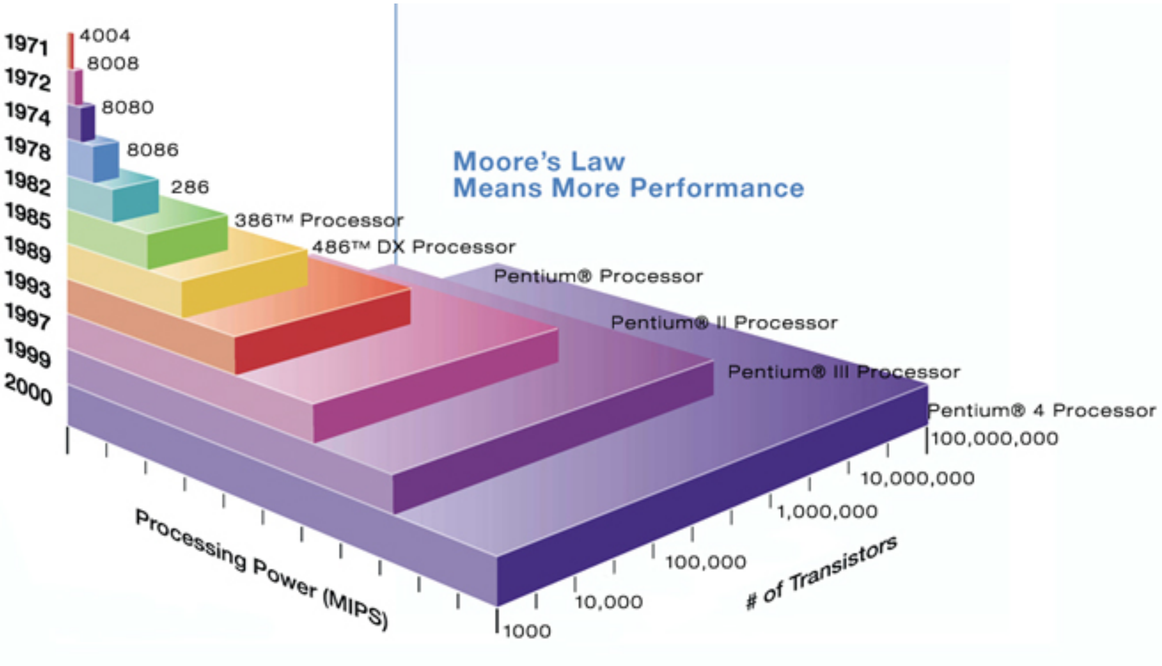
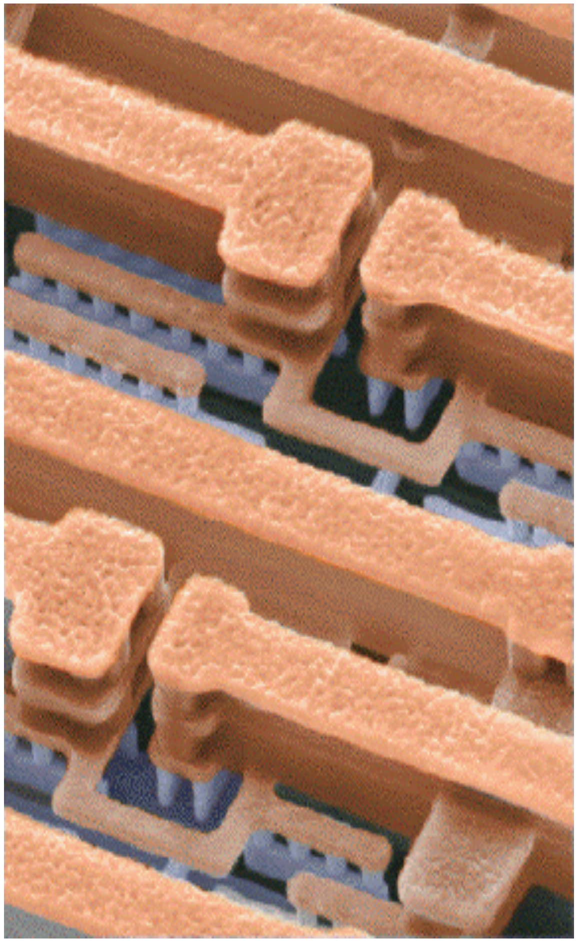
ALD and CVD of Copper-Based Metallization for Microelectronic Fabrication

Yeung Au, Youbo Lin, Hoon Kim, Zhengwen Li,
and Roy G. Gordon
Department of Chemistry and Chemical Biology
Harvard University

Introduction

- Periodic improvements in performance of microelectronic devices have been achieved through device-scaling



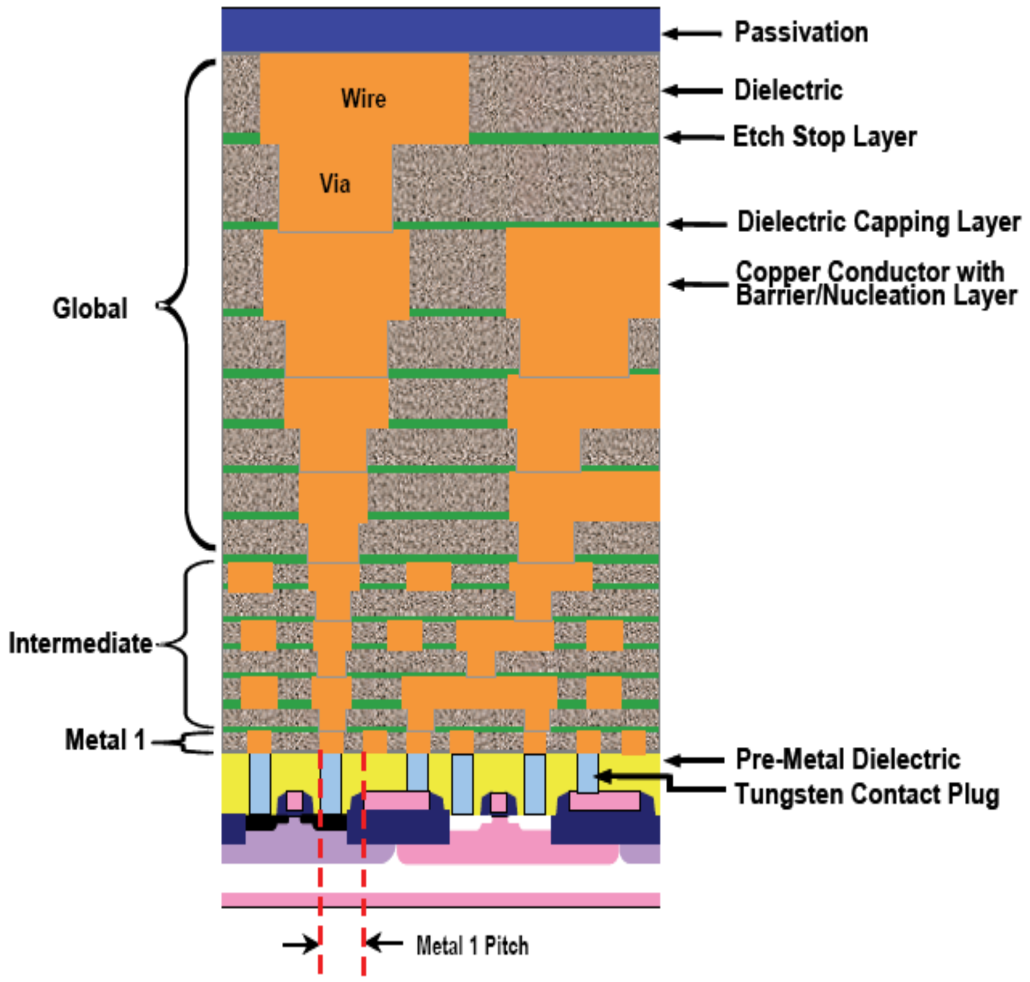


- Copper was selected because of its (1) abundance, (2) low resistivity, and (3) better electromigration reliability
- Damascene process (EP and CMP) is commonly adopted for patterning copper

Outline

In today's presentation:

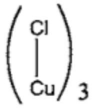
- ALD and CVD of Cu films from a Cu(I) amidinate precursor
- Formation of Cu seed layer by ALD of Cu and by CVD of CuON
- Bottom-up filling of CVD-Cu and CuMn alloy in nanoscale features
- Summary



