Co & Ru Precursors Chemistry for Advanced Metallization. Challenges & Opportunities

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Outlines

1. Preliminary remarks on new ALD/CVD precursors development
2. Insights on Co precursors chemistry
3. Insights on Ru precursors chemistry & selective processes

The background problem / opportunity

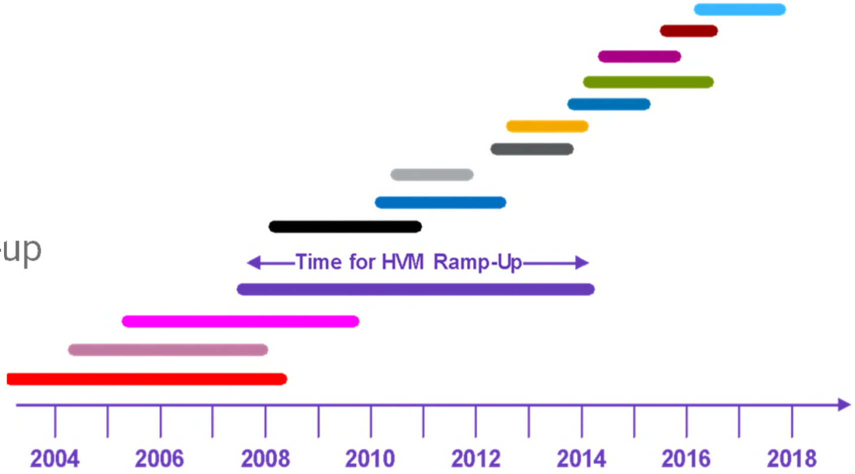
- Many new ALD/CVD chemicals introduced in semi industry have no applications in other industries

- Hence
  - No established supply chain
  - No metrology knowledge available
  - Little to no information on safety and regulatory aspects
  - Uncertainty about adoption, intense R&D effort w/ limited success rate
  - Uncertainty about lifecycle - is it a one node material?
    - Worst case, is it a single customer, single node material?

The birth of a new molecule – Time to Market

- Time to market **shrunk by ~50%** in the last 15 years from 4-6 to 2-3 years.

- Productization includes multiple steps
  - « High energy » synthesis reactions scale-up
  - Metrology development
  - EHS, physical & chemical properties
  - Regulatory management
  - QA/QC, SPC implementation



Source: Air Liquide Internal Data

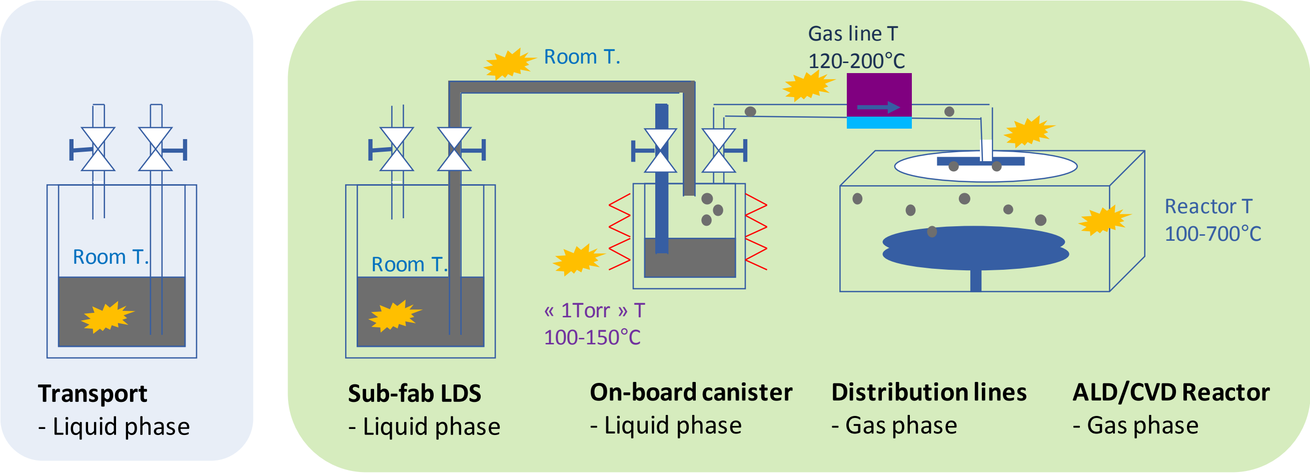
→ intensification of productization and concentration of 1st move players
Upfront investment is required to minimize late learnings

The precursor design conflicts

Process	Facilitization	Quality/Procurement
Extreme T budget xLT for BEOL metals	**Stable**	**Cost efficient**
Extreme geometry <10nm CD structures, HAR>10	**Liquid, volatile**	**Scalability « within 6 months » w/o iterations**
High deposition rate	**Not toxic**	**Metrology developed**
Composition tuning	**Not pyrophoric**	**No variability from Day 1**
	Not water-reactive	

Low stability high reactivity precursors are often required for extra Low T processes
Strong impact on quality, metrology, supply chain → **strong collaboration need**

