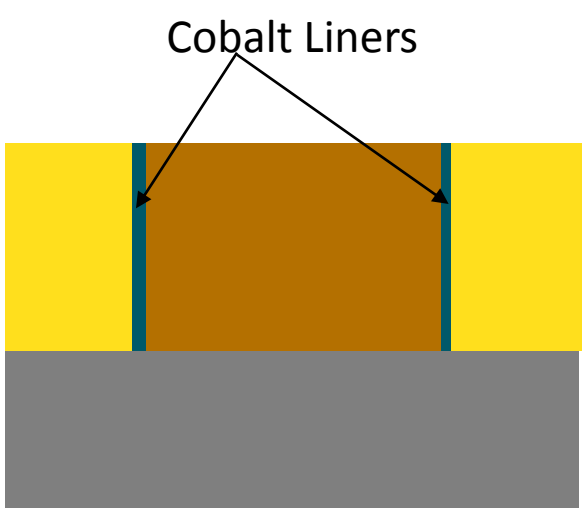
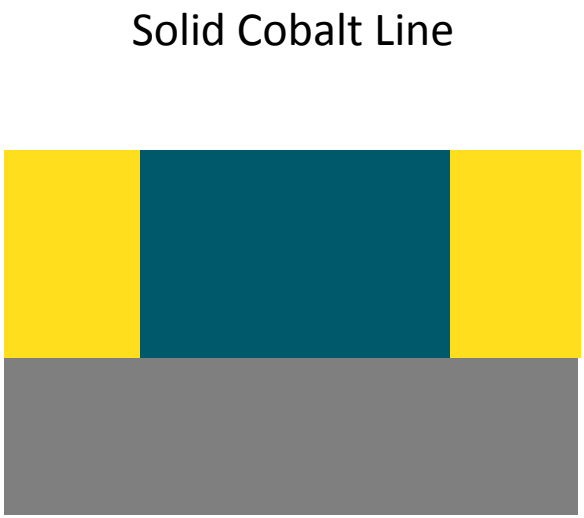
Changes due to Cobalt

- Two Type of potential post polish Cobalt Structures





The Cleaning will be very different for these two structures

- Reduce the etch of Cobalt and the cobalt ions in the cleaning solution
- Lower Galvanic effects between the copper and cobalt

- Reduce the cobalt ions in the cleaning solution during cleaning
- Controlled etch to clean the surface.

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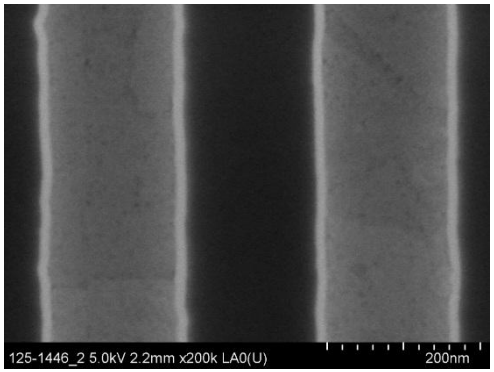
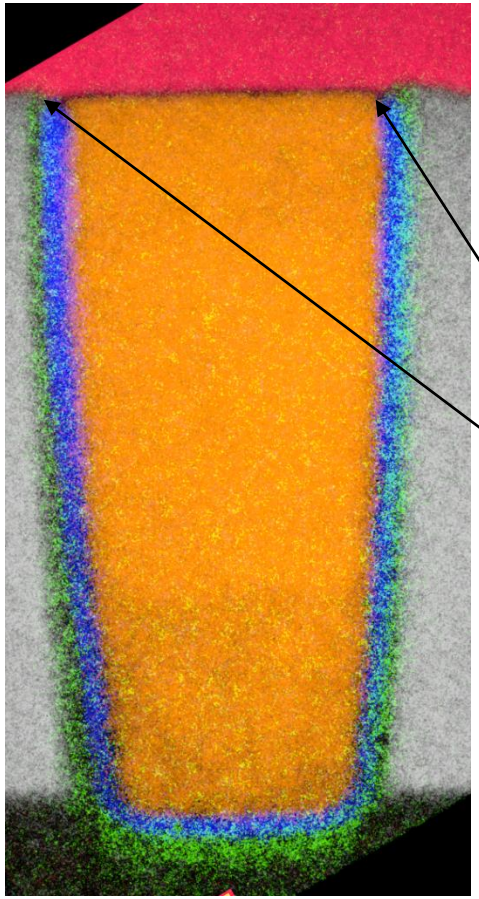
NT 3300 cleaned copper lines with cobalt liner
TEM – EDX Element Map (overlay)

