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Selective Chemical Vapor Deposition (CVD) of Manganese Self-aligned Adhesion and Barrier Layers for Cu Interconnections in Microelectronics

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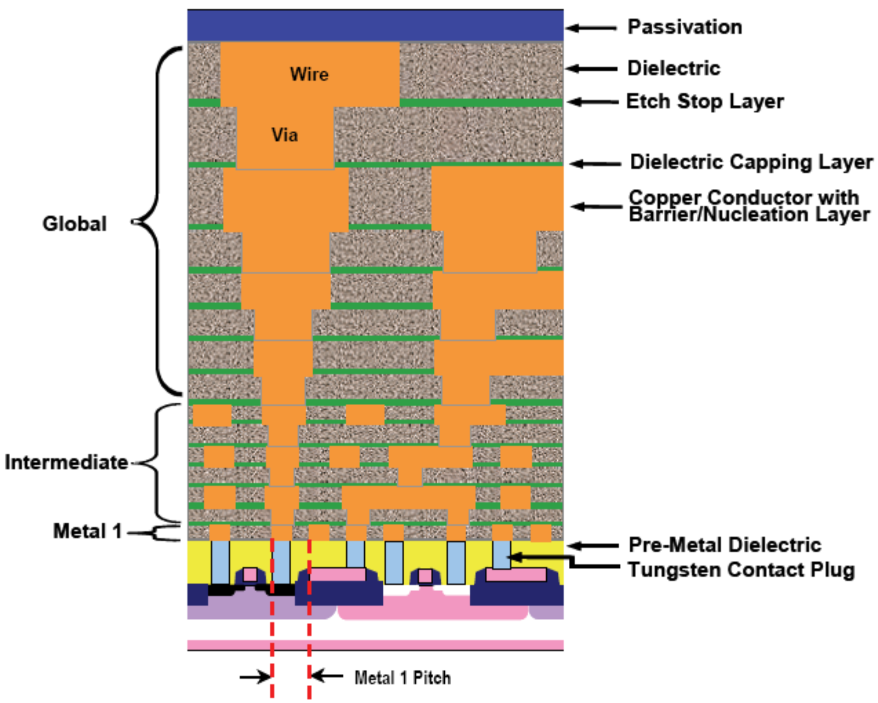
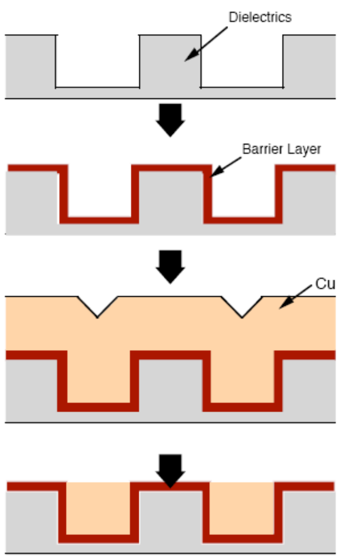
Introduction

- Interconnect (RC) delay will be dominant in determining the overall device performance
- Copper was chosen to replace aluminum alloy in metallization due to its low resistivity and better electromigration reliability
- **Electromigration**: A reliability problem of metal atoms moving in the direction of the current flow due to momentum transfer



Cross-Section of Microprocessors

Typical Damascene Process

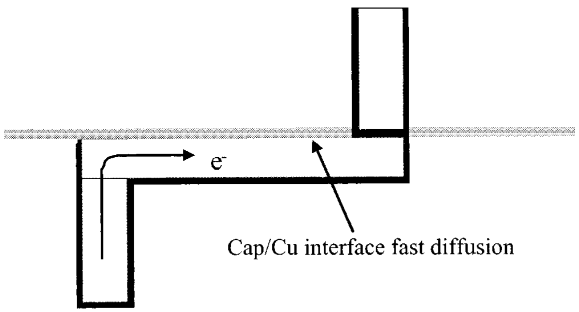


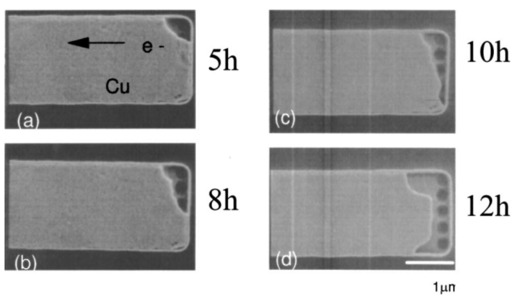
- Deposit dielectric materials
- Pattern & etch
- Deposit barrier/seed stack
- Fill with electroplated Cu
- Anneal to stabilize the microstructures
- Polish the excess Cu away using CMP
- Deposit capping layer/etch stop

The International Technology Roadmap for Semiconductors, http://public.itrs.net, (2007).

Introduction

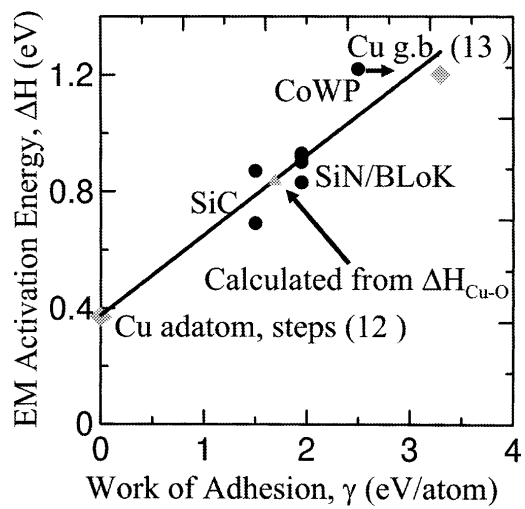
- The Cu/capping layer interface has found to be responsible for electromigration failure due to lack of protection liner





Black's Equation

$$MTTF = Awj^{-n} e^{\left(\frac{\Delta H}{k_B T}\right)}$$



$$\Delta H = 0.35 + 0.26\gamma$$

- Adhesion at Cu/capping layer interface must be improved to achieve longer lifetime

