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Vapor Deposition of Highly Conformal Copper Seed Layers for Plating through-Silicon Vias (TSVs)

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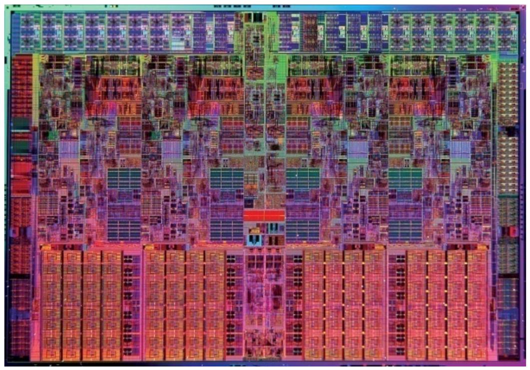
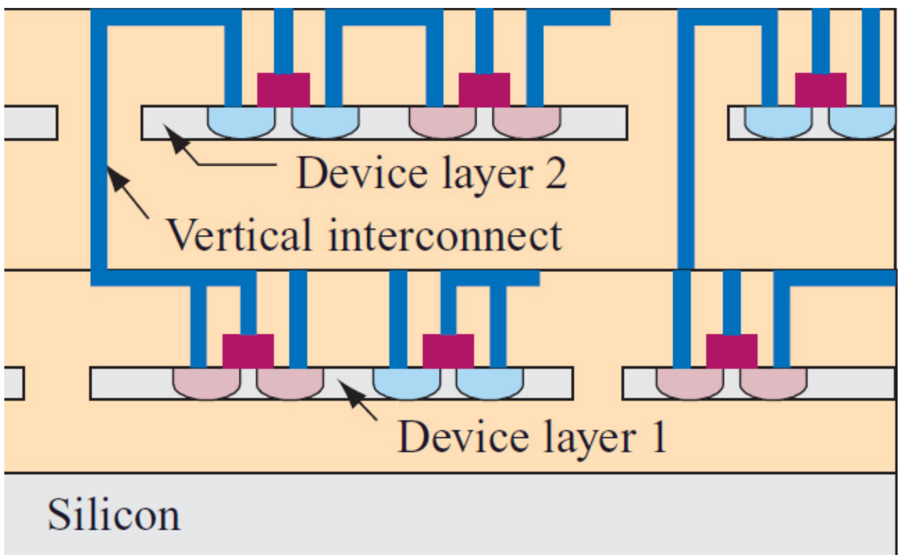
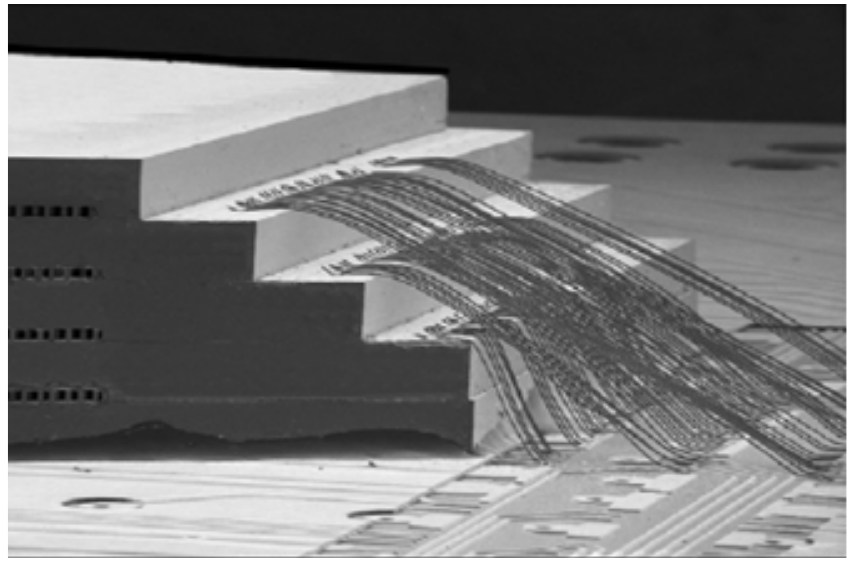
Introduction

- IC integration has traditionally been done using 2D approaches
- More efficient and compact packages with greater integration flexibility can be achieved by vertical (3D) integration





3D Integration



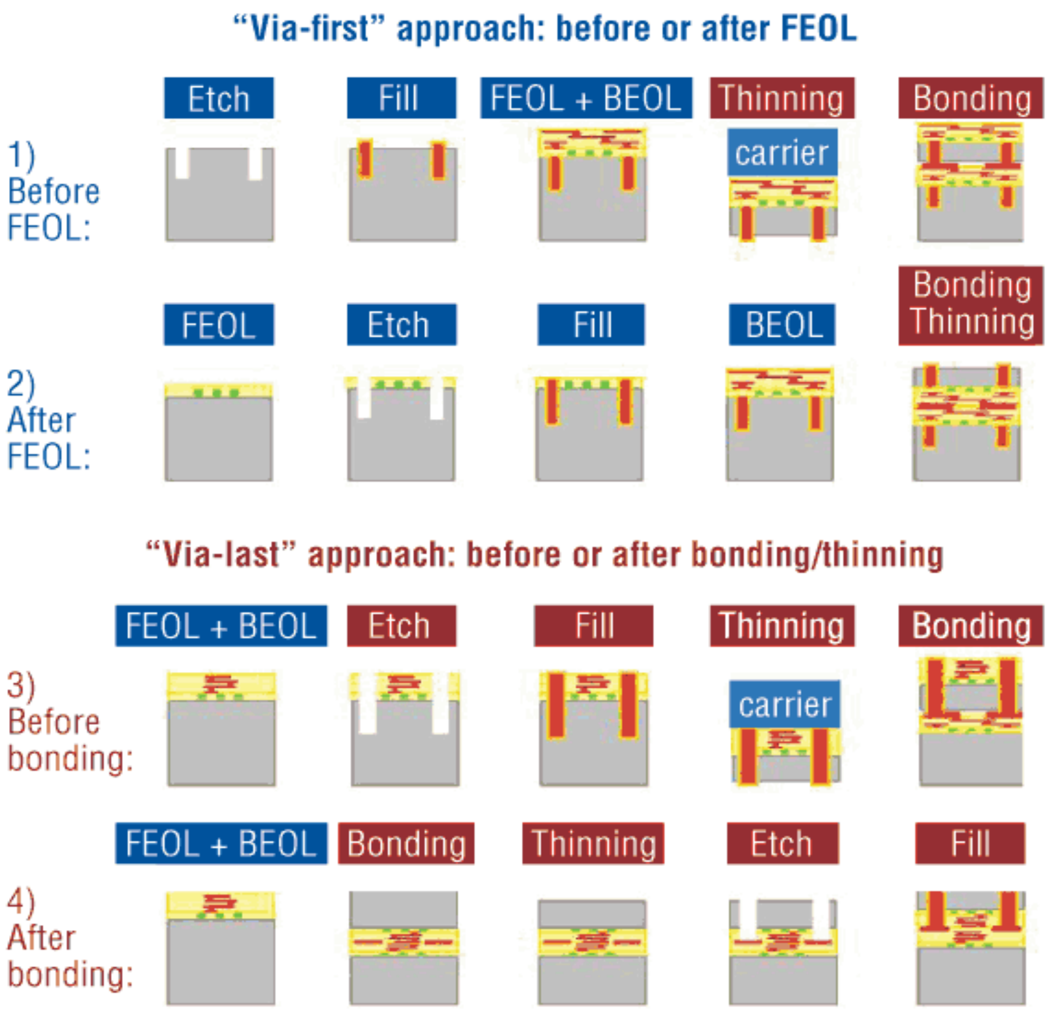
3D Wire Bonding

Limitations of wire bonding

- Long connection
- Excess resistance
- Not scalable

Introduction

- Through-silicon vias (TSV) enable the formation of higher density and higher aspect ratio connections, allowing better packing density than traditional 3D methods



Main Process Steps

- Via etching in Si
- Insulator deposition
- **Barrier deposition**
- **Copper seed layer deposition**
- Via filling
- Surface copper removal
- Wafer thinning
- Wafer alignment, bonding, and dicing

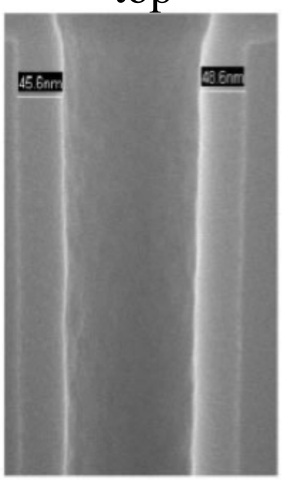
- The 2009 ITRS roadmap calls for copper vias with AR of 10:1 by 2012 and 20:1 by 2015

Introduction

- Rapid atomic layer deposition (ALD) of alumina-doped silica insulating layer
- Chemical vapor deposition (CVD) of manganese nitride barrier/adhesion layer
- ALD of copper seed layer, or
- Direct liquid injection (DLI) CVD of copper manganese alloy seed layer

SiO_2(Al)

top



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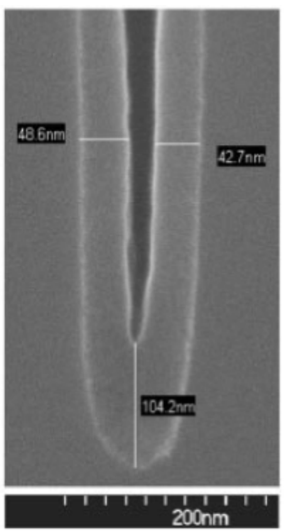
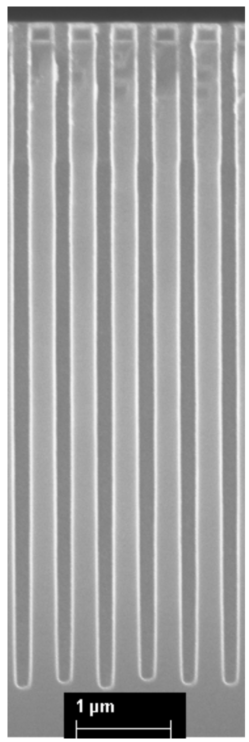
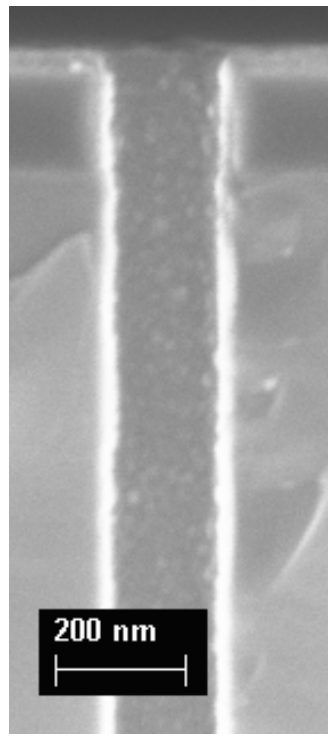


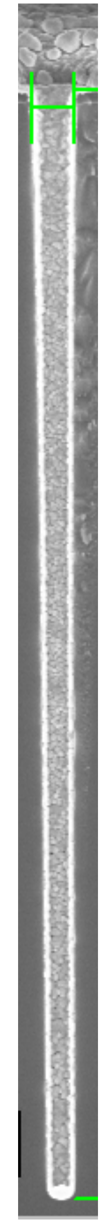
Mn_4N





CuMn

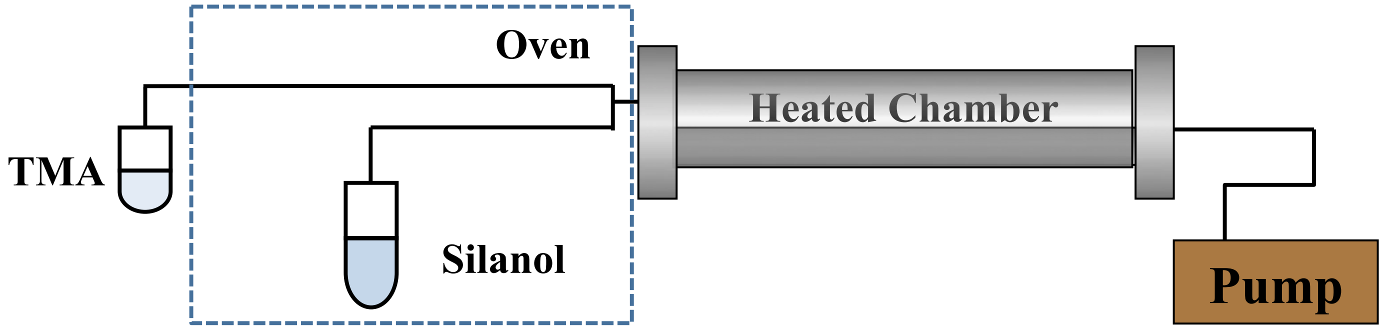
in vias with very high aspect ratios > 25:1



