

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

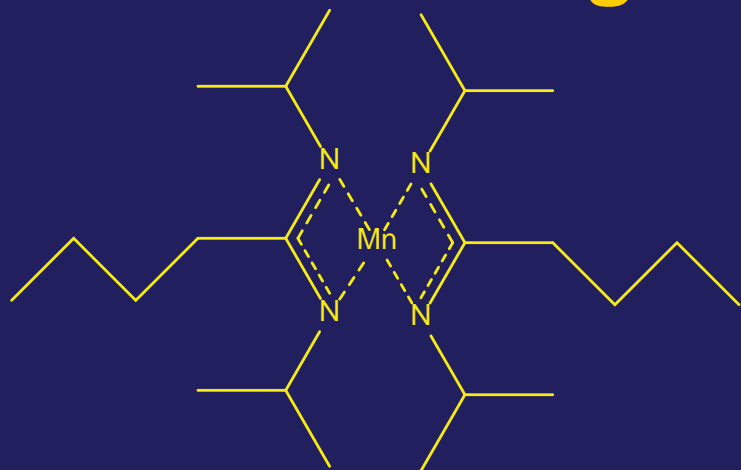


Potential Applications of MnSi_xO_y

Copper wires in computer chips could use MnSi_xO_y as a

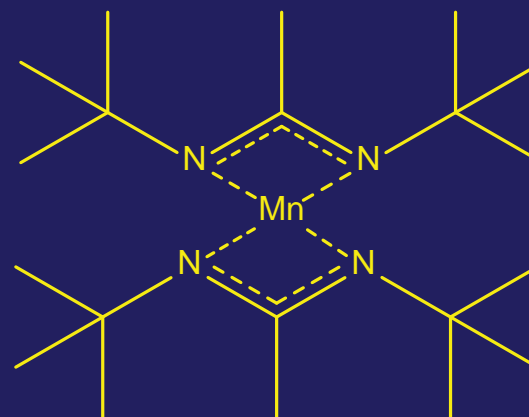
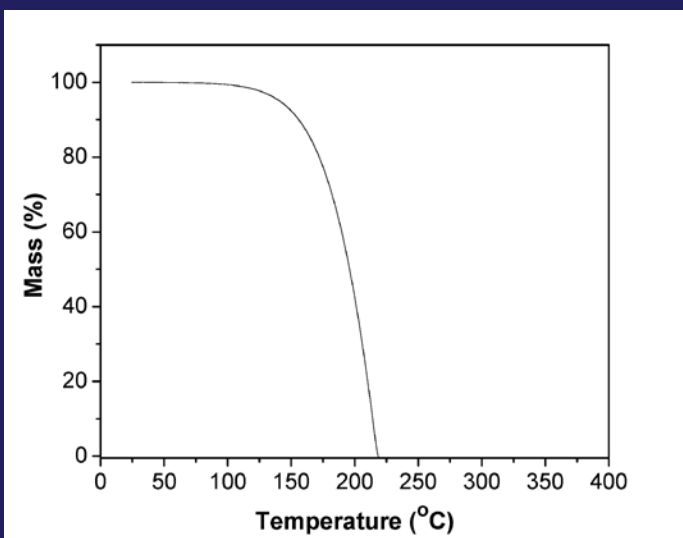
- barrier to diffusion of copper, water and oxygen
- adhesion promoter between copper and insulators
- nucleating layer for vapor deposition of copper

Manganese Precursors



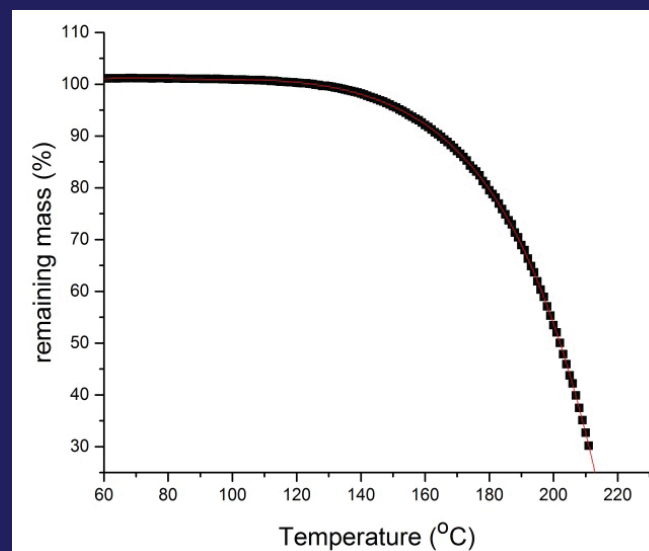
manganese(II)
bis(*N,N'*-diisopropylpentamidine)

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



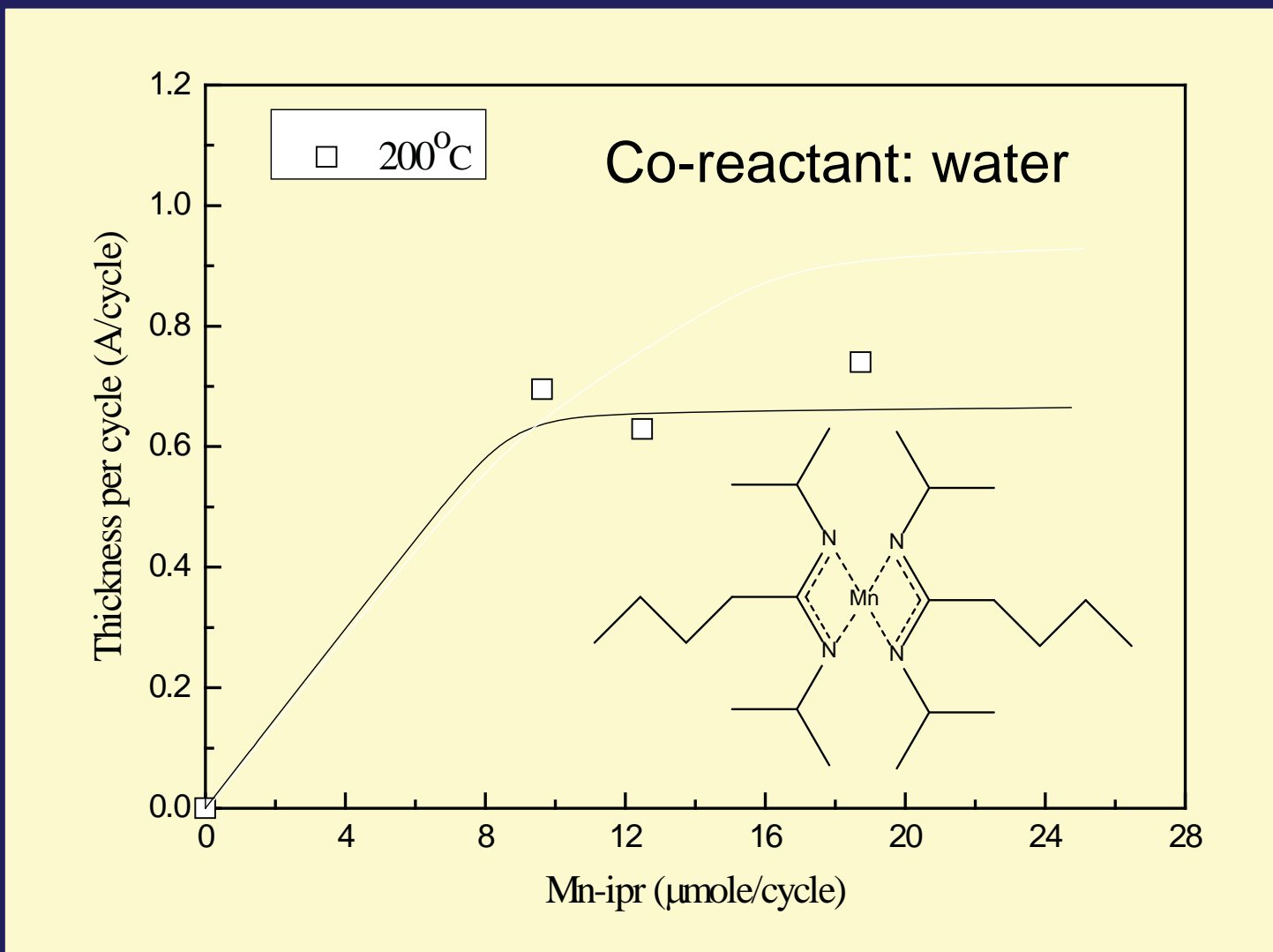
manganese(II)
bis(*N,N'*-di-*tert*-butylacetamidine)