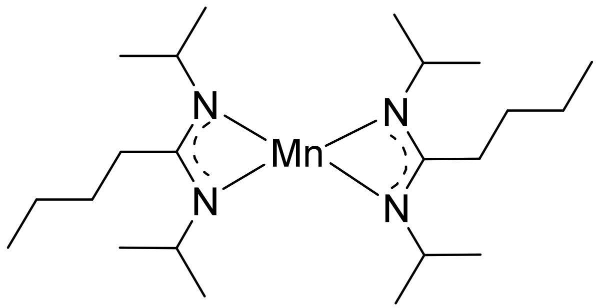
M. W. Lane, E.G. Liniger, and J.R. Lloyd, "Relationship between interfacial adhesion and electromigration in Cu metallization," *J. Appl. Phys.*, **93 (3),** 1417-1421, (2003).

Outline

- Chemical vapor deposition of manganese (Mn)
- CVD-Mn Self-aligned Adhesion and Barrier Layer
  - Diffusion of Mn in polycrystalline Cu
  - Manganese silicate ($MnSi_xO_y$) self-aligned diffusion & oxidation barrier
  - Adhesion enhancement at Cu/capping layer interface
  - Selective deposition by surface passivation
- Summary

Chemical Vapor Deposition of Manganese

Precursor



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

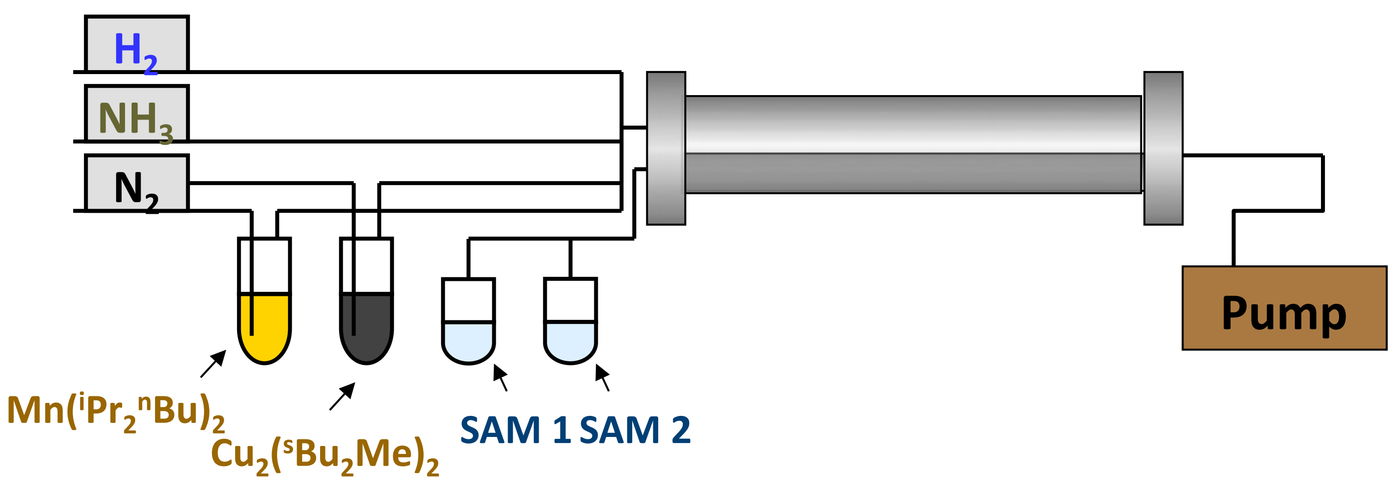
Advantages of using transitional metal amidinates as CVD precursors:

- Bidentate chealting effect enhances thermal stability
- Tunable reactivity and volatility
- Minimal carbon incorporation
- Ability to make metal-nitrogen bonds
- No corrosive byproducts

Booyong S. Lim, Antti Rahtu, Jin-Seong Park, and Roy G. Gordon, "Synthesis and characterization of volatile, thermally stable, reactive transition metal amidinates," *Inorg. Chem.*, **42 (24),** 7951-7958, (2003).