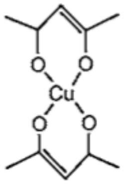
Cross-Section of Microprocessors

Copper Precursors

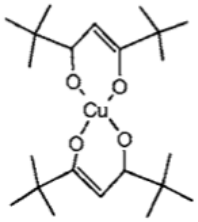
- Requirements for good ALD Cu precursors: (1) thermally stable, (2) volatile, and (3) minimal contaminations



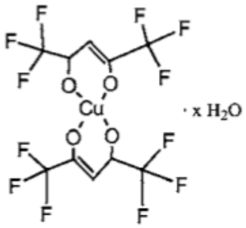
(a) CuCl



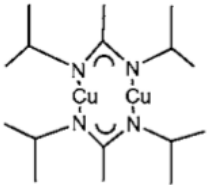
(b) Cu(acac)$_2$



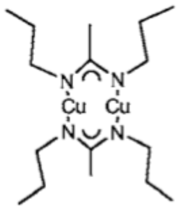
(c) Cu(thd)$_2$



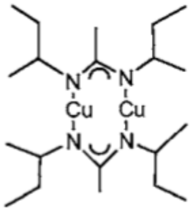
(d) Cu(hfac)$_2$ · xH$_2$O



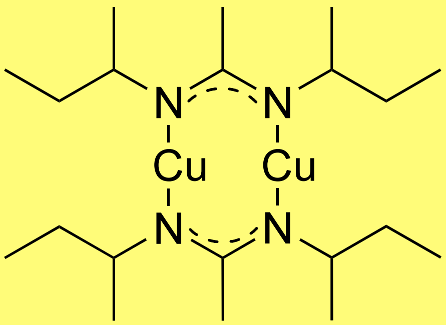
(e) [Cu(^{i}Pr-amd)]$_2$



(f) [Cu(^{n}Pr-amd)]$_2$



(g) [Cu(^{s}Bu-amd)]$_2$



Copper (I) N,N'-di-sec-butylacetamidinate
Melting Point: ~75°C
Bubbler Temperature: 130°C
Vapor Pressure: ~0.25 mbar at 95°C

Advantages of metal amidinates precursors:

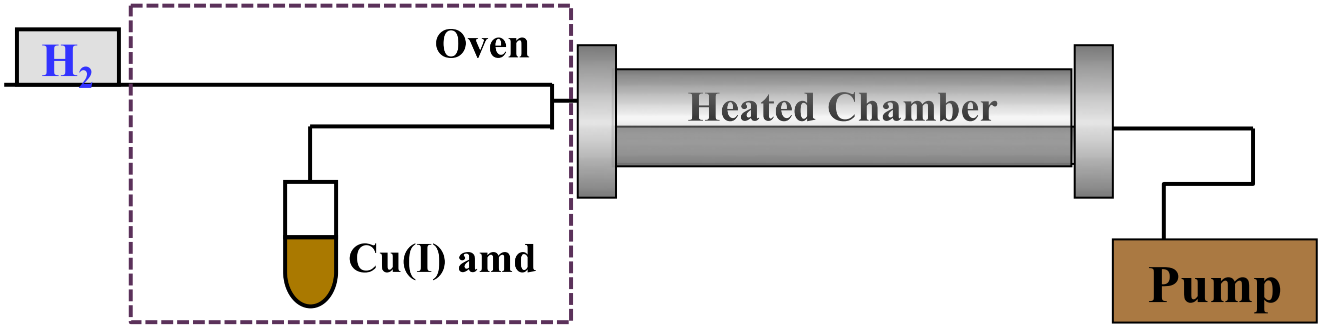
- Bidentate chealting effect enhances thermal stability
- Tunable reactivity and volatility
- Minimal carbon and oxygen contamination

B. S. Lim, A. Rahtu, J. S. Park, and R. G. Gordon, *Inorg. Chem.,* **42** (24), 7951-7958, (2003).

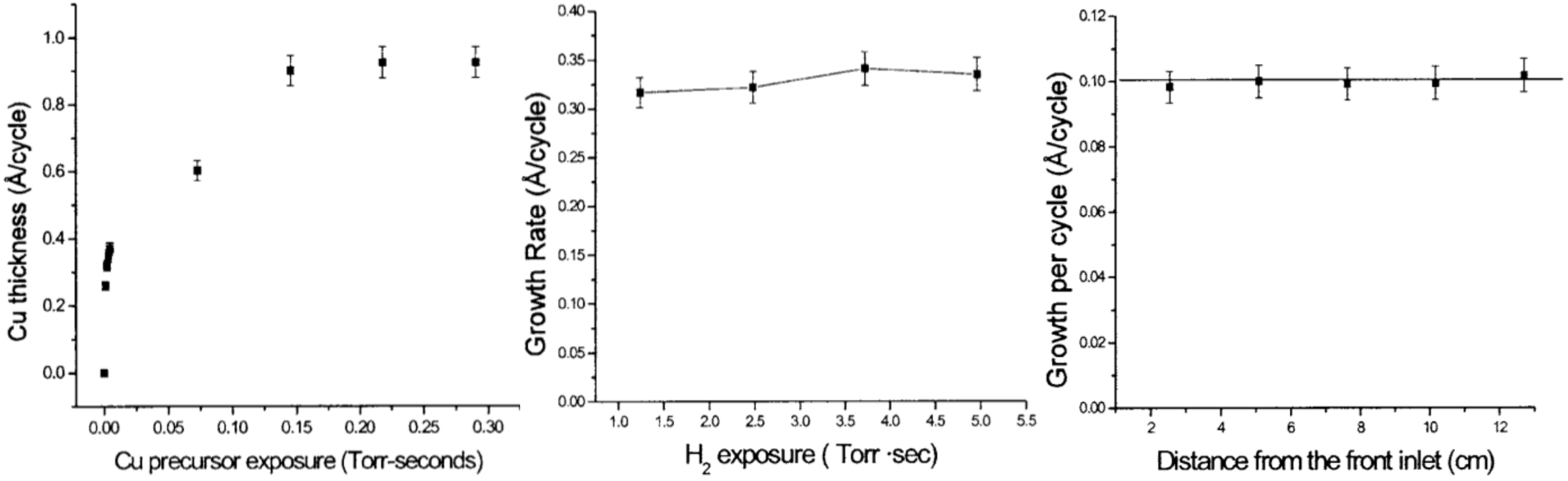
ALD of Copper

- Copper films could be deposited by ALD using molecular hydrogen as reducing agent

ALD System



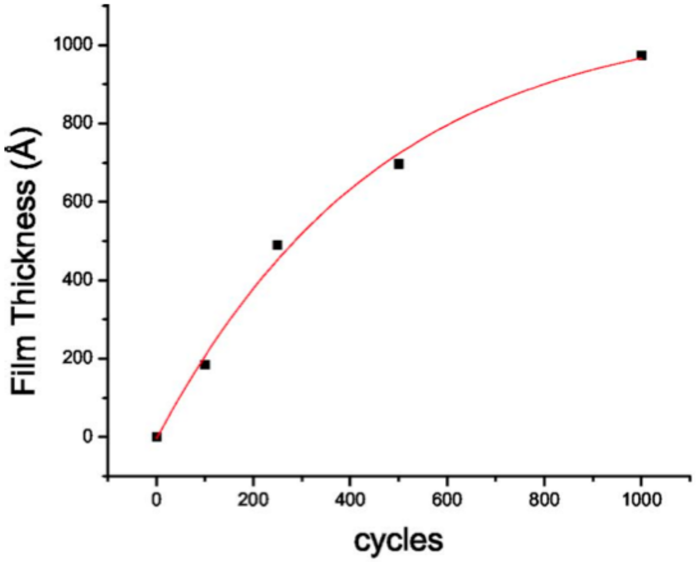
- Copper deposited on ALD-Al_2O_3 substrate at low temperatures (150-190°C):



