ASD 2017

Area-selective Deposition of Metal Films

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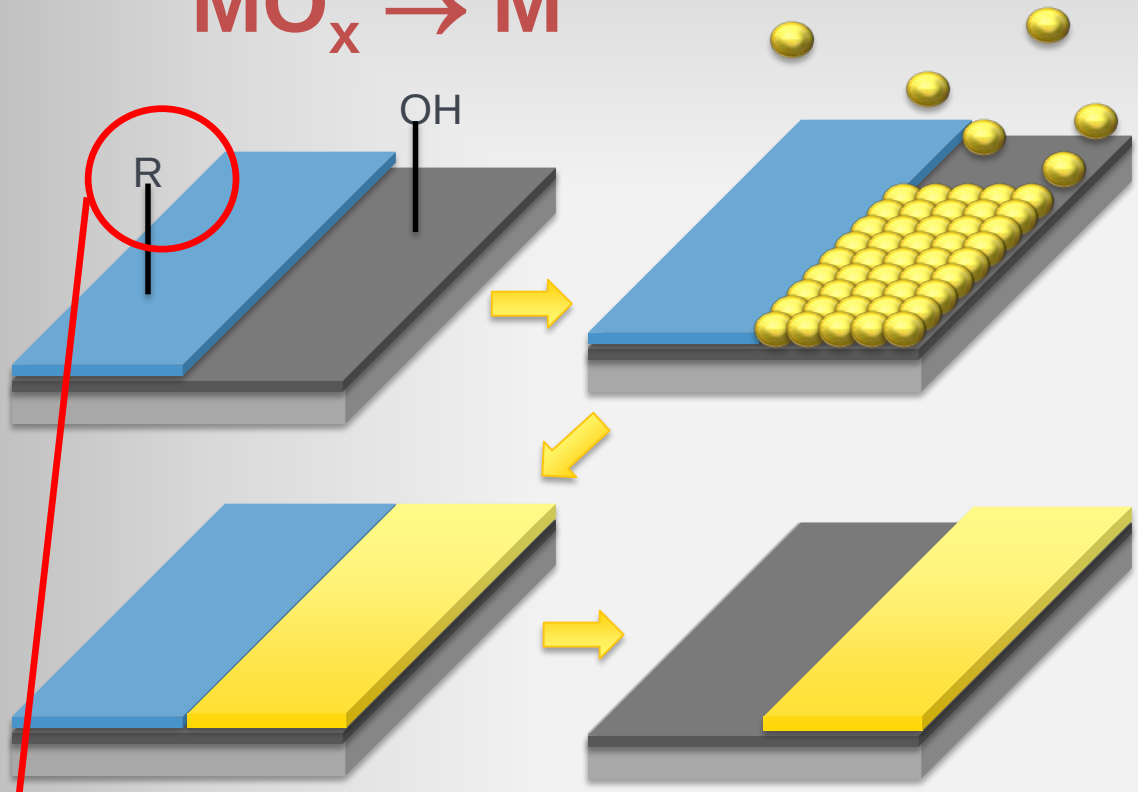
NASCENT - An NSF-funded Engineering Research Center

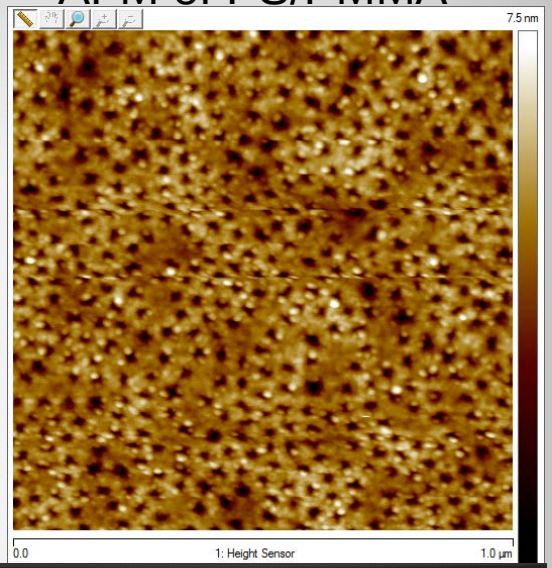
Raytheon

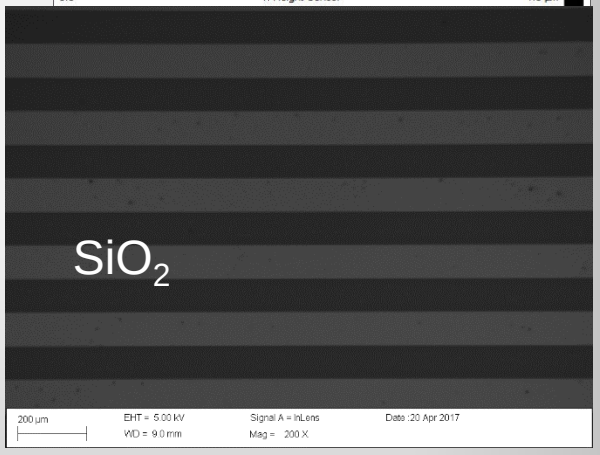
Area Selective ALD (AS-ALD)