From lab to wafer: the temperature journey



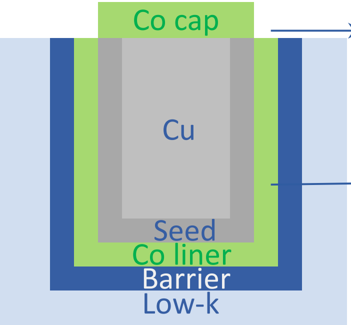
Transport	Sub-fab LDS	On-board canister	Distribution lines	ALD/CVD Reactor
20-50°C	**Room T**	**50-150°C**	**120-200°C**	**100-700°C**
1-3 months	**1-3 months**	**1 month**	**1-10s**	**0.1-10s**

Less stable precursors create challenges on the full delivery chain
→ Illustrations on Co & Ru chemistries for BEOL metallization

Insights on Co CVD Precursors Chemistry

Cobalt applications and requirements

BEOL Cu metallization: <22nm →



Co capping layer
✓ Prevents Cu EM

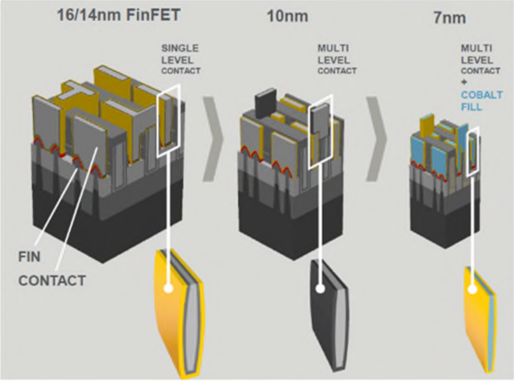
Co liner
✓ Improve wettability
✓ Prevents voids

Source: Applied Materials Inc.
http://www.appliedmaterials.com/products/endura-volta-cvd-cobalt

Challenges for <10nm integration

- Conformality (low **stability** precursors)
- Adhesion becomes more challenging
- Selectivity

MOL contact fill: <10nm →



Source: Applied Materials Inc.

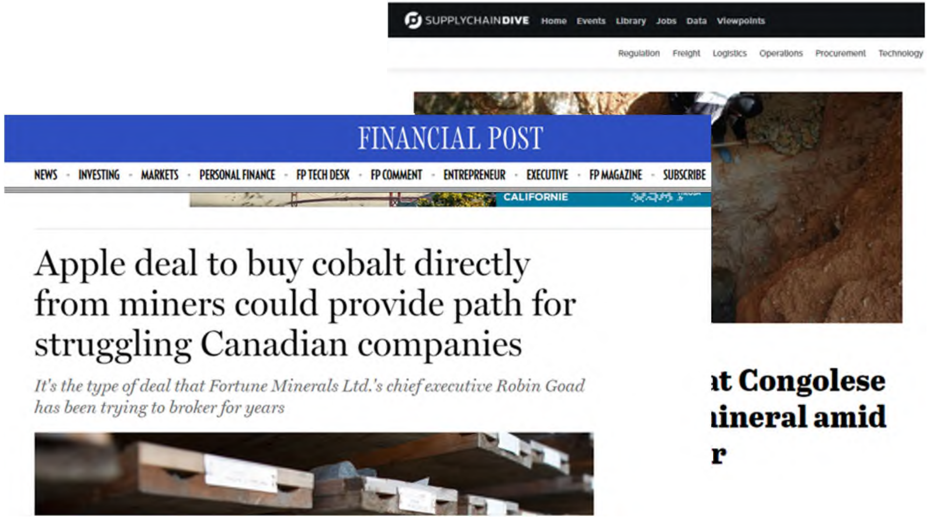
Challenges

- Conformality, void-free deposition
- Contact resistance

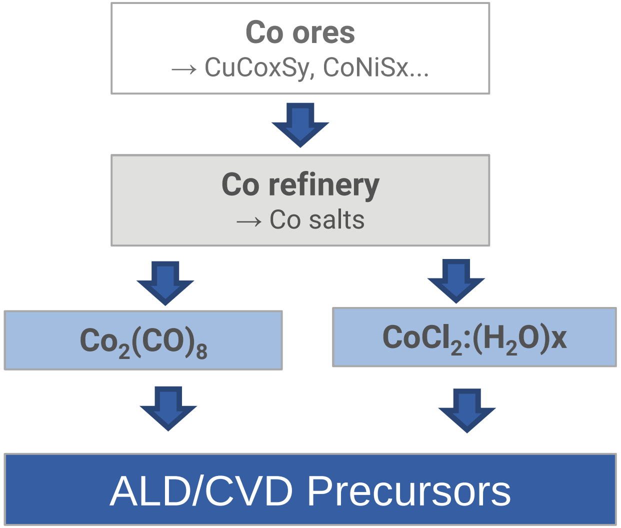
Cobalt - from mine to precursor

Cobalt mining

- 120,000TPY production, usually a Ni, Cu by-product
- DRC (50%), CN, CA, US, RU….