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



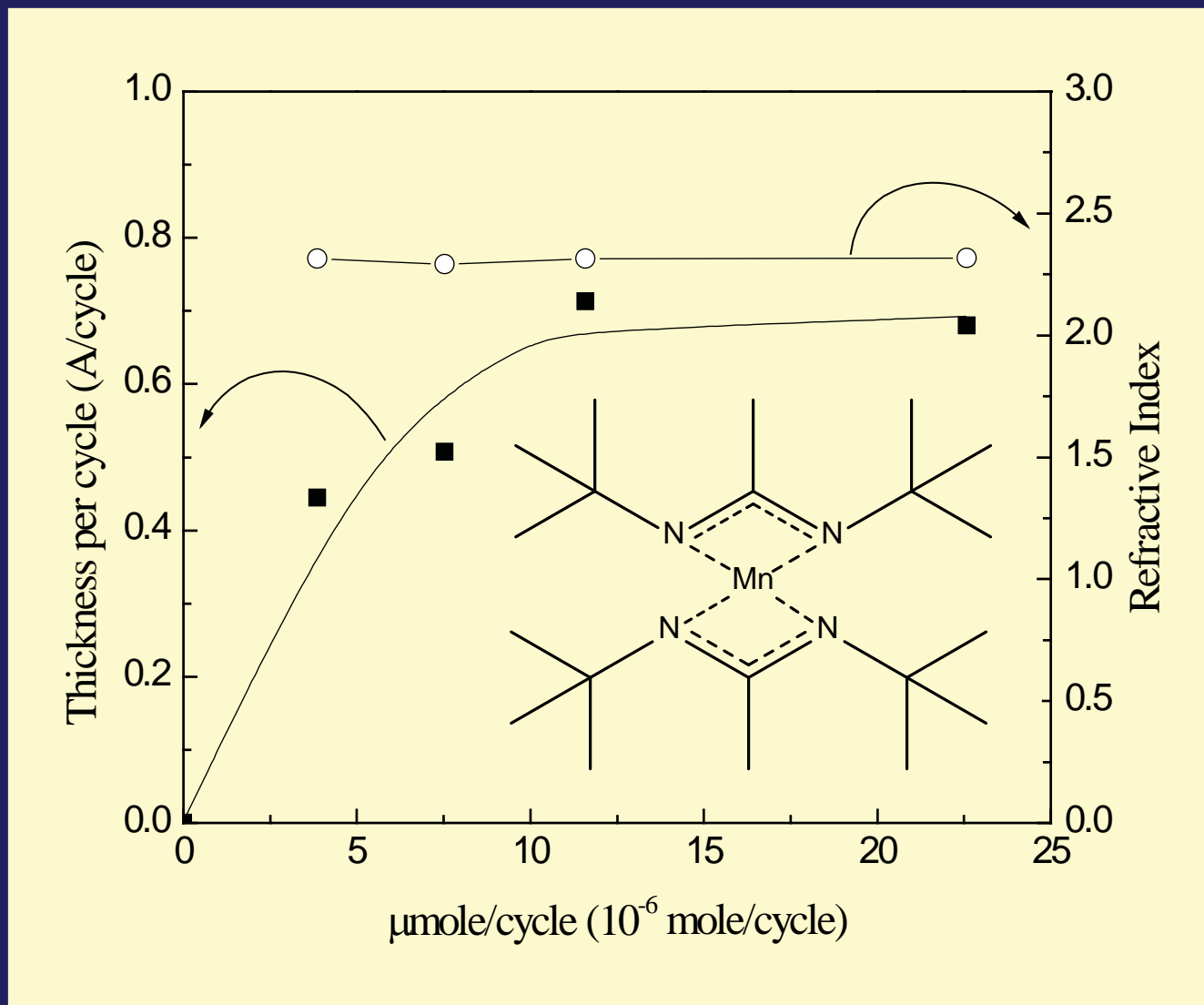
Saturation Curve for Manganese Oxide

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

