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ALD of Manganese Silicate

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Citation	Gordon, Roy G., Lu Sun, Qiang Chen, Jin-Seong Park, Sang Bok Kim. 2015. ALD of Manganese Silicate. In Proceedings of the AVS Atomic Layer Deposition Conference, Portland, Oregon, June 28 - July 1.
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ALD of Manganese Silicate

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Outline

Potential Applications of Manganese Silicate

ALD Process for Manganese Oxide, MnO

ALD Process for Manganese Silicate

Properties of Manganese Silicate

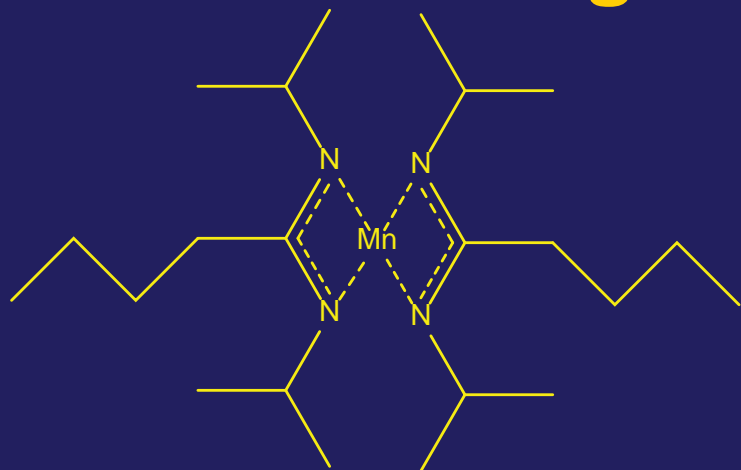


Potential Applications of MnSi_xO_y

Copper wires in computer chips could use MnSi_xO_y as a

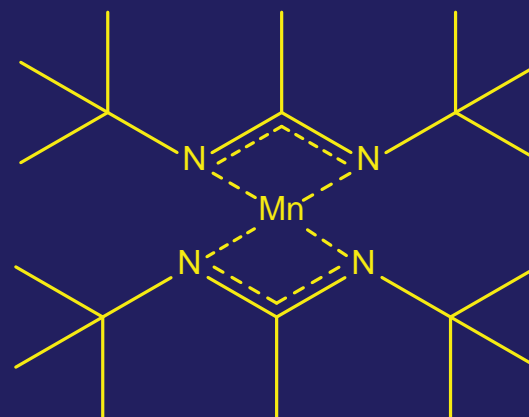
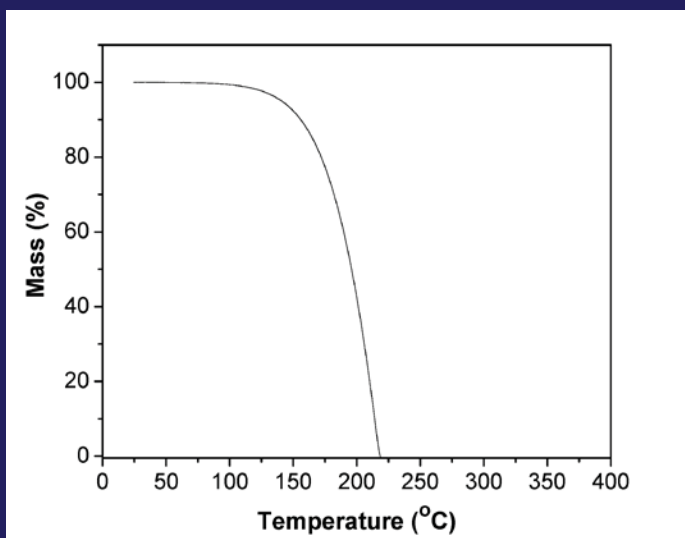
- barrier to diffusion of copper, water and oxygen
- adhesion promoter between copper and insulators
- nucleating layer for vapor deposition of copper

Manganese Precursors



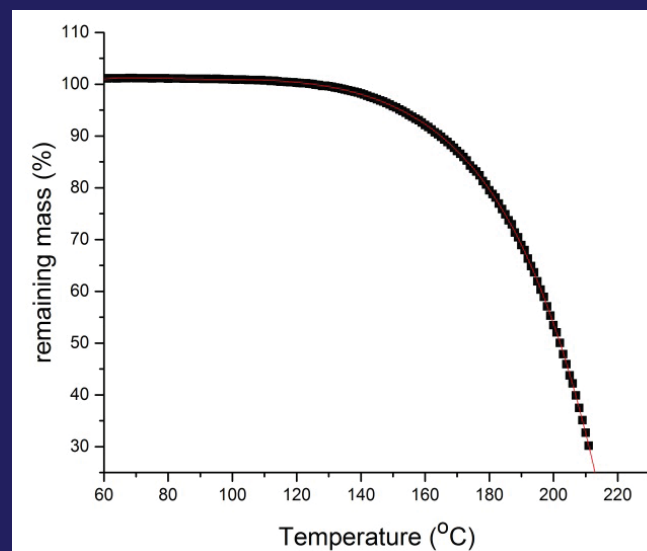
manganese(II)
bis(*N,N'*-diisopropylpentamidine)

melting point: 60 °C
boiling point: 120 °C / 0.02 torr



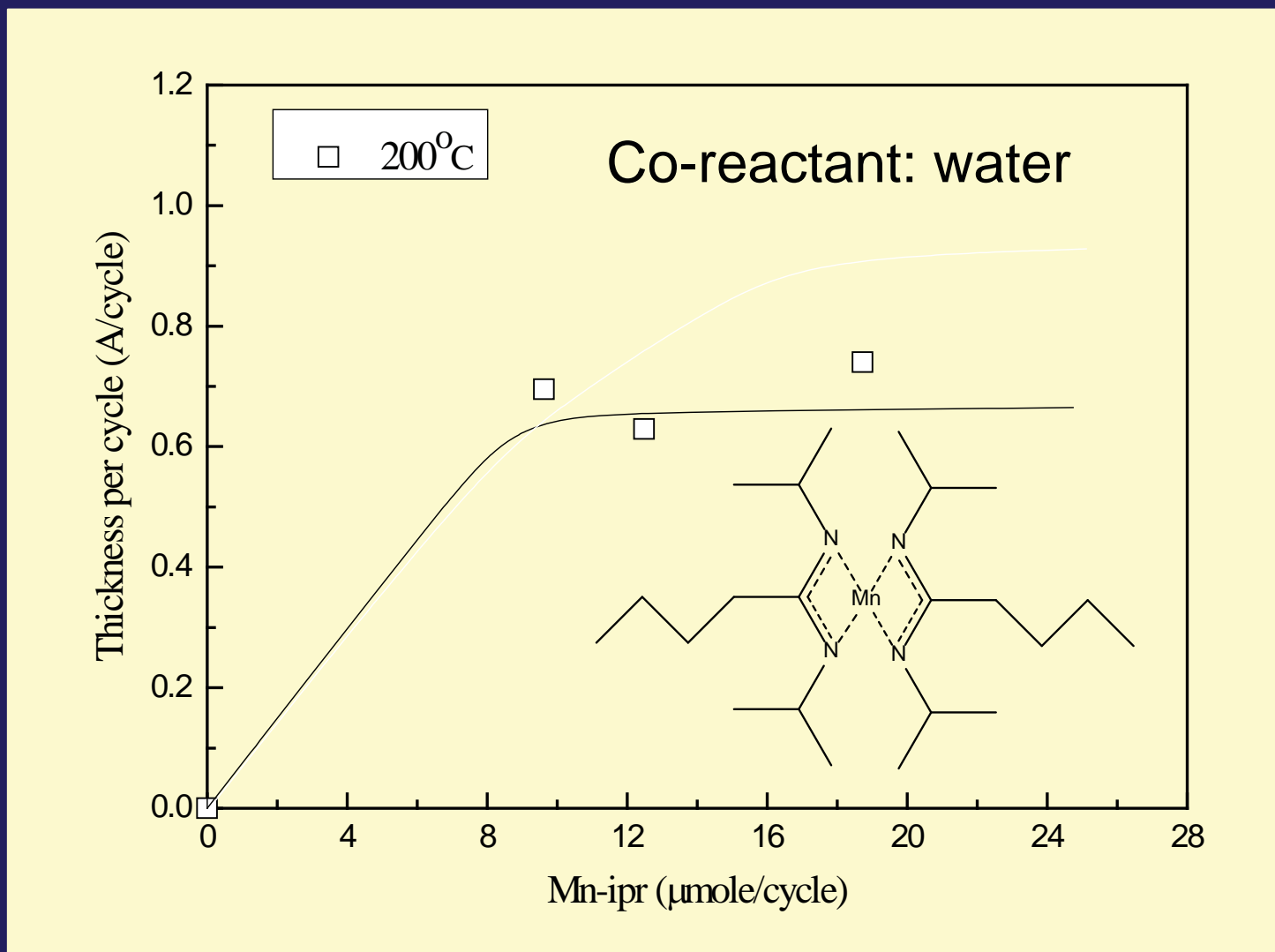
manganese(II)
bis(*N,N'*-di-*tert*-butylacetamidine)