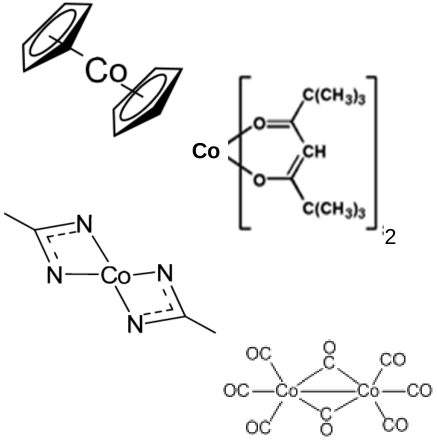


Cobalt supply chain



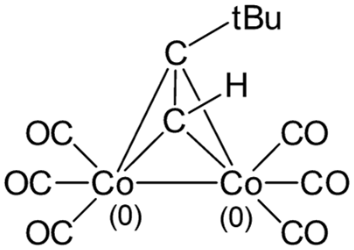
Co precursors families options

	Physical state	Volatility	Stability	Co-metal access
Cyclopentatienyls				
β-diketonates				
Amidinates				
Carbonyl				
Carbonyl derivatives				



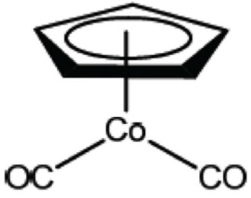
Industry examples: CCTBA and CODCP

CCTBA



- Volatile liquid
- Co metal LT-CVD
- High Growth-rate (2 Co)
- Non selective
- No ALD window
- Limited stability

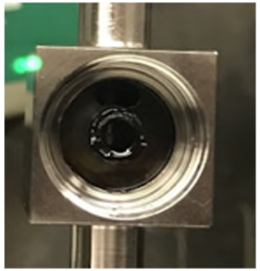
$CpCo(CO)_2$

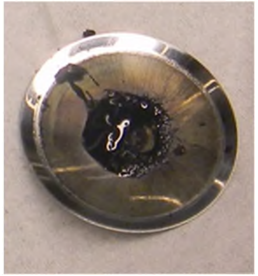


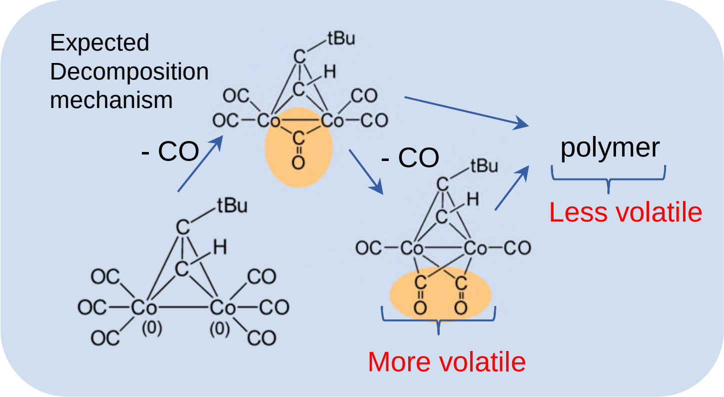
- Volatile liquid
- Co metal **PE**ALD
- Selective → capping
- Good thermal stability

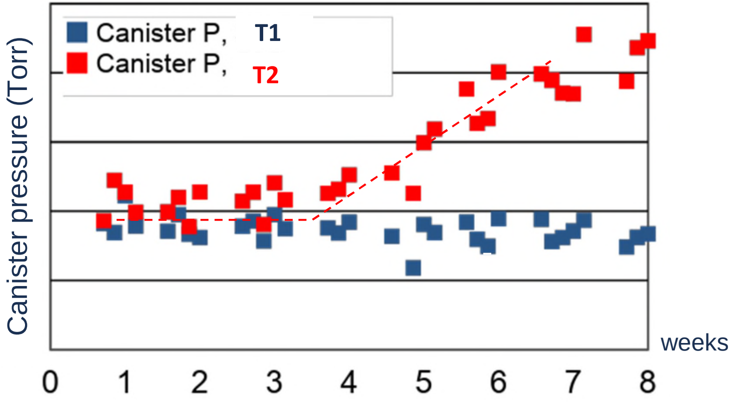
CCTBA – Challenges

- Excellent T-CVD process performance, but….:
- In-ampoule decomposition during utilization
  - Formation of low volatile polymers
  - …. leads to in-wafer particle contamination
  - …. decreases ampoule utilization efficiency