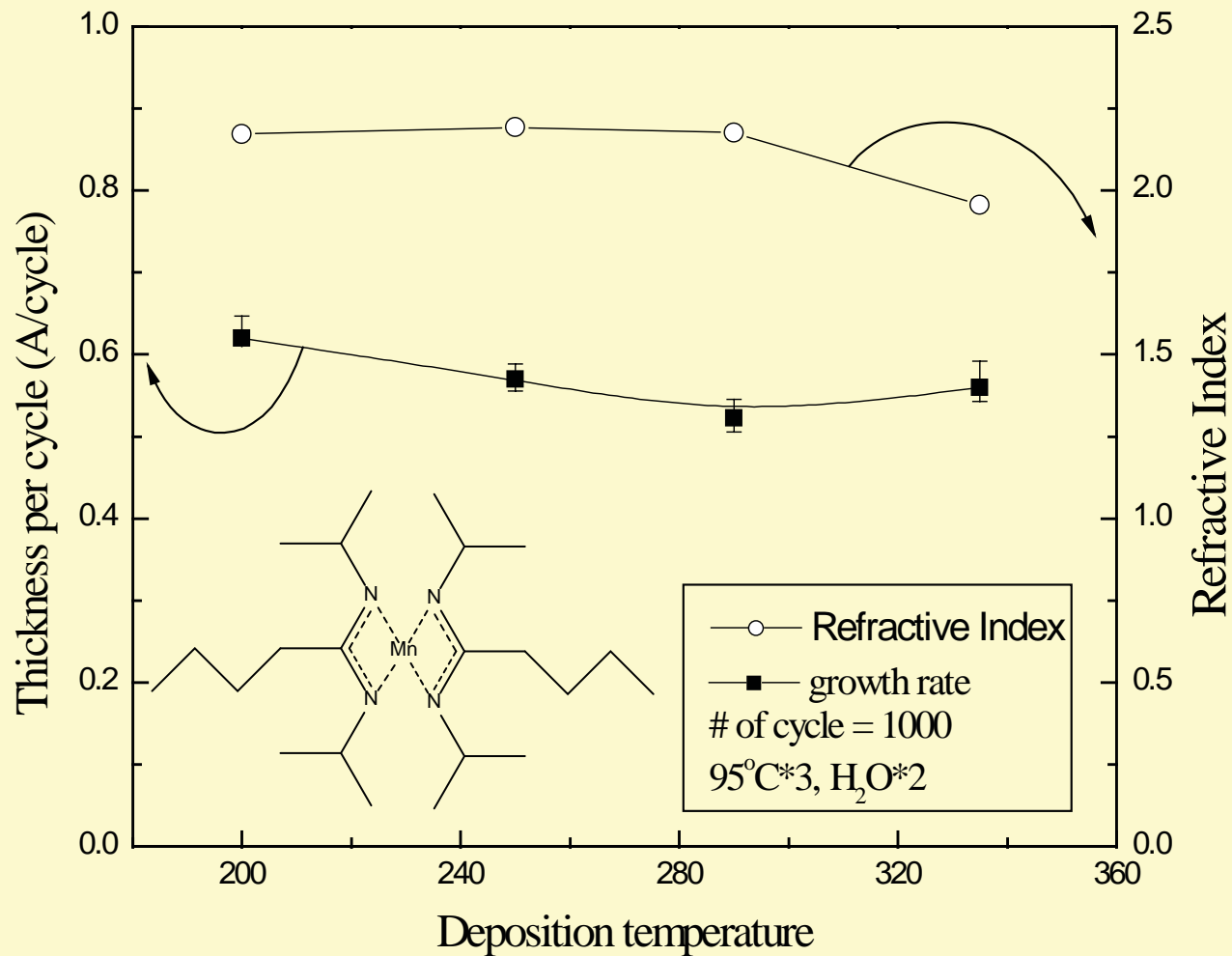


Saturation Curve for Manganese Oxide

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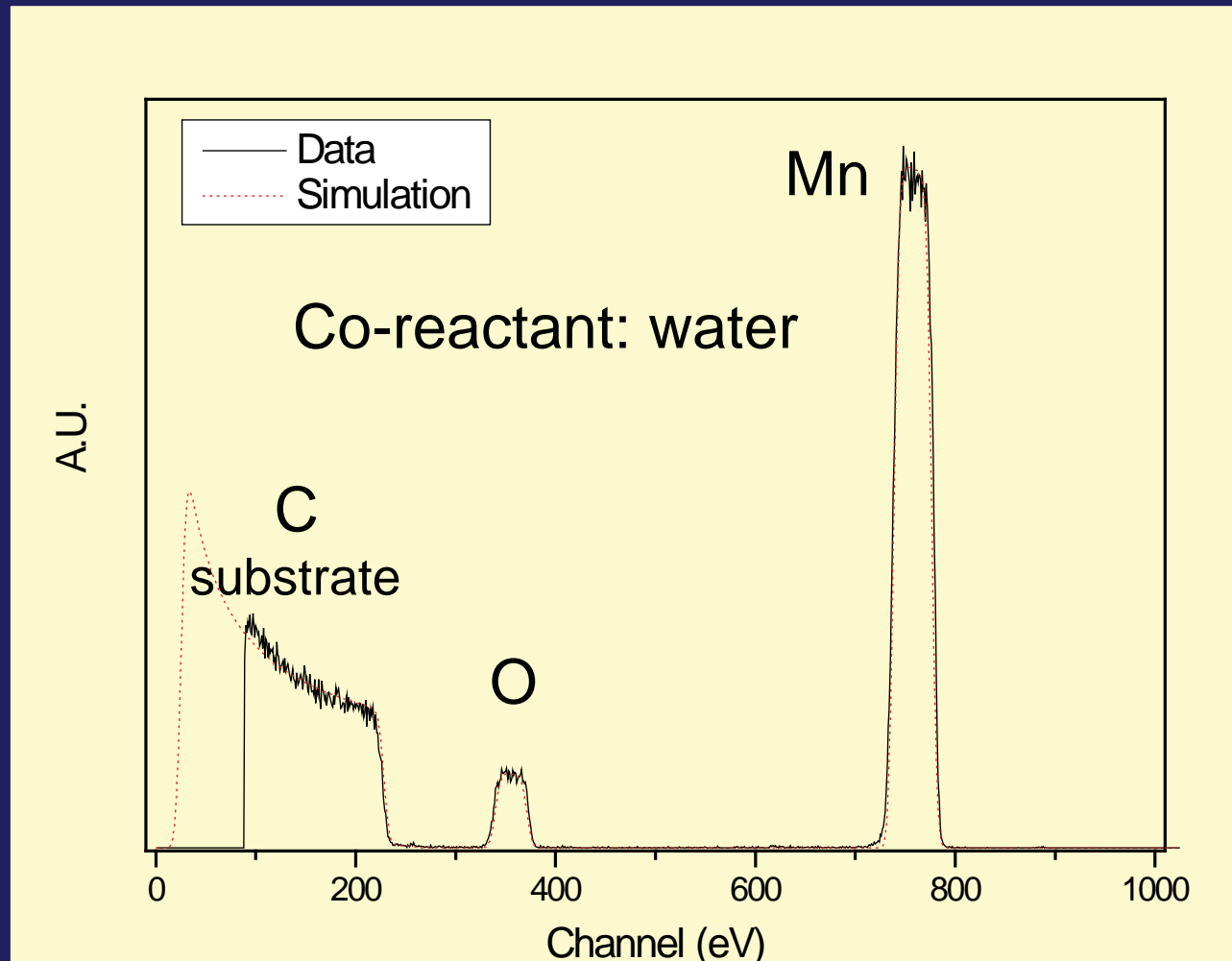