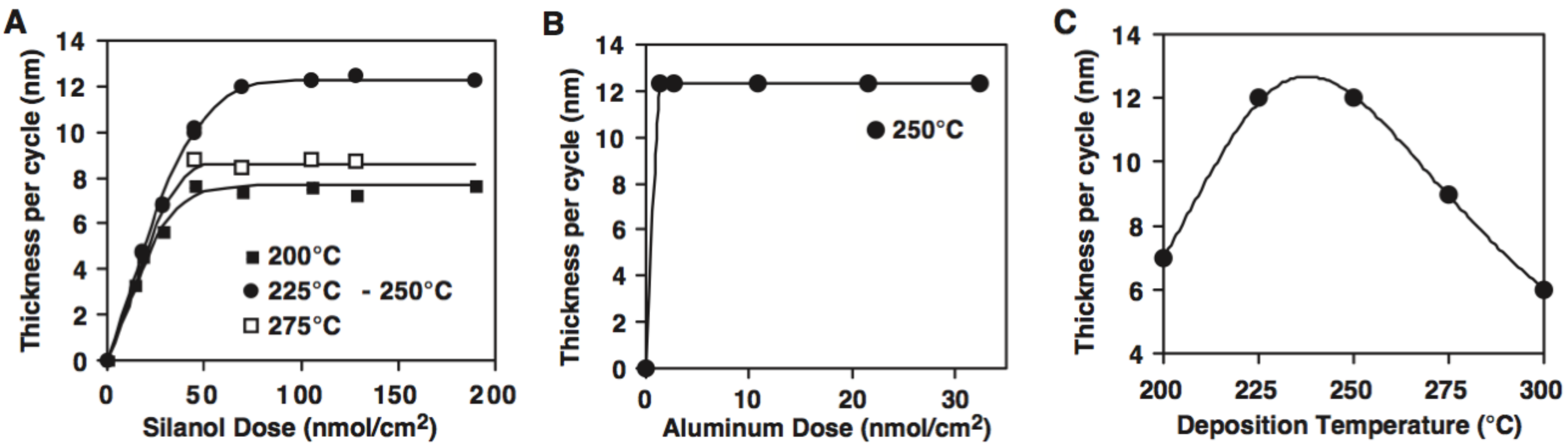
ALD of Aluminum-doped Silica

- Highly conformal silica film can be deposited using trimethyl aluminum (TMA) and tris(*tert*-butoxy) silanol [$(Bu^tO)_3SiOH$]

ALD System



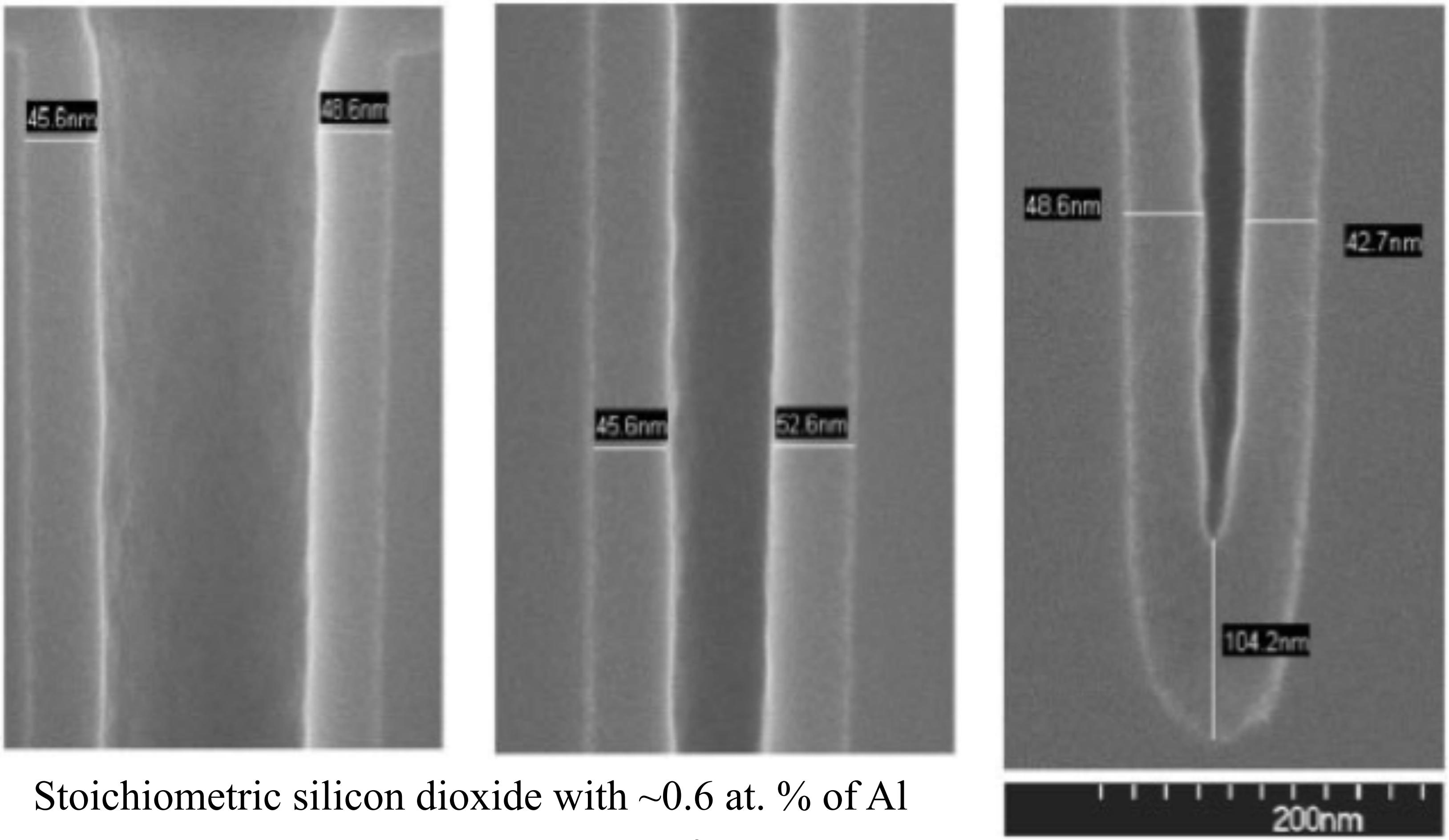
- Saturation behavior and temperature dependence of growth rate:



D. Hausmann, J. Becker, S. Wang, and R. G. Gordon, *Science*, **298** 402-406 (2002)

ALD of Aluminum-doped Silica

- ALD-silica process allows uniform lining of long narrow holes, aspect ratio > 50:1



- Stoichiometric silicon dioxide with ~0.6 at. % of Al
- Amorphous film with density 2.0 g/cm^3 (~91% of bulk silica)

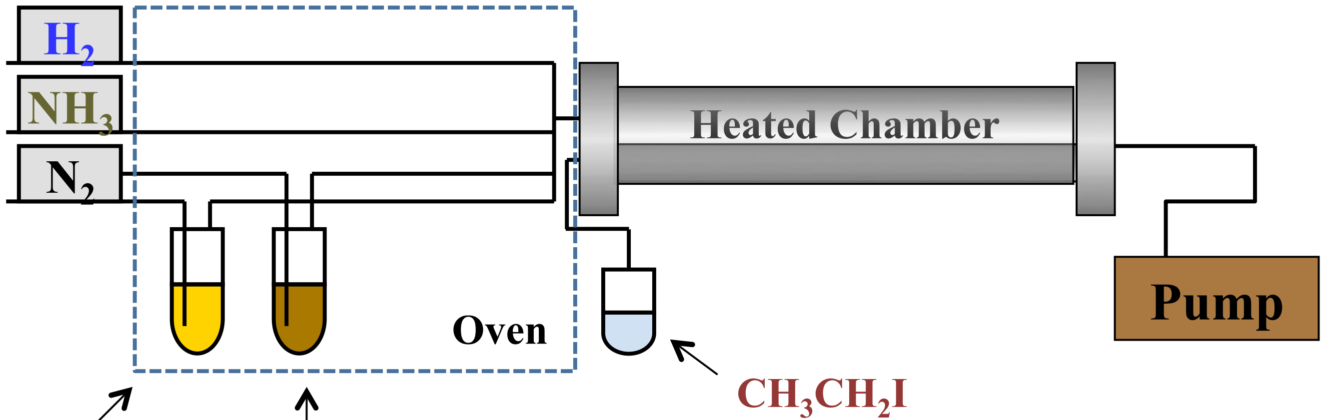
D. Hausmann, J. Becker, S. Wang, and R. G. Gordon, *Science*, **298** 402-406 (2002)

Highly conformal silica insulating film can be deposited using rapid (up to 12 nm/cycle) **ALD in vias with AR over 50:1**

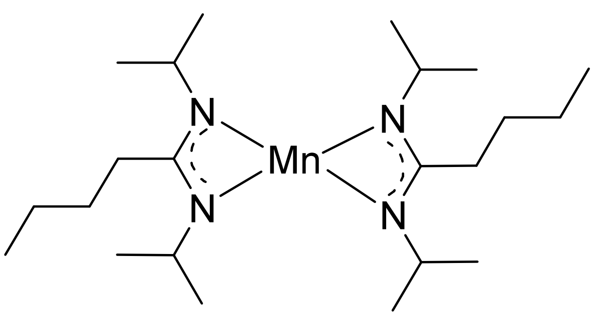
CVD of Manganese Nitride

CVD System

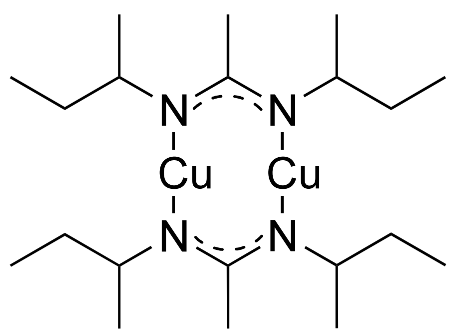
Temperature: 130°C
Pressure: 5 Torr



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

Advantages of metal amidinate precursors:

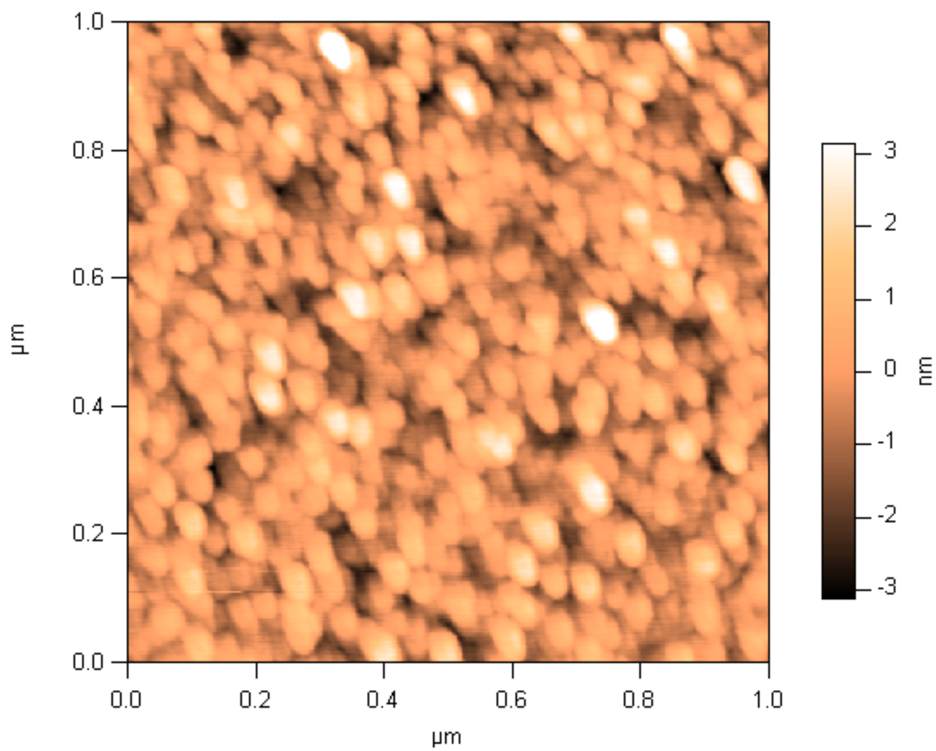
- Chelating effect enhances thermal stability
- Low carbon and oxygen contamination
- Tunable reactivity, volatility, and melting point