melting point: 107 °C
boiling point: 100 °C / 0.07 torr



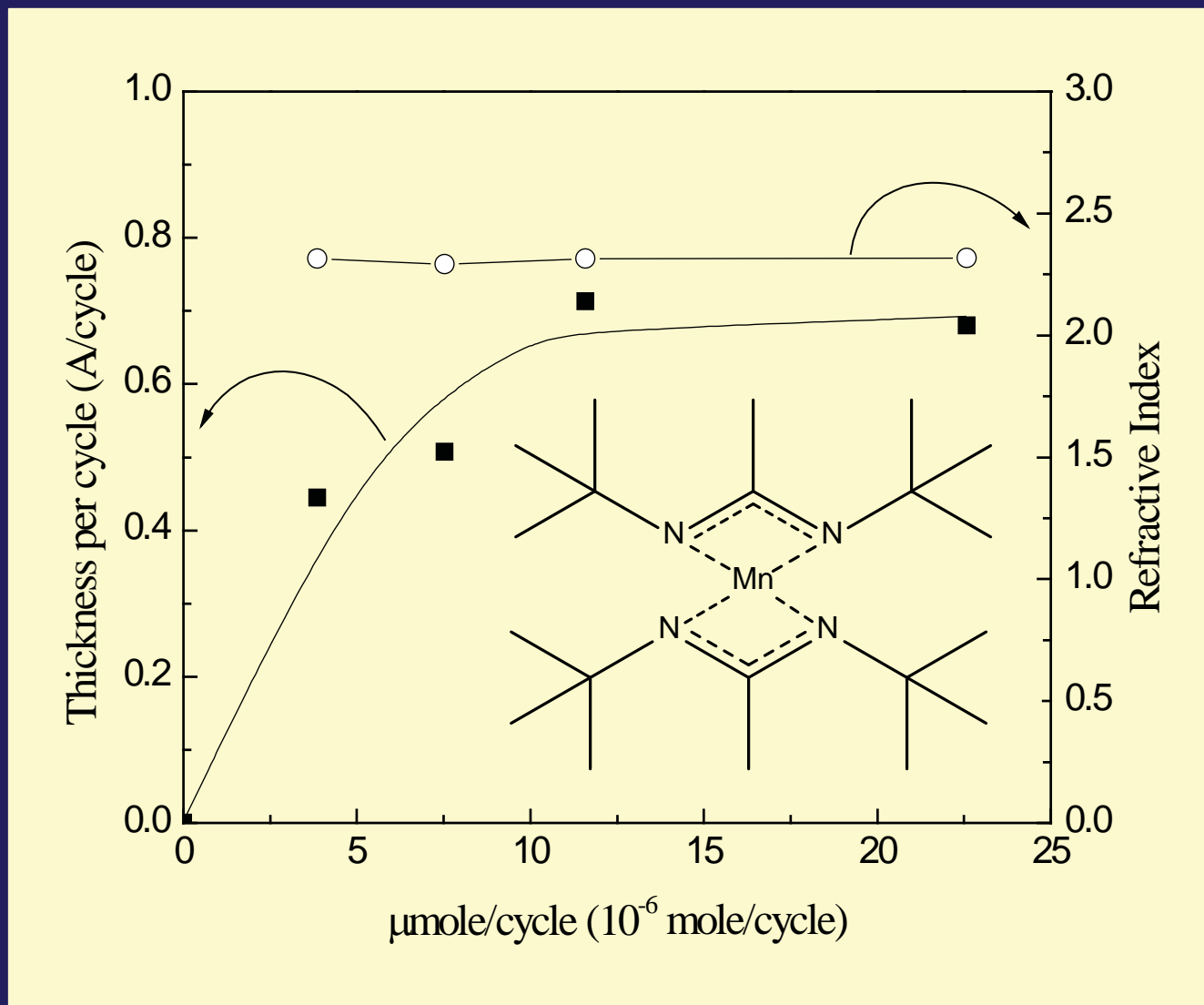
Saturation Curve for Manganese Oxide

Saturated for doses $> 10^{-5}$ moles/cycle

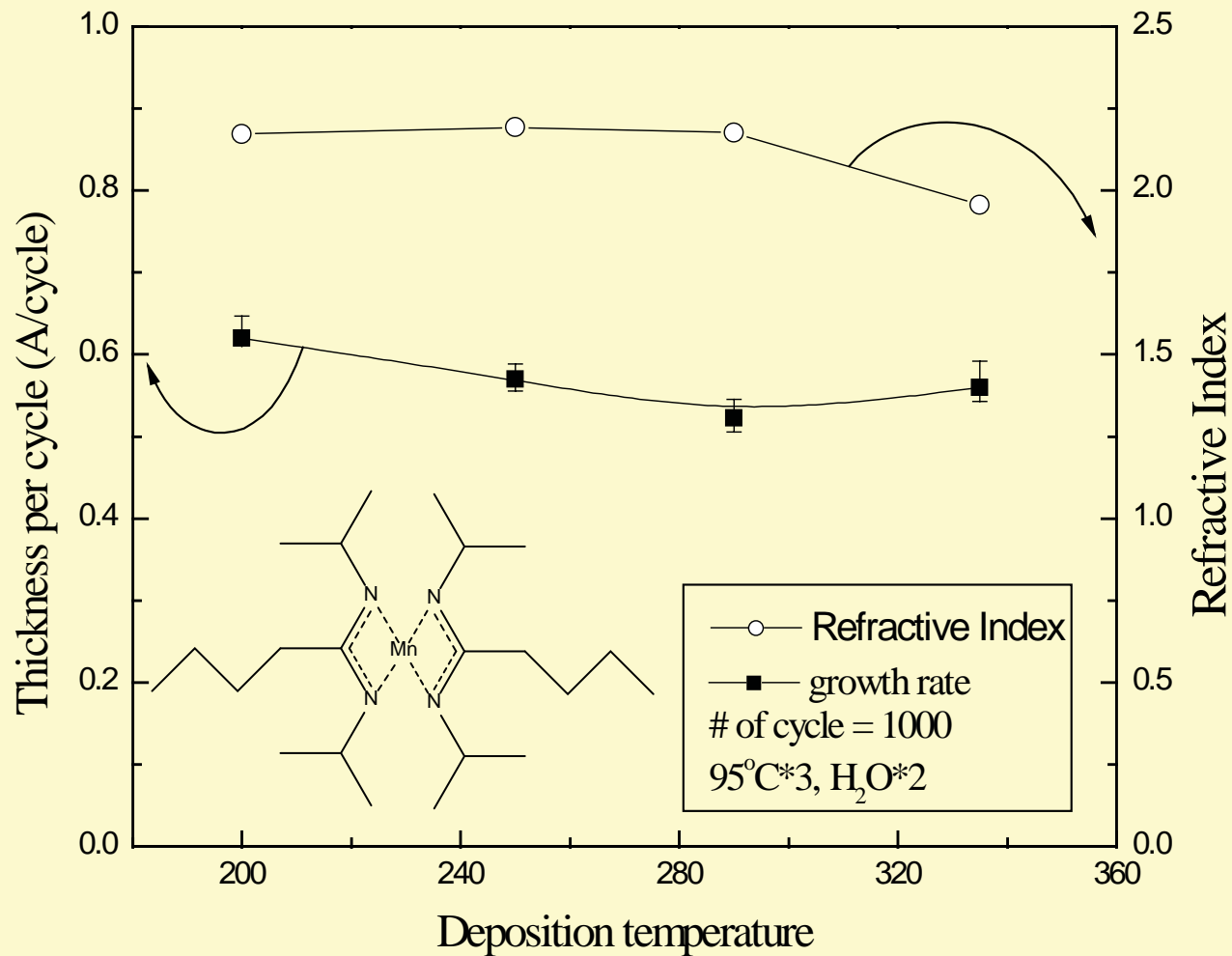


Saturation Curve for Manganese Oxide

Saturated for doses $> 10^{-5}$ moles/cycle

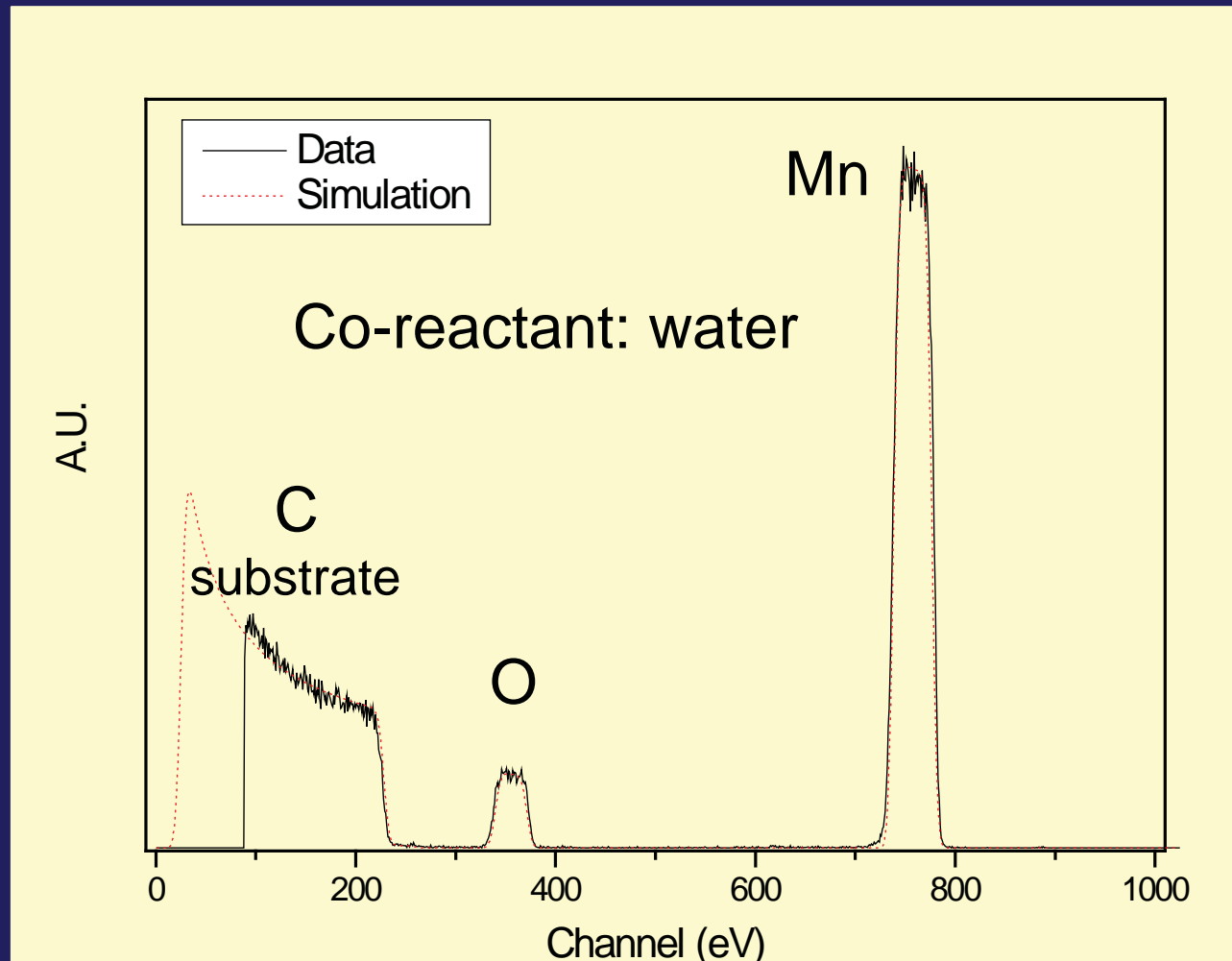


