Novel EHS-Friendly Ru Etch and SPM Alternatives for 5nm Applications

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Presentation Outline

1. ***Ruthenium (Ru) – Cu Interconnect Alternative***

2. **Ru Etch – Current Options**

3. **EHS-Friendly Ru Etch Development**
   - **RSE-1 Chemistry Platform Design**
   - **Selective Ru Etch with Broad Substrate Compatibility**
   - **Other Selective Etch Examples – WNx, W Selective Etch**

4. **Study of SPM Alternatives and Their Applications**

5. **Summary**

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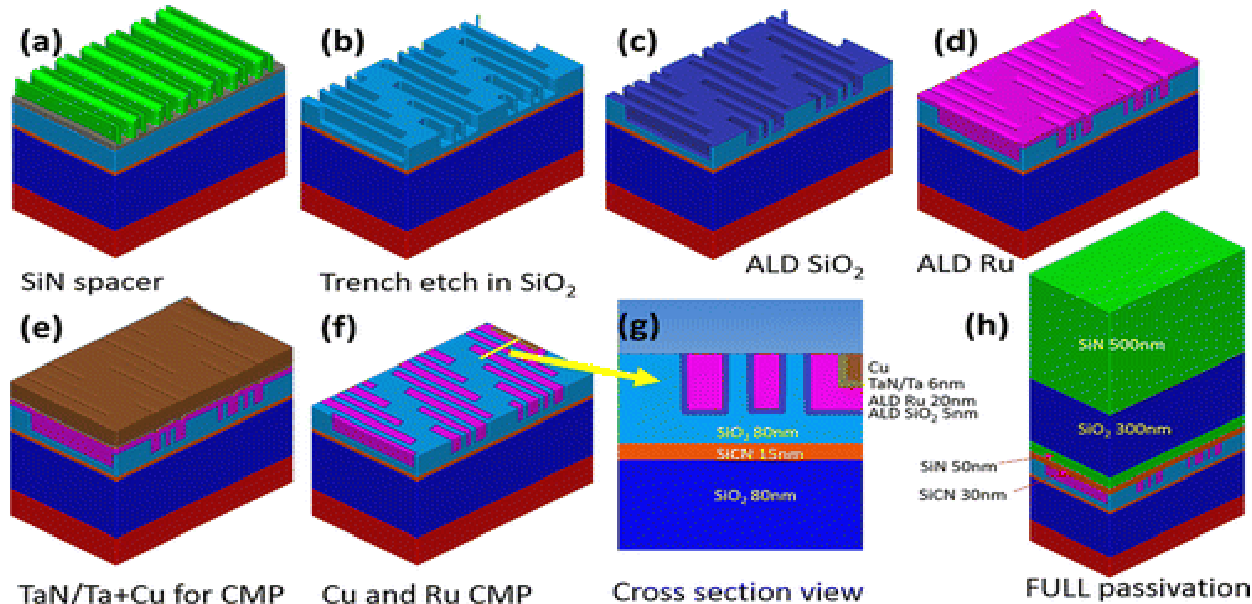
Ruthenium – Potential Cu Replacement in Interconnect



[Source: L.G. Wen et.al., ACS Appl. Mater. Interfaces, 2016, *8* (39), pp 26119–26125}

- **Ru – Good effective resistance; candidate as barrier-less metallization in interconnect; replacing Cu**
- **Ru lines – excellent EM behavior, no Ru ion drift into low-k**