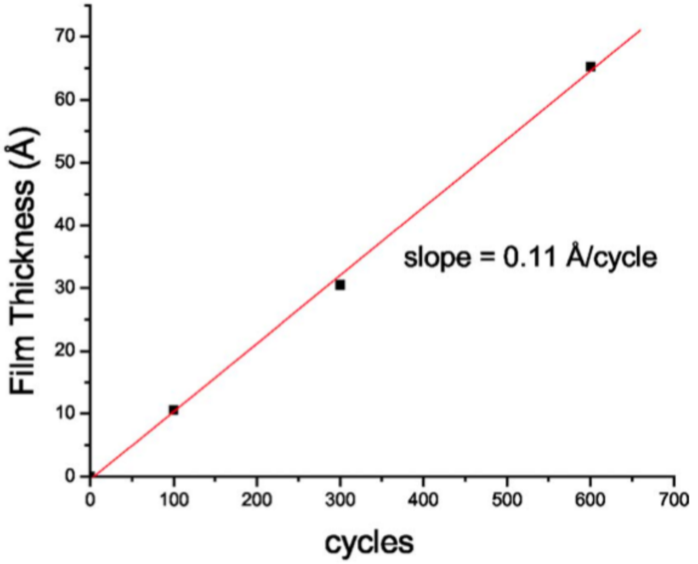
Z. Li, A. Rahtu, and R. G. Gordon, *J. Electrochem. Soc.*, **153** (11) C787-C794 (2006)

ALD of Copper

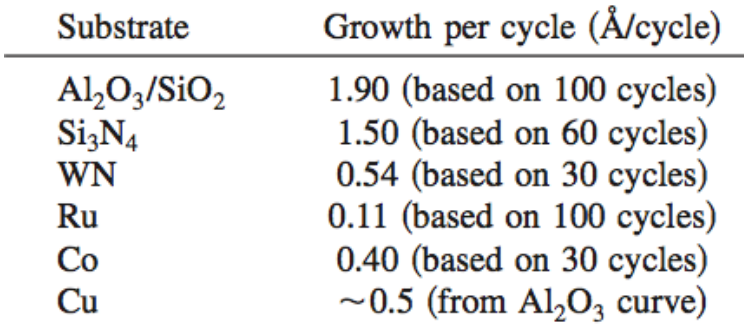
- Growth behavior can be affected by many factors: surface chemistry, precursor exposure, deposition temperature, etc.



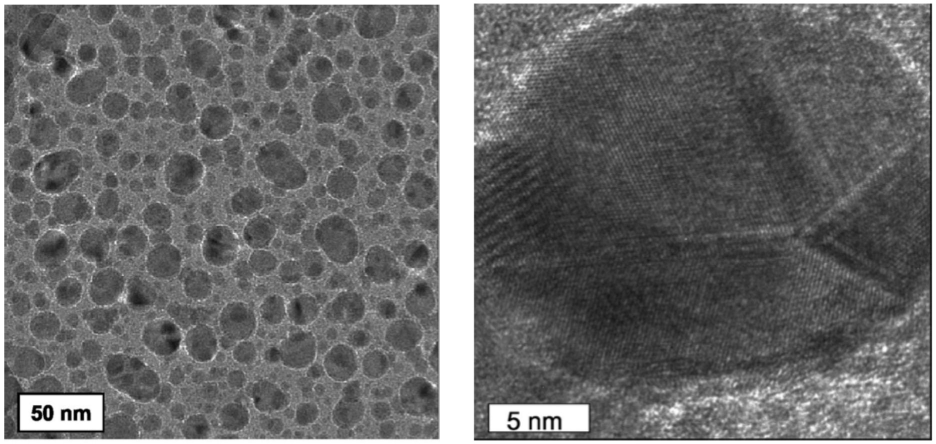
ALD-Al_2O_3, ALD-HfO_2, Thermal SiO_2
Initially ~2Å/cycle, ~0.5Å/cycle when surface is fully covered by Cu



Ru Substrates
0.11Å/cycle

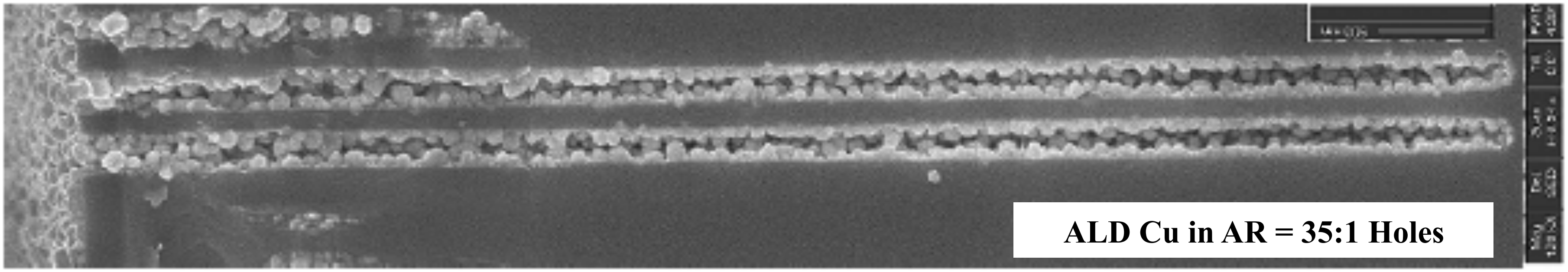


Substrate	Growth per cycle (Å/cycle)
Al_2O_3/SiO_2	1.90 (based on 100 cycles)
Si_3N_4	1.50 (based on 60 cycles)
WN	0.54 (based on 30 cycles)
Ru	0.11 (based on 100 cycles)
Co	0.40 (based on 30 cycles)
Cu	~0.5 (from Al_2O_3 curve)



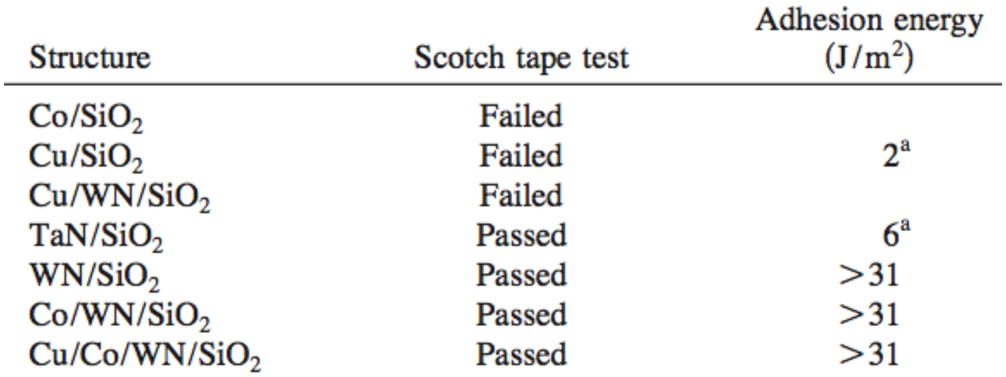
Copper Seed Layer Using ALD

- ALD has the ability to grow films conformally and uniformly over high aspect ratio holes and trenches



ALD Cu in AR = 35:1 Holes

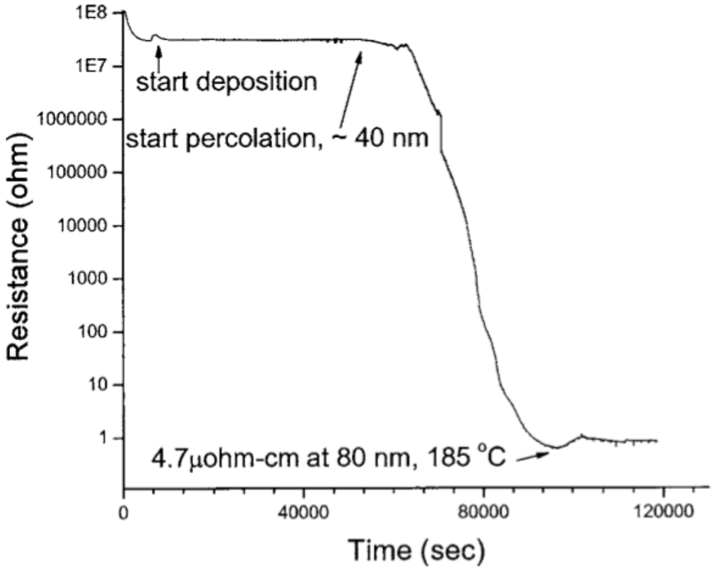
- Four-point bend experiment showed high adhesion energies for Cu/Co/WN/SiO_2