Thickness per Cycle for Manganese Oxide nearly constant from 200 to 340 °C



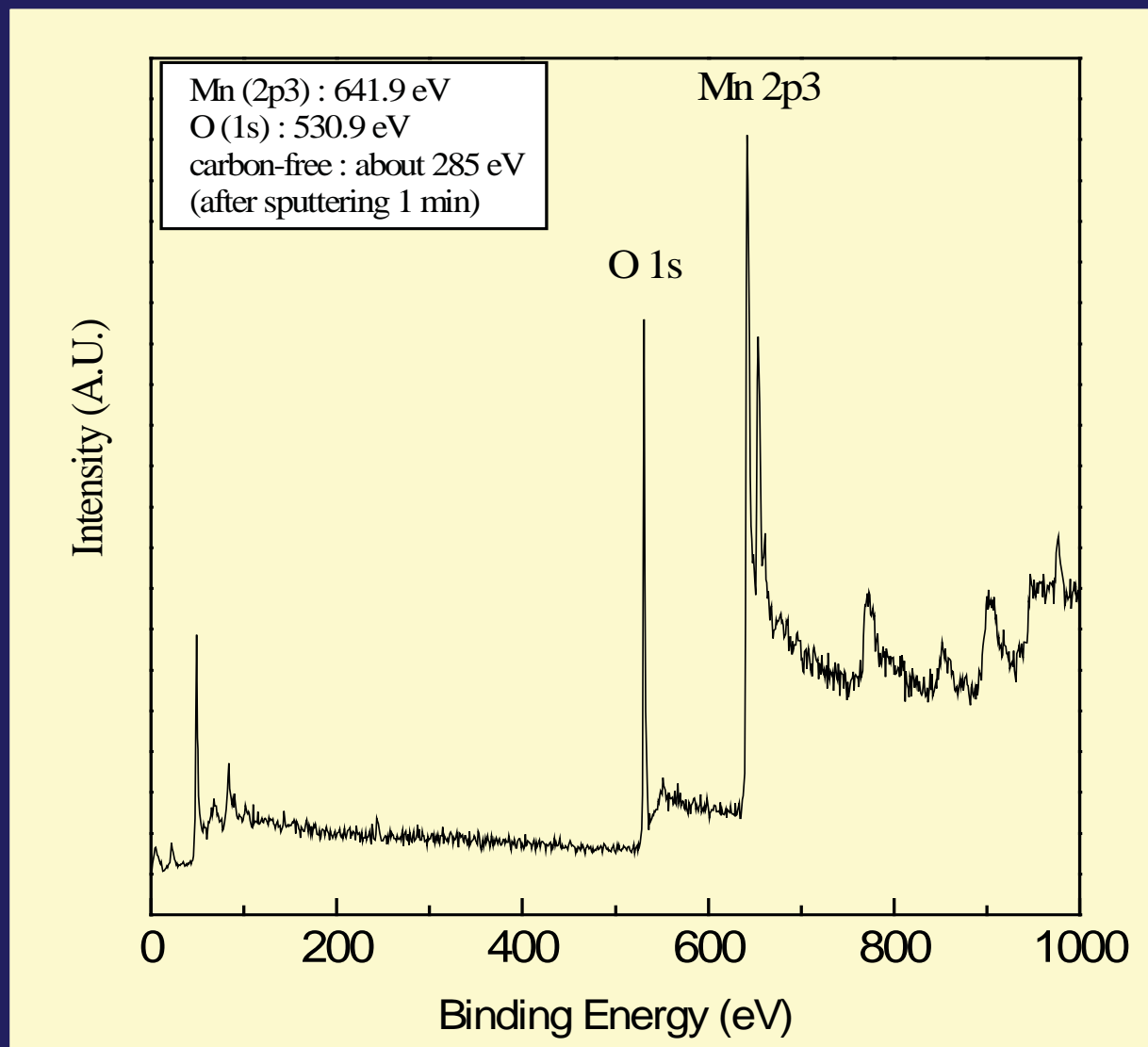
Rutherford Backscattering Spectroscopy

=> Stoichiometry MnO Adding O₂ cycles => MnO₂

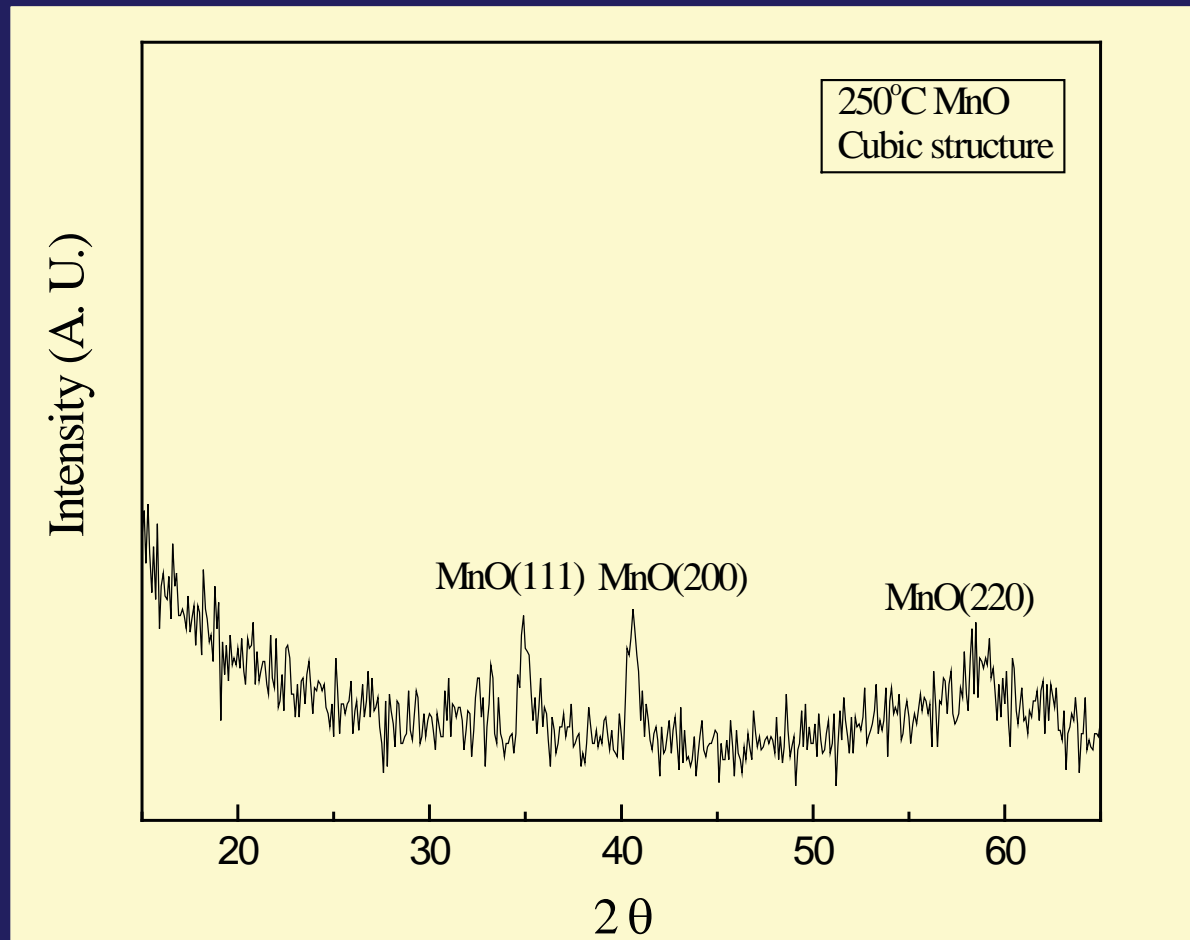


X-Ray Photoelectron Spectroscopy

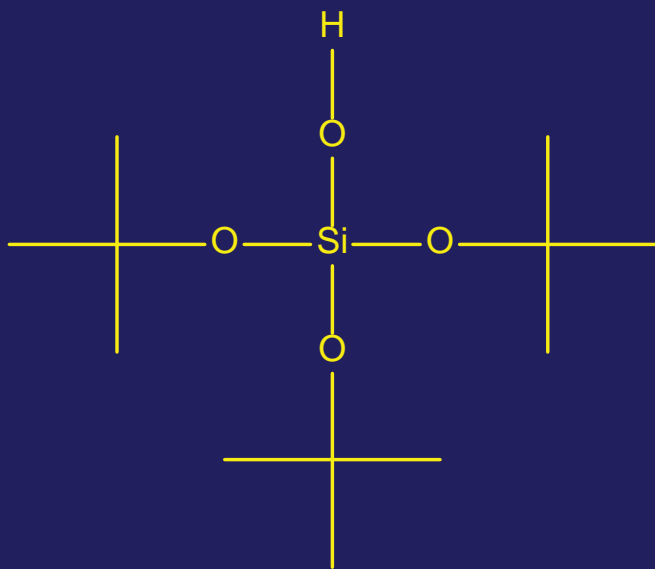