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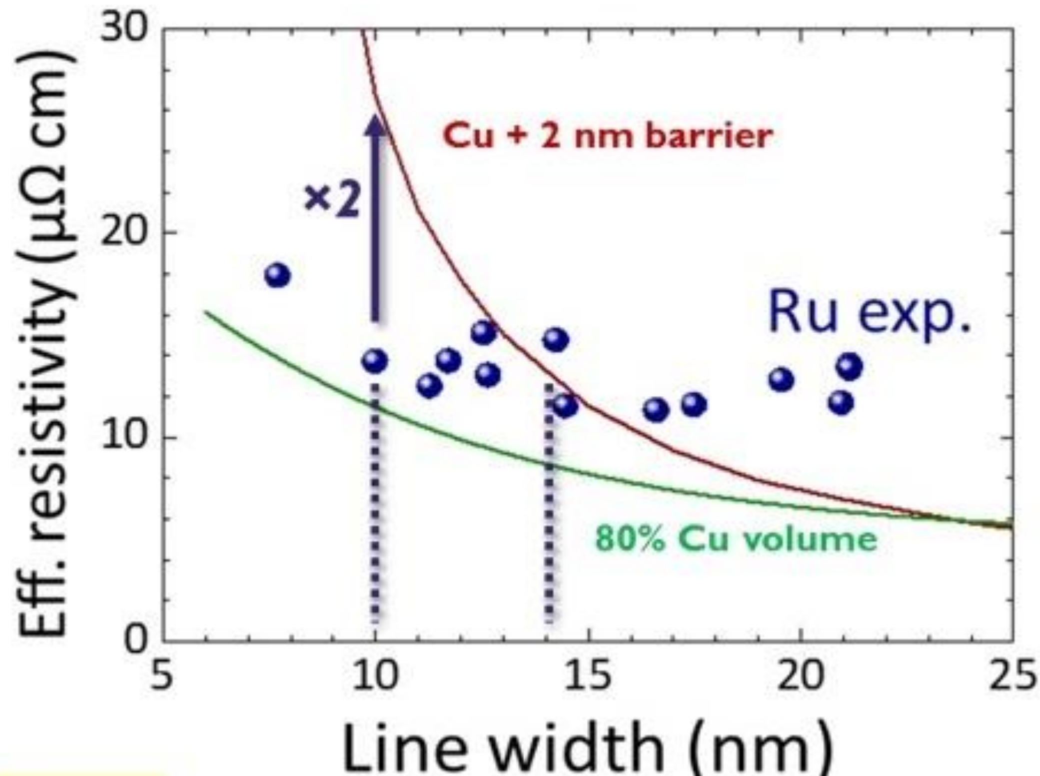
Ru as Cu Interconnect Alternatives



- **Effective resistivity as a function of line width for copper and ruthenium.**
- **At 10nm narrow lines, Ru interconnects has 2X better resistivity than Cu**

Source: courtesy of IMEC

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Ru Wet Etch Chemistry Options

- **Ru is a hard metal; resistant to common etch chemistries**
- **Ru can be oxidized to various oxides. RuO_2 is most common oxide of ruthenium**
- **Conventional etch chemistries do not provide enough Ru etch rates: SPM, HNO_3, Aqua Regia, HF, SC-1…**

- **Ru integration in advanced nodes has big challenges**
  - **Need high Ru etch selectivity vs. a number of substrates and metallization**
  - **Need better Ru CMP solutions**

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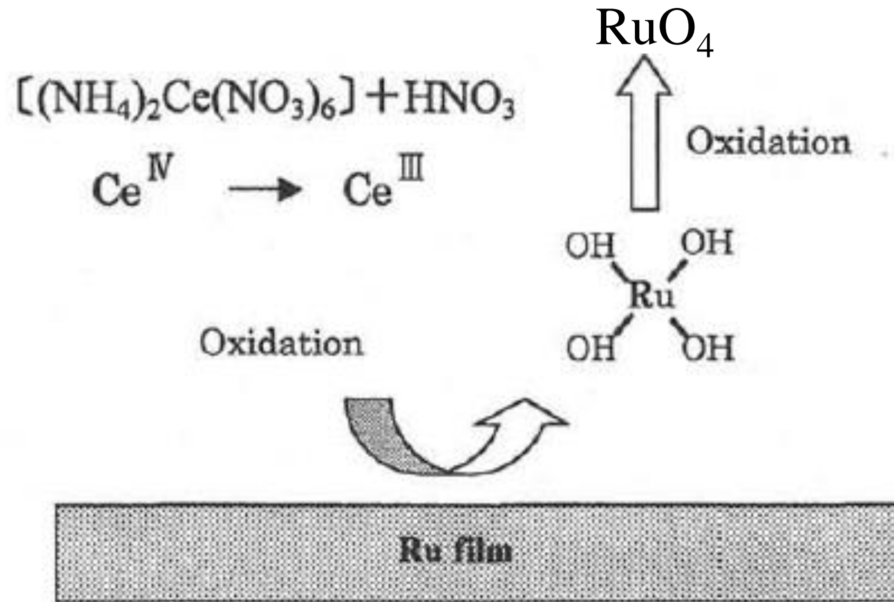
Ru Wet Etch Chemistry Options



