Copper CVD: Applications and Potential Recycle

John Norman

PRESENTATION OUTLINE

- Applications for copper CVD.
- Introduction to precursor chemistry.
- Chemical delivery, processing issues.
- Abatement versus recycle of CVD effluent.
- Summary.

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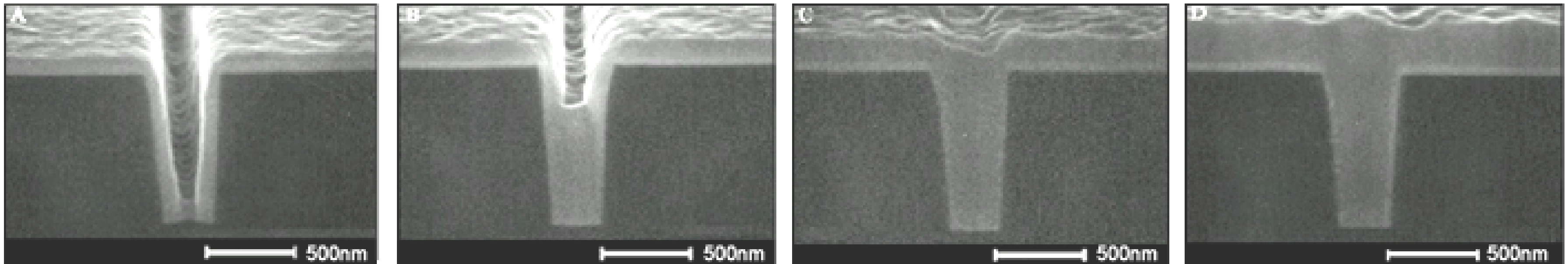
Applications for copper CVD

- Provide ultra-thin conformal copper seed layers for electroplated copper.
- Enable new copper CVD Superfill.
- All ‘dry’ CVD copper full-fill capability vs. electroplated copper
  - Avoids the use of stand alone e-plating tool.
  - All metal film processing from diffusion barrier to copper seed to full-fill achieved on one tool without vacuum break.

Copper CVD superfill using CupraSelect

- Use of catalytic iodine surfactant. E.S. Hwang, J. Lee, Chem. Mater. 2000, 12, 2076- 2081.
- Copper fills from the bottom of the feature first.



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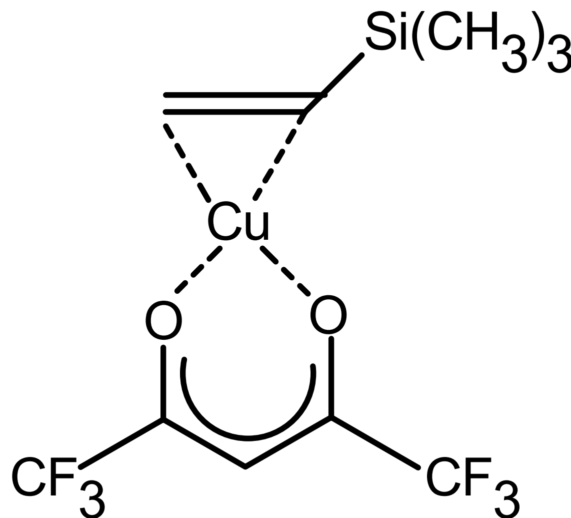
CUPRA SELECT®

- Stable yellow liquid Cu(hfac)(tmvs), premier copper precursor.
- Vapor pressure 1 Torr @ 60°C.
- Provides 99.99% copper , 1.85 µohm cm[1], 5000 A/min.
- Conformality > 90%