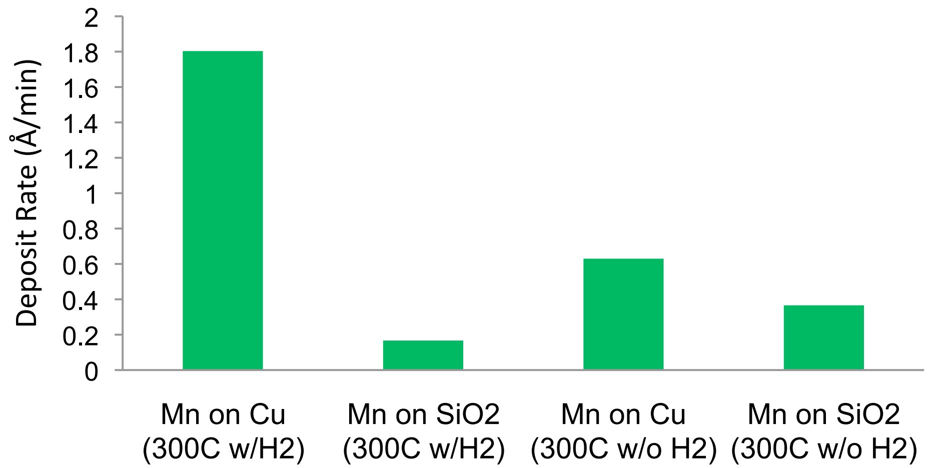
CVD System

Temperature
300-350°C for Mn
200°C for Cu
Pressure: 5 Torr

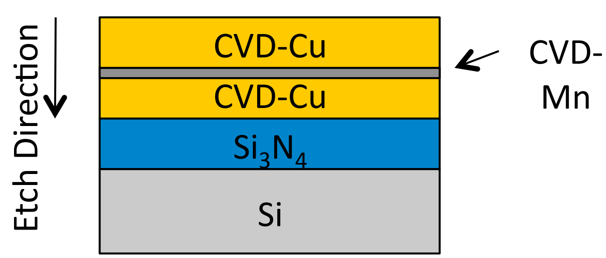


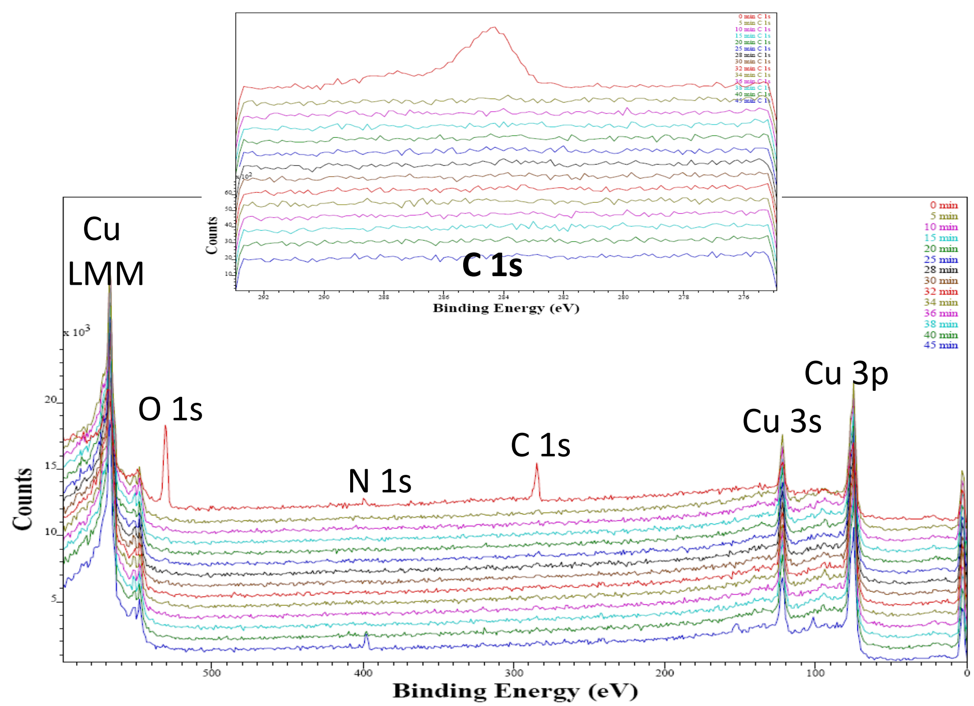
Chemical Vapor Deposition of Manganese

Mn can be deposited with or without supplying hydrogen



Evaluation of Carbon Contaminations

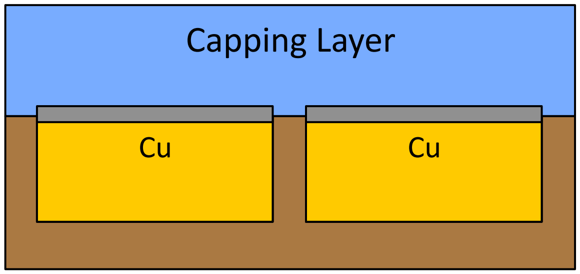




- Minimal carbon contamination found in film when hydrogen is supplied

CVD-Mn Self-aligned Adhesion and Barrier Layer

Motivation

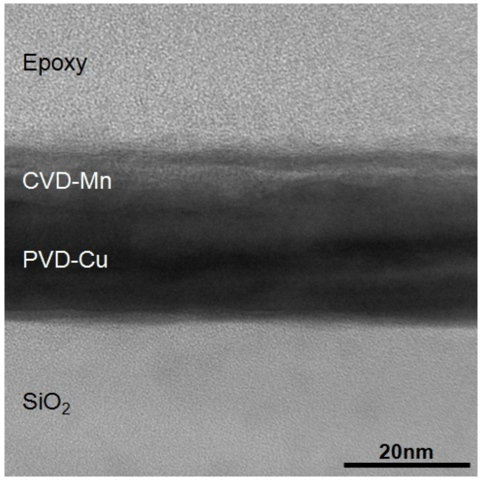


Advantages

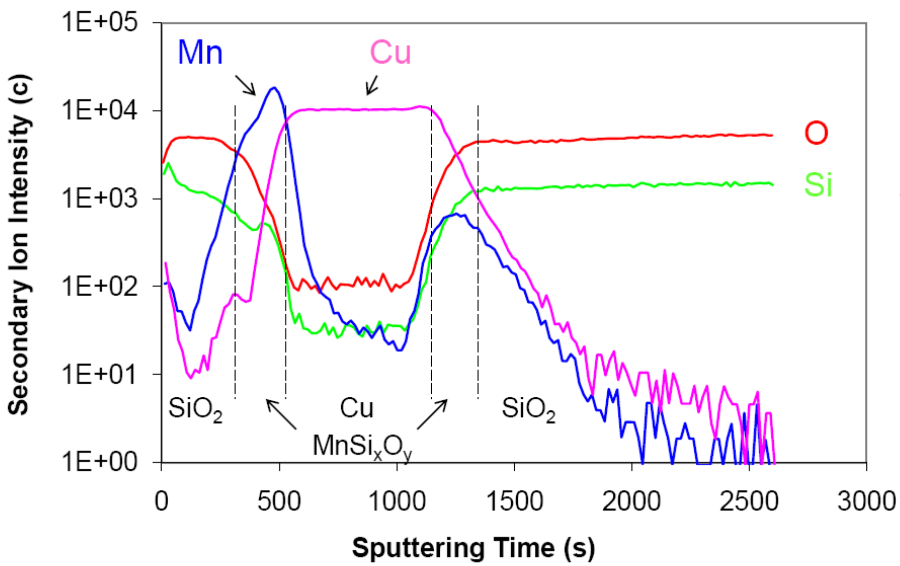
- Inexpensive fabrication processes
- Does not increase the resistivity of copper
- Formation of interfacial layer prevents copper diffusion and enhances adhesion at the Cu/capping layer interface
- High selectivity can be achieved to prevent line-to-line leakage between copper wires