< 1% C or N impurities



XRD shows polycrystalline MnO

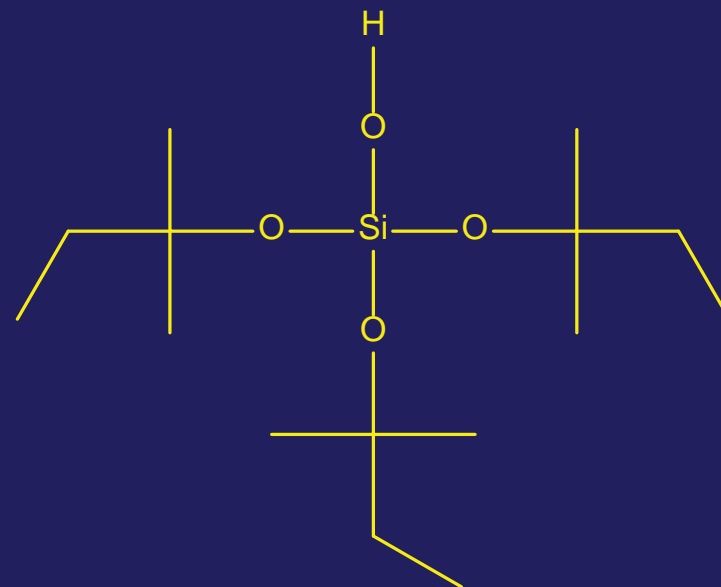


Precursors for Silicon and Oxygen



tris-*tert*-butoxysilanol (TBS)

melting point: 63 - 65 °C
boiling point: 205 - 210 °C/ 760 torr



tris-*tert*-pentoxysilanol (TPS)

melting point: < 20 °C
boiling point: 96-99 °C/ 2-3 torr