[1]J. Norman et al Thin Solid Films 262 (1995) 46-51



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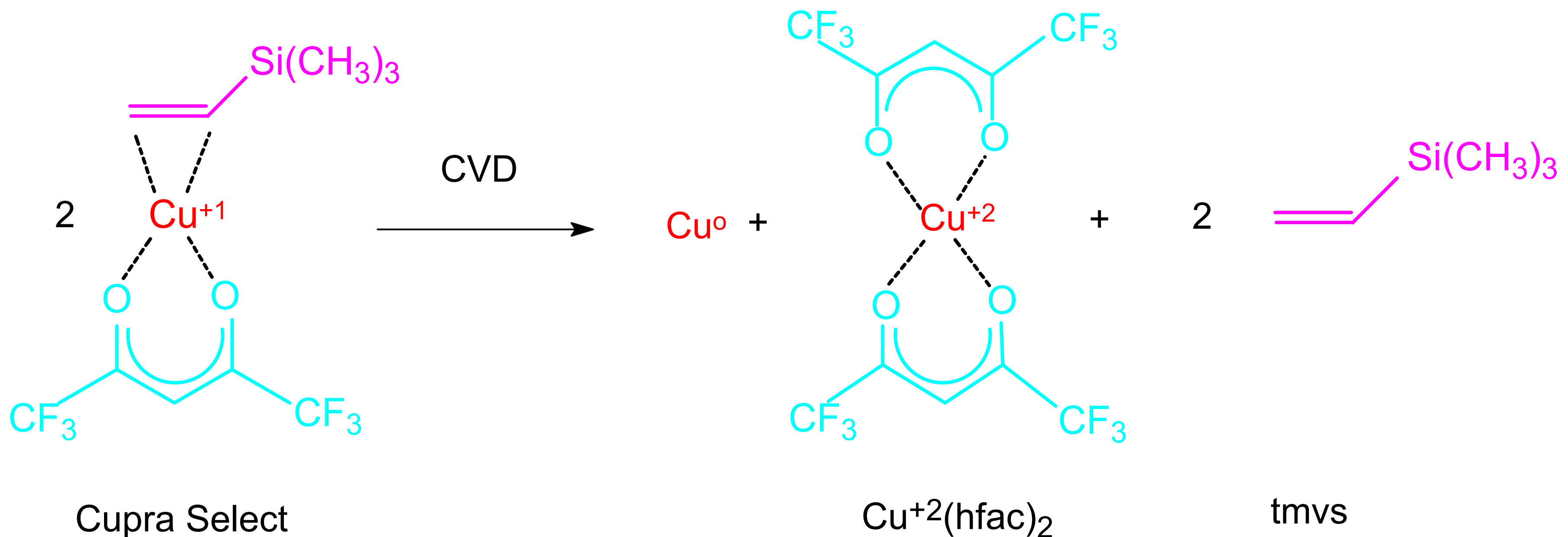
CVD COPPER FILM GROWTH

- Metallization by disproportionation



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METALLIZATION CHEMISTRY

- Selective deposition onto conductors due to key electron transfer step.
- Superior metallization process by the use of additives.
  - tmvs for stable precursor delivery.
  - hfac and water (separately or as HDH) for enhanced metallization.
  - water addition alone promotes adhesion.

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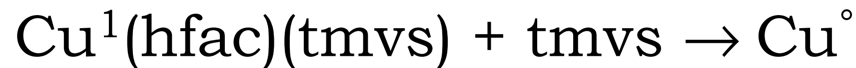
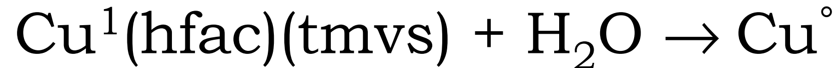
EVOLUTION OF CUPRA SELECT PROCESSING WITH ADDITIVES

- Enhanced thermal stability during DLI evaporation.



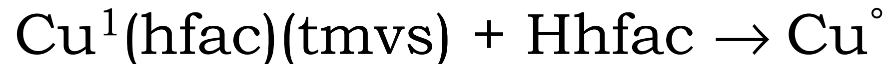
T. Omstead (Sandia)

- Enhanced deposition rate for copper.



A. V. Gelatos et al Appl Phys Lett., 63 (20) (1993) 2842.

- Enhanced deposition rate, uniformity and reflectivity.