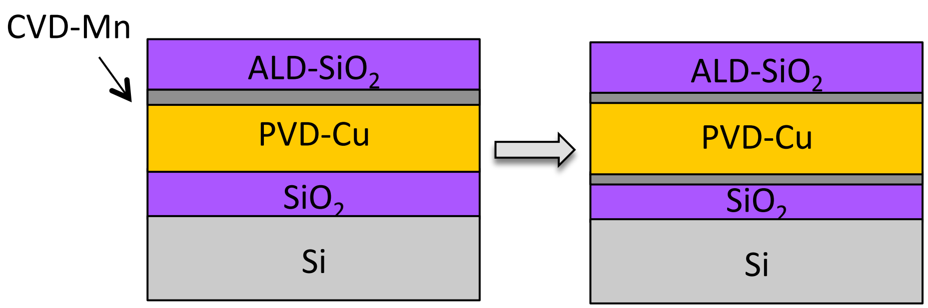
Diffusion of Mn in Polycrystalline Cu

- A continuous and uniform layer of CVD-Mn is deposited on PVD-Cu



Diffusion of manganese into copper



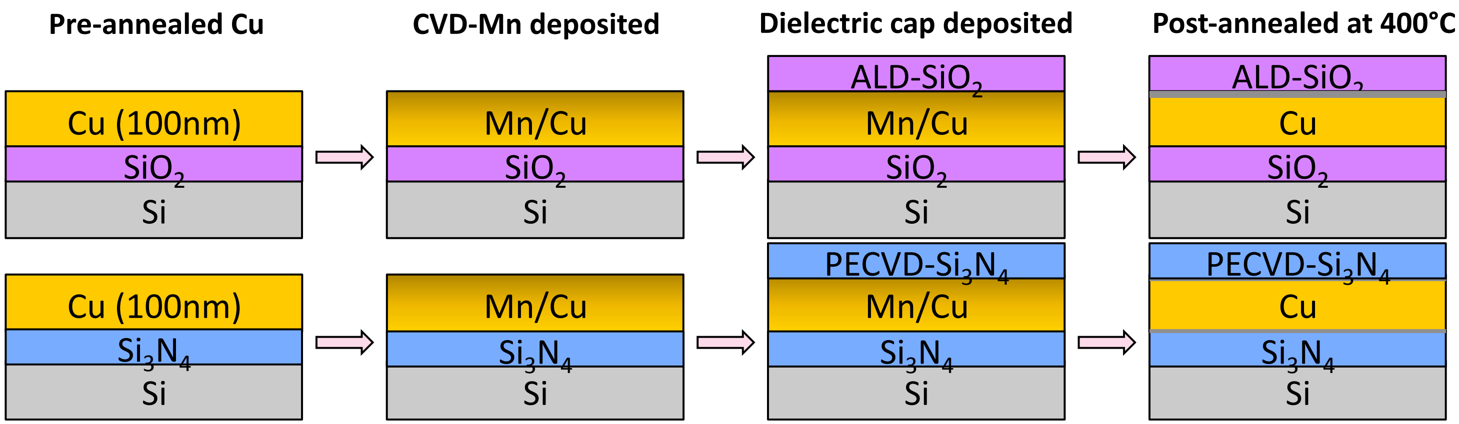


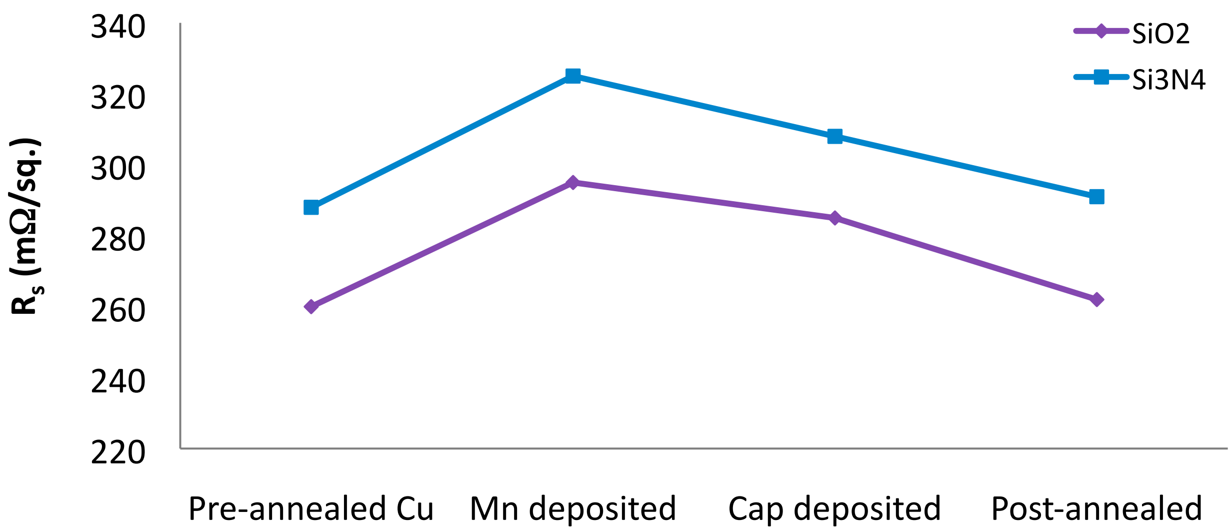
- XPS depth-profiling: by assuming constant concentration maintained by CVD condition, **D = 3×10^{-21} m²/s** at 300°C
- Manganese readily diffuses in copper through grain boundaries