Structure	Scotch tape test	Adhesion energy (J/m^2)
Co/SiO_2	Failed	
Cu/SiO_2	Failed	2[a]
Cu/WN/SiO_2	Failed	
TaN/SiO_2	Passed	6[a]
WN/SiO_2	Passed	>31
Co/WN/SiO_2	Passed	>31
Cu/Co/WN/SiO_2	Passed	>31

***In-situ* Resistance Measurement**

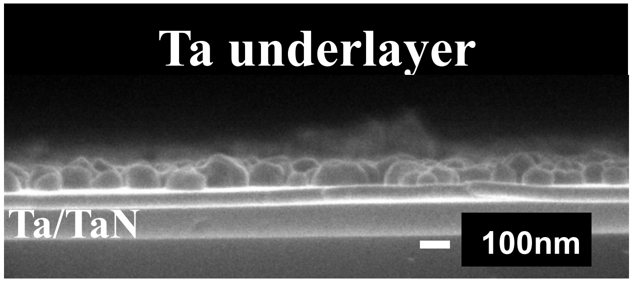
ALD Cu on Glass (185°C)

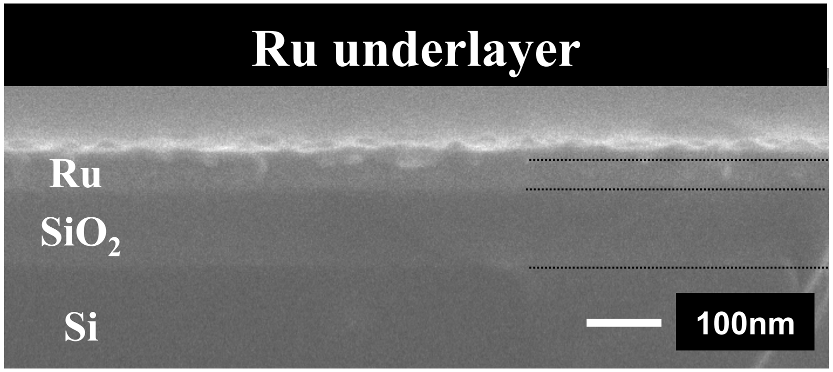


Z. Li, R. G. Gordon, D. F. Farmer, Y. Lin, and J. Vlassak, *Electrochem. Solid-State Lett.,* **8** (7) G182-G185 (2005)

Cu Seed Layer Using CVD-CuON and Plasma Reduction

- Copper seed layers must have conformal step coverage, strong adhesion and <u>smooth surface morphology</u>





- Island growth of CVD-Cu on Ta underlayer
- Cu has fairly high wettability on Ru, but requires >20nm to form a continuous film due to island growth

- New approach:

Cu precursor + $H_2O \rightarrow Cu_2O$
Cu precursor + $NH_3 \rightarrow Cu_3N$

Cu precursor + H_2O + $NH_3 \rightarrow$ CuON

Remote Hydrogen Plasma Reduction near RT

Thin (<10 nm), Smooth (RMS ~1 nm), High Density (95%) CVD Cu Seed Layer

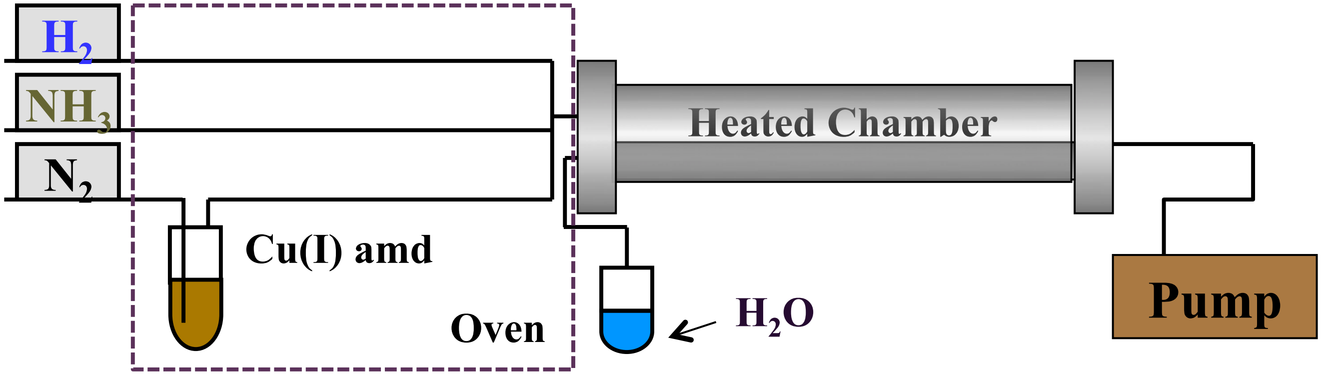
Low Surface Energy (22-26 mJ/m^2 for Cu_2O and Cu_3N, compared to 1700-1900 mJ/m^2 for Cu)

H. Kim, H. B. Bhandari, S. Xu, and R.G. Gordon, *J. Electrochem. Soc.*, **155** (7) H494-H503 (2008).

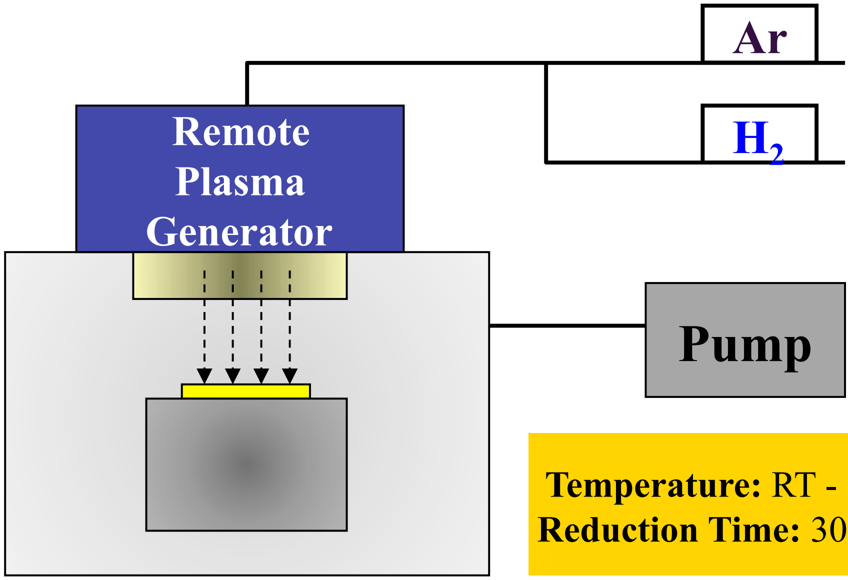
Cu Seed Layer Using CVD-CuON and Plasma Reduction