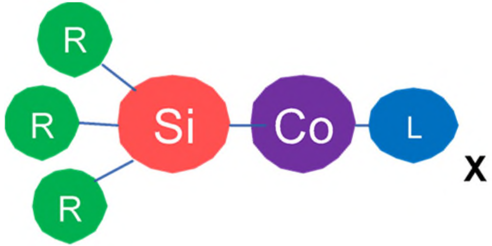




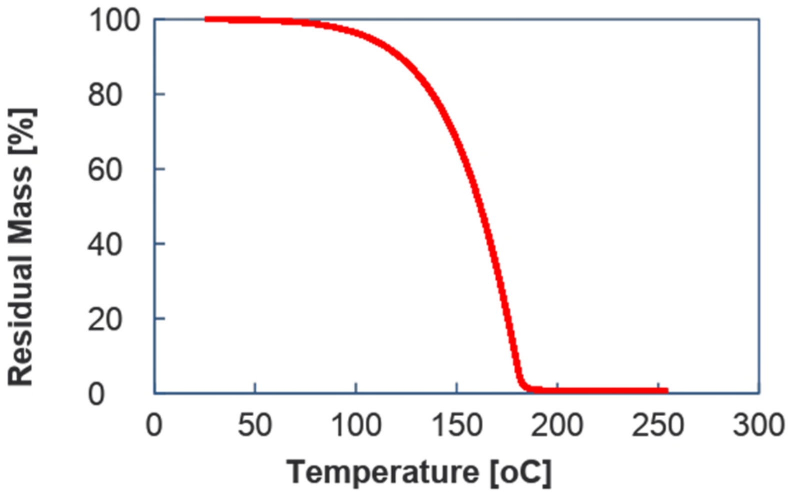


The new chemical approach – CoSine™

- Principle: thermally stable yet highly reactive bond

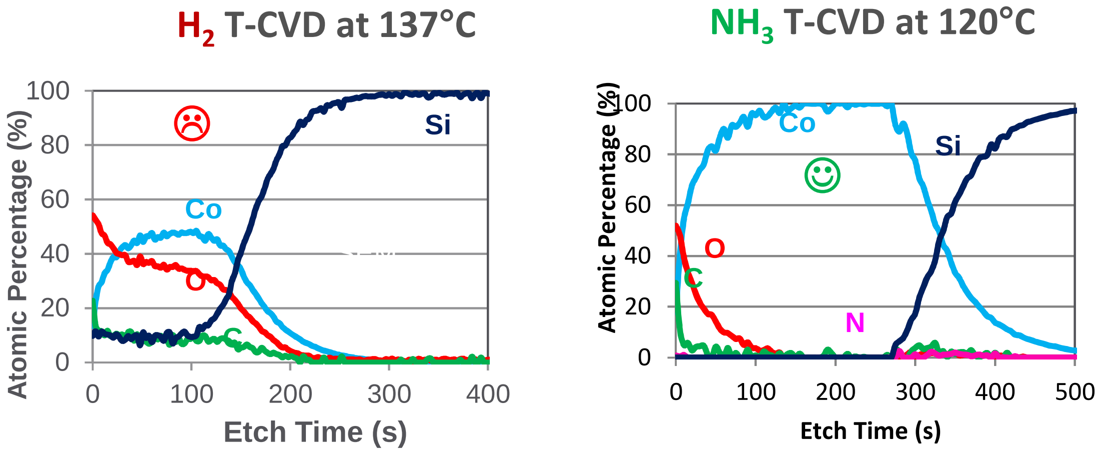


  - Contains a **Co-Si functionality**
  - Co-Si bond strength tuned by R groups
  - Liquid, melting point -9°C
  - Volatile, 1Torr @ 57°C
  - Thermally stable



Co-reactant selection

- NH_3 is require to achieve clean, Si free, film

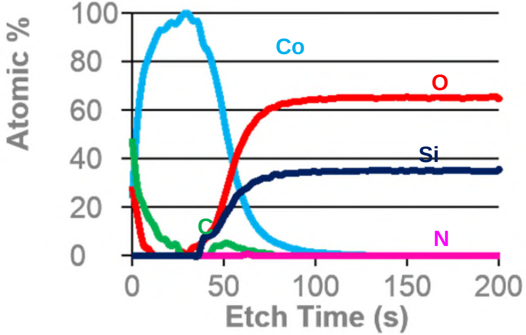


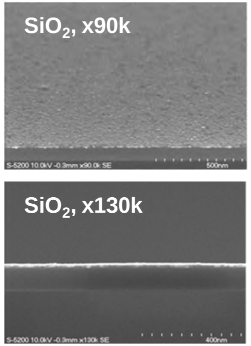
NH_3 is optimum co-reactant / suggest to release Si as NH_2-SiR_3
Clean reaction: **N and Si below XPS detection limit , C ~1%**

Co Low Temperature CVD from Cosine™

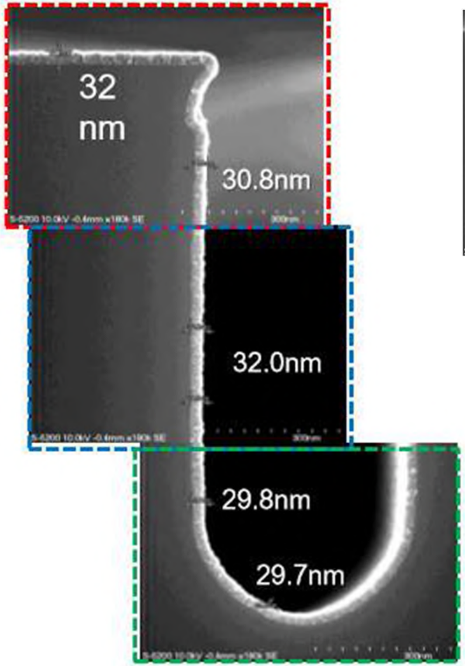
o T-CVD w/ NH_3 at 120°C

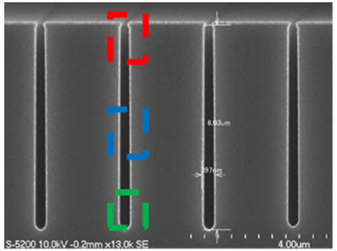
Post-deposition anneal: 30min, H_2, 400°C





Substrate	Thickness (nm)	Growth Rate (nm/min)	Resistance (Ω)	Resistivity (µΩ·cm)
SiO2	15	**0.76**	4.2	**29**