Y. Au, Y. Lin, H. Kim, E. Beh, Y. Liu and R.G. Gordon, "Selective Chemical Vapor Deposition of Manganese Self-Aligned Capping Layer for Cu Interconnections", *J. Electrochem. Soc.*, **157** (6) D341-D345 (2010)

Diffusion of Mn in Polycrystalline Cu

Diffusion of manganese from copper to interface



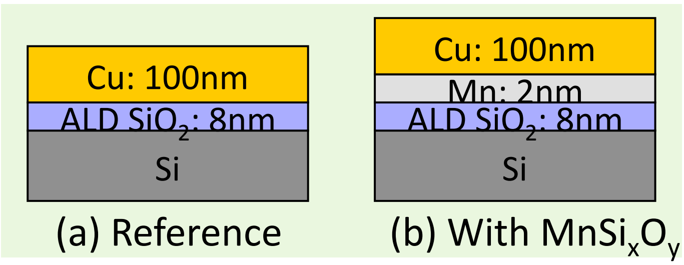


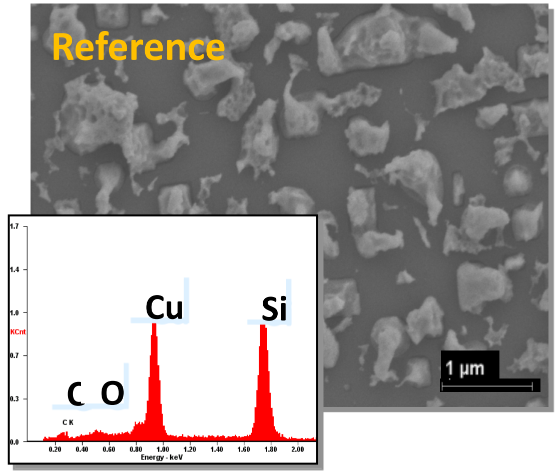
- Capping layers (SiO_2 and Si_3N_4) encourages diffusion of Mn from Cu to interface
- CVD-Mn process does not increase the resistivity of copper

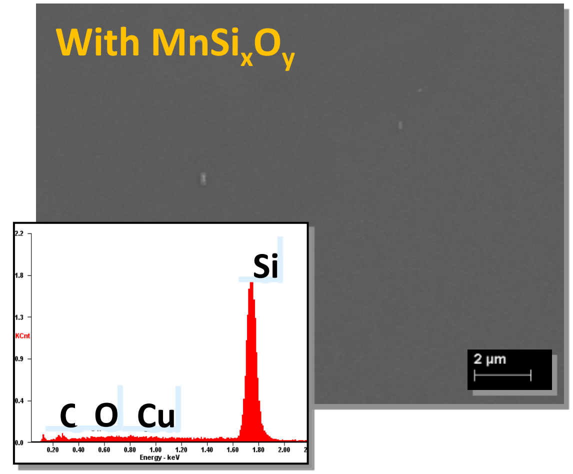
Manganese Silicate Diffusion Barrier

- Manganese reacts with SiO_2 to form an amorphous, insulating $MnSi_xO_y$ layer
- $MnSi_xO_y$ layer is found to be an excellent barrier against Cu diffusion