Thickness per Cycle for Manganese Oxide nearly constant from 200 to 340 °C



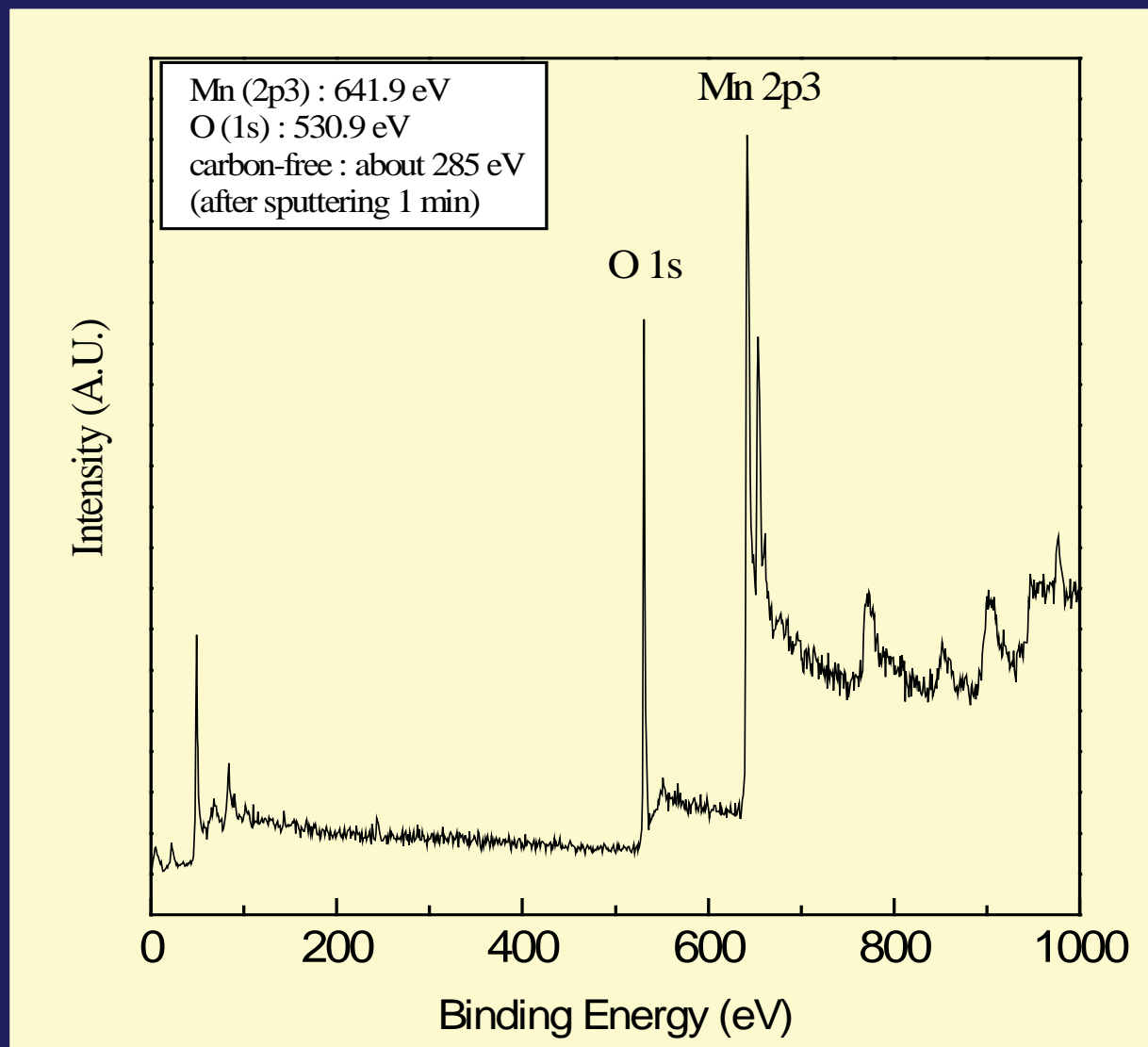
Rutherford Backscattering Spectroscopy

=> Stoichiometry MnO Adding O₂ cycles => MnO₂

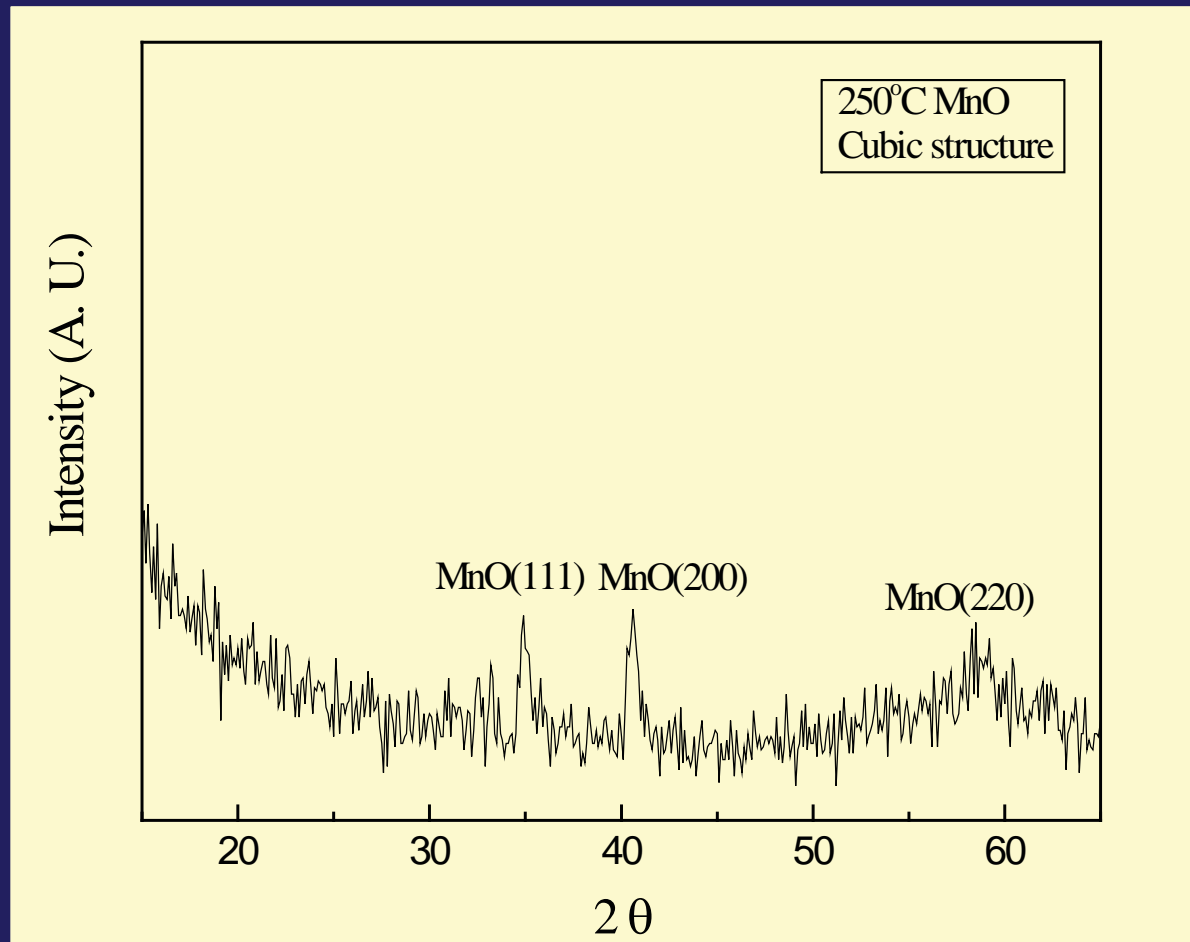


X-Ray Photoelectron Spectroscopy

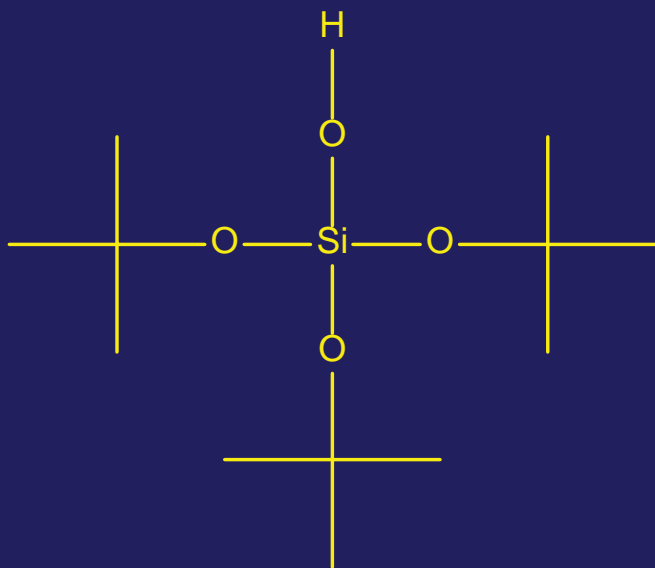