CVD System

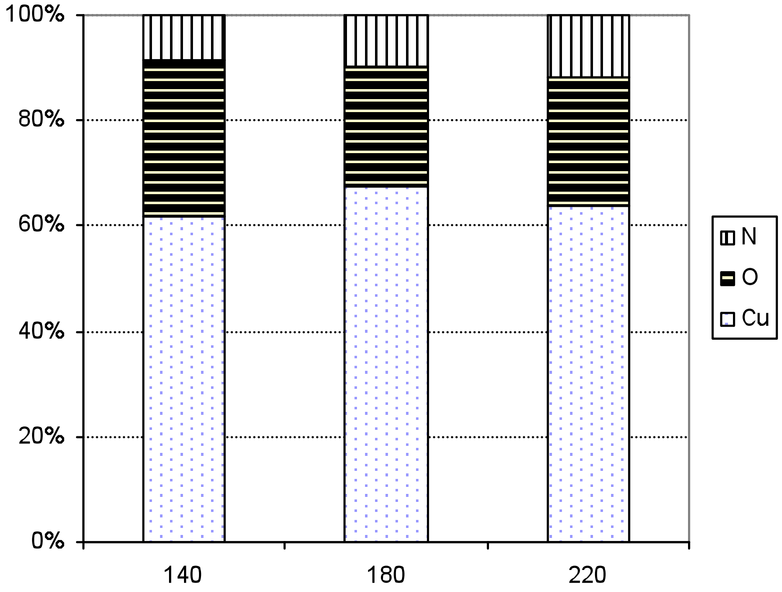
Temperature: 140-220°C
Pressure: 8 Torr



Plasma System



Temperature: RT - 50°C
Reduction Time: 30-180s

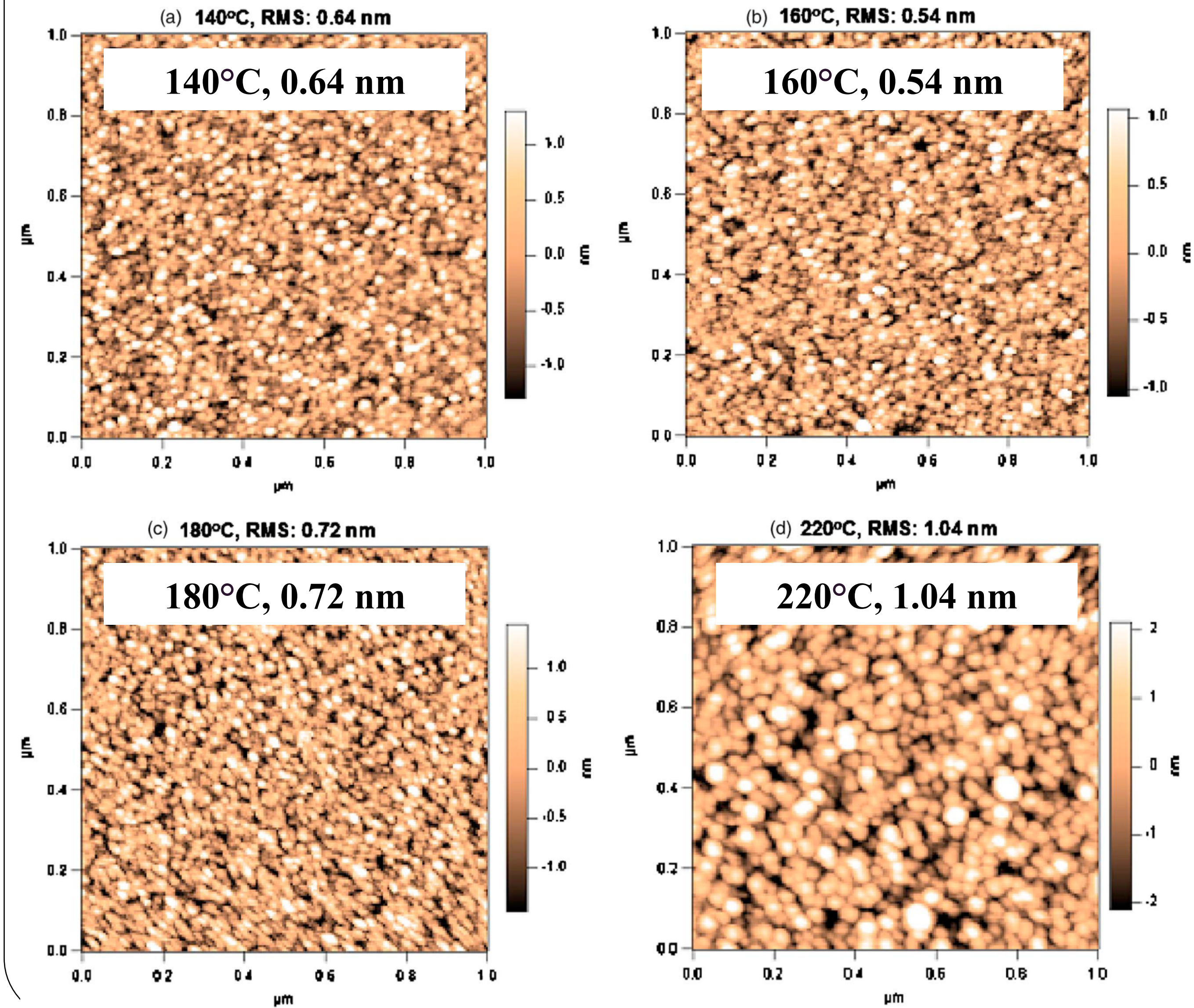


Composition of CVD-CuON Films
($H_2O:NH_3$=30:10)

Cu Seed Layer Using CVD-CuON and Plasma Reduction

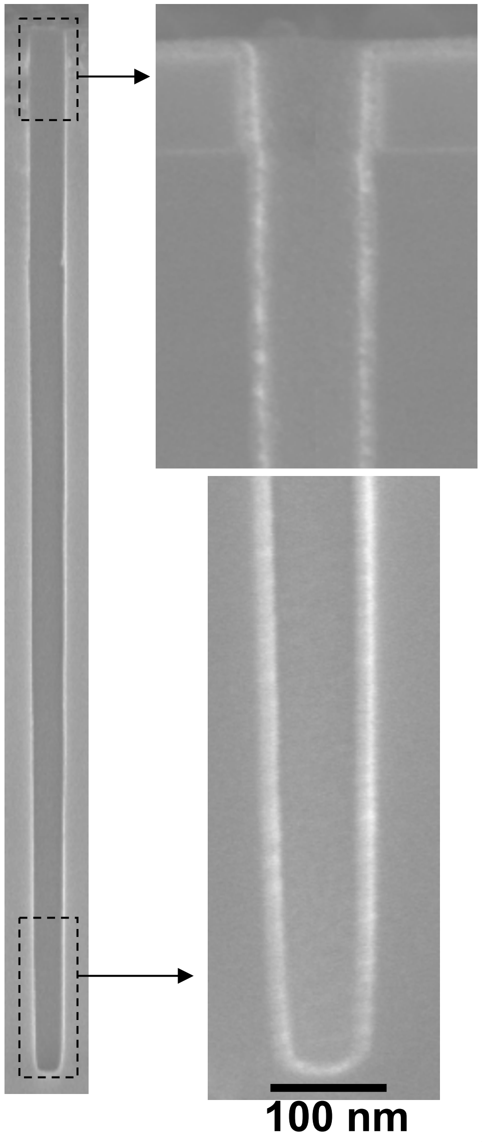
Surface Morphology of 20nm of CVD-CuON Films

($H_2O:NH_3$=30:10)



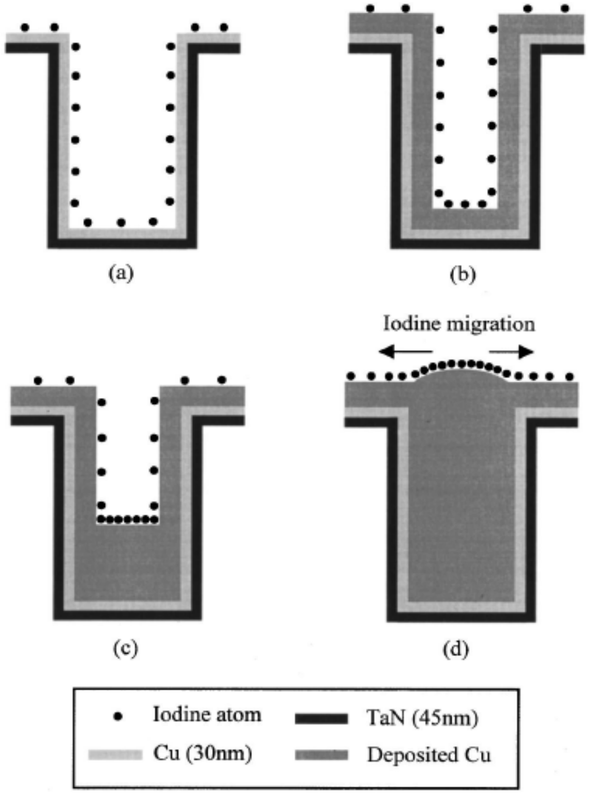
Step Coverage in High AR Holes

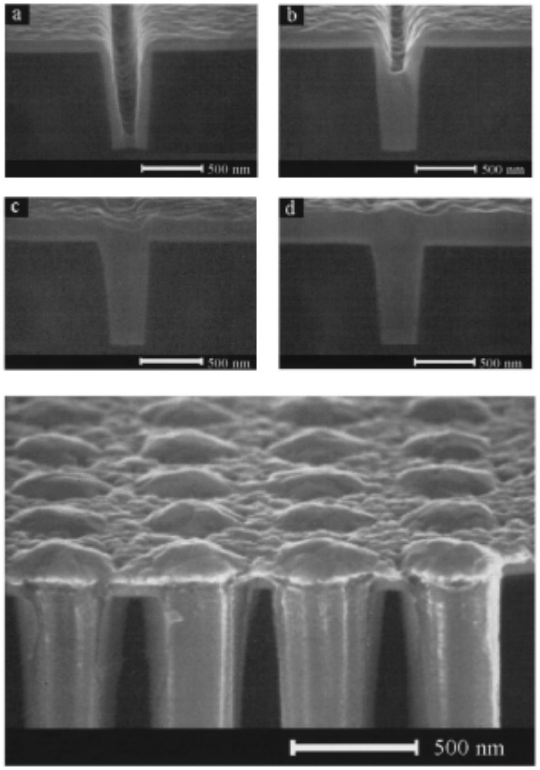
($H_2O:NH_3$=30:10, 140°C)