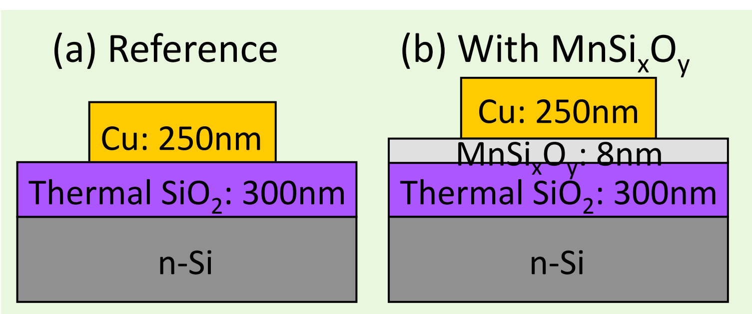
SEM:EDX Analysis

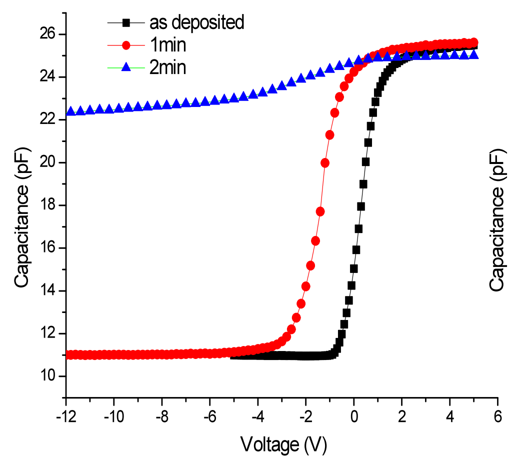


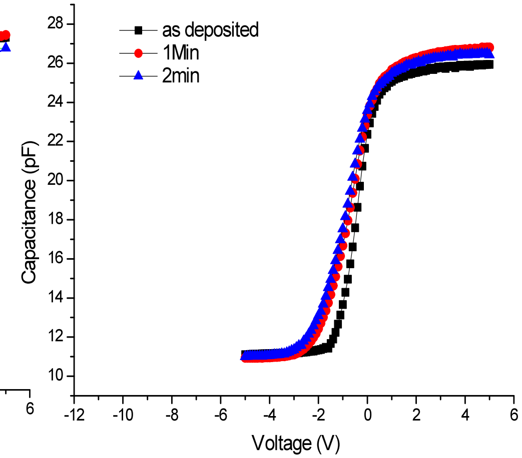




Electrical Analysis



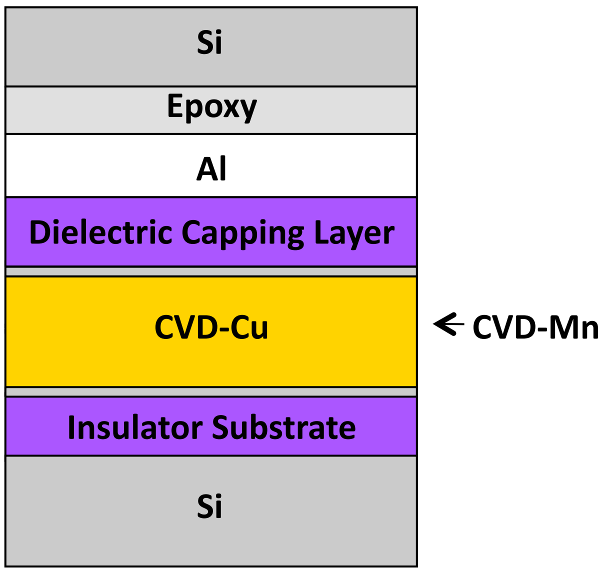




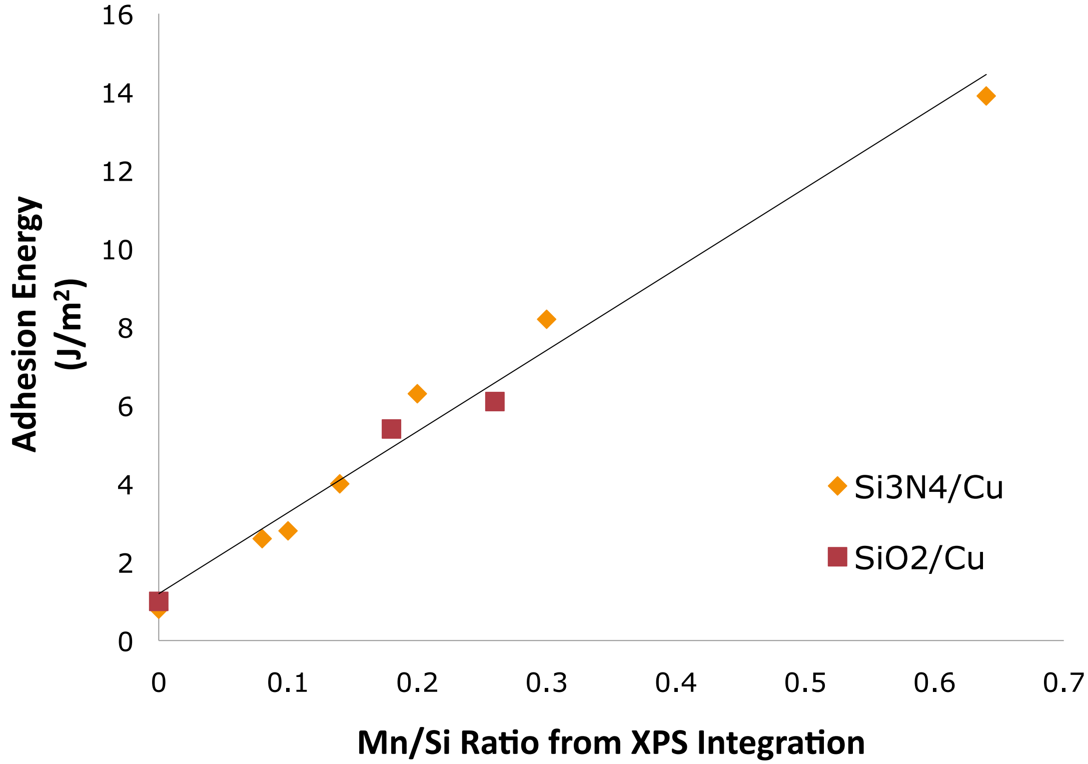
Roy G. Gordon, Hoon Kim, Yeung Au, Hongtao Wang, Harish B. Bhandari, Yiqun Liu, Don Keun Lee, and Youbo Lin, "Chemical vapor deposition of manganese self-aligned diffusion barriers for Cu interocnnections in microelectronics," *Adv. Met. Conf. 2008, Proc.*, p. 321 (2008).

Adhesion Enhancement at Cu/Capping Layer Interface

- Four-point bend technique to evaluate adhesion enhancement at Cu/capping layer interfaces



Adhesion Test Structure

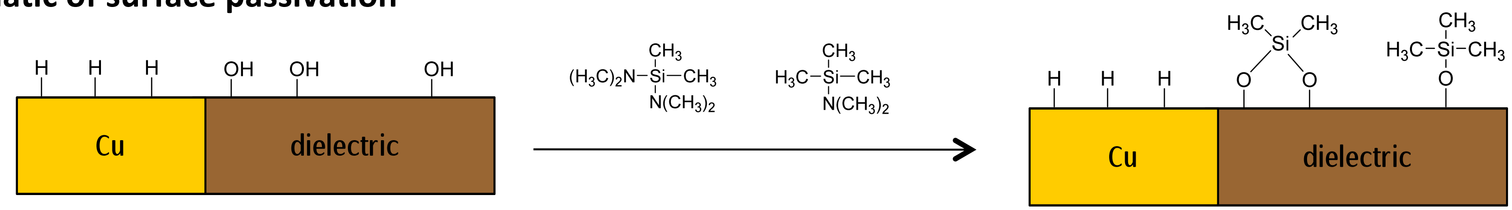


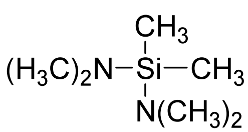
Debonding energy at Cu/dielectric interface increases linearly with the amount of manganese at the interface

Selective Deposition of CVD-Mn by Surface Passivation

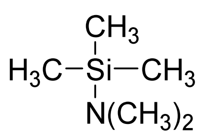
- Selective deposition is desired in order to avoid line-to-line leakage caused by metal deposited on insulator between copper lines
- Approach: deactivation of reactive sites on insulator surfaces by applying alkylsilanes