20:1 structures
CD: 350nm

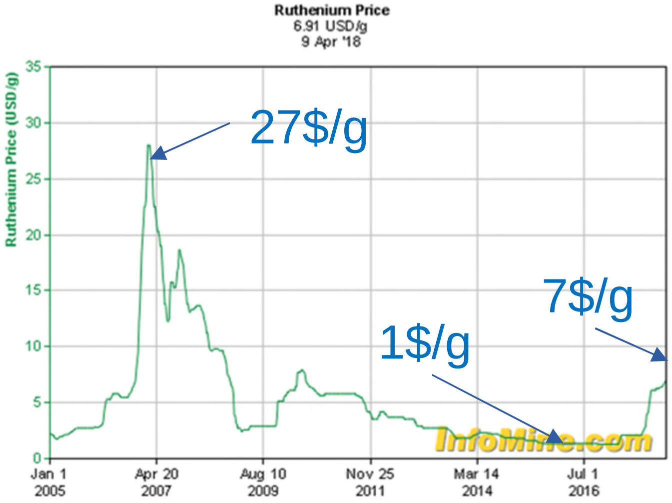
Step coverage
Cosine: 93%
CCTBA ref: 56%

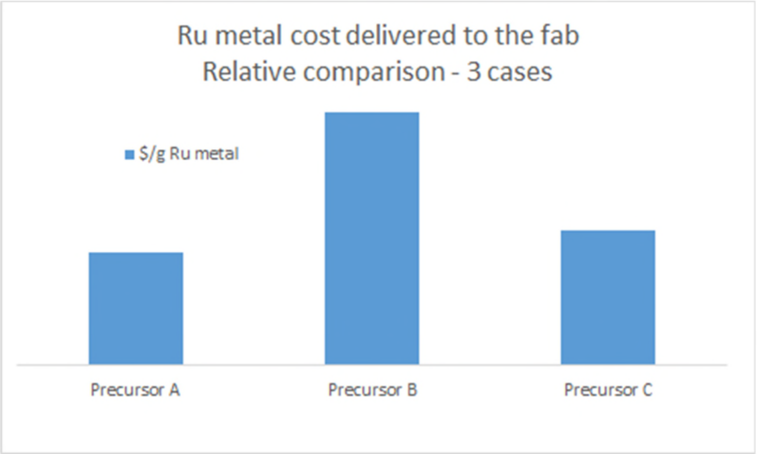
Smooth, low resistivity, conformal films obtained by LT-CVD

Insight on Ru CVD Precursors Chemistry

Ru Supply Chain Considerations

- Ru mining ~20-30Tons/year: South Africa (>>50%), Russia mainly
- Applications in Data storage, electrical, chemical industries
- **Ru metal cost is very volatile**
- Delivered Ru function of Ru metal cost, yield, properties, ligands



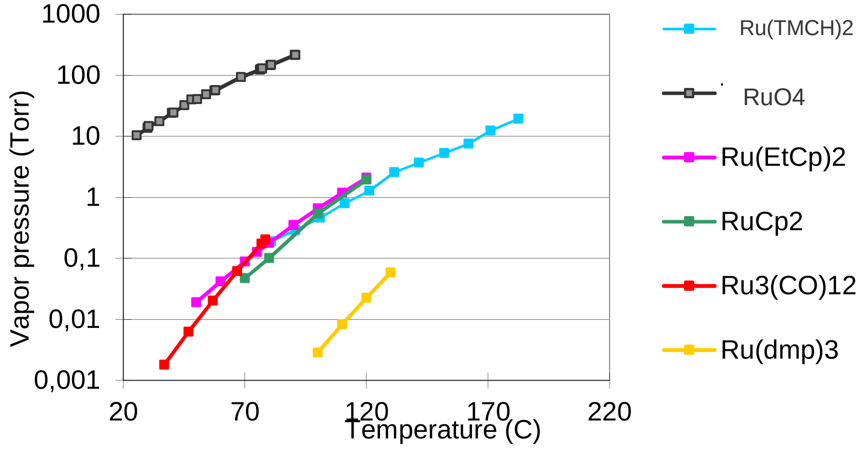


Ru precursors families options

- Ru ALD/CVD is investigated since >10years

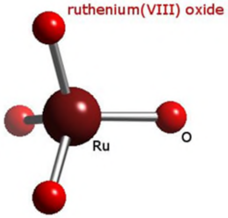
	Physical state	Volatility	Stability
Ru3(CO)12			
Ru(EtCp)2			
Ru(TMCH)2			
Amidinate			
β-diketonates			
RuO4			

Vapor pressure of selected Ru precursors



Ruthenium Tetroxide - RuO_4

- Used in solution as fingerprinting agent in the 90s.



- Key challenges
  - Low mp solid
  - Unstable in pure form
  - Can explosively decompose
  - RuO4 → RuO2 + O2
- Key advantages
  - Stable in diluted form
  - Extremely volatile (BP @ 100°C)
  - Synthesis pathway

Latent Fingerprint Processing by Ruthenium Tetroxide Method

Article in Japanese journal of science and technology for identification
2(1):21-25 · January 1997 with 71 Reads
DOI: 10.3408/jasti.2.21