Filling Narrow Features with CVD of Copper

- Conventional techniques lead to formation of voids and seams in very narrow features
- Iodine is a catalytic surfactant that promotes smoother morphology and higher deposit rate
- Bottom-up filling of sub-micrometer features could be achieved by CVD



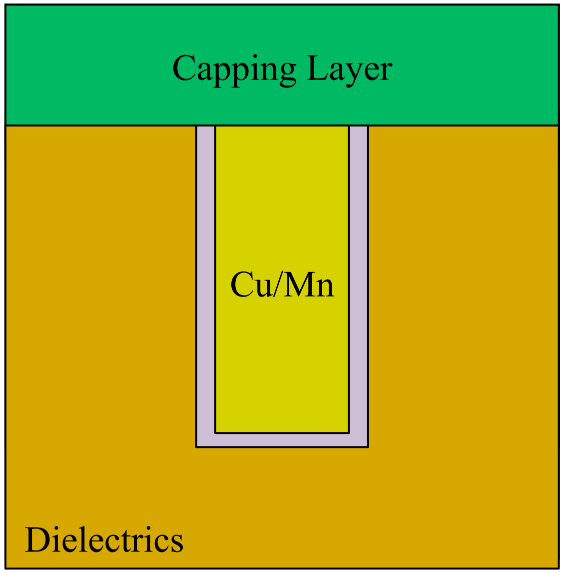


- This process requires a conformal Cu seed layer on top of the diffusion barrier and adhesion layer

E. S. Hwang and J. Lee, *Chem. Mater.*,**12**, 2076 (2000).
K. Shim, O. Kwon, H. Park, W. Koh, and S. Kang, *J. Electrochem. Soc.*, **149** (2) G109-G113 (2002) .

Surfactant Catalyzed CVD Cu and CuMn in Narrow Trenches

Motivation



Key Points

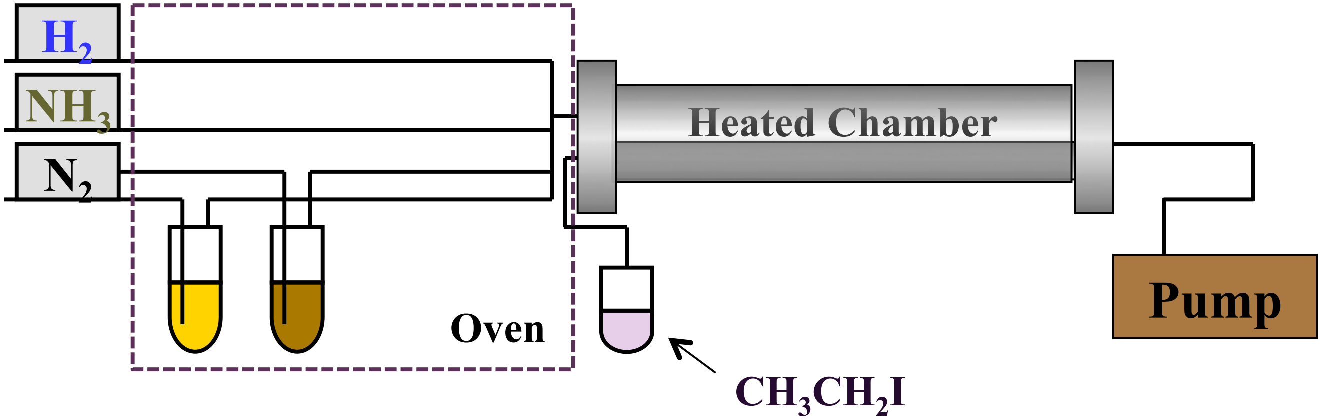
- Conformally deposited manganese nitride serves as a barrier/adhesion layer
- Iodine acts as a surfactant catalyst to promote Cu and Mn growth
- Void-free, bottom-up filling of Cu or Cu-Mn alloy in narrow trenches with AR up to at least 5:1
- Mn diffuses out from Cu during post-annealing to further improves adhesion and barrier properties at Cu/insulator interface

Y. Au, Y. Lin and R. G. Gordon, *J. Electrochem. Soc.*, **158** (5) D248-D253 (2011).

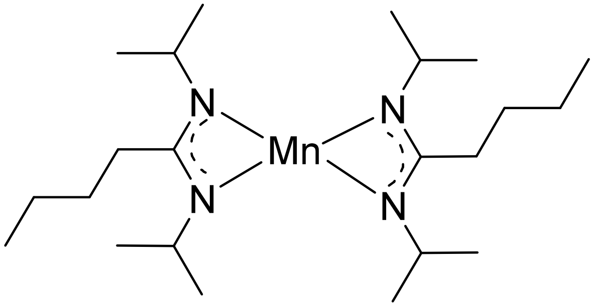
Chemical Vapor Deposition of Copper

CVD System

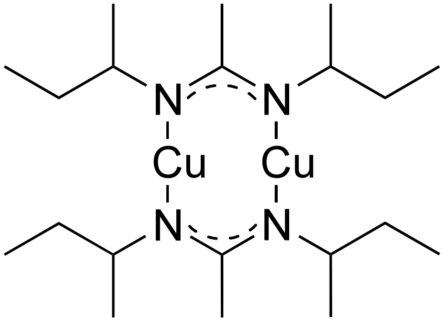
Temperature
130°C for Mn_4N
180°C for Cu and CuMn
Pressure: 5 Torr



Precursors



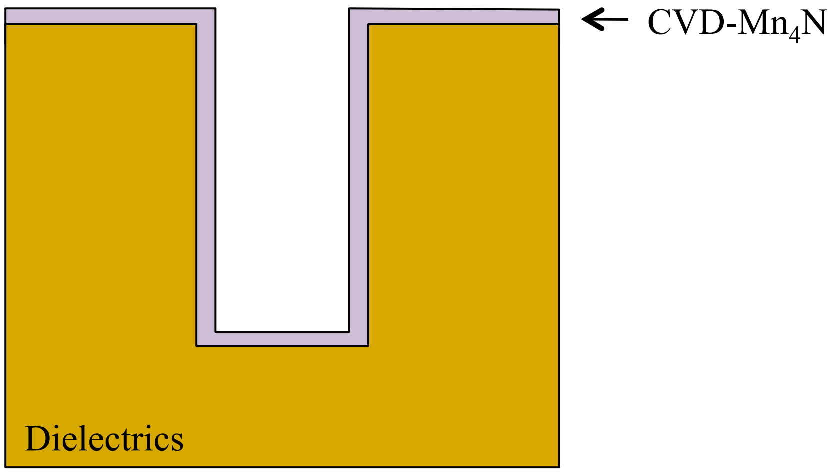
Bis (*N,N'-diisopropylpentylamidinato) manganese(II)*
Melting Point: ~60°C
Bubbler Temperature: 90°C
Vapor Pressure: ~0.1 mbar at 90°C

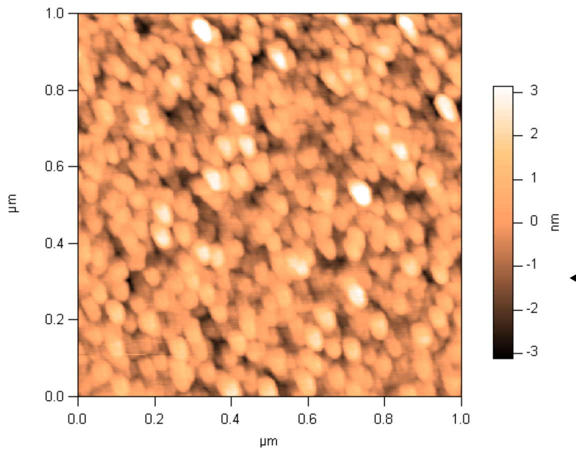


Copper (I) N,N'-di-sec-butylacetamidinate
Melting Point: ~75°C
Bubbler Temperature: 130°C
Vapor Pressure: ~0.25 mbar at 95°C