Schematic of surface passivation



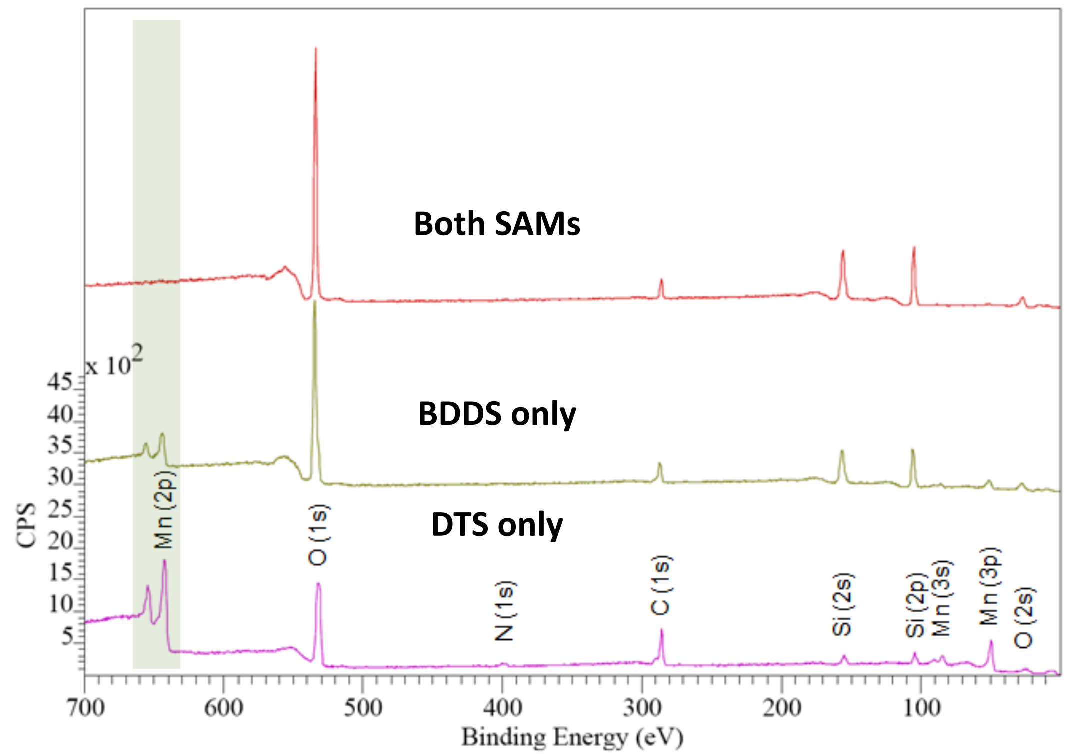


Bis(dimethylamino) dimethylsilane



(N,N-dimethylamino) trimethylsilane

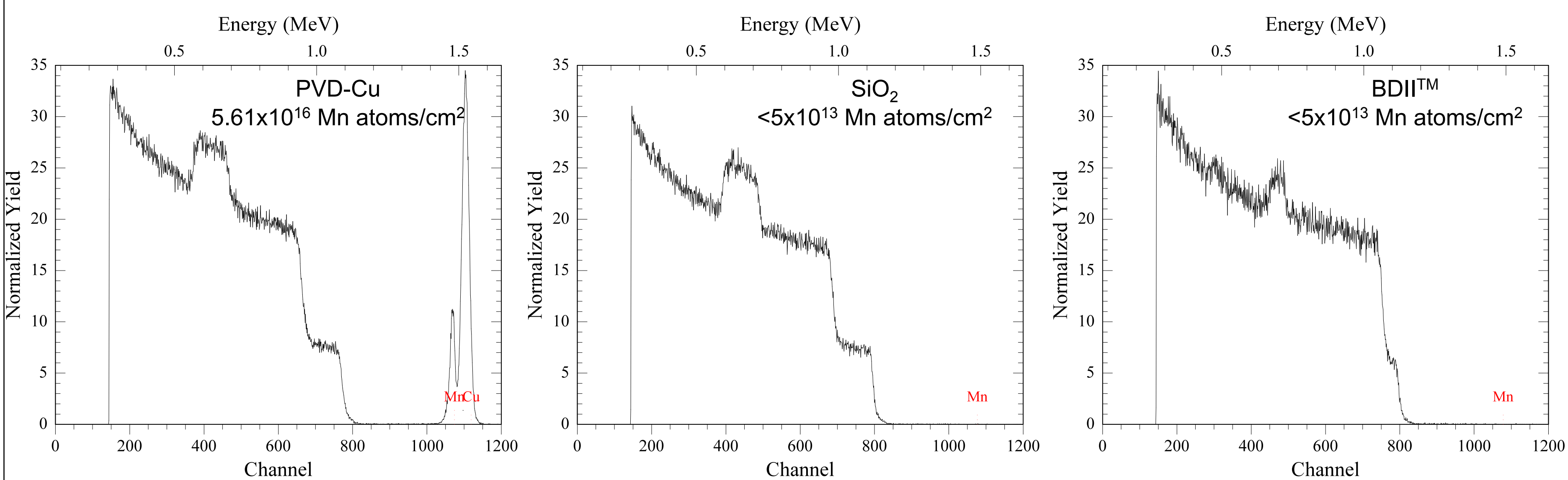
- Effect of passivation and reduction of reactive sites are maximal when both SAMs are applied



Selective Deposition of CVD-Mn by Surface Passivation

Drying under N_2 (250°C, 350°C) → Reduction by H_2 (250°C) → Surface Passivation by SAMs (90°C) → CVD-Mn Deposition (300°C)