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

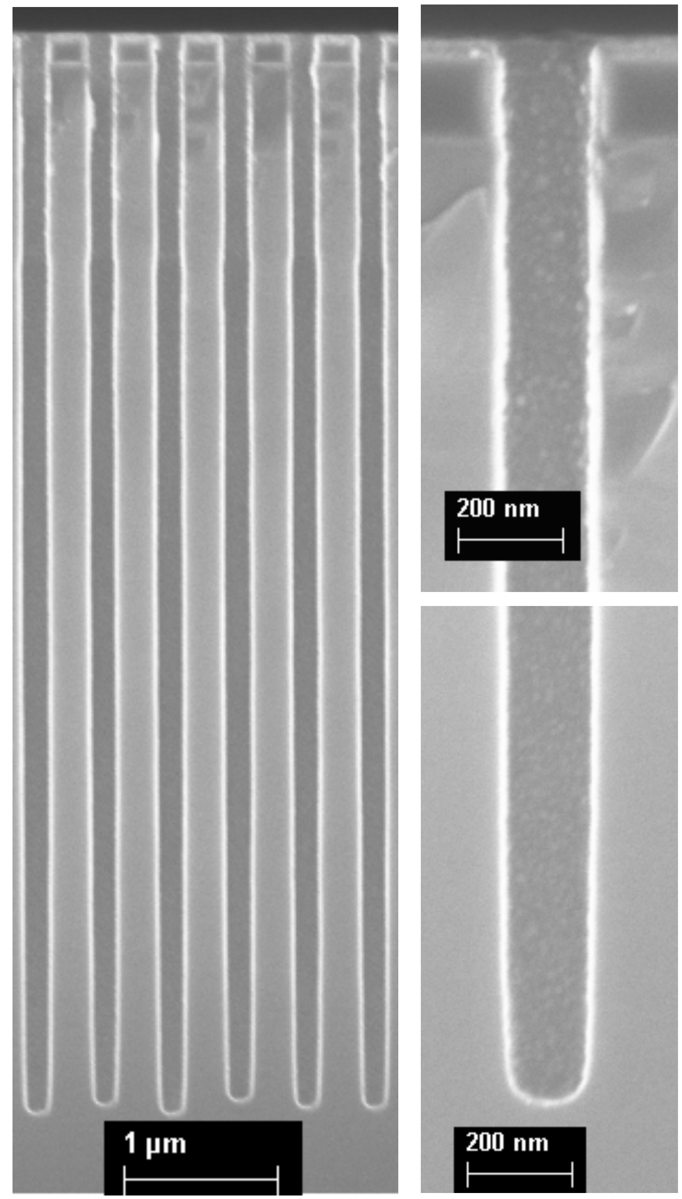
CVD of Manganese Nitride

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

Excellent step coverage holes with AR = 52:1 →



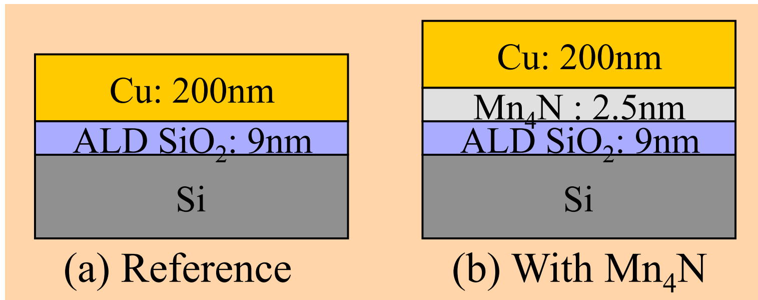
RMS roughness = 0.97 nm for a 13.5 nm film

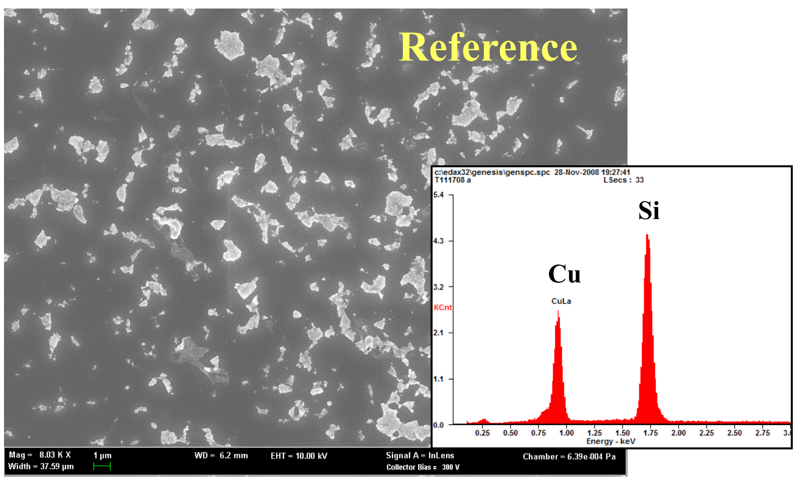


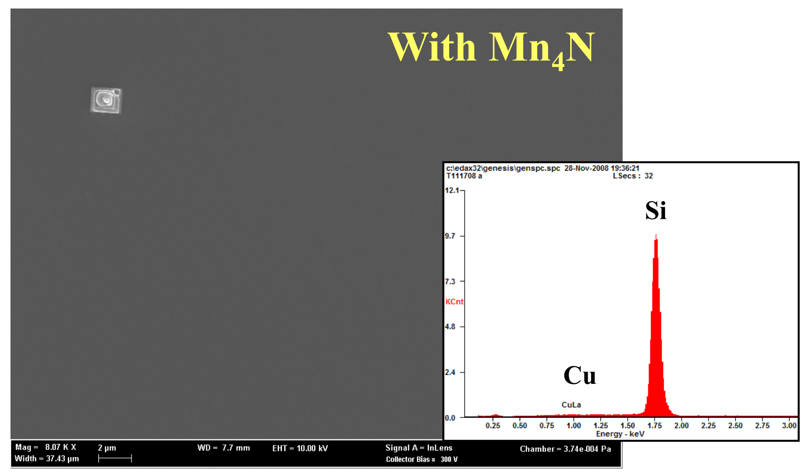
Y. Au, Y. Lin and R. G. Gordon, *J. Electrochem. Soc.*, **158** (5) D248-D253 (2011)

CVD of Manganese Nitride

- Mn_4N layer as thin as 2.5 nm can significantly improve adhesion between Cu and SiO_2
- Four point bend: debonding energy = 6.5 J/m^2 (D.E. ≥ 5 J/m^2 to survive CMP)
- Thin Mn_4N layer also shows barrier properties against Cu diffusion



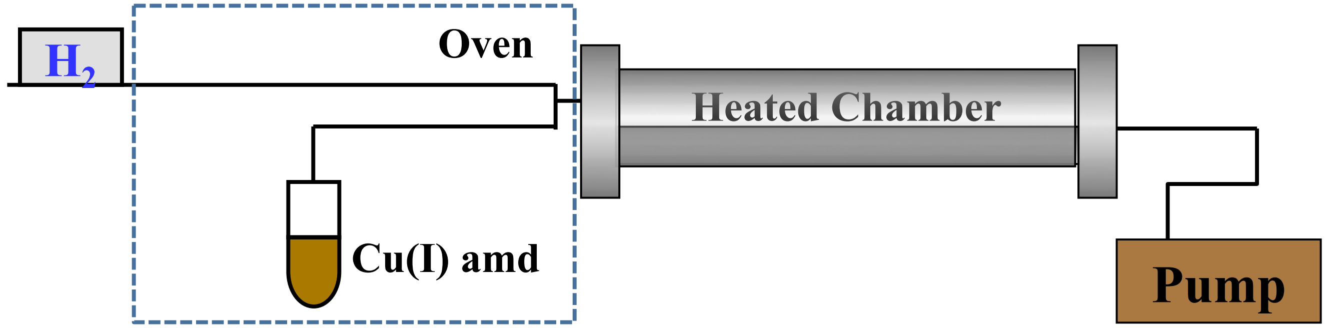




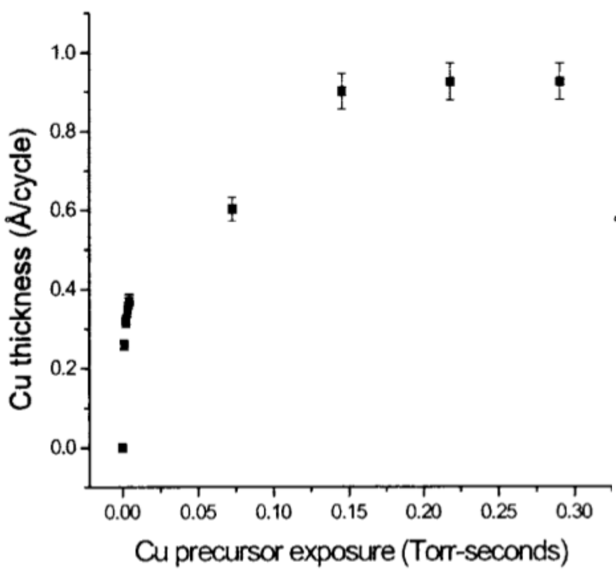
ALD of Copper

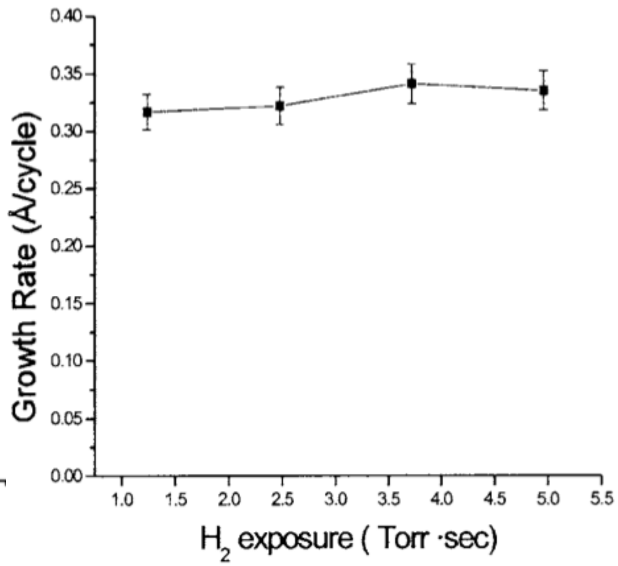
- Copper films could be deposited by ALD using molecular hydrogen as reducing agent

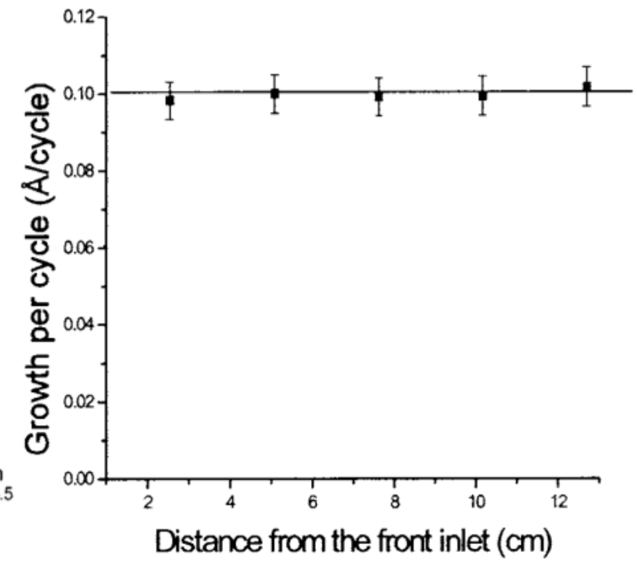
ALD System



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





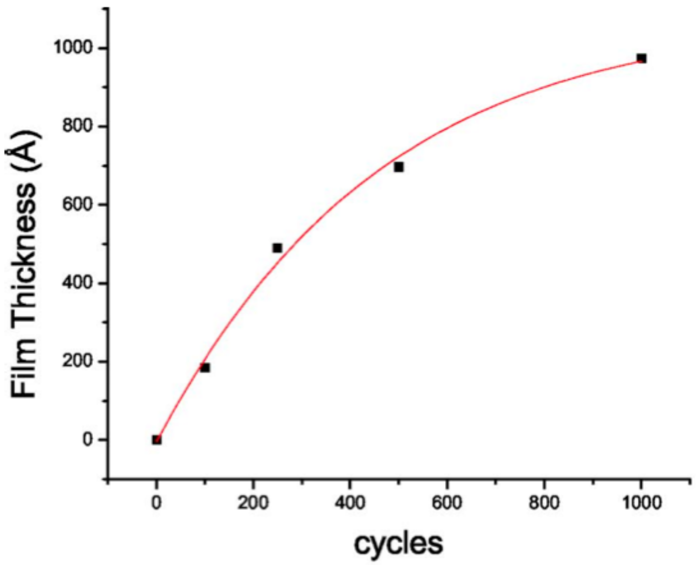


- Slow surface reaction suggests the possibility of highly conformal CVD reactions