< 1% C or N impurities



XRD shows polycrystalline MnO

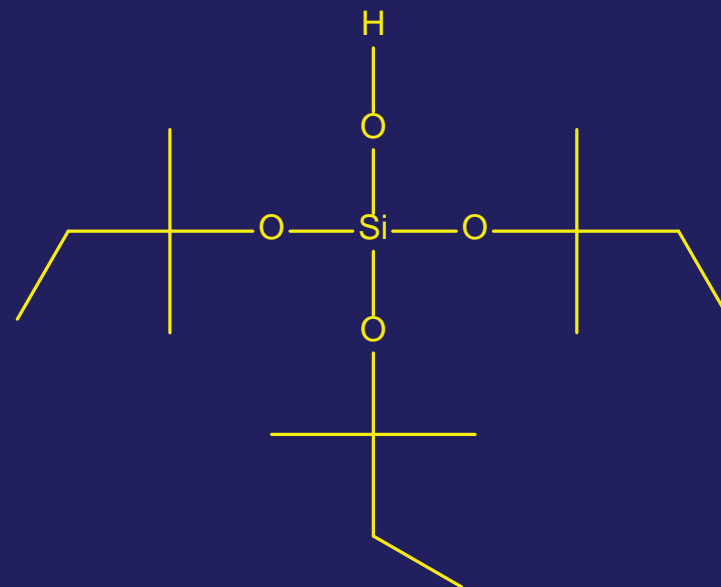


Precursors for Silicon and Oxygen



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

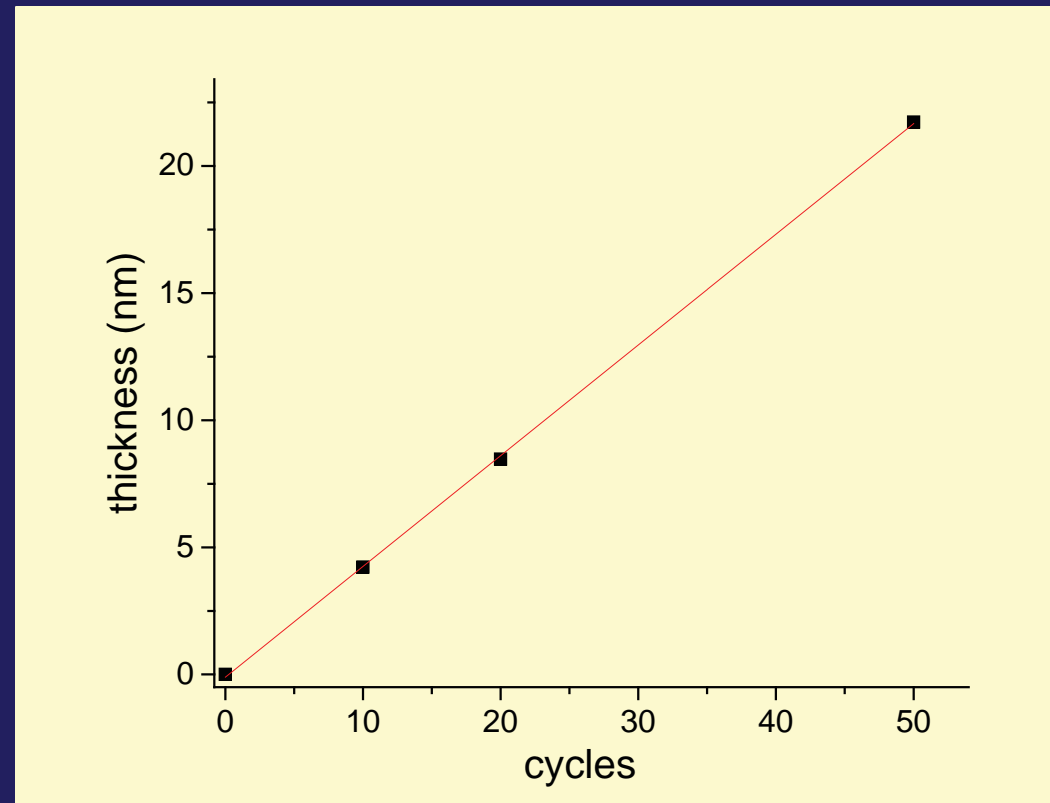
Si/O source (TPS)=120°C

T(substrate)= 350°C

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