Orange – Cu
Blue – Co
Green – Ta
Red – C



Cu Lines with Co/Ta Barriers

Top Down SEM



Co liner touches Cu Barrier in this example with no gap between them.

This example needs great Cu cleaning and low Co Etching.

Key Requirements of the pCMP Cleaner

- No Etching of the Co Liner
- Good Cleaning of the Copper lines
- Low Cu/Co Galvanic etching

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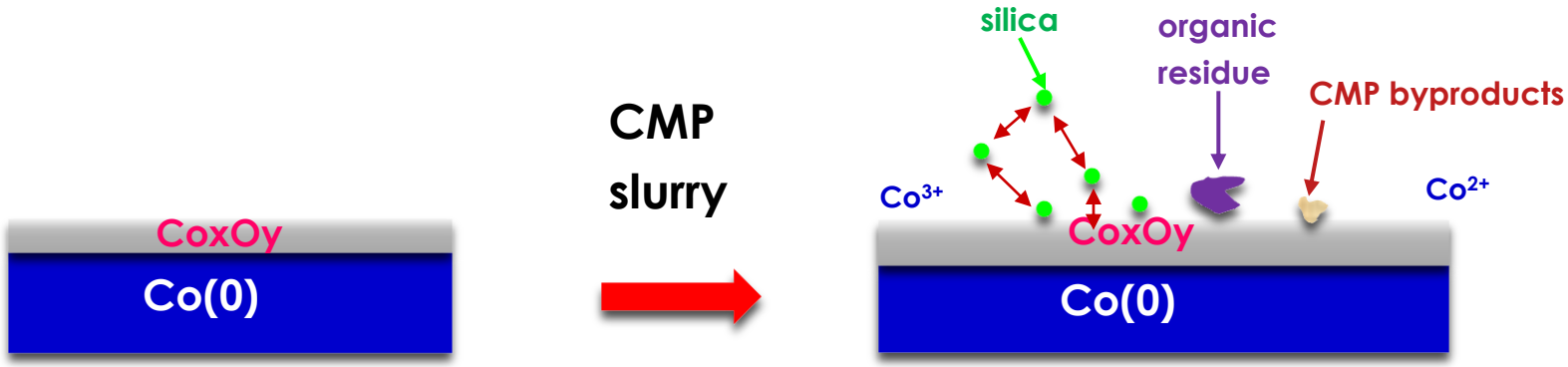
Advanced pCMP clean for Solid Co Lines



- Abrasive particles (e.g. silica)
- RR Promoters (aminoacids)
- Corrosion inhibitors (BTA, SHA)
- Oxidizers
- CMP pad and brush debris

contaminated wafer

The ratio of the Co^{3+} to Co^{2+} ions is very important

Particles adhesion mechanisms

- **Physisorption** (van der Waals attraction – increases with PS)
- **Electrostatic** attraction or repulsion (zeta potential)
- **Chemisorption** (chemical reaction particle-surface, e.g ceria/TEOS)
- **Capillary condensation**