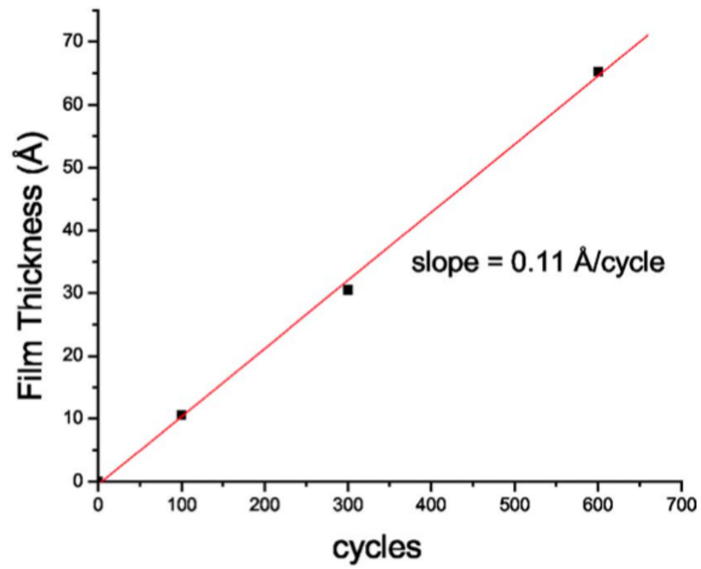
Z. Li, A. Rahtu, and R. G. Gordon, *J. Electrochem. Soc.*, **153** (11) C787-C794 (2006)

ALD of Copper

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

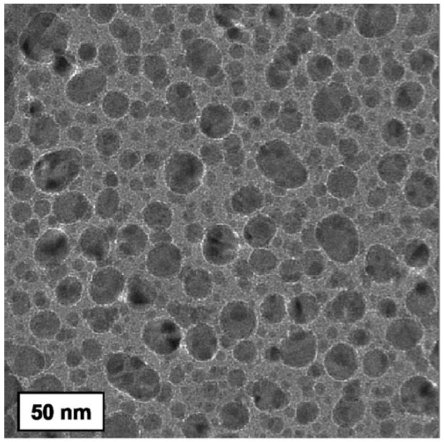


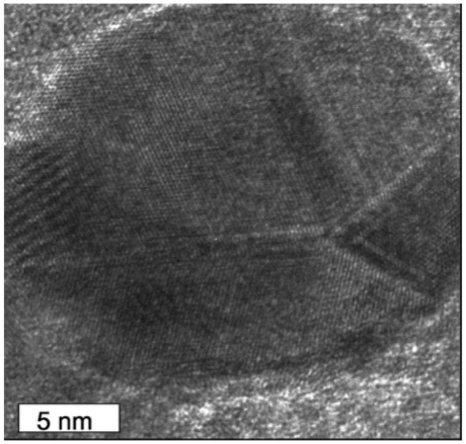
ALD-Al_2O_3, ALD-HfO_2, Thermal SiO_2
Initially ~2Å/cycle, ~0.5Å/cycle when surface is fully covered by Cu



Ru Substrates
0.11Å/cycle

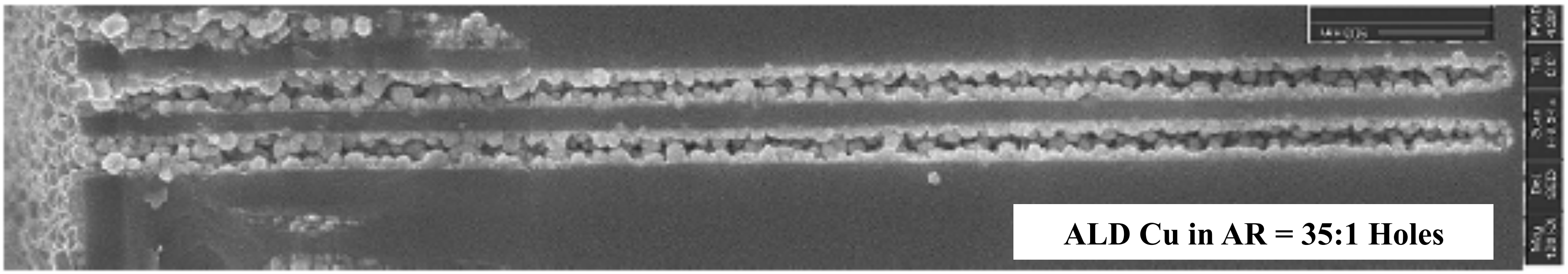
Substrate	Growth per cycle (Å/cycle)
Al_2O_3/SiO_2	1.90 (based on 100 cycles)
Si_3N_4	1.50 (based on 60 cycles)
WN	0.54 (based on 30 cycles)
Ru	0.11 (based on 100 cycles)
Co	0.40 (based on 30 cycles)
Cu	~0.5 (from Al_2O_3 curve)





ALD of Copper

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

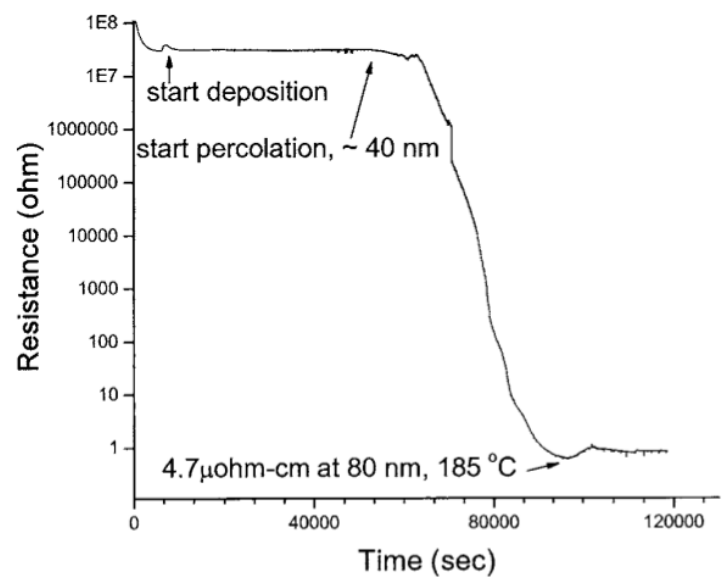


- Four-point bend experiment showed high adhesion energies for $Cu/Co/WN/SiO_2$

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

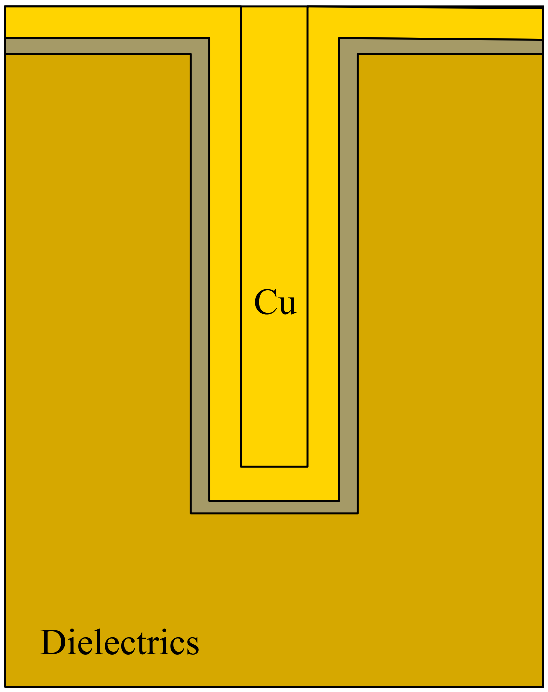
***In-situ* Resistance Measurement**

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)

CVD of Copper Manganese Alloy Seed Layer

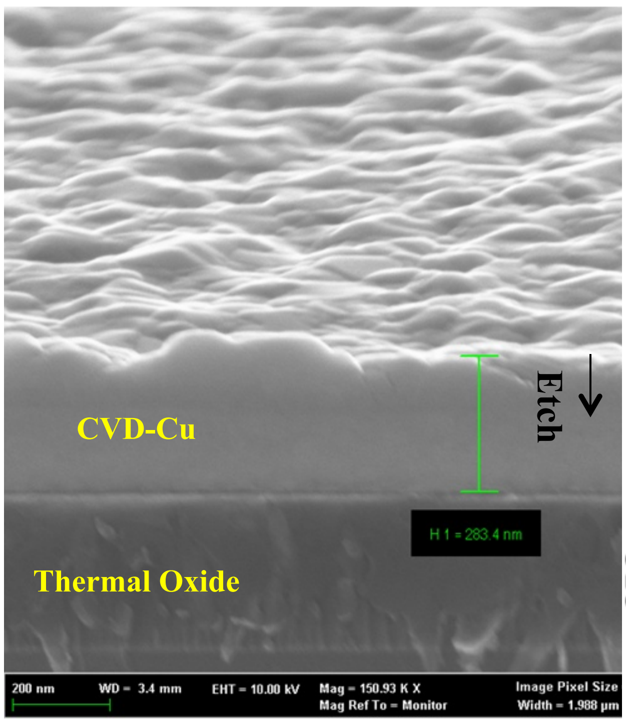


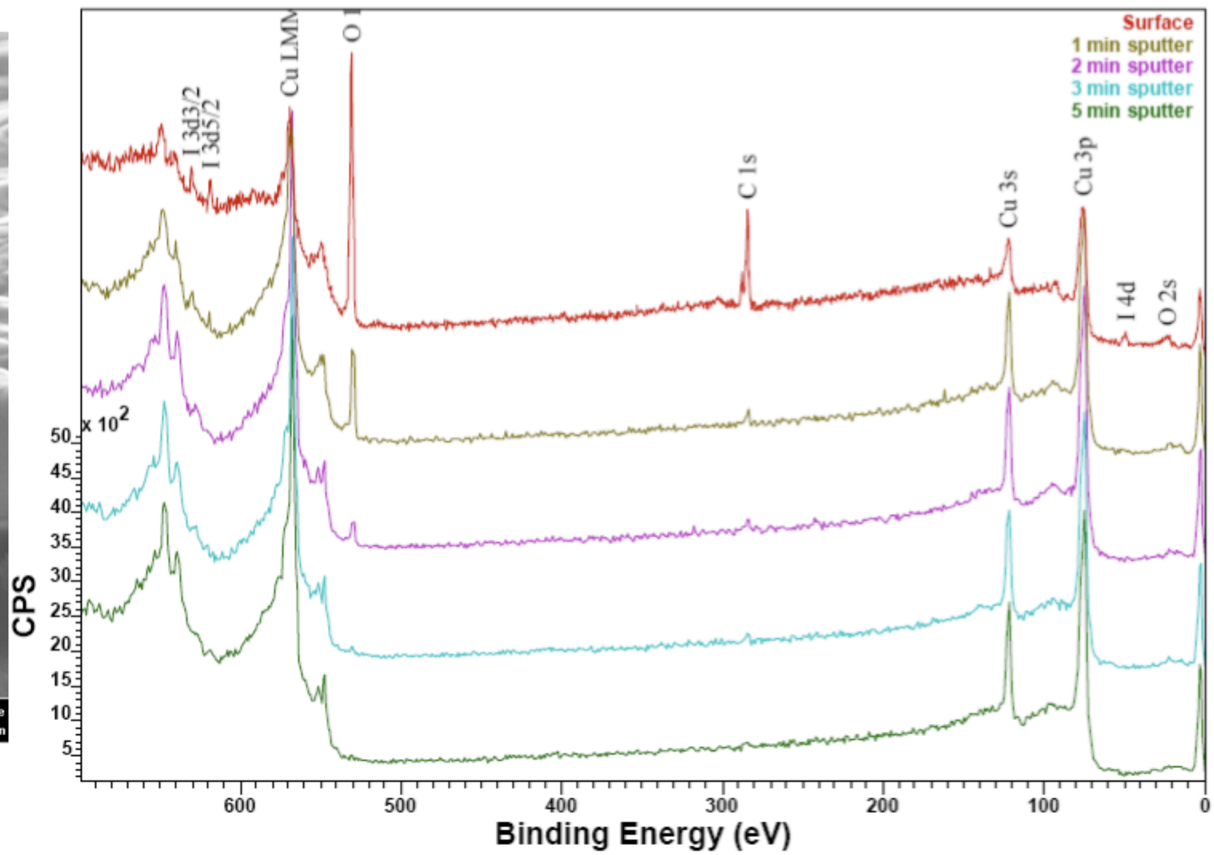
- Conformally deposited silica insulating layer plugs pores and makes clean SiO_2 surface
- Conformally deposited manganese nitride serves as a barrier/adhesion layer
- Iodine acts as a surfactant catalyst to increase Cu growth rate and make a smooth surface
- Conformally deposited copper-manganese alloy seed layer on manganese nitride
- Mn diffuses out from Cu during post-annealing to further improve adhesion and barrier properties at Cu/insulator interface

Y. Au, Y. Lin, H. Kim, E. Beh, Y. Liu and R. G. Gordon, *J. Electrochem. Soc.*, **157** (6) D341-D345 (2010).
Y. Au, Y. Lin and R. G. Gordon, *J. Electrochem. Soc.*, **158** (5) D248-D253 (2011).