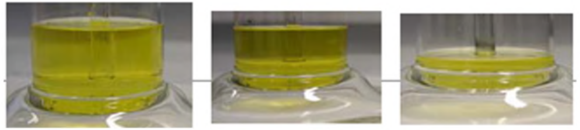
Kenzo Mashiko
Takashi Miyamoto

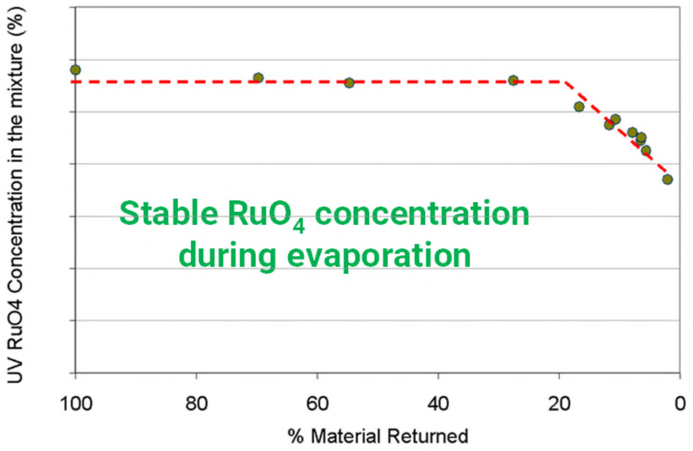
Abstract

The method studied in this paper is developing latent fingerprints based on ruthenium tetroxide (RuO4) method. Ruthenium tetroxide fuming promptly react with various organic compound, particularly oils or fats contained in sebaceous secretions in latent print and producing brownish black or black ruthenium dioxide (RuO2). Ruthnium Tetroxide is yellow, volatile crystails (melting point; 25.5°C, boiling point; 100.8°C) at room temperature. Conventional methods using RuO4 have been almost impractical because it is very difficult to handle by its strong oxidizability. Additionally because of the two liquid method, it is not only troublesome to produce RuO4 fumes immediately before developing latent fingerprints, but also is difficult to produce necessary ammounts of RuO4 fumes. In this method, these problems were resolved by utilizing a saturated hydrocarbon halogenid solution of RuO4

TORUS™

- RuO_4/solvent blend behaving as an ideal mixture and simultaneously evaporating
- Key characteristics
  - o RuO_4/solvents mixture
  - o Clear yellow liquid
  - o Vapor pressure 10 Torr @ 25°C
  - o Boiling point 61-76°C
  - o Viscosity 0.6cP @ 23°C
  - o LC_{50} (inh - rat) > 20 mg/L
    - – *ToRuS is not considered a toxic substance*
- US7906175B2, WO2006035281

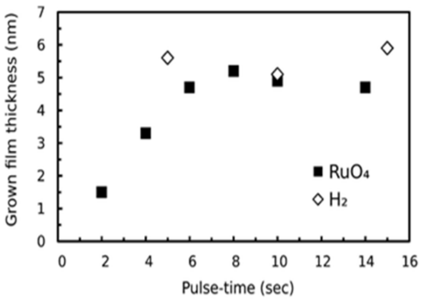


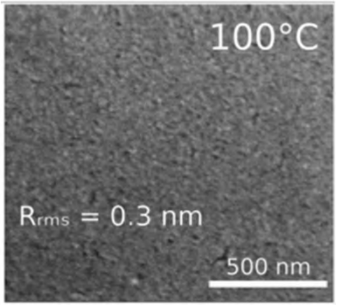


Non-flammable, non toxic, liquid solution for stable RuO_4 gas phase delivery

TORUS™ – Process Results

T-ALD @ 100°C

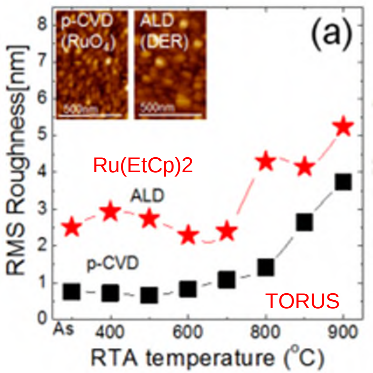


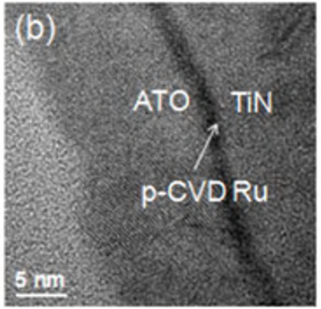


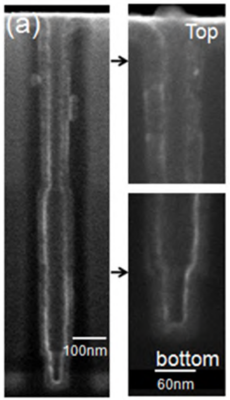
Minjauv et.al., J. Mater. Chem. C, 2015, **3**, 132-137

T-ALD at 100°C – GPC of 1A/cy
ρ18µΩ.cm @ 18nm (at. % level O)
Excellent conformality

Pulsed-CVD @ 250°C



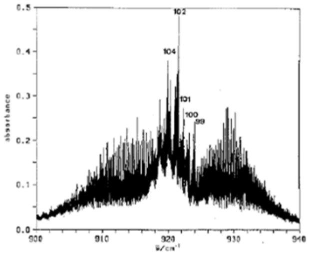




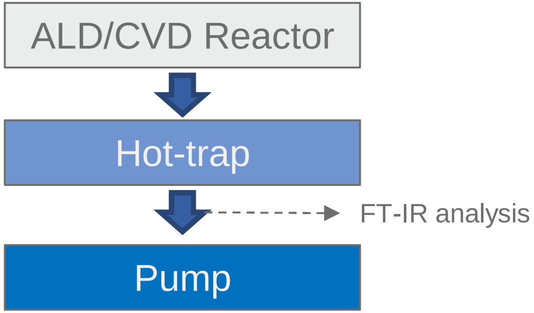
Han et al., ECS Transactions, 58 (10) 171-182 (2013)