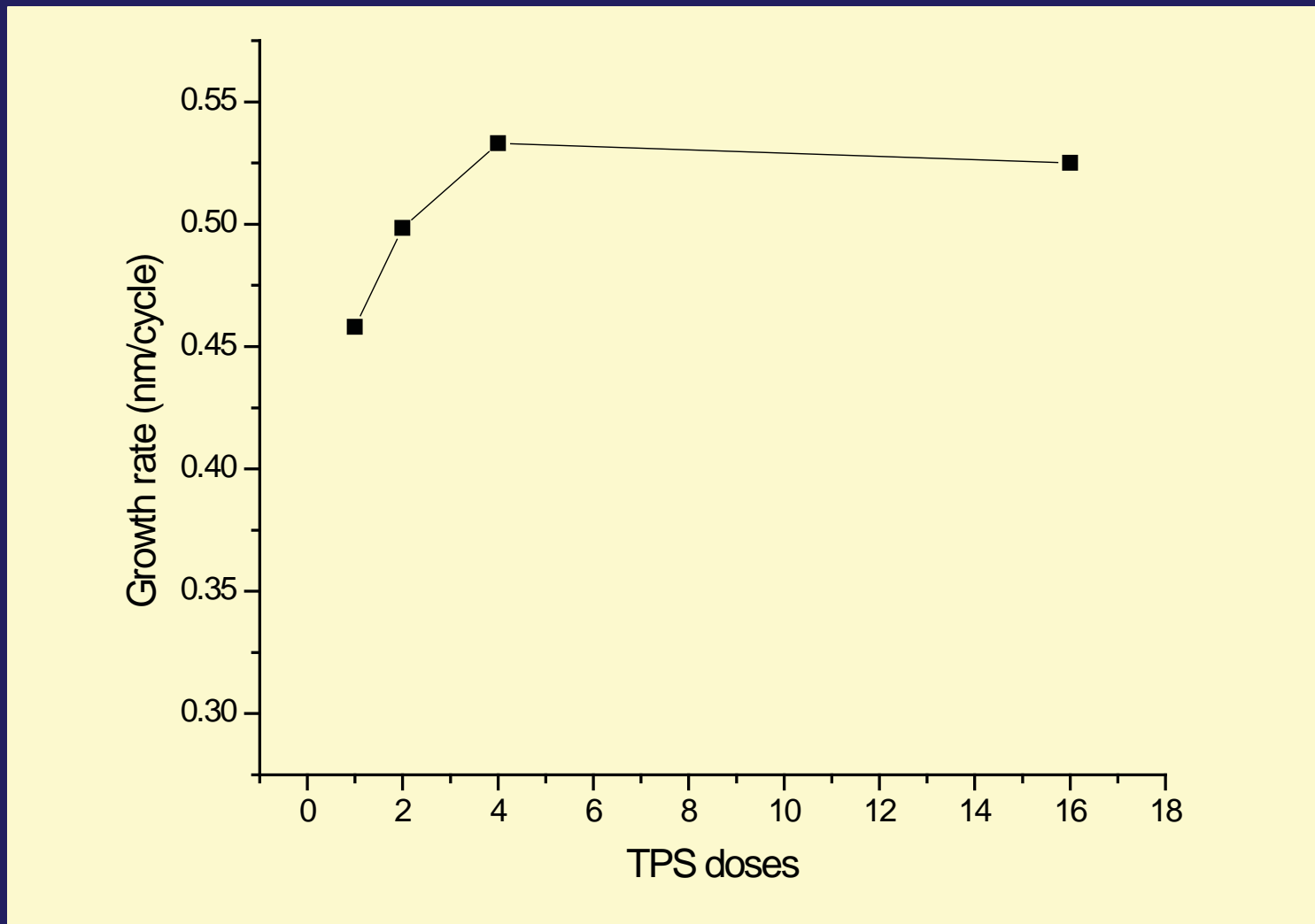
(Mn(amd)/purge/TPS/purge)

growth per cycle = 0.43 nm

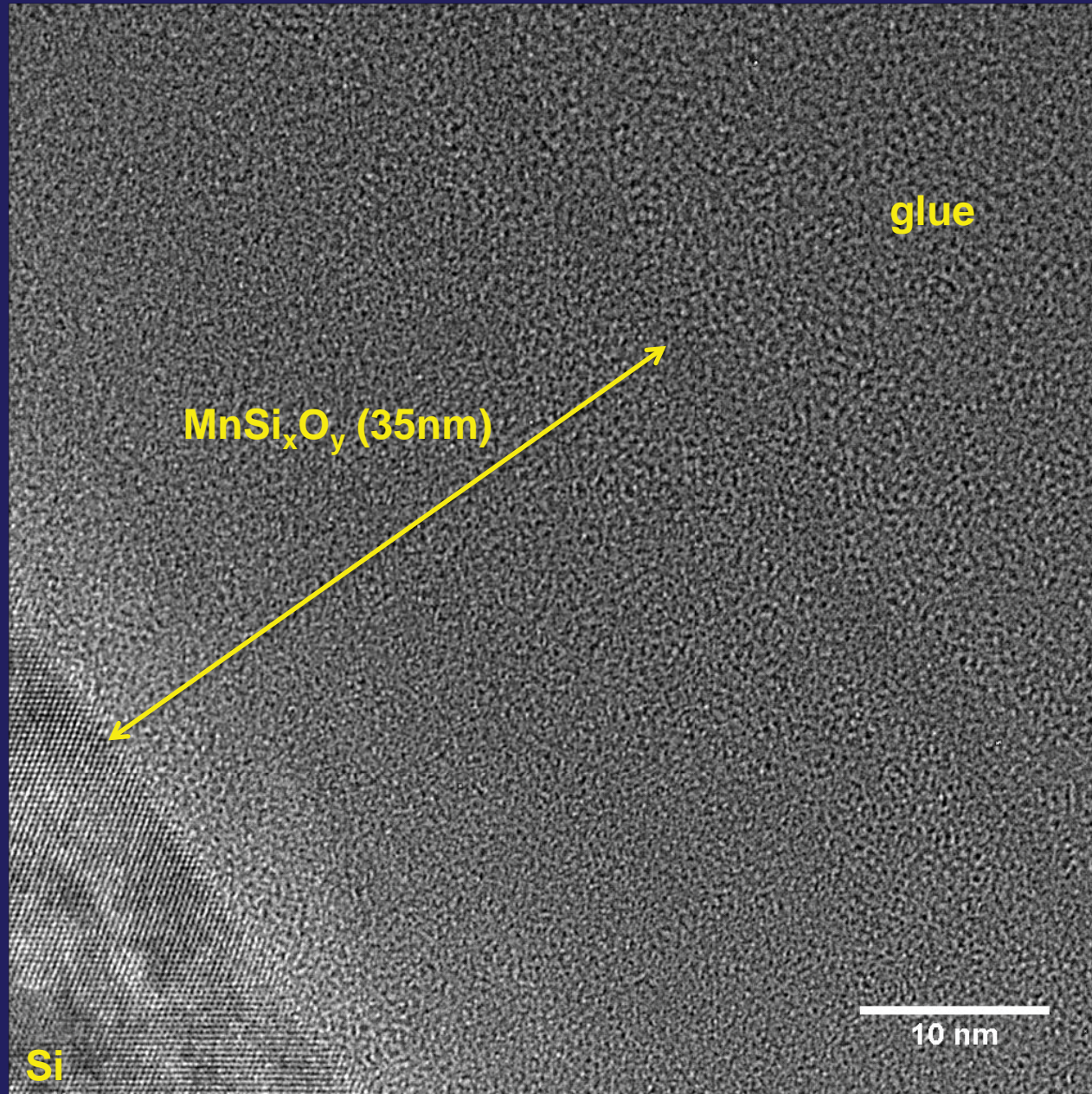


High growth per cycle due to a catalytic mechanism similar to that of aluminum-catalyzed silica: Dennis Hausmann, Jill Becker, Shenglong Wang, Roy G. Gordon, Science 298, 402 (2002)