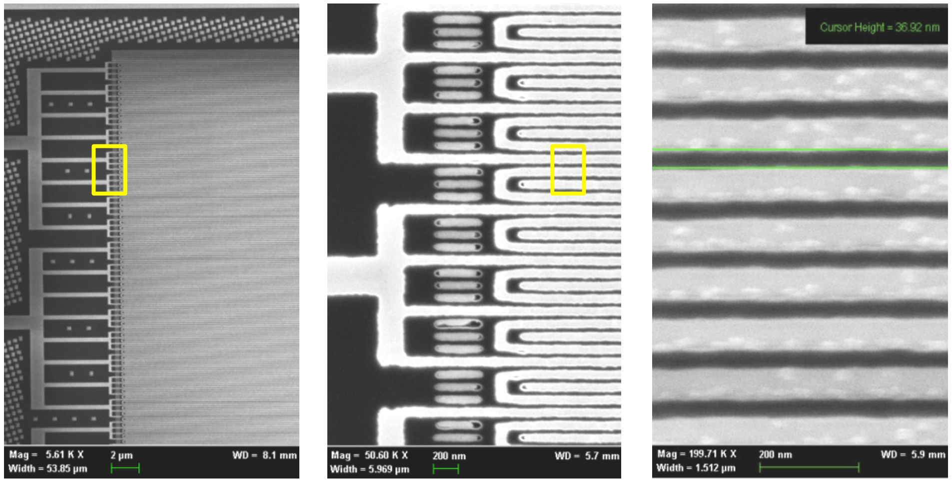
RBS

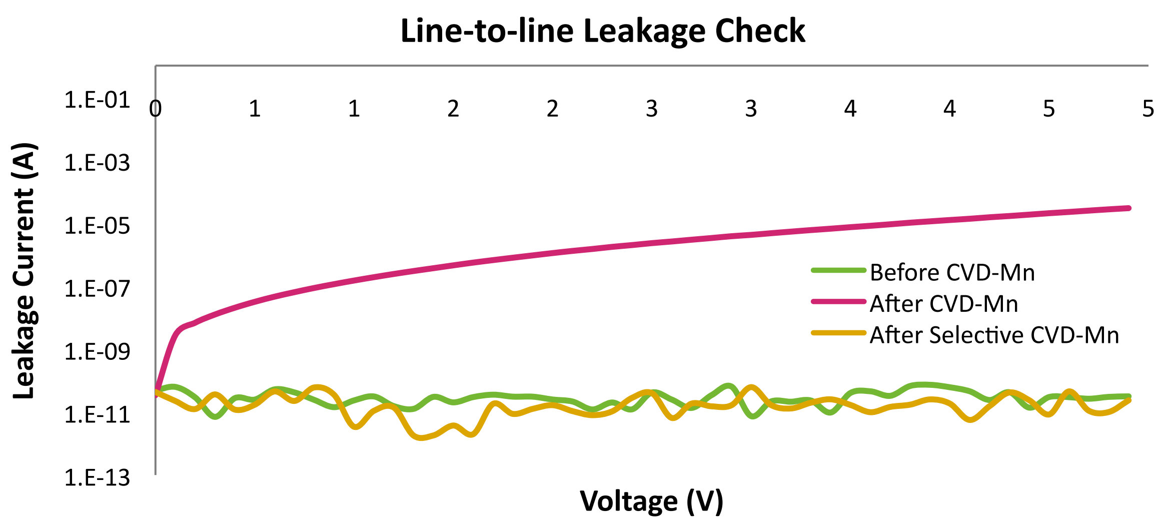


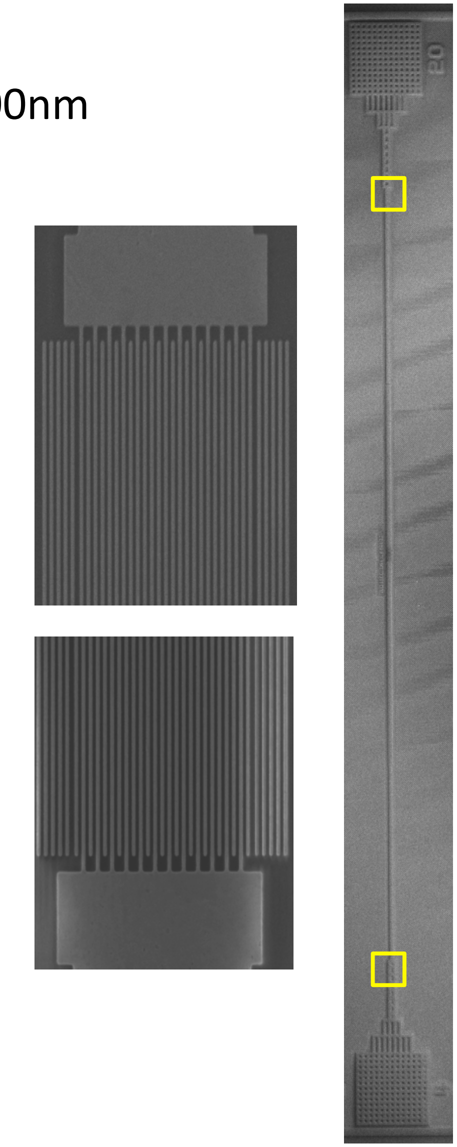
Manganese contents on passivated insulators are below RBS detection limit
A selectivity of >1100:1 can be achieved

Selective Deposition of CVD-Mn by Surface Passivation

- Leakage check with comb structures from *Selete* and IBM
  Dielectrics: SiO_2 and porous low-k, Pitch size = 200, 140, and 100nm







Selective deposition of CVD-Mn can sufficiently prevent line-to-line leakage

Summary

- Manganese can be deposited by CVD using a manganese amidinate precursor
- Manganese diffuses quickly in copper through grain boundaries
- Manganese silicate ($MnSi_xO_y$) interfacial layer shows excellent barrier properties against Cu diffusion
- Manganese can strengthen the interface between Cu and dielectric capping layer without increasing the resistivity of Cu
- Selective deposition of CVD-Mn can be achieved by surface passivation to avoid line-to-line leakage

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

- Copper Precursor: Dow Chemical Company
  Substrates: IBM, Selete, and Applied Materials

- Members of Gordon Group