Iodine Catalytic Surfactant

- Presence of iodine surfactant catalyst promotes higher (10x) deposition rate and smoother surface morphology
- Iodine is not incorporated into the film

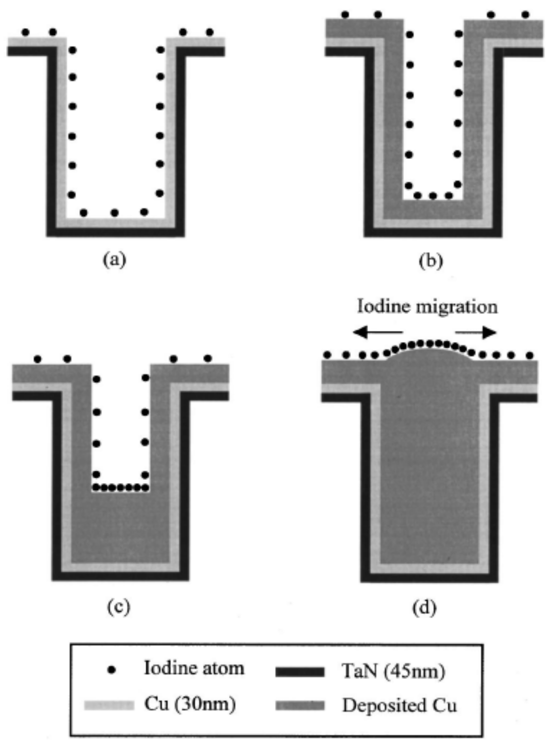


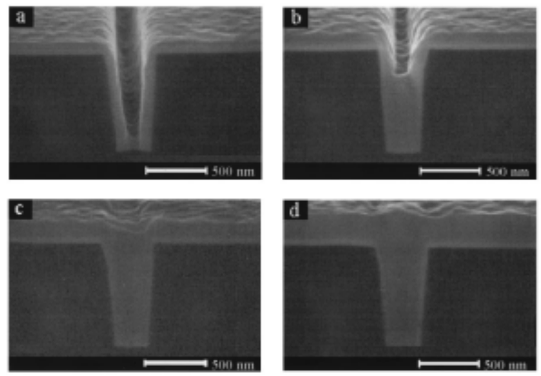


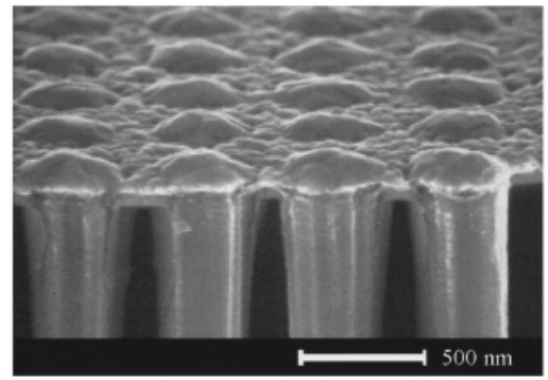
Y. Au, Y. Lin and R. G. Gordon, *J. Electrochem. Soc.*, **158** (5) D248-D253 (2011)

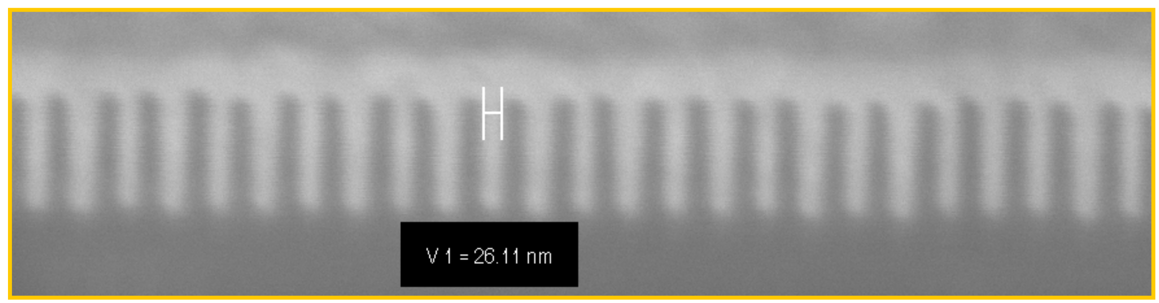
Void-free Bottom-up Filling of CVD-Cu

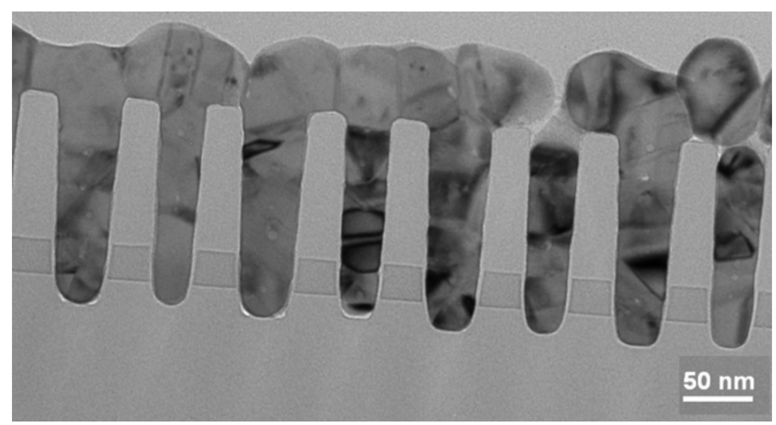
- Bottom-up filling of nanoscale features could be achieved with iodine catalyst









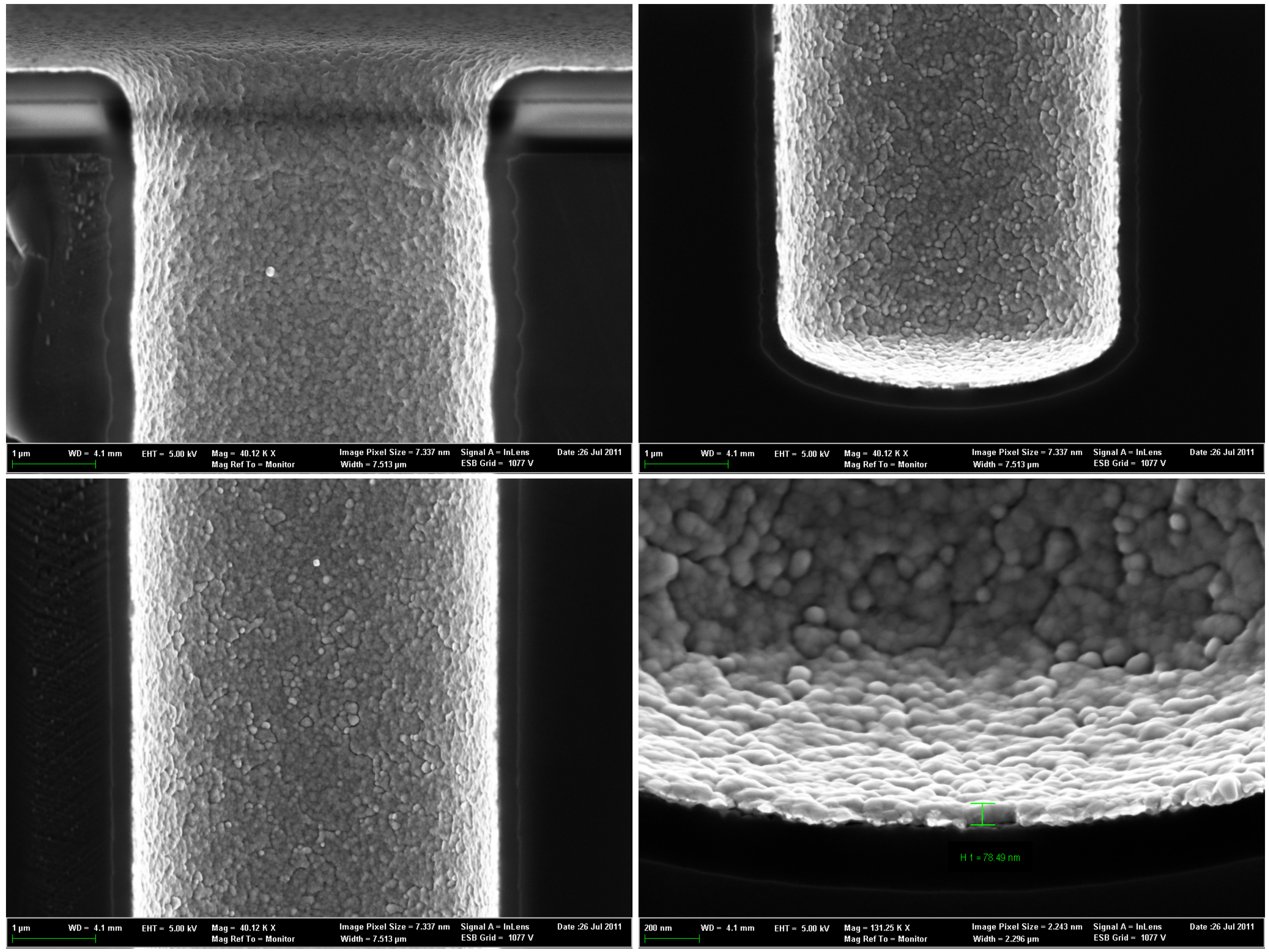


E. S. Hwang and J. Lee, *Chem. Mater.*,**12**, 2076 (2000).
K. Shim, O. Kwon, H. Park, W. Koh, and S. Kang, *J. Electrochem. Soc.*, **149** (2) G109-G113 (2002) .
Y. Au, Y. Lin and R. G. Gordon, *J. Electrochem. Soc.*, **158** (5) D248-D253 (2011).

Formation of Cu Seed Layer in High Aspect Ratio TSVs

CVD-Mn_xN (130°C)	Iodine Exposure (Room Temp.)	CVD-CuMn (180°C)	Post-annealing (350°C)

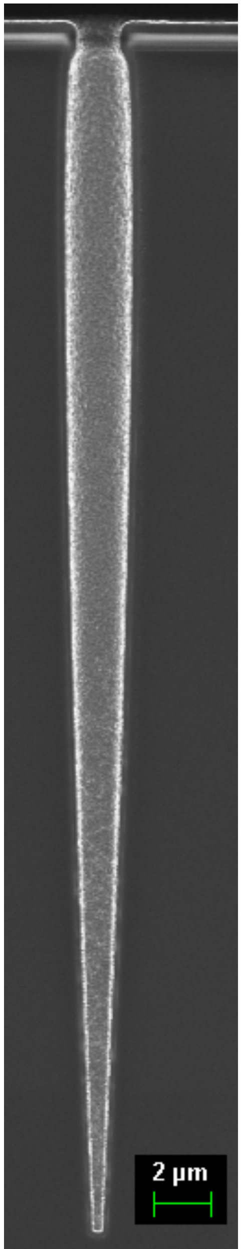
Aspect Ratio = 10:1 TSV (IMEC)

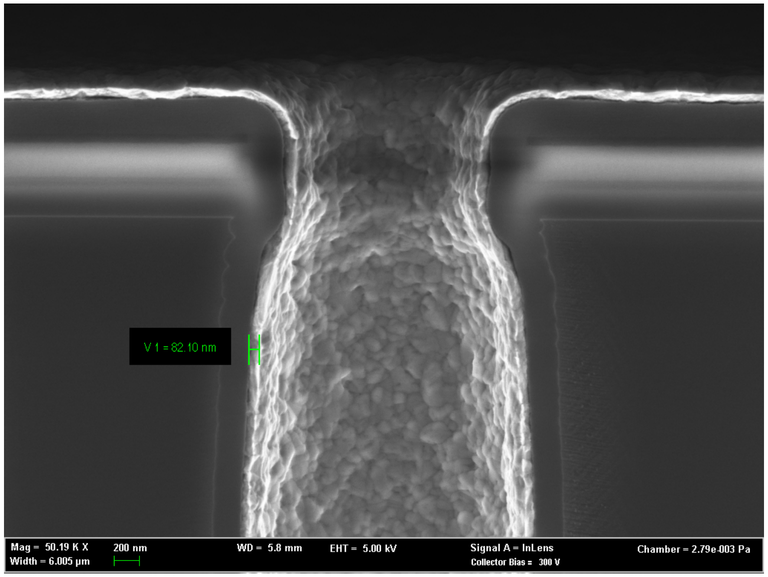


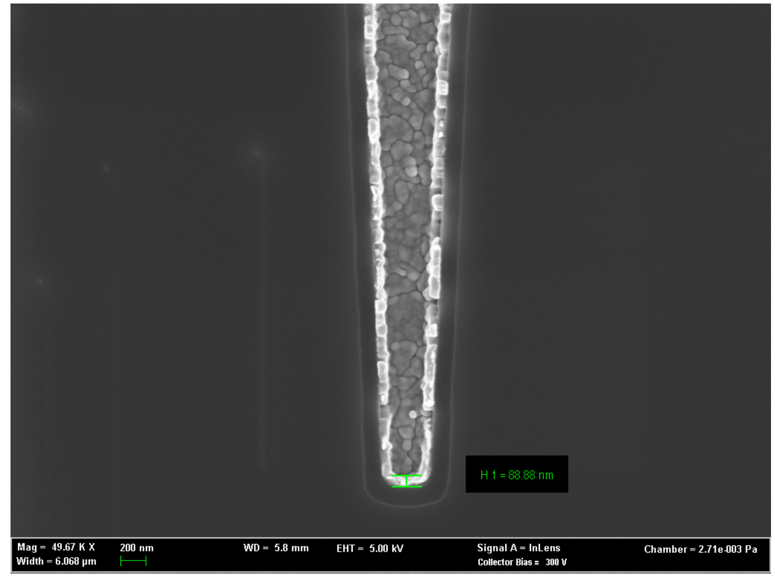
- 70-80 nm of seed layer deposited conformally (~1 atomic % Mn)
- Sheet Resistance = 350-380 mΩ/sq.
- Strong adhesion