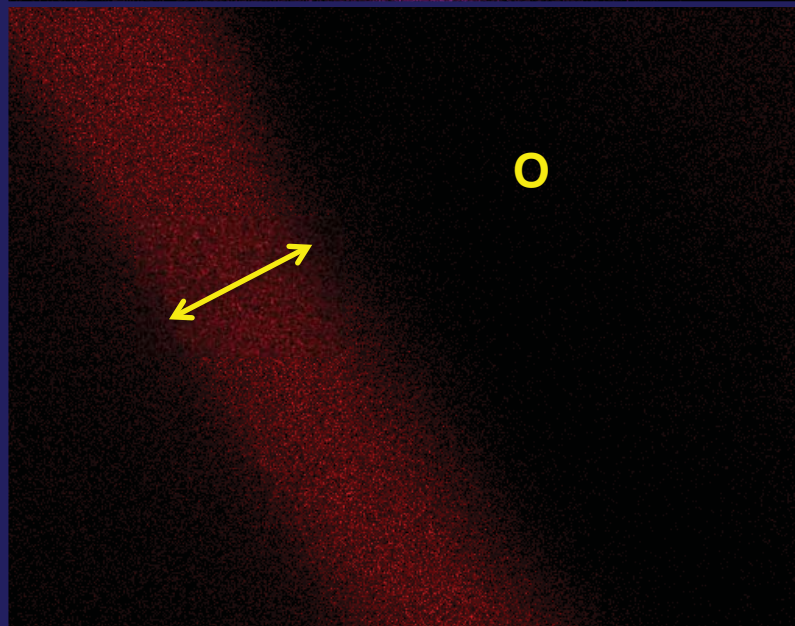
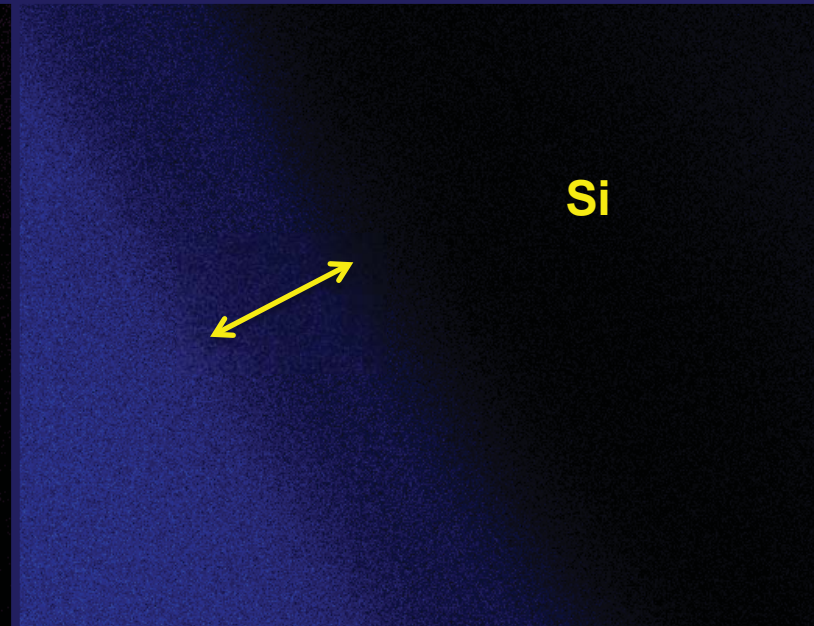
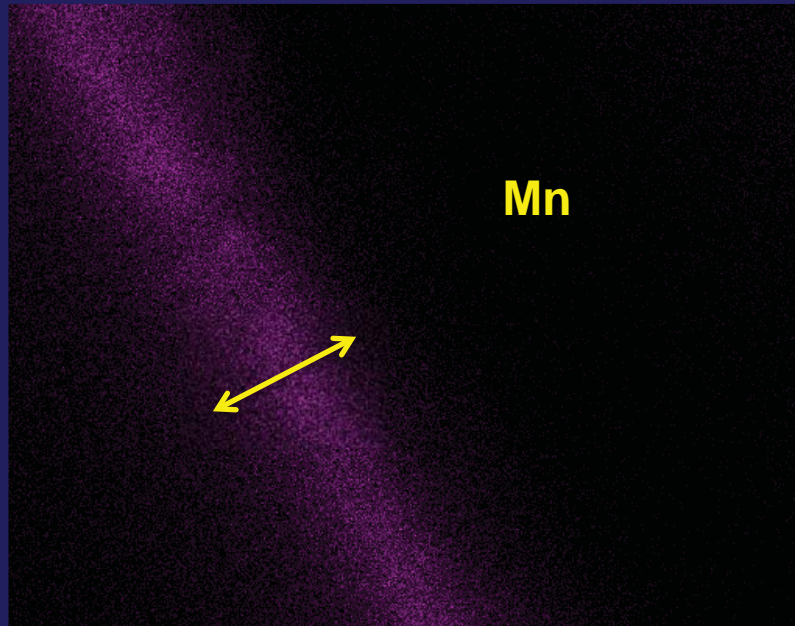
Saturation Curve for MnSi_xO_y vs. Silicate Precursor



TEM => Amorphous Structure



STEM EDX Mapping of Elements



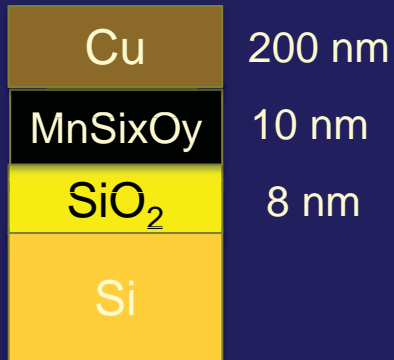
Composition by Rutherford Backscattering Spectroscopy