J. Norman et al Conference proceedings ULSI-lX 1994 MRS

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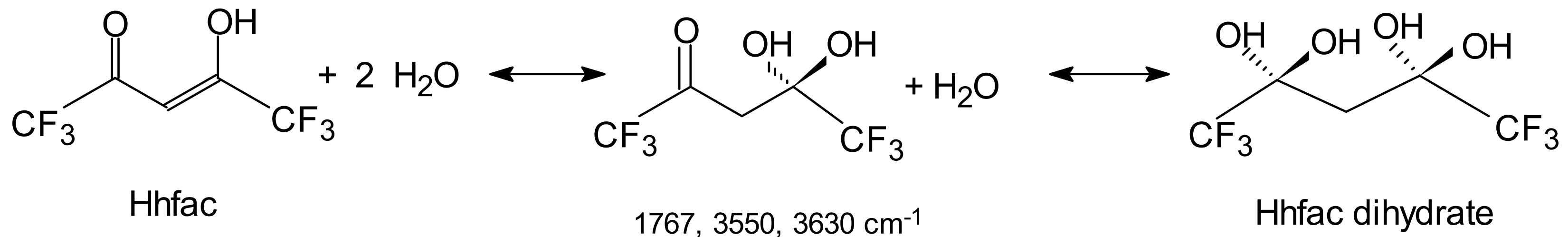
COMBINING THE ACCELERANT ADDITIVES Hhfac AND WATER INTO ONE COMPOUND: Hhfac DIHYDRATE

- Release of Hhfac and H_2O occur under CVD conditions, assuming adequate residence times for dissociation in the CVD chamber.
- Cu(hfac)(tmvs)/hydrate blend can be stabilized by tmvs addition.
- Improved adhesion of copper to some TiN, but additional water needed for Ta and TaN.



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SUMMARY OF ADDITIVE TRENDS

	Adhesion	Uniformity	Dep. Rate	Resistance	Reflectivity	DLI Performance
tmvs	0	0	(-)[1]	(-)[2]	(-)[3]	+
Hhfac	0	+	+	0	+	(-)
H_2O	+	(+)	+	(-)[4]		(-)
HDH	(+)[5]	+	+	0	+	(-)

Legend:
+ = improves
- = degrades
0 = no effect
( ) = lesser effect

1) Disproporation suppressed.
2) Resistance can appear higher due to film roughness.
3) Degraded by higher roughness.
4) Excess water yield copper oxides.
5) Improves adhesion on some TiN.

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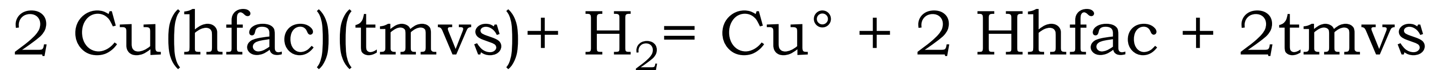
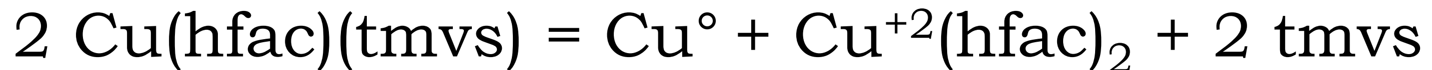
Hydrogen as a reducing agent:



$$2\ Cu(hfac)(tmvs) + H_2 = Cu^{\circ} + 2\ Hhfac + 2tmvs$$

Arita et al J. Electrochem. Soc., Vol 142, No9, 3173 (1995)

- Compare to disproportionation:



$$2\ Cu(hfac)(tmvs) = Cu^{\circ} + Cu^{+2}(hfac)_2 + 2\ tmvs$$

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WAFER METALLIZATION SCENARIO

- At 2000A/min, 0.25m 6:1 AR
- On an 8 inch wafer 0.5 microns copper film corresponds to 0.144g copper metal.
- Assume 30% utilization efficiency of copper precursor entering the reactor.
- 2.5g of CupraSelect will be consumed during the process step, but approx 70% of this remains unchanged as it exits the process chamber as effluent.