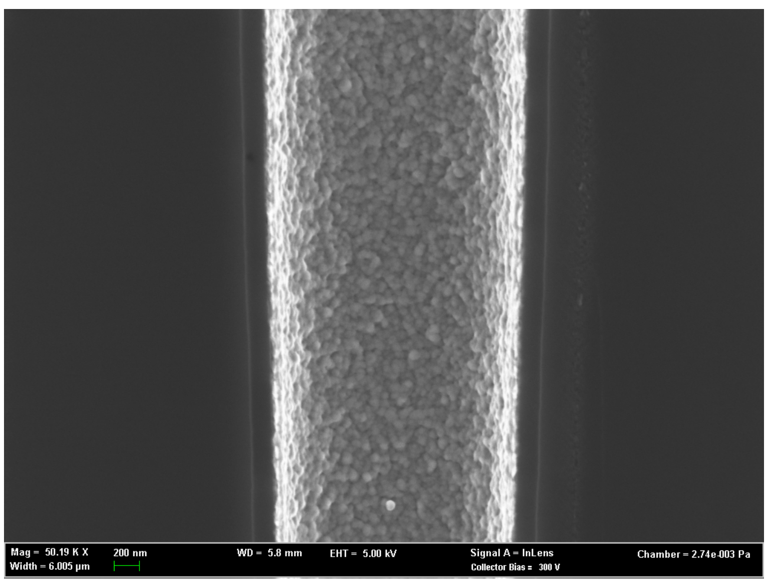
Formation of Cu Seed Layer in High Aspect Ratio TSVs

CVD-Mn_xN (130°C) → **Iodine Exposure (Room Temp.)** → **CVD-CuMn (180°C)** → **Post-annealing (350°C)**







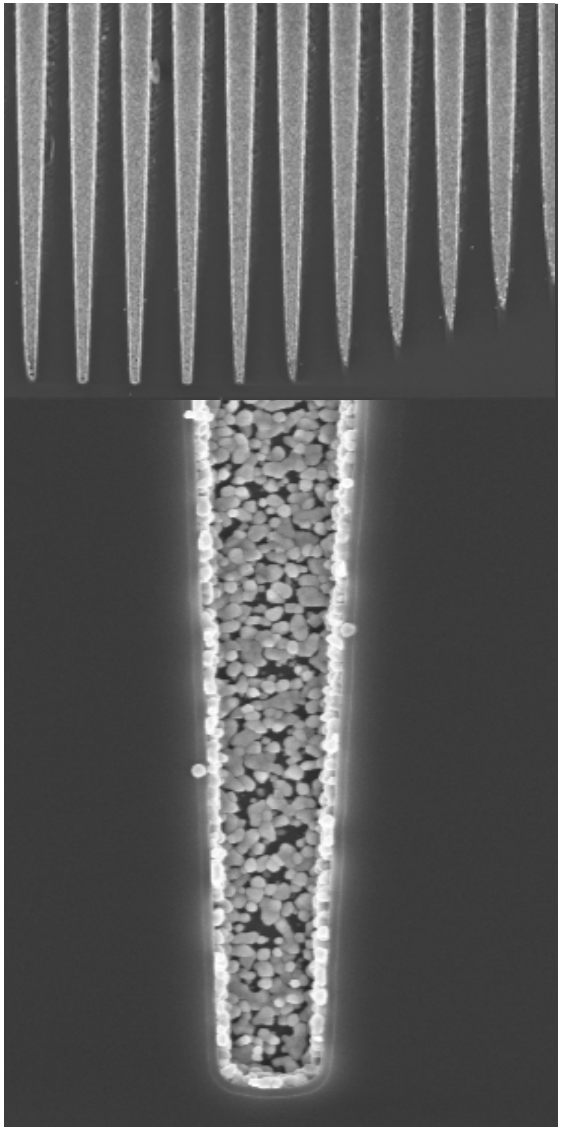


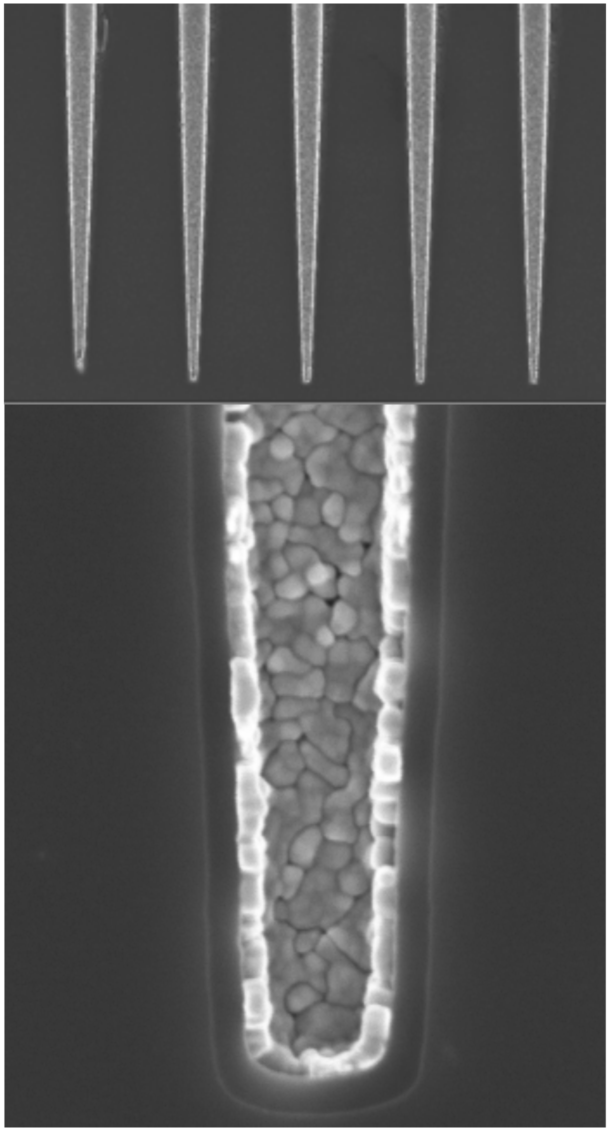
Aspect Ratio = 20:1 TSV (IMEC)

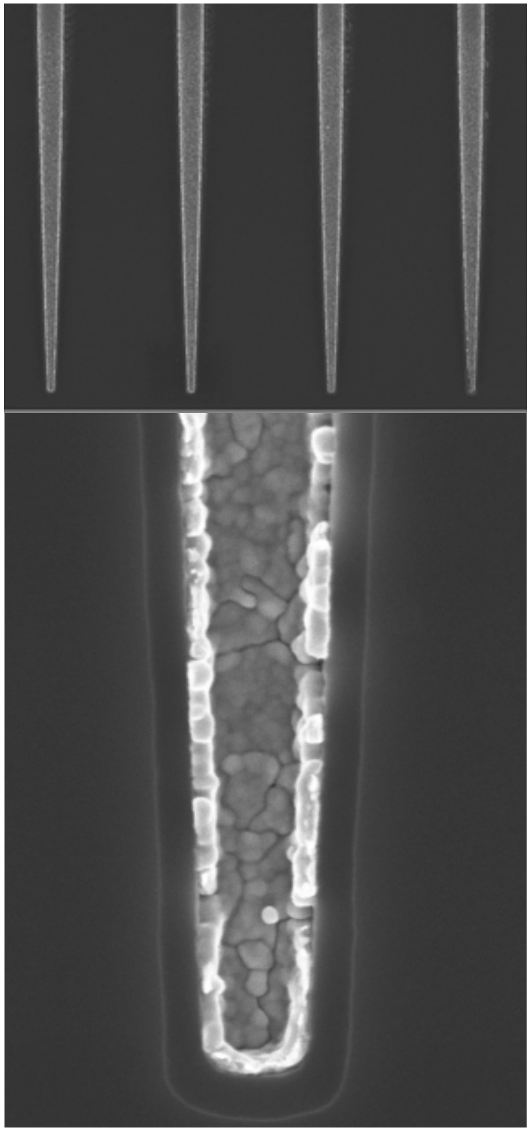
70-80 nm of Seed Layer is Conformally Deposited
Sheet Resistance = 350-380 mΩ/sq.

Formation of Cu Seed Layer in High Aspect Ratio TSVs

- Vapor delivery from a bubbler fails to nucleate densely at the bottoms of 20:1 TSV holes with extremely high density



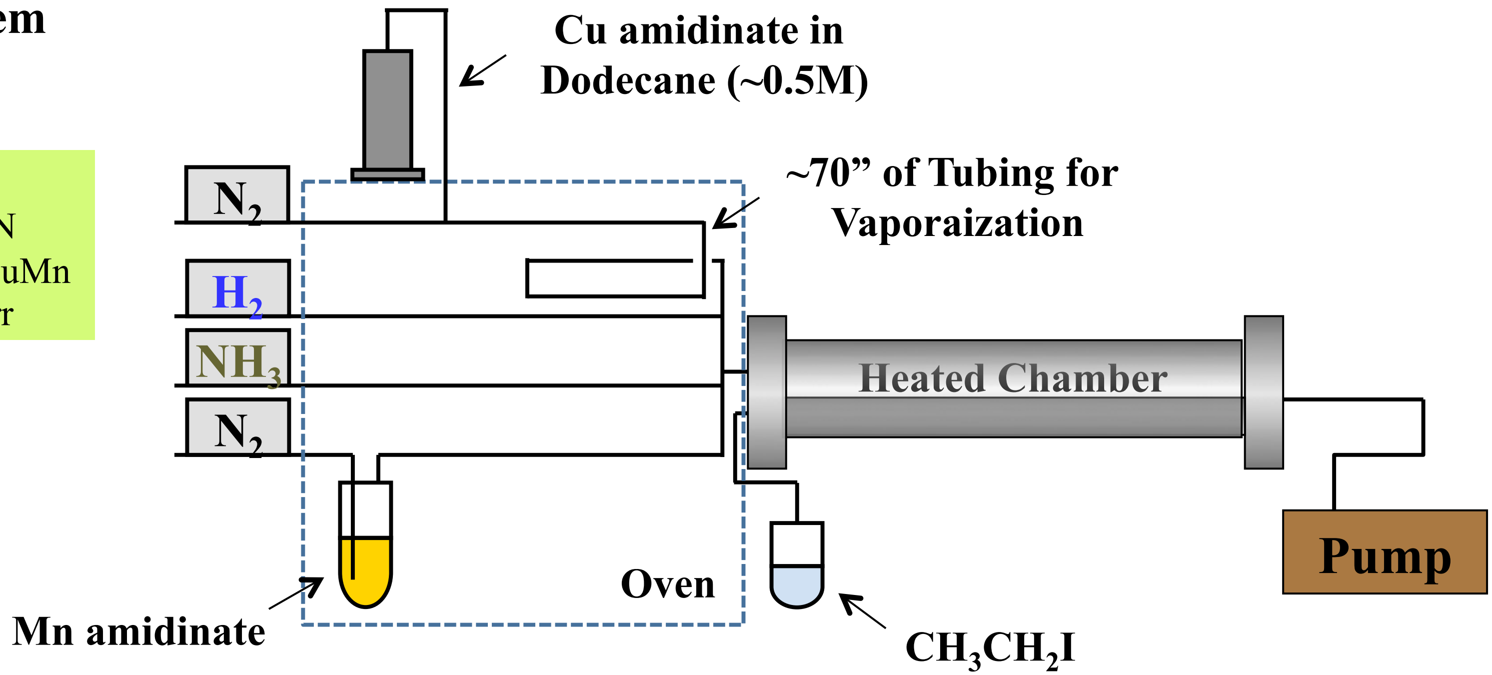




Direct Liquid Injection (DLI) CVD of Copper

DLI-CVD System

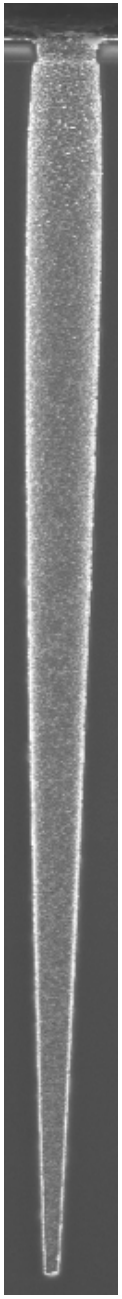
Temperature
130°C for Mn_4N
180°C for Cu and CuMn
Pressure: 5 Torr