ALD Conditions for Manganese Silicate

Substrate: SiO₂/Si

UV ozone cleaning: 2 min

Drying at 350°C: 1 hour

Mn amidinate source =105°C

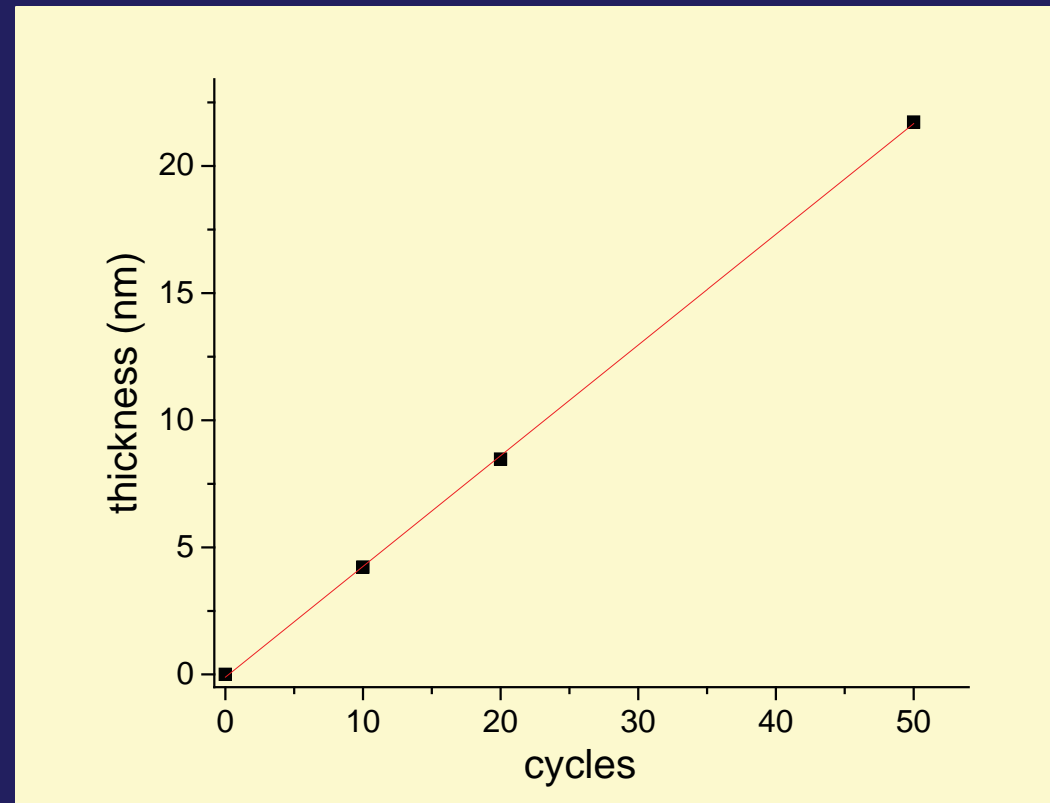
Si/O source (TPS)=120°C

T(substrate)= 350°C

Cycle times (s): 1/30/4/30

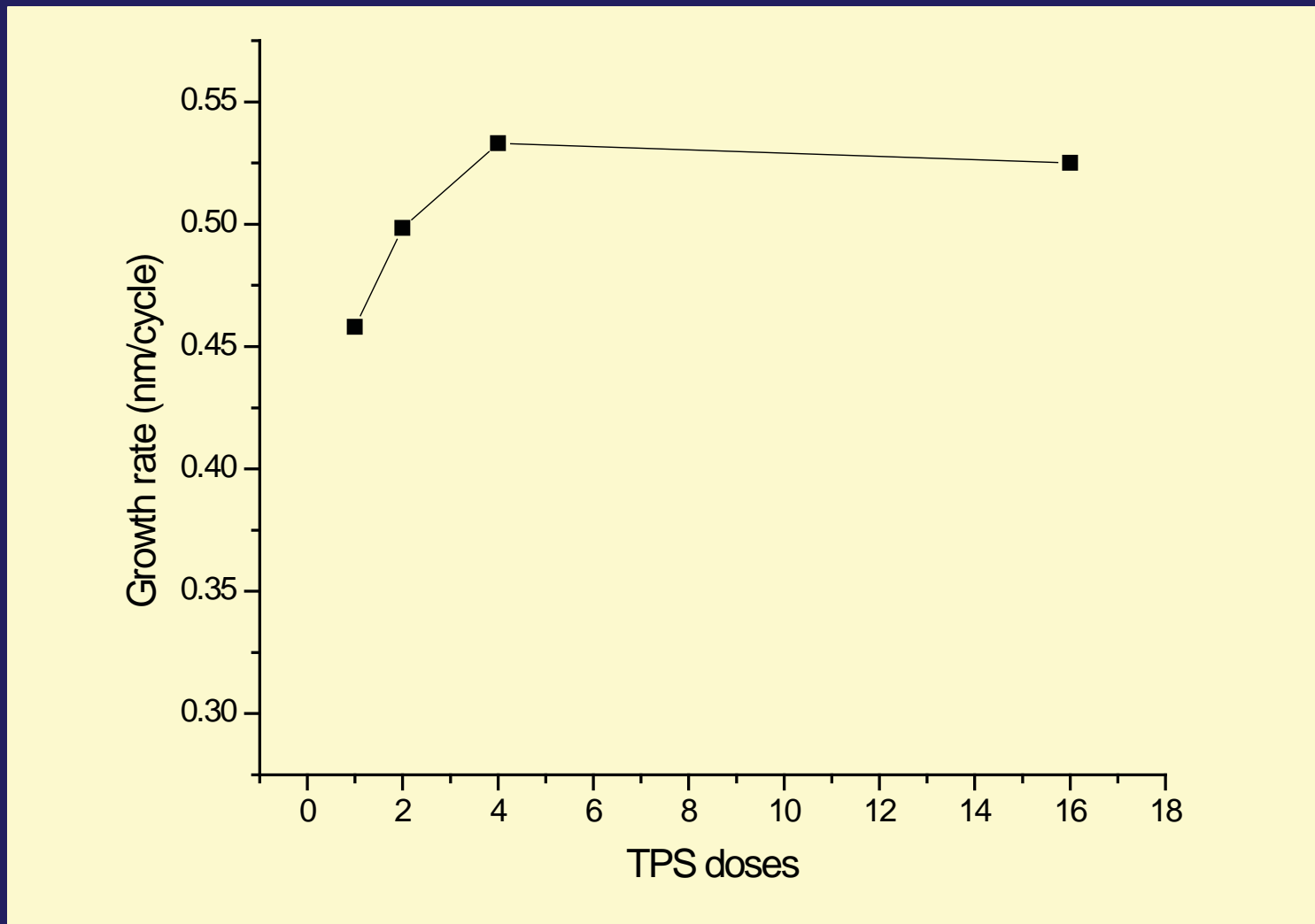
(Mn(amd)/purge/TPS/purge)