[H. Aoki et.al. Extended Abstracts of the 2001 International Conference on Solid State Devices and Materials. 2001]

- **Cerium ammonium nitrate (CAN) and nitric acid etch Ru.**
- **By-product: volatile RuO_4 (m.p. 25.4°C; b.p. 40°C; toxic); Formulation contains metal (Ce)**

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Ru Selective Etch by RSE-1 Chemistry

- **Aqueous, alkaline oxidative chemistry design**
- **Convert Ru to RuO_4^-; Fully dissolution mode. No toxic RuO_4 release**
- **Utilize a unique oxidant to boost Ru etch efficiency, but minimize alkaline bases' attack on low-k and TEOS**
- **Proposed mechanism – based on Pourbaix diagrams**

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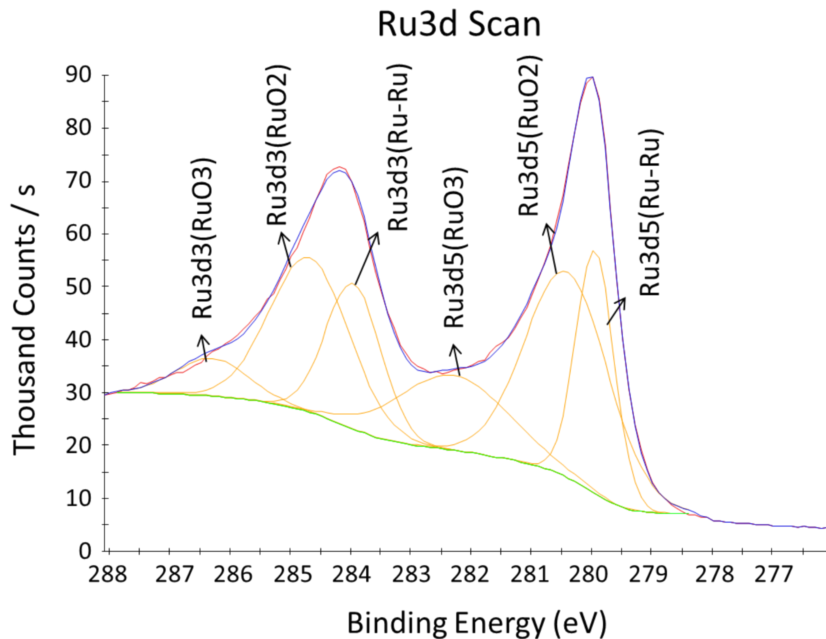
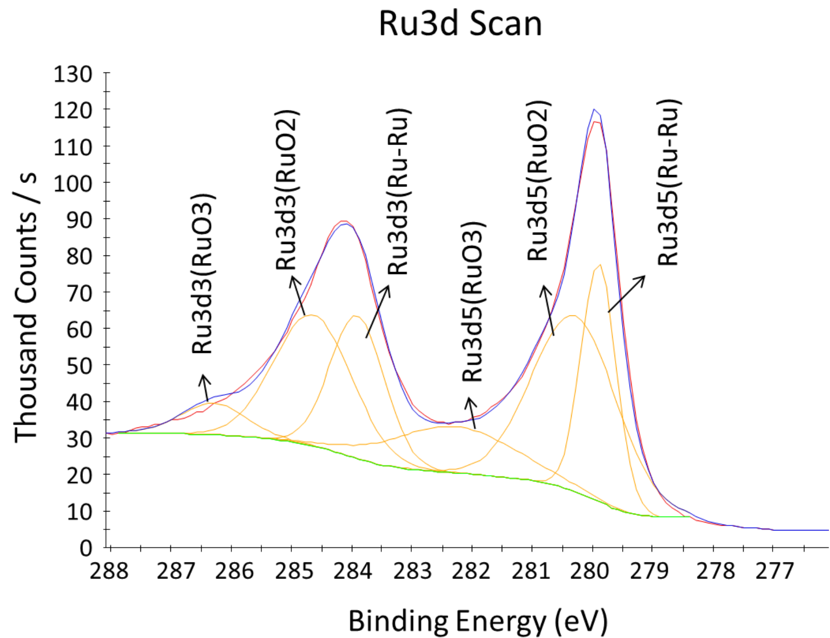
Ru Selective Etch by RSE-1
(with Ru – XPS analysis)