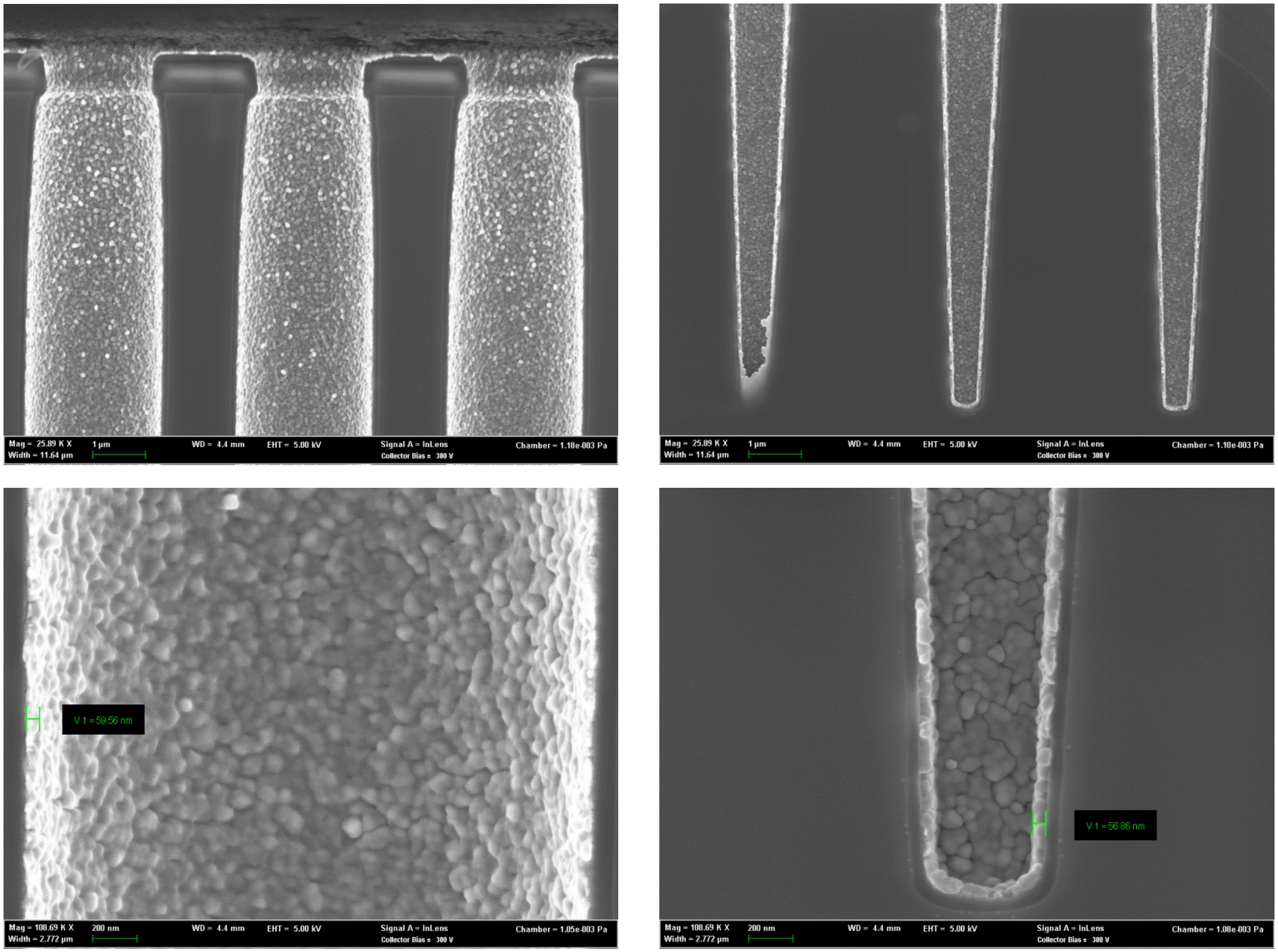
Advantages of DLI-CVD Systems:

- High growth rate
- Predictable and consistent vapor delivery
- Good control of chemical composition of films
- Possibility to coat complex and porous substrates

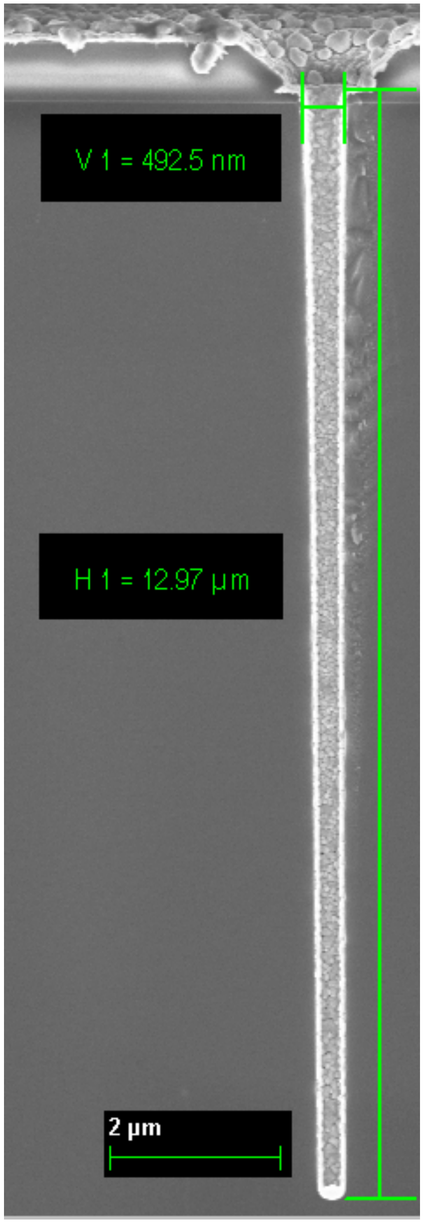
DLI Cu-Mn Seed Layer in Dense 20:1 Aspect Ratio TSVs



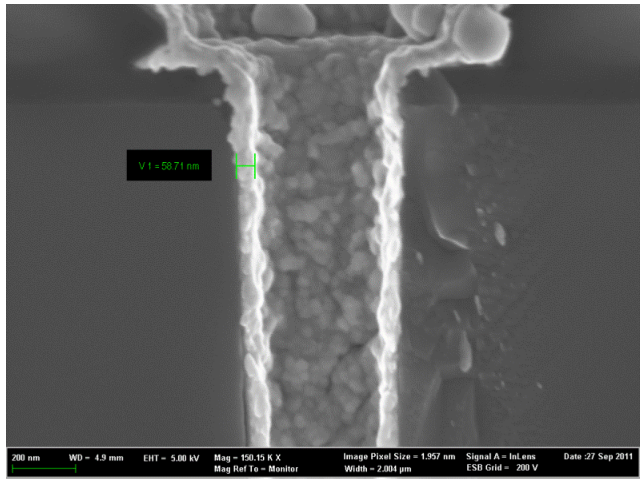
CVD-Mn_xN (130°C)	Iodine Exposure (Room Temp.)	CVD-CuMn (190°C)	Post-annealing (350°C)

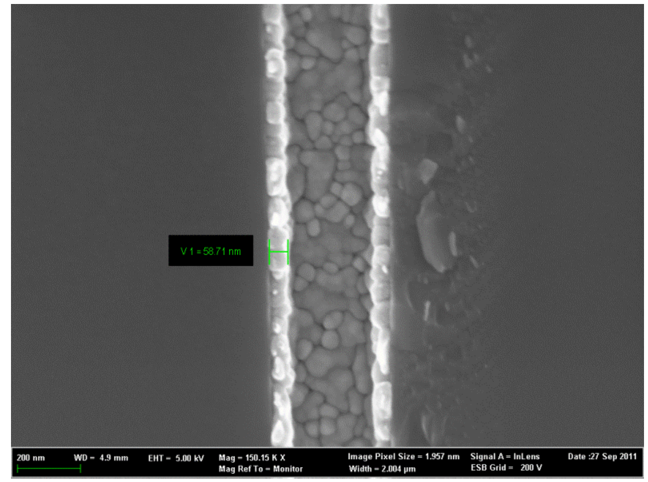


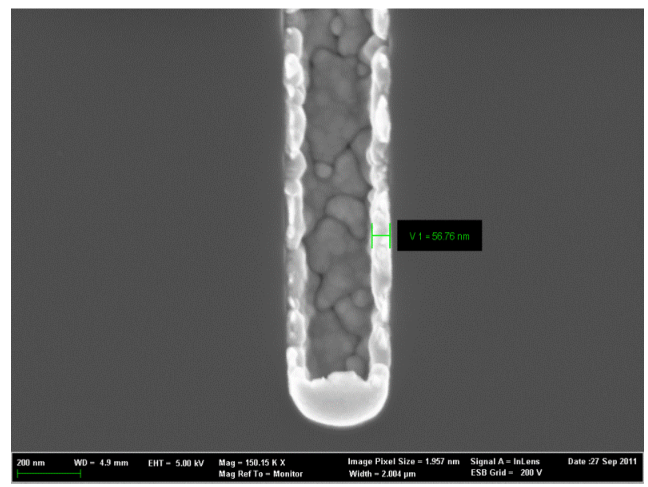
DLI Cu-Mn Seed Layer in Dense 25:1 Aspect Ratio TSVs



$ALD-SiO_2$ (250°C) → **$CVD-Mn_xN$ (130°C)** → **Iodine Exposure (Room Temp.)** → **CVD-CuMn (190°C)**





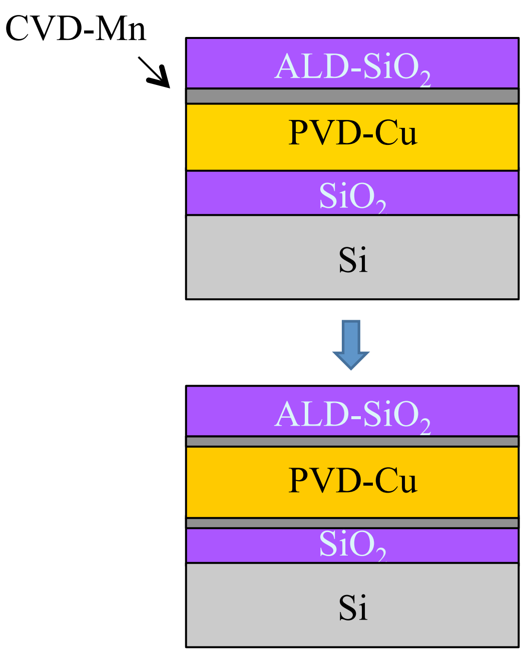


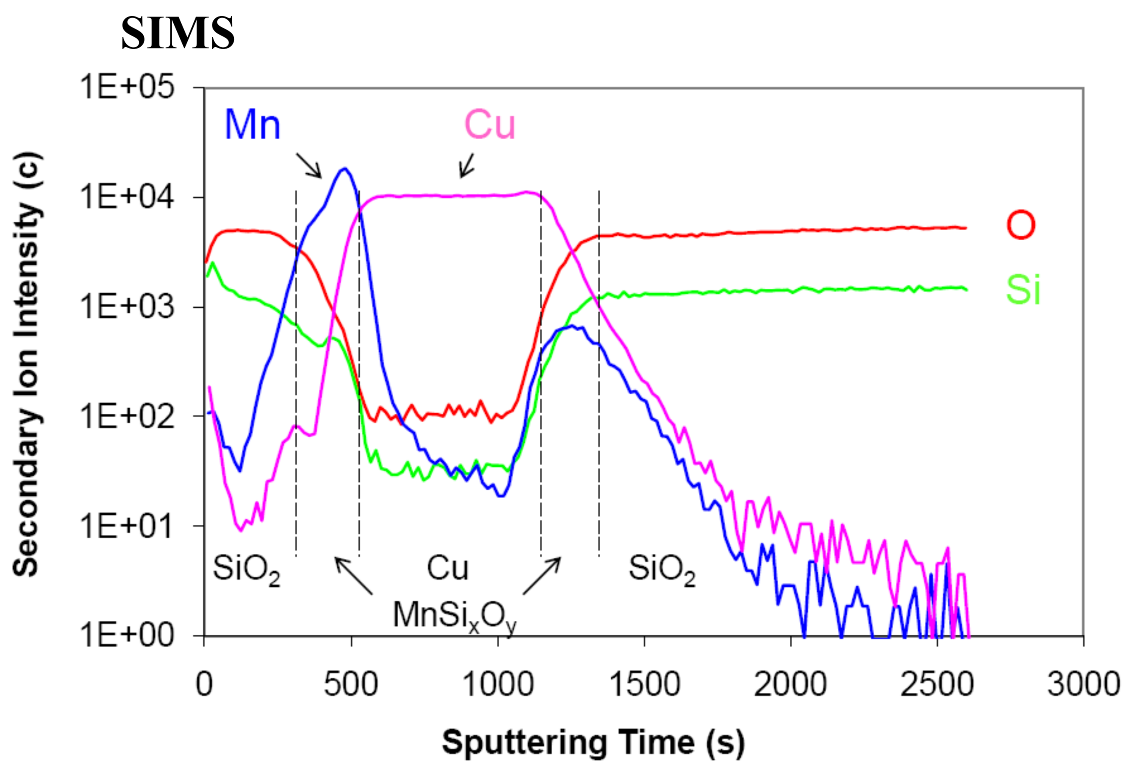
Aspect Ratio > 25:1 Holes

TSV features with AR > 25:1 are conformally Coated by CuMn

Diffusion of Mn in Polycrystalline Cu

- Insulators (SiO_2 and Si_3N_4) encourage diffusion of Mn through Cu grain boundaries to Cu/SiO_2 and Cu/Si_3N_4 interfaces