growth per cycle = 0.43 nm

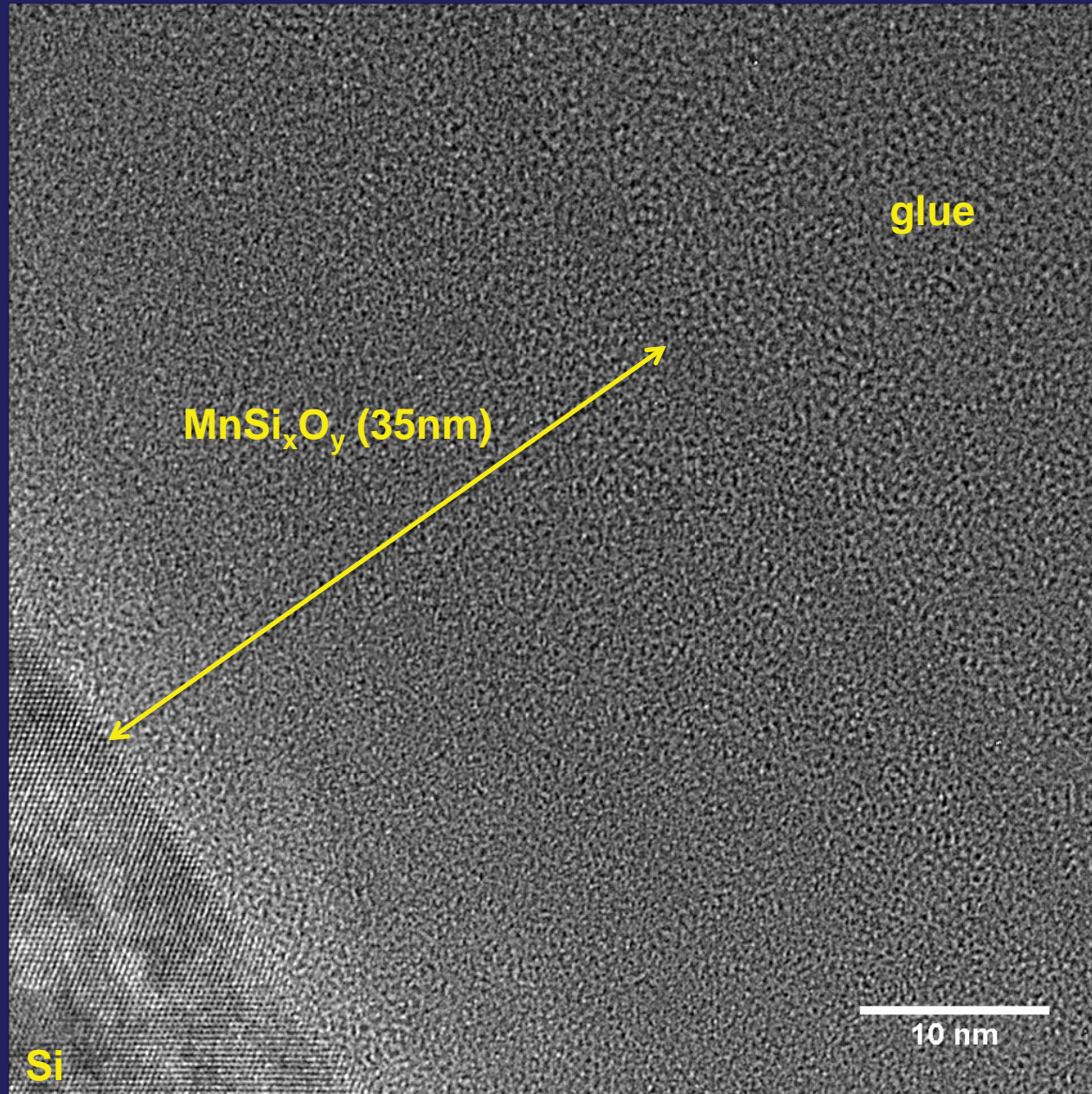


High growth per cycle due to a catalytic mechanism similar to that of aluminum-catalyzed silica: Dennis Hausmann, Jill Becker, Shenglong Wang, Roy G. Gordon, Science 298, 402 (2002)