CVD-Mn_4N Barrier/Adhesion Layer

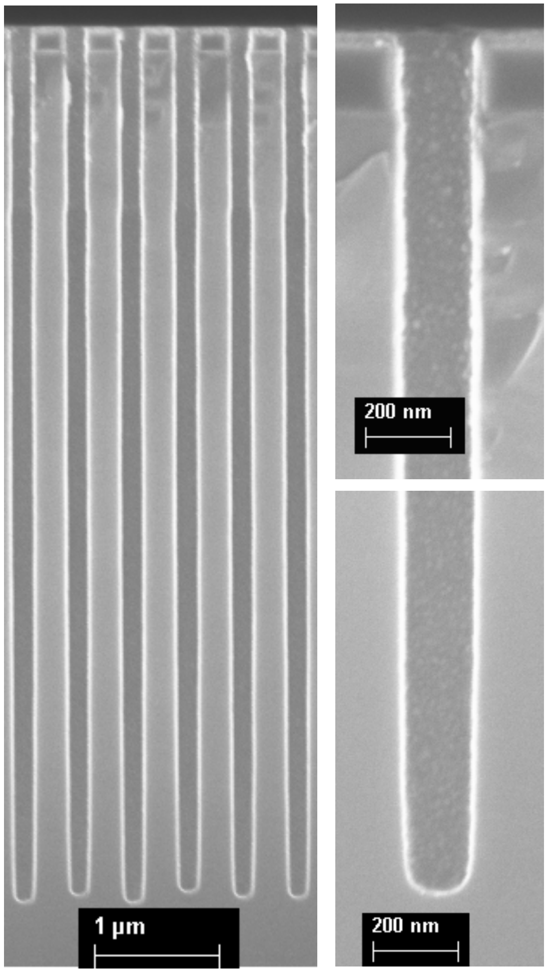
- CVD-Mn_4N (ε phase, FCC structure) can be prepared by reacting manganese amidinate precursors with NH_3





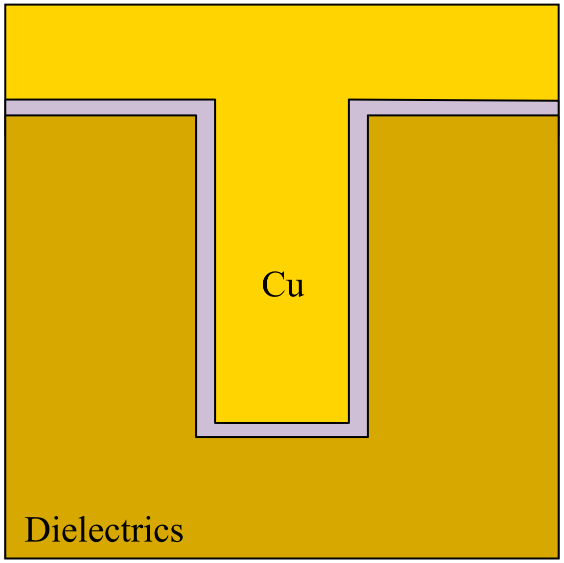
RMS roughness = 0.97 nm for a 13.5 nm film

Excellent step coverage holes with AR = 52:1

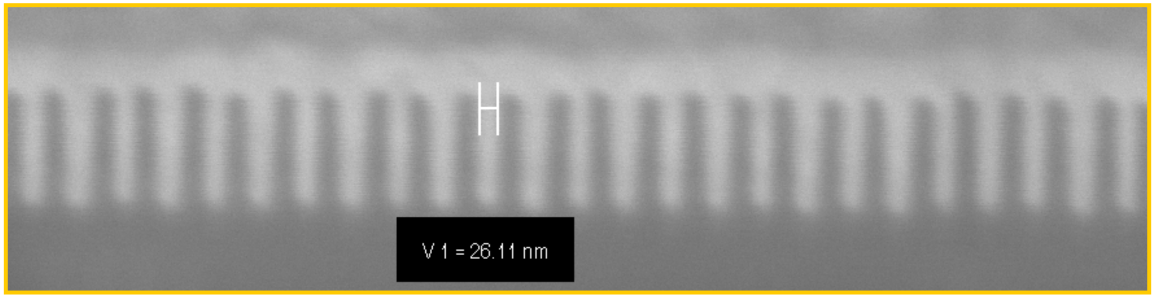


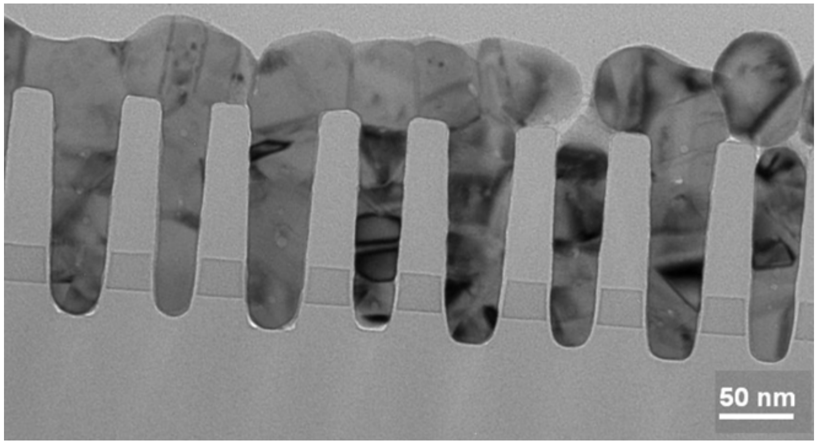
- Mn_4N layer as thin as 2.5 nm (1) shows barrier properties against Cu diffusion, (2) significantly improve adhesion (debonding energy = 6.5 J/m^2) between Cu and SiO_2
- Release of iodine and catalytic effects are observed on Mn_4N underlayer

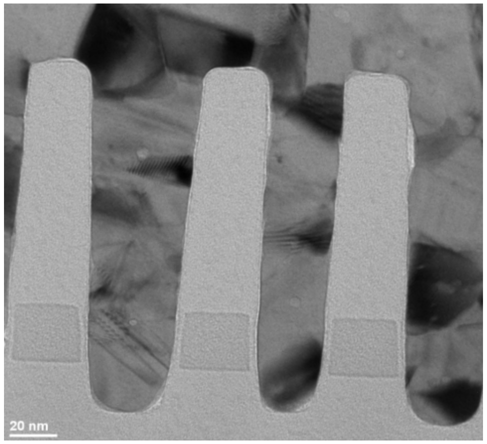
Surfactant Catalyzed Bottom-up Filling of CVD-Cu



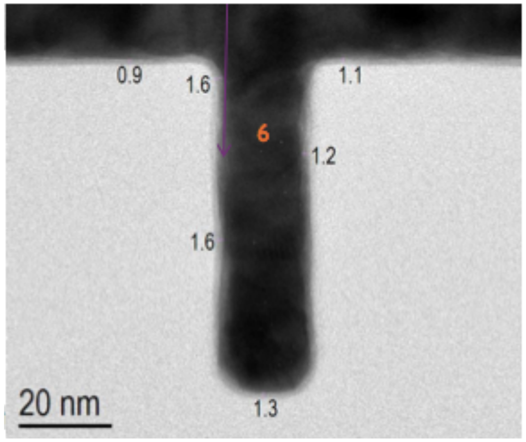
CVD-Mn_4N Deposition → Iodine Exposure → CVD-Cu Deposition







26 nm Structure



18 nm Structure

With CVD-Mn_4N liner layer and iodine catalyst, trenches with width ≤ 20 nm and aspect ratio over 5:1 can be completely filled with CVD-Cu