ABATEMENT SCENARIOS FOR REACTOR EFFLUENT

- Destructive capture of CVD effluent.
  - pyrolysis in a hot-box.
  - chemical absorption by a caustic scrubber.
  - ultimate disposal of copper waste.
- Reversible physical entrapment for recycle
  - no copper waste for disposal, environmentally benign.
  - complete recycle for copper containing CVD byproducts.
  - lowered COO to end user.

Destructive abatement

- Precursor vapor contacted with alkaline metal oxides at high temperature to fragment fluorocarbon ligands to give metal fluorides, HF,CHF_X etc.
- Any residual flammable vapors are combusted in burn box to give carbon dioxide, water and HF
- HF vapors and carbon dioxide need alkaline scrubber for absorbtion
- Copper deposited as waste metal or metal fluoride for disposal.
- High value-added molecules irreversibly consumed.

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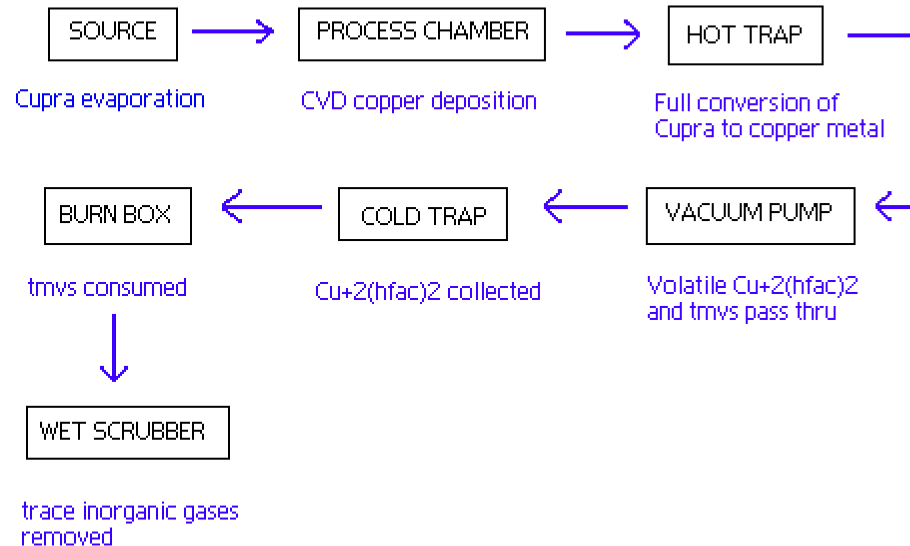
Collection of copper metal and $Cu^{+2}(hfac)_2$

- Applied Materials US 6099649



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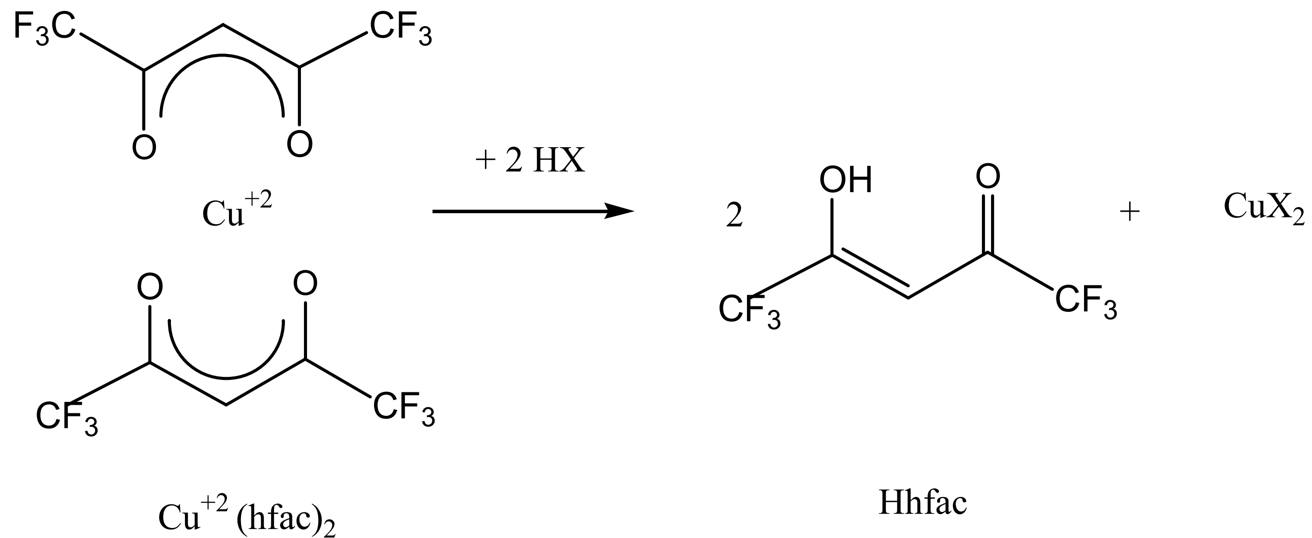
Regeneration of Hhfac ligand