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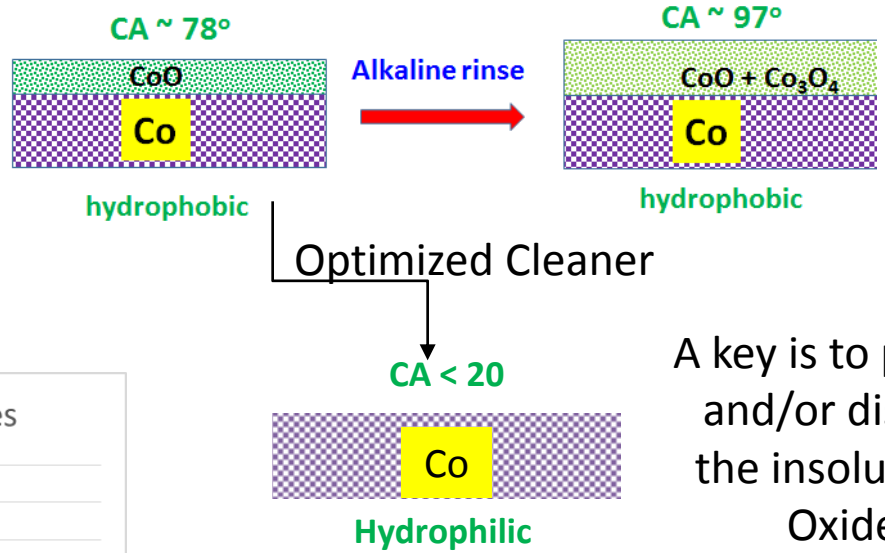
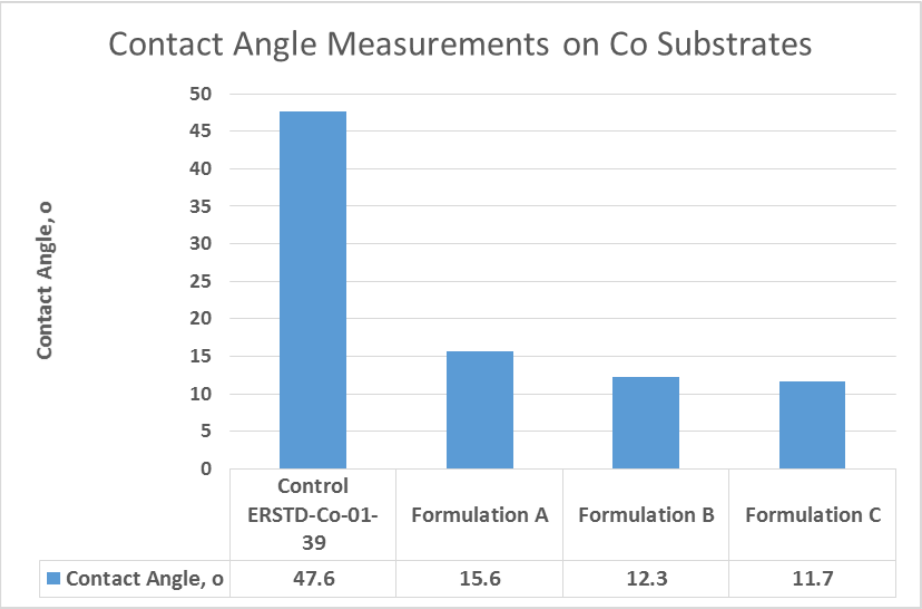
Cobalt pCMP Cleaner of Co solid lines

After pCMP cleaning films need to be clean with no to thin oxide layers and no Co_3O_4; plus, be hydrophilic.



A key is to prevent and/or dissolve the insoluble Co Oxides



Small Contact Angle (CA) indicates good clean surfaces and hydrophilic.

Formulation A, B & C are developmental cleaners that have been used to clean Cobalt films. This same technology can be applied to pCMP.