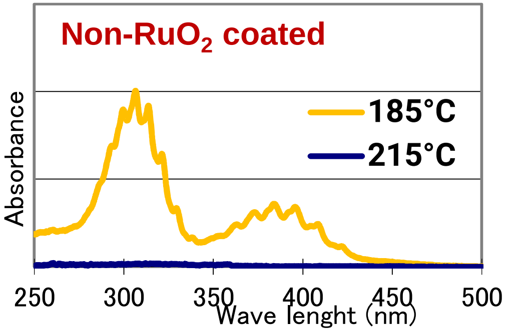
P-CVD down to ultrathin Ru layer. ρ25µΩ.cm
Conformality > 90% in 10:1 structures
Also reported for crystalline SrRuO3 ALD

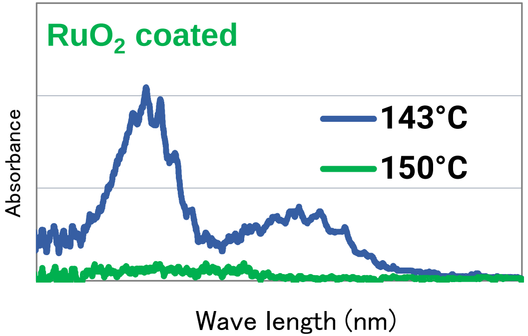
RuO_4 Abatement and Recycling



- FT-IR analysis of RuO_4 effluent downstream to a hot furnace
  - *$RuO_4 \rightarrow RuO_2 + O_2$, catalysed by RuO_2*





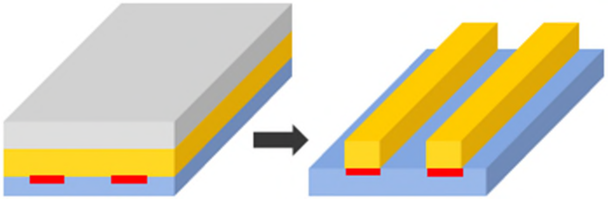


RuO_4 can be decomposed to RuO_2 in a simple hot furnace, no co-reactant required
$\rightarrow$ Ru could be recovered as RuO_2.

Ru Selective ALD/CVD processes

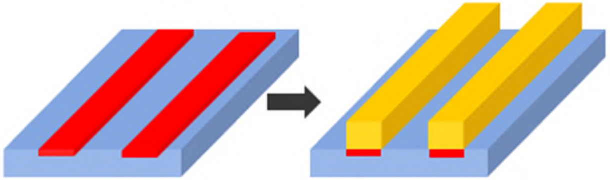
Selective Deposition

Conventional top-bottom approach



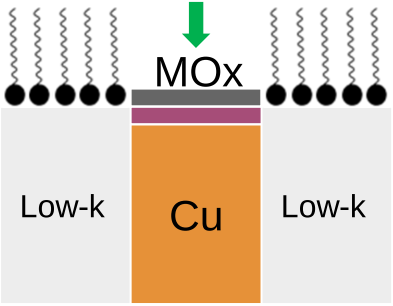
6 steps

Selective bottom-top approach

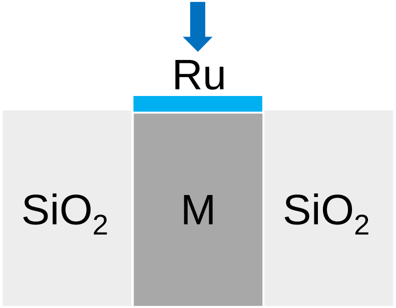


1-3 steps

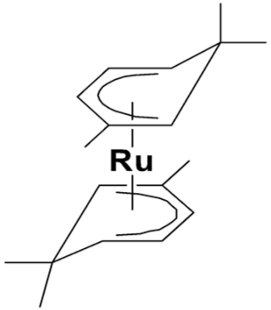
Dielectric-on-**Metal** (DoM)
→ Self-Assembled Monolayers



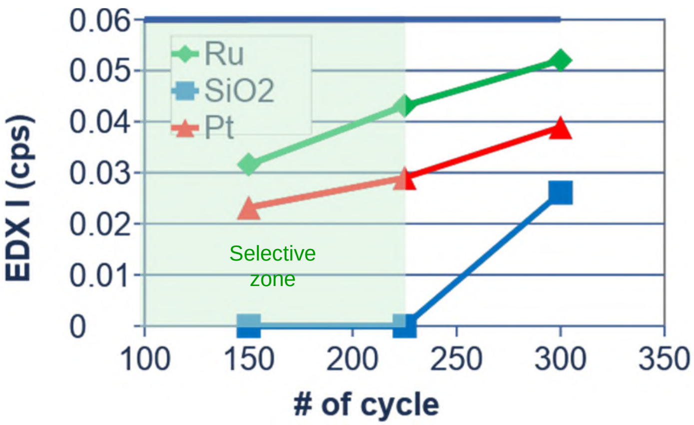
Metal-on-**Metal** (MoM)
→ Inherent or enhanced selectivity