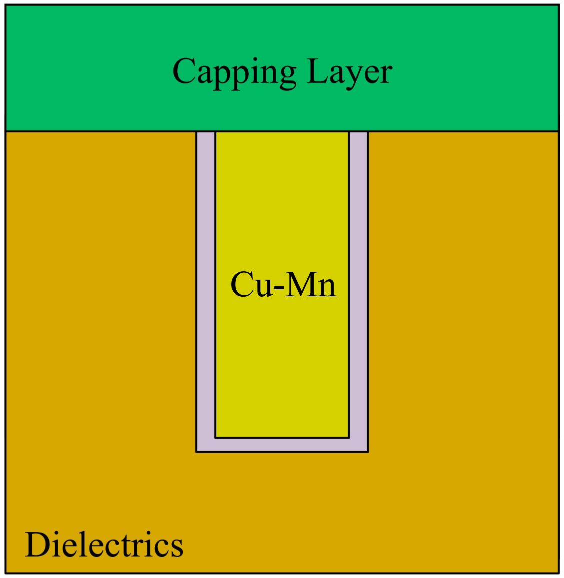
Surfactant Catalyzed Bottom-up Filling of CVD-CuMn Alloy

- Cu-Mn alloy can be formed by (1) alternating CVD-Cu and Mn or (2) co-depositing Cu and Mn

CVD-Mn_4N Deposition

Iodine Exposure

CVD-CuMn Alloy

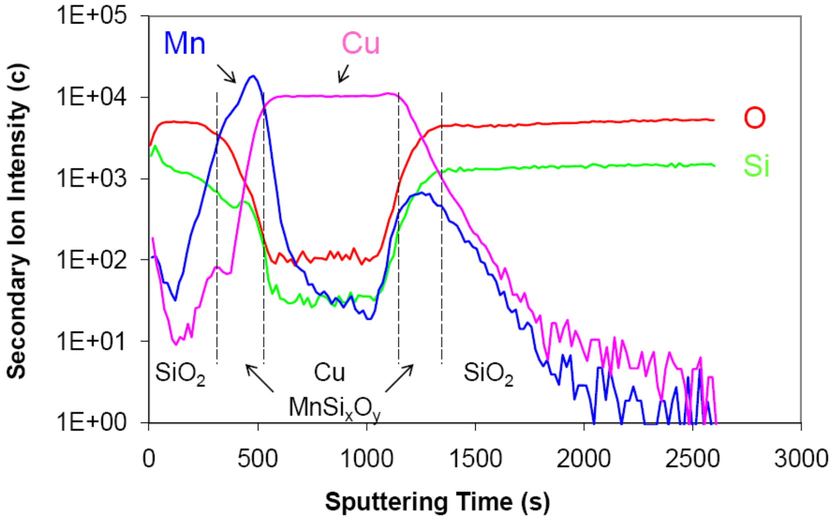


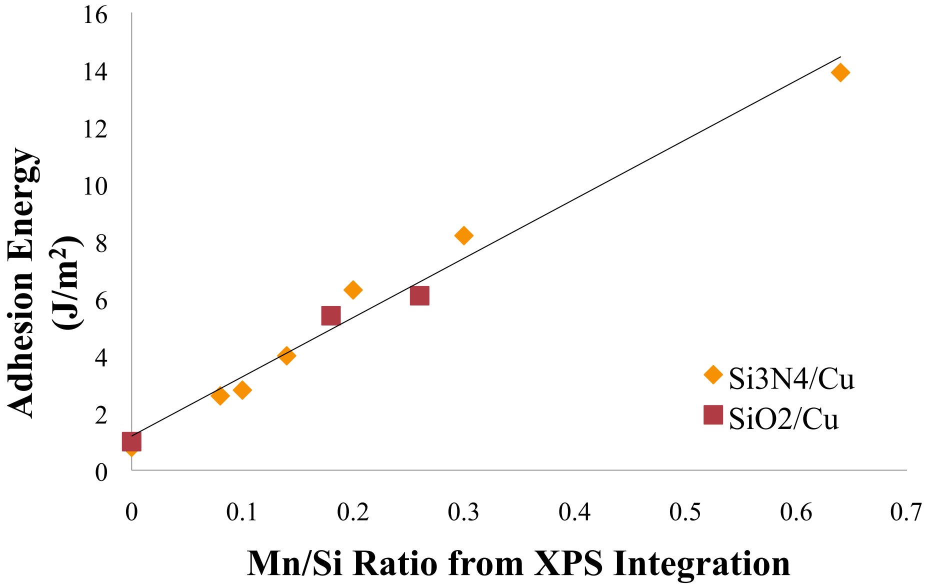
Trenches with width ≤ 30 nm can be completely filled with CuMn alloy

Manganese concentration: 0.5-2.0 atomic %

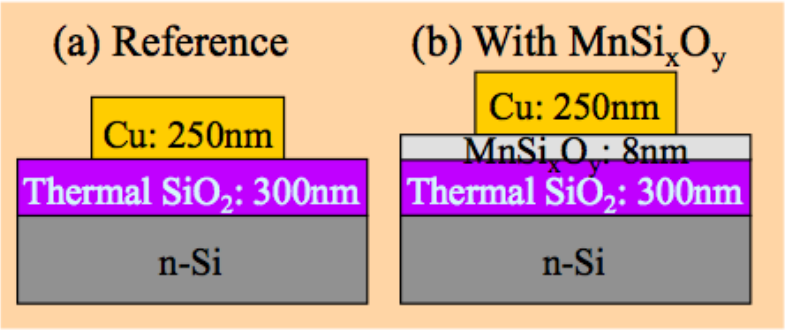
Enhancement by Diffusion of Mn from Cu to Interface

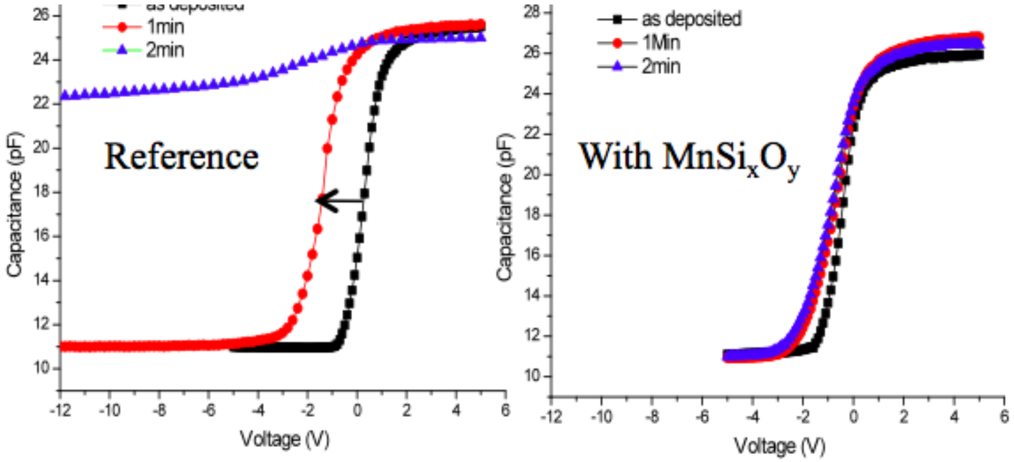
- Insulators encourages diffusion of Mn through Cu grain boundaries to interface
- Mn improves both adhesion and barrier properties at the interface





Cu Diffusion Barrier Test





Y. Au, Y. Lin, H. Kim, E. Beh, Y. Liu and R. G. Gordon, *J. Electrochem. Soc.*, **157** (6) D341-D345 (2010).

Summary

- ✓ Copper can be deposited by ALD or CVD using a Cu(I) amidinate precursor
- ✓ Conformal and uniform seed layers can be prepared by ALD-Cu or by CVD-CuON followed by remote hydrogen plasma reduction
- ✓ Nanoscale trenches can be superconformally filled by CVD-Cu and CVD-CuMn alloy with an iodine surfactant on Mn_4N liner layer
- ✓ Manganese in Cu-Mn alloy diffuses out to strengthen the interface between Cu and insulators without increasing the resistivity of Cu
- ✓ Manganese silicate ($MnSi_xO_y$) interfacial layer shows excellent barrier properties against Cu diffusion and protects Cu from corrosion by H_2O and O_2

Acknowledgements

- Facilities at Harvard's Center for Nanoscale Systems (CNS), a member of the National Nanotechnology Infrastructure Network (NNIN), supported by the National Science Foundation

- Precursors: Dow Chemical Company
  Substrates and Analyses: Applied Materials, IMEC and IBM

- Members of Gordon Group