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SUMMARY

- Integration of Cobalt requires new understanding of ….
  - Stability /selectivity of Co precursor
  - Surface preparation prior to deposition
  - Co compatible post CMP & post etch cleans

- Mechanism of deposition & residual impurities in cobalt film influence effectiveness of subsequent cleaning steps

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Deposition Conditions

- 150 - 290 °C deposition temperatures
- 50 -150 μmole/min delivery
- 10 - 30 Torr pressures
- 110 - 130 °C vaporizer temperature
- 90 °C chamber temperature
- 0.5 – 3.0 lpm H_2 co-reactant
- 5 - 30 minutes
- Substrates: ULK, PVD Cu & TiN

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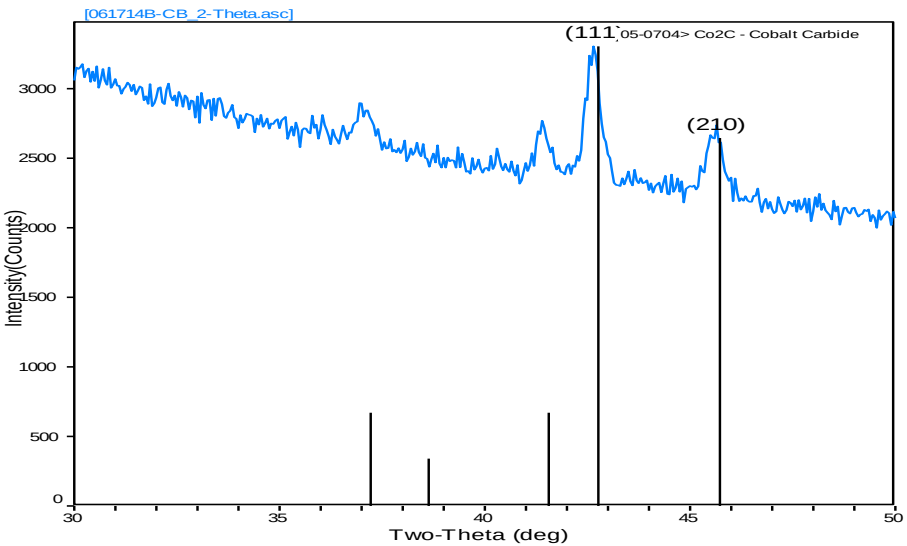
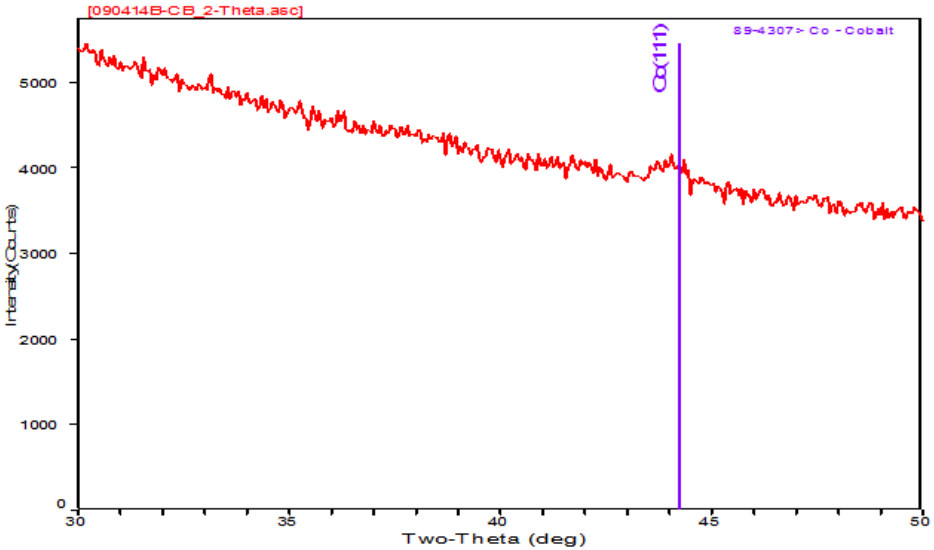
Film Composition Varies with Substrate and Deposition Temperature





- Film deposited on SiO_2 at 250 °C
- XRD shows orthorhombic Co_2C peaks

- 120 A Co deposited on Cu at 150 °C
- XRD now shows Co (111) peak

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