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

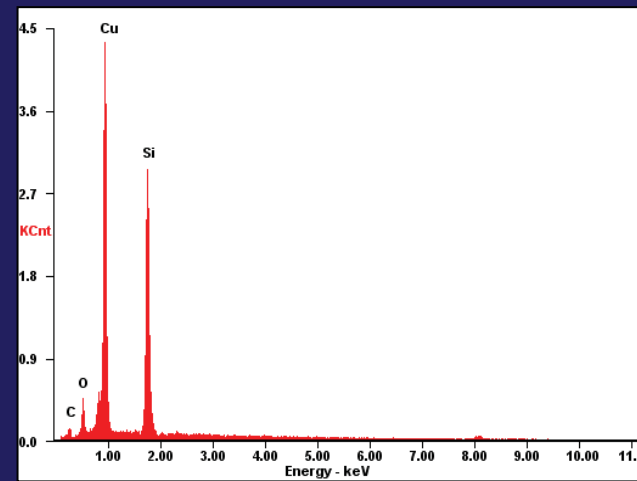
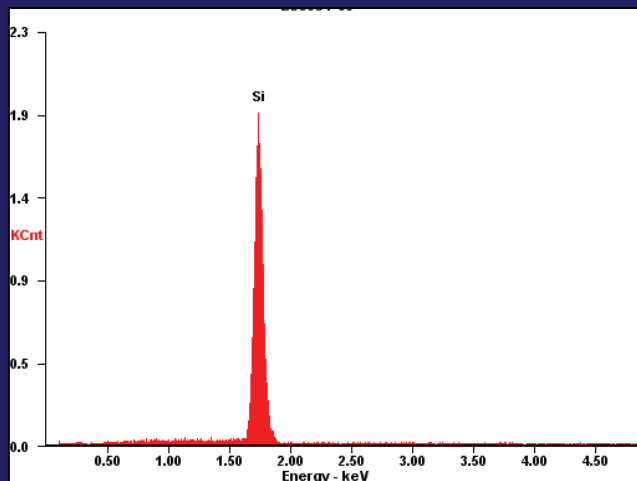
Stoichiometry ~ $\text{MnSi}_{2.7}\text{O}_{7.6}$ so Mn is oxidized to Mn^{4+}

Cu diffusion test

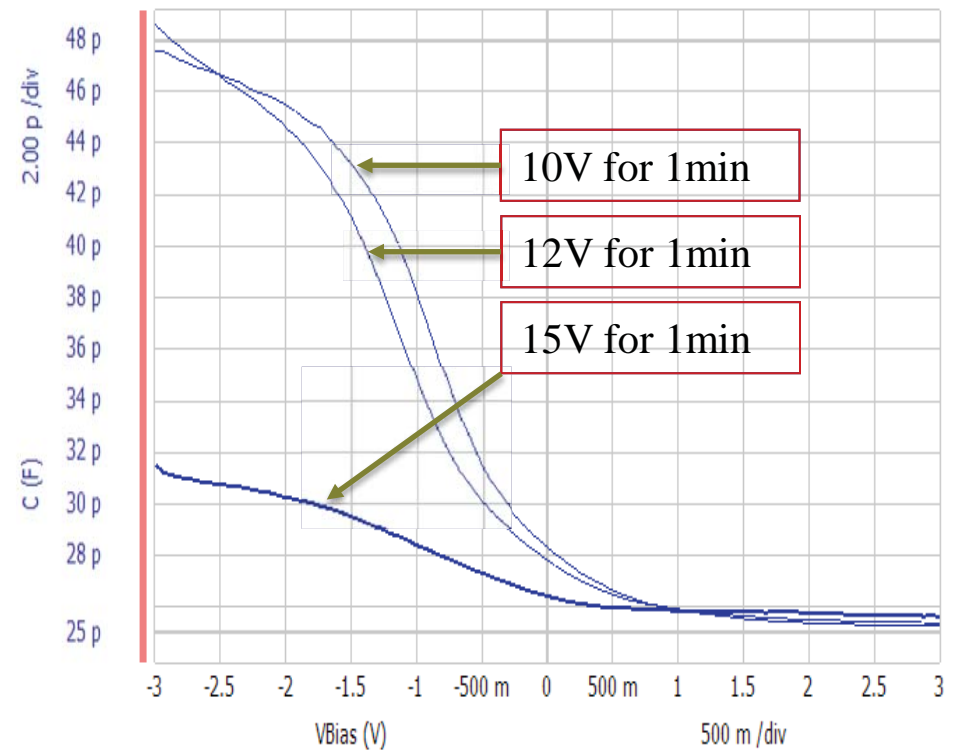
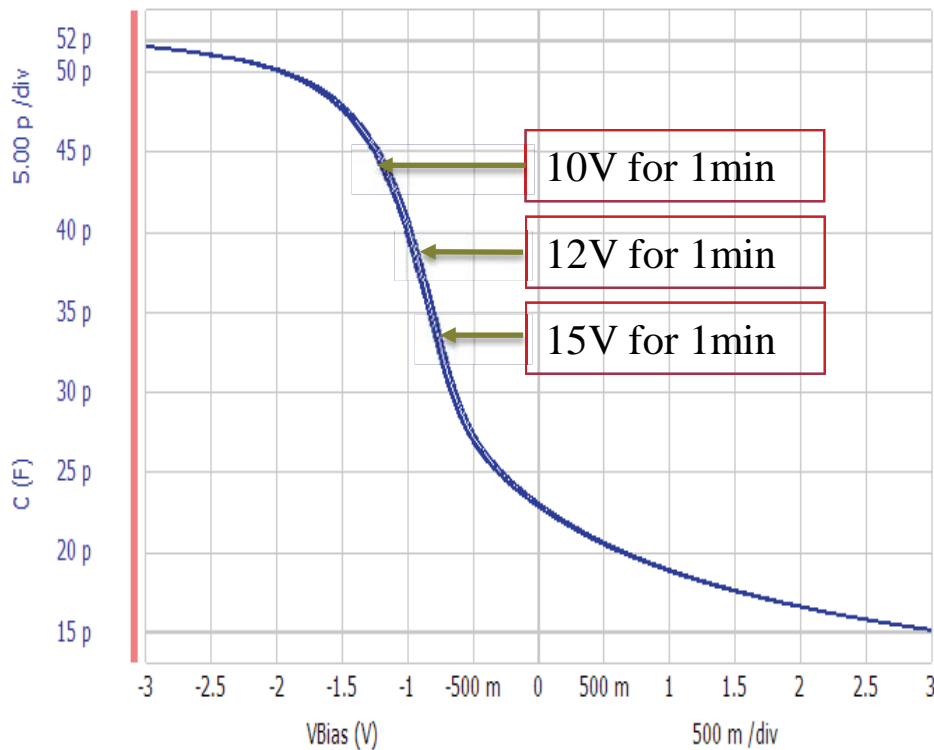
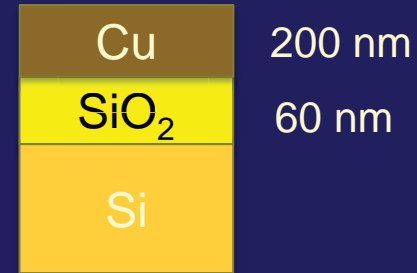
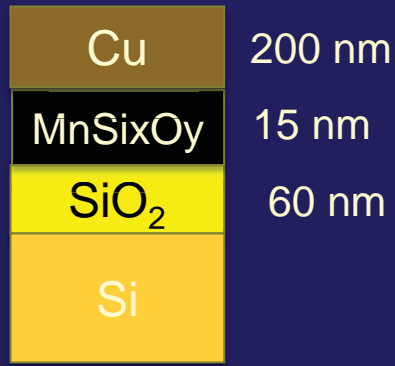
anneal samples in N_2 for 1h at 450 C, use Ni etchant to remove Cu film, then EDX



visible appearance



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

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