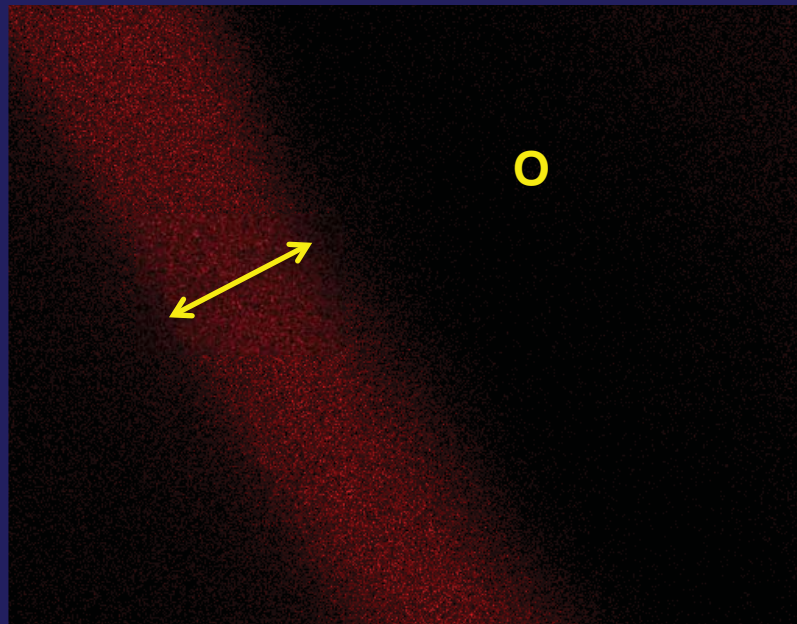
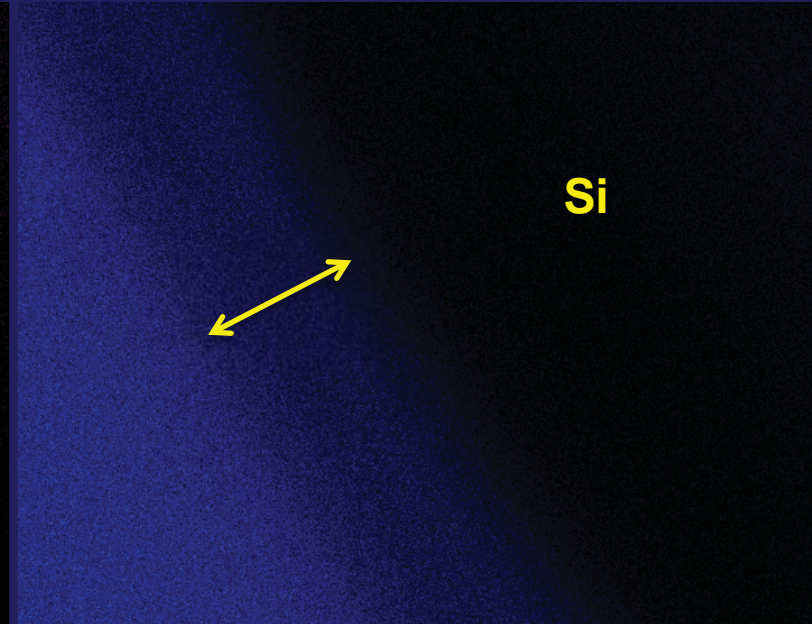
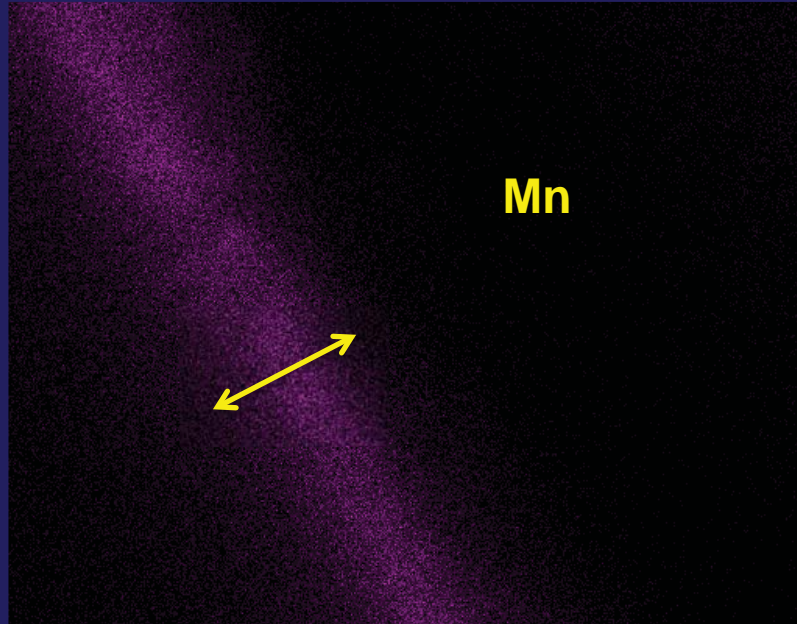
Saturation Curve for MnSi_xO_y vs. Silicate Precursor



TEM => Amorphous Structure



STEM EDX Mapping of Elements



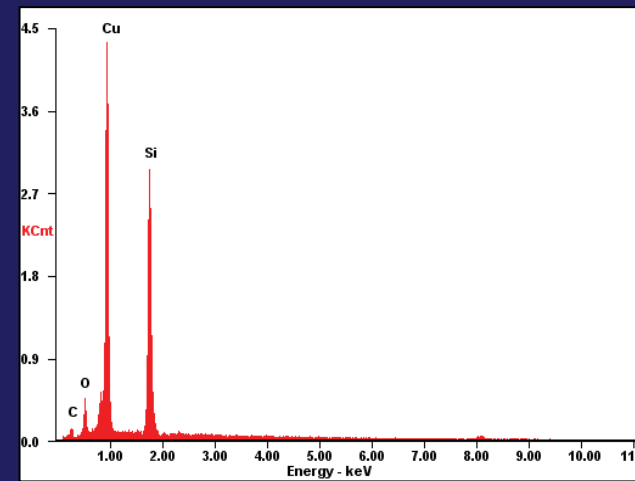
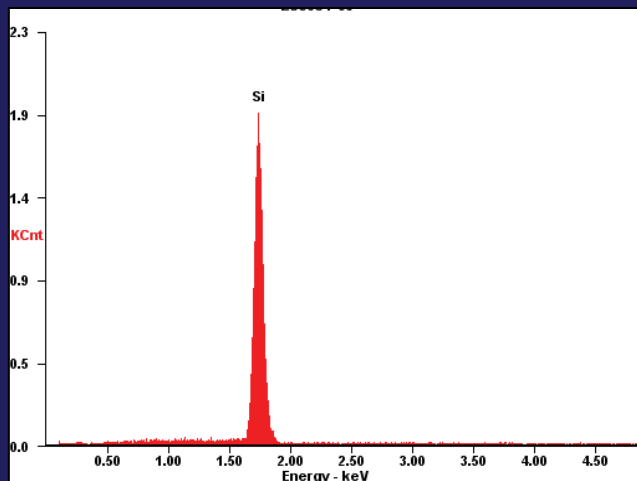
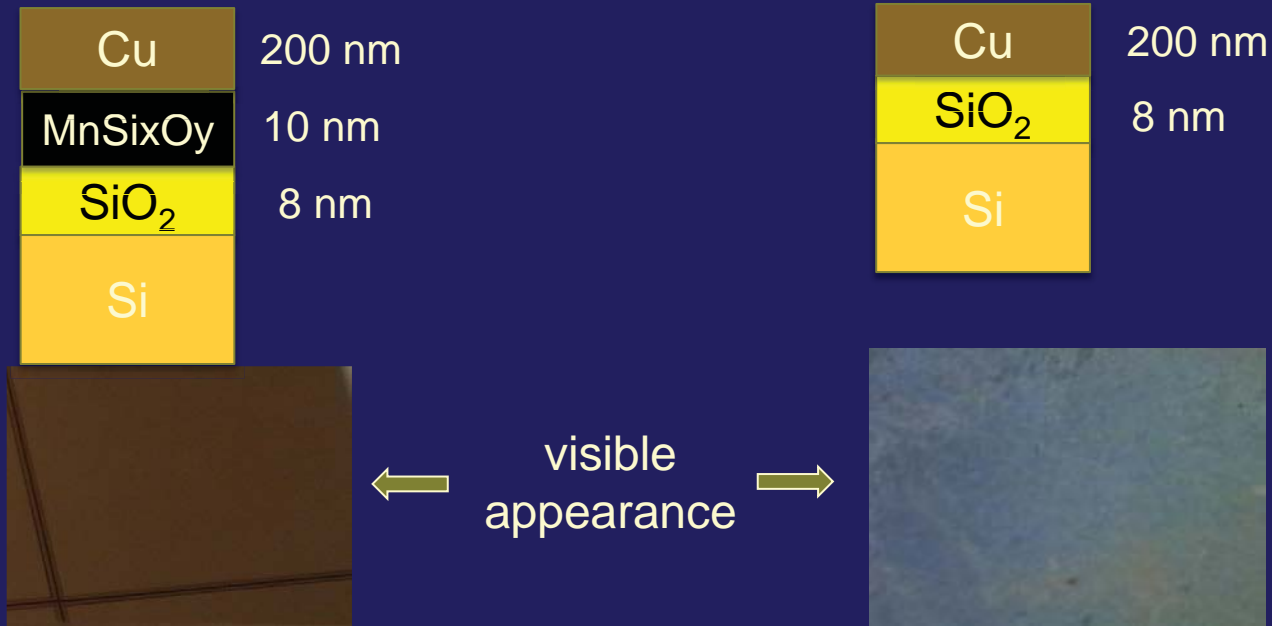
Composition by Rutherford Backscattering Spectroscopy