Untreated Ru film



RSE-1, 65°C, 5m

*** Ru 3d XPS -**

Similar Ru-Ru, RuO_2 and RuO_3 are primary bonding in both Ru samples

* Ru oxide is also conductive

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RSE-1 – Powerful PR/Residue Cleaner and Selective Ru Etch

RSE-1 etch rates at 65°C (Å/min)										
Cu	Ta	SiN	TEOS	SiC	Black Diamond II	SiOC	FSG	General CDO	Ru (PVD)	Ru (CVD/ALD)
<1	<1	<1	<1	<1	<1	<1	<1	<1	90-170	15-25
Co	Ti	TiN	TaN	WN	B-Doped Si		P-Doped Si	W	BARC	
<1	<1	<1	<1	>100	0		10	> 70	Compatibility Depends on BARC Types	

- RSE-1 is fully aqueous, but offers improved PR removal (high dose, highly cross linked polymer structure)
- RSE-1 is EHS friendly. No toxic RuO_4 gas release.
- RSE-1 has unique high Ru etch rates and broad compatibility with other materials ⇒ Expected applications: Selective Ru etch, Ru CMP & pCMP….
- Other Selective Etch examples: WNx etch selectivity vs. TiN, HfOx, LaOx --- from >2500 to >10,000

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RSE-1: Selective W, WNx Etch vs TiN

Etch rate comparison

Chemistry Description	Process Temp. (°C)	WNx (A/min)	W (A/min)	TiN (A/min)	WNx/TiN Selectivity	W/TiN Selectivity
10:1 H_2O-(RSE-1)	35	> 100	-	0.04	> 2,500: 1	-
RSE-1	60	-	>100	0.8	-	> 125:1

- **RSE-1 Chemistry platform (10:1 dilution): Excellent WNx Etch selectivity vs. TiN; Selectivity: >2,500:1**
- **RSE-1 Chemistry platform: Excellent W Etch selectivity vs. TiN; Selectivity: >125:1**

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RSE-1 Construction Material Compatibility

Compatible Materials		
Chemraz	PFE	PVC
Glass	Polyethylene	PVDF
Kalrez	Polypropylene	Quartz
PFA	PTFE	Telfon

* Viscosity: 1.30 mPa.s (30°C); 0.58 mPa.s (65°C)

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RSE-1: Cu Compatible SPM Alternative

	Chemistry Description	Cu ER (Å/min)	TiN ER (Å/min)	Co ER (Å/min)	Ti ER (Å/min)
A	**SPM, 90°C**	**>1000**	**>340**	**>80**	**>60**
B	**SC-1 (5:1), 65 °C**	**>25**	**>230**	**>15**	**>60**
C	**RSE-1, 65°C**	**<1**	**<1**	**<1**	**<1**

Process Description	N5, Implanted BARC	Sub-20nm, PR/Organic BARC Bi-Layer
RSE-1, 65C, 5min	**Implanted BARC film is removed**	**PR is removed; Organic BARC film remains**
RSE-1, 65C; DHF (Multi-step)	**---**	**PR and organic BARC film is removed**

- **RSE-1: Broad substrate compatibility (Cu, Co, Ti, TiN, TaN, TEOS, low-κ…)**
- **Fully aqueous, more environmentally friendly**
- **RSE-1 alone or RSE-1/DHF multi-step --- Effective bi-layer or tri-layer PR & BARC layers (100% removal, dissolution mode; including high dose, highly cross linked polymer structure)**
- **Suitable for typical FEOL/BEOL Single Spin Wafer Processors**

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Summary

- **Ru has been proposed as a potential Cu interconnect replacement. Ru selective etch and its CMP present integration challenges.**

- **Novel chemistry, RSE-1, delivers highly selective Ru etch and excellent compatibility with a broad range of substrates, such as Cu, Co, Ti, TiN, TaN, low-k and others. It also provides excellent W or WNx selective etch vs. TiN.**

- **Another application of RSE-1 chemistry platform is used for PR and BARC implant removal. It is fully aqueous, organic solvent-free, thus an EHS-friendly SPM alternative.**

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