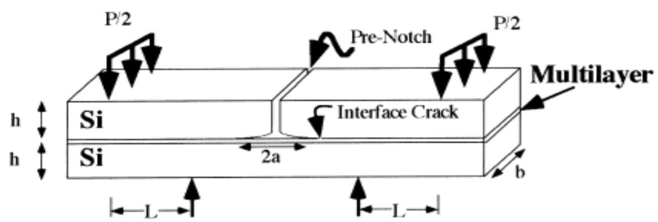
- XPS depth-profiling: **D ≈ 3x10^{-21} m^2/s** at 300°C

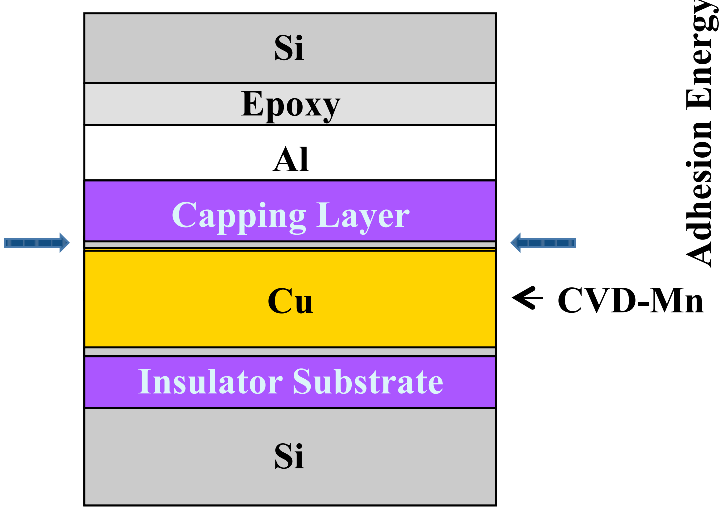
- CVD-CuMn process does not increase the resistivity of copper

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

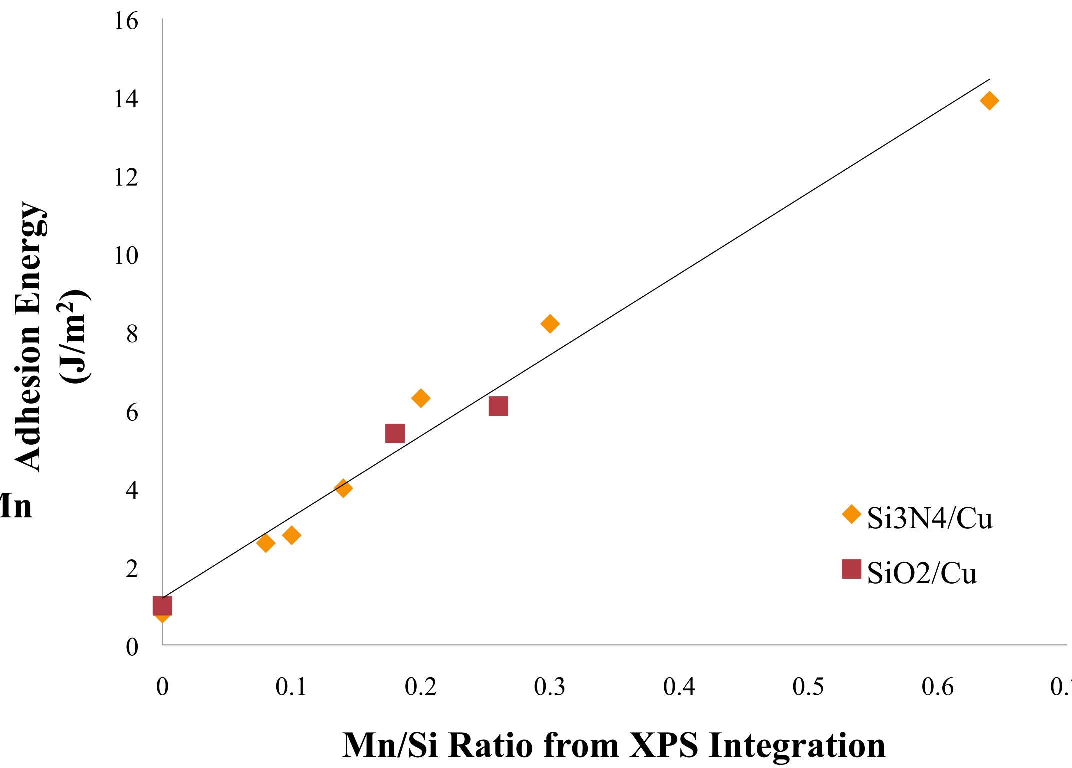
Adhesion Enhancement at Cu/Insulator Interface

- Four-point bend technique evaluates adhesion enhancement at Cu/insulator interfaces





Adhesion Test Structure

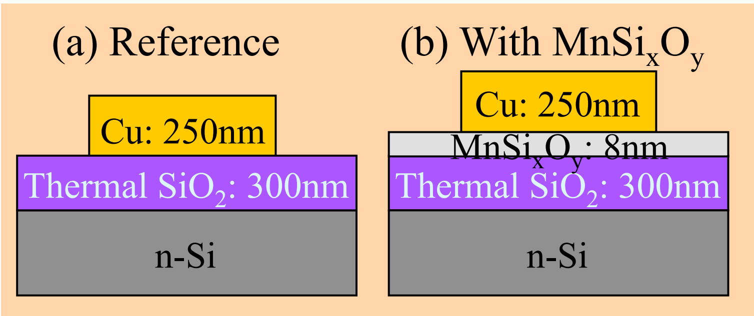


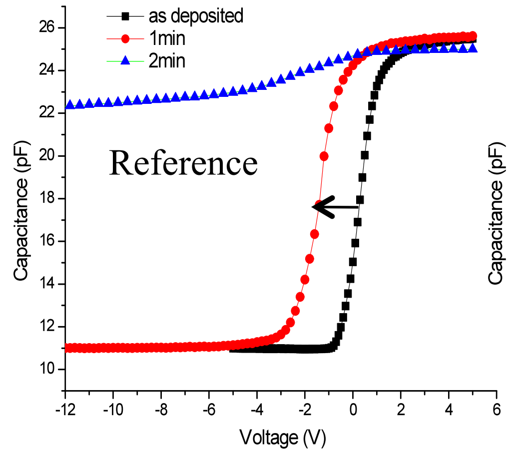
Debonding energy at Cu/dielectric interface increases linearly with the amount of manganese at the interface

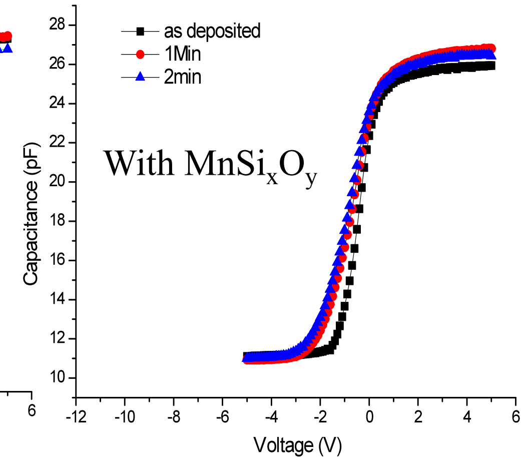
Y. Au, Y. Lin, H. Kim, E. Beh, Y. Liu and R. G. Gordon, *J. Electrochem. Soc.*, **157** (6) D341-D345 (2010).

Manganese Silicate Diffusion Barrier

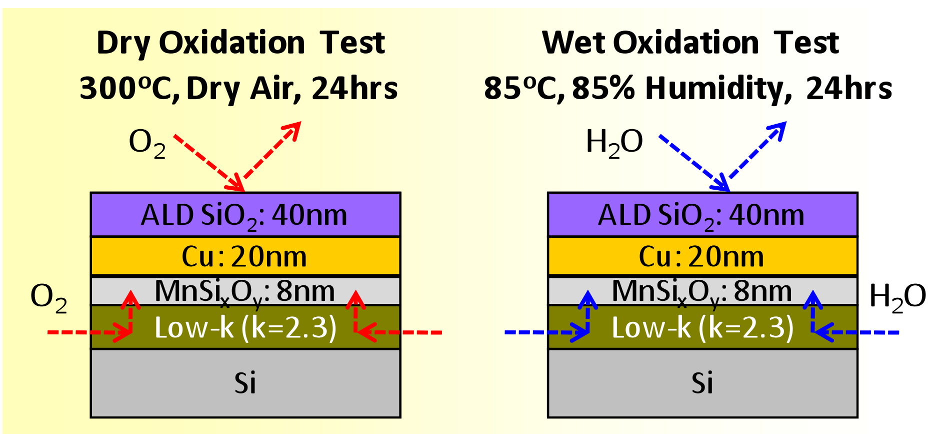
Cu Diffusion Barrier Test

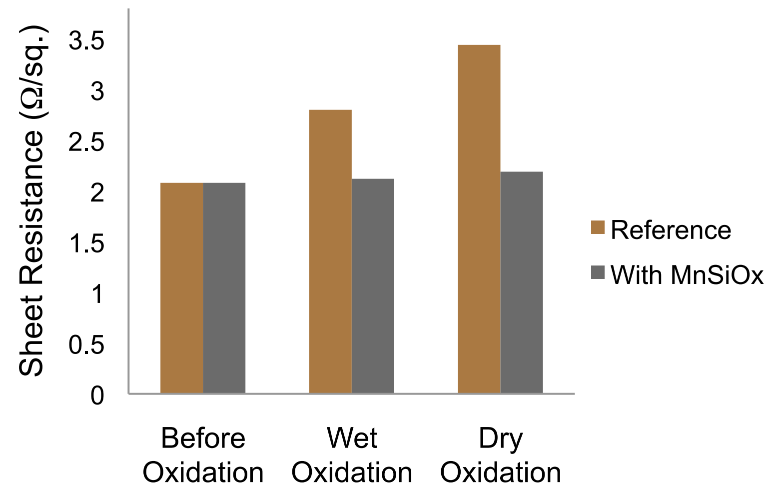






Oxidation Barrier Test





$MnSi_xO_y$ layer formed at the interface is an excellent barrier against diffusion of Cu, H_2O and O_2

R. G. Gordon, H. Kim, Y. Au, H. Wang, H. B. Bhandari, Y. Liu, D. K. Lee, and Y. Lin, *Adv. Met. Conf. 2008, Proc.*, p. 321 (2008)

Summary

- ✓ Conformal ALD-silica can be deposited using TMA and silanol
- ✓ Conformal CVD-manganese nitride barrier/adhesion layer can be prepared by reacting amidinate precursors with ammonia
- ✓ TSV features with AR > 25:1 can be conformally coated by CuMn seed layer using a direct liquid injection (DLI) CVD method
- ✓ Manganese in CuMn 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

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  Substrates and Analyses: IMEC, TEL and IBM

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- Rapid ALD of Silica: Dennis M. Hausmann, Jill S. Becker
- Synthesis of Metal Amidinates: Booyong S. Lim
- ALD of Cu: Antti Rahtu, Zhengwen Li
- CVD of Cu and Mn: Hoon Kim
- CVD of Manganese Nitride and Adhesion: Youbo Lin