- Air Products US 6046364



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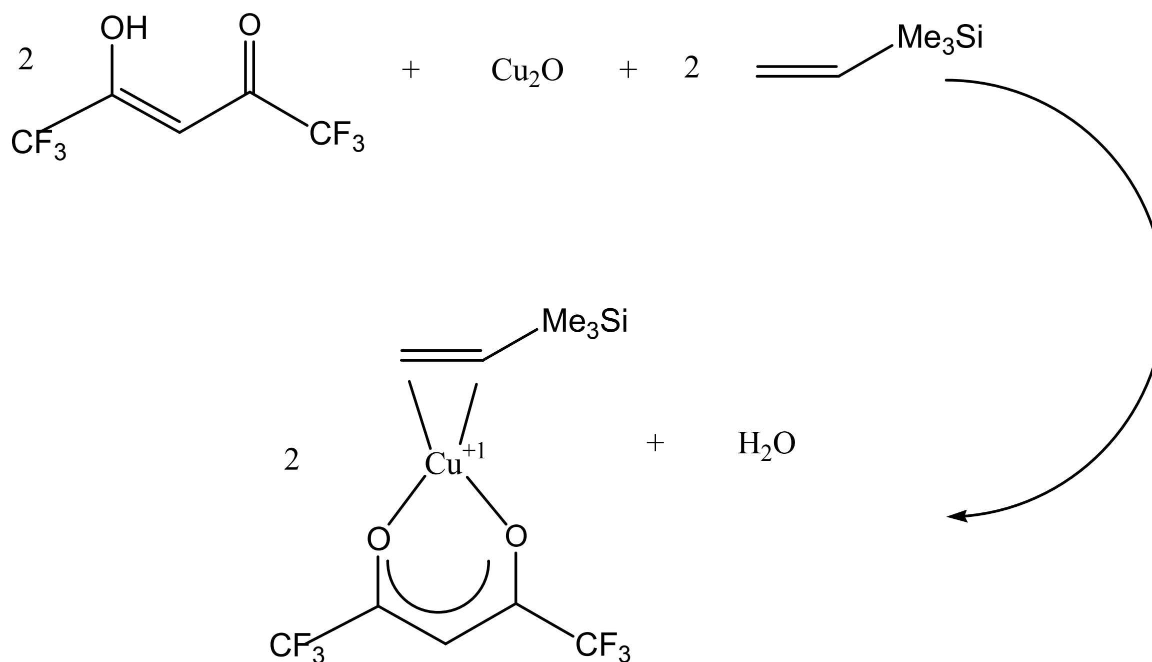
Production of CupraSelect

- Regenerated Hhfac recycled back to give fresh precursor. Air Products US 6096913.



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SUMMARY

- CupraSelect is attractive for commercial implementation of copper CVD for e-plate seed, CVD superfill, all 'dry' full-fill CVD .
  - Adaptable precursor properties
  - Simple thermal CVD process.
  - Excellent film properties.
  - Potential for minimal environmental impact via fluorinated ligand and copper recycle.