Cycles	Mn 10^{15} at/cm ²	Si 10^{15} at/cm ²	O 10^{15} at/cm ²	Mn:Si:O
10	2.32	6.2	24	1 : 2.7 : 10
20	5.56	15	47	1 : 2.7 : 8
50	15.4	41	117	1 : 2.7 : 7.6

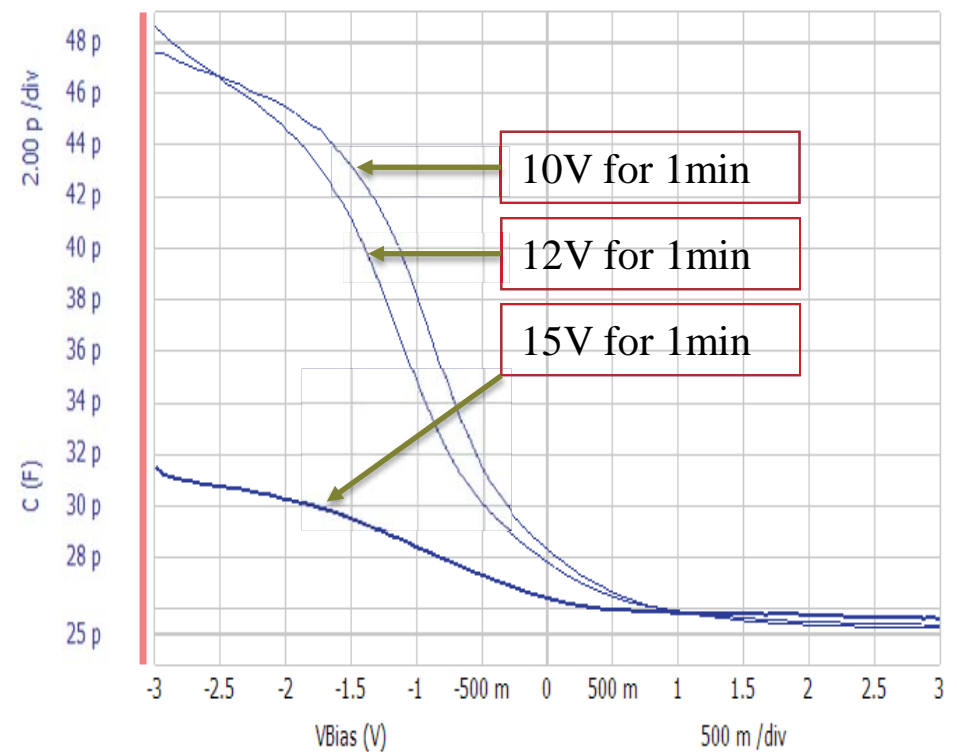
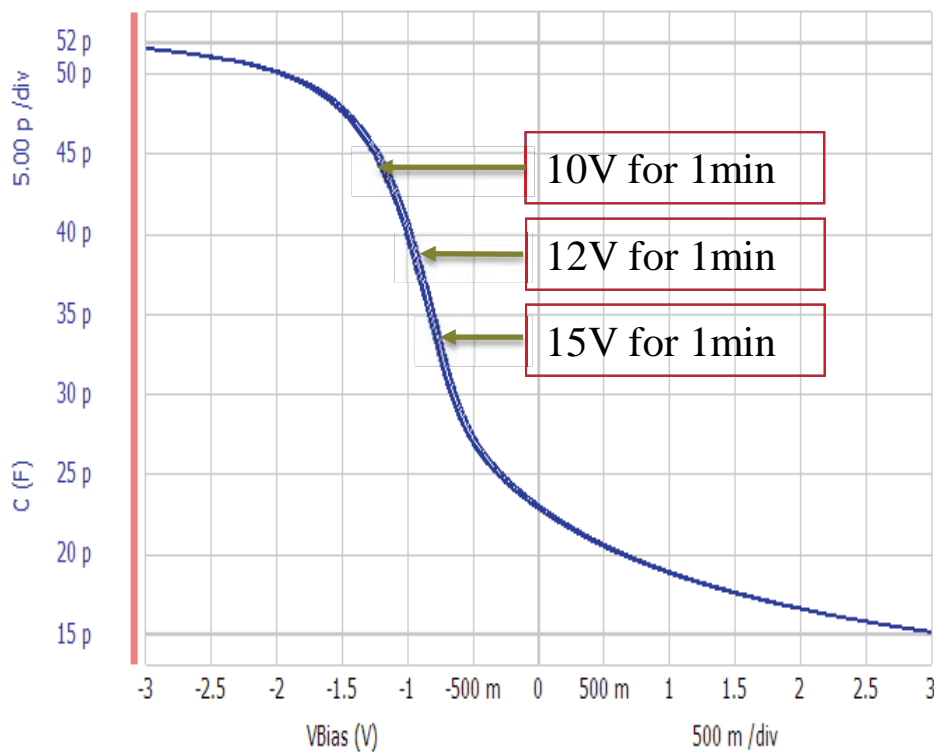
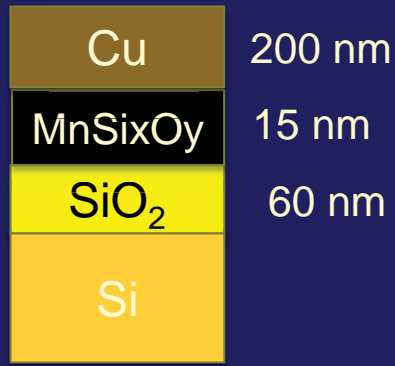
Stoichiometry ~ $\text{MnSi}_{2.7}\text{O}_{7.6}$ so Mn is oxidized to Mn^{4+}

Cu diffusion test

anneal samples in N_2 for 1h at 450 C, use Ni etchant to remove Cu film, then EDX



CV tests after electric field at room temperature



Effectiveness of MnSi_xO_y as a Cu Diffusion Barrier

Composition	Structure	Cu Barrier	Diffusion Pathway
SiO_2	amorphous	no	open tetrahedral network
$\text{MnSi}_{2.7}\text{O}_{7.6}$	amorphous	yes	paths blocked by Mn ions
MnO	polycrystalline	no	grain boundaries

Acknowledgements

Precursors supplied by Dow Chemical, Sigma-Aldrich and Strem Chemical

The work was supported as part of the Center for the Next Generation of Materials by Design, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science

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