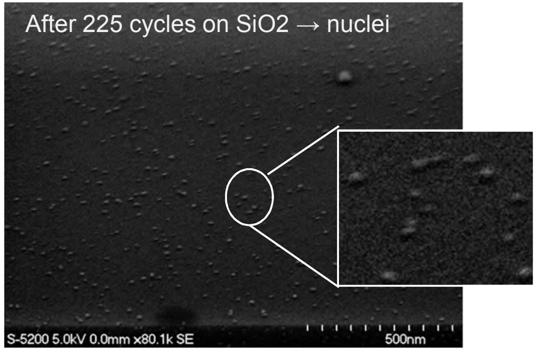


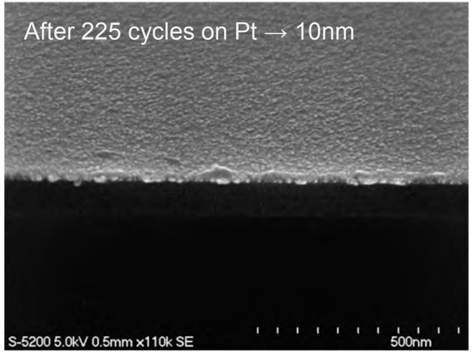
Ru Metal-Organics – AS-ALD MoM



- Ru(II) precursor
  - ALD w/ O_2 at 325°C - « Combustion » type (same w/ $Ru(EtCp)_2$)
  - Bis(2,2,6,6-trimethylcyclohexadienyl)Ruthenium – $Ru(TMCH)_2$





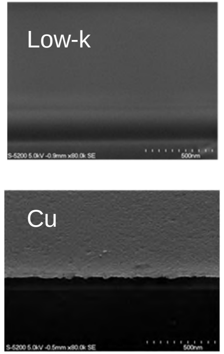


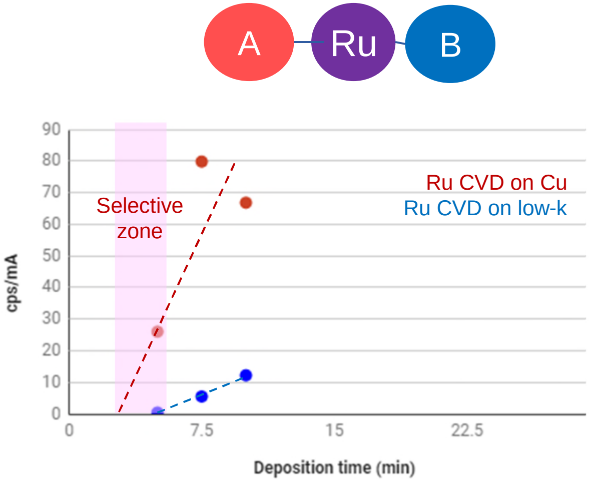
Good selectivity achieved 10nm Ru on Pt. Ru nucleation sites observed on SiO_2
Likely to be combined w/ ABC etch-back process to maximize contrast

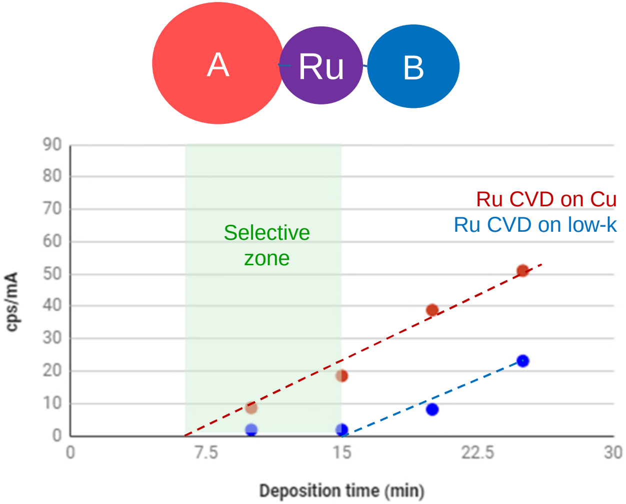
Ru Metal-Organics – AS-CVD MoM

- Increasing inherent selectivity by ligand size (H_2 based CVD Ru)

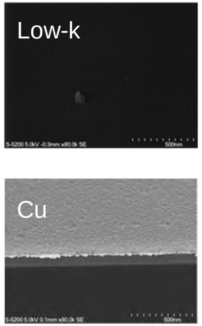
SEM after 5min







SEM After 20min



Lower precursor reactivity → increased selectivity
Likely to be combined w/ ABC etch-back process to maximize contrast

Conclusions

- For BEOL metallization Lower stability precursors cannot be avoided in most cases.
  - Chemical innovation can address stability issue in some cases.
  - Otherwise a robust metrology and manufacturing control is required to ensure reproducibility

- Cobalt precursors chemistry
  - Existing precursors have demonstrated **successful** integration down to 10-7nm nodes
  - Development is still required to achieve **~nm conformal thermal ALD**

- Ruthenium precursors chemistry
  - Ru ALD/CVD chemistry has been investigated since ~20+ years
  - Existing options **allow deposition of ~nm Ru layers by CVD/ALD w/ O_2 or H_2 co-reactants**
  - Ru ALD/CVD is promising for selective MoM deposition
  - Challenges focused on integration

THANK YOU