$MO_x \rightarrow M$



AFM of PS/PMMA





Patterned PS on SiO_2 before ALD

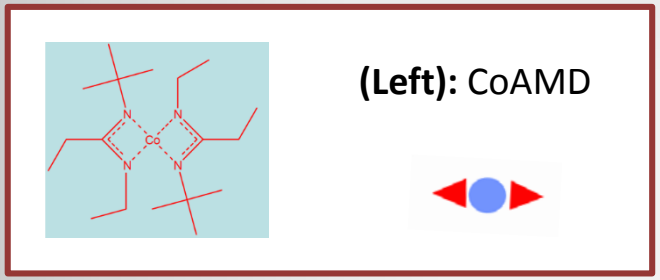
- AS-ALD advantages
  - Eliminates post deposition etch step
  - Eliminates alignment

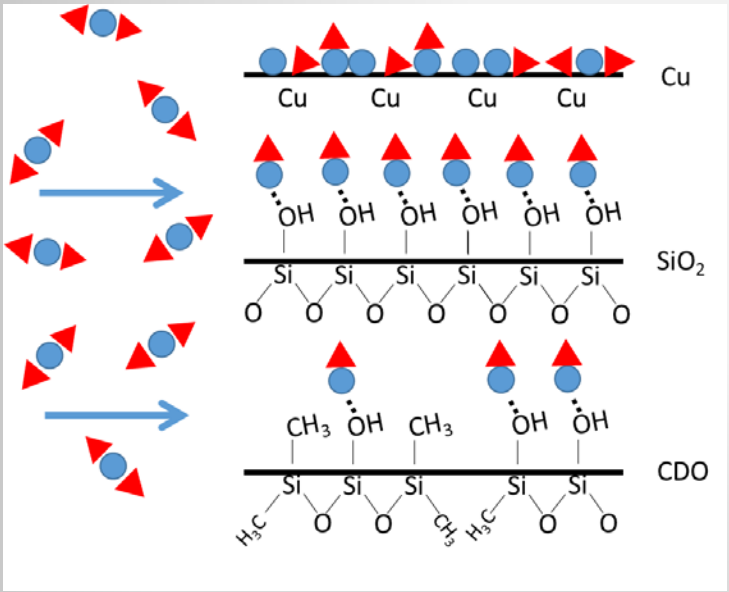
Every R-group studied blocked CoO and NiO ALD.

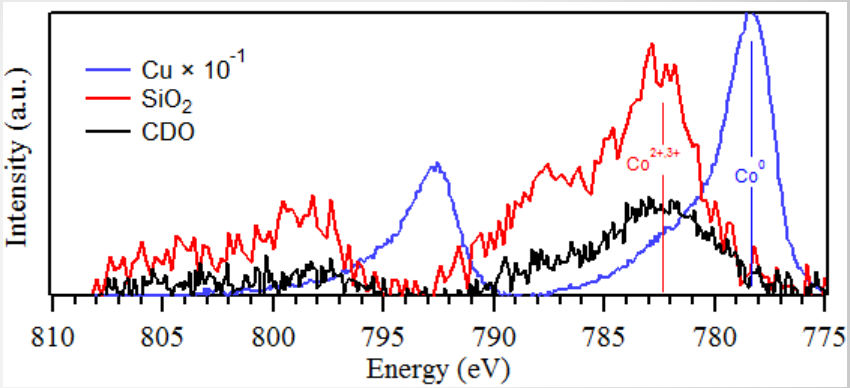
After extended O_2 RIE "PMMA" is active !

Lee, H; Bent, S (2012). Nanopatterning by Area-Selective Atomic Layer Deposition. In *Atomic Layer Deposition of Nanostructured Materials.* John Wiley & Sons.
George, Steven M. "Atomic Layer Deposition: An Overview." *Chemical Reviews* 110, no. 1 (2009): 111–31

CoAMD Adsorption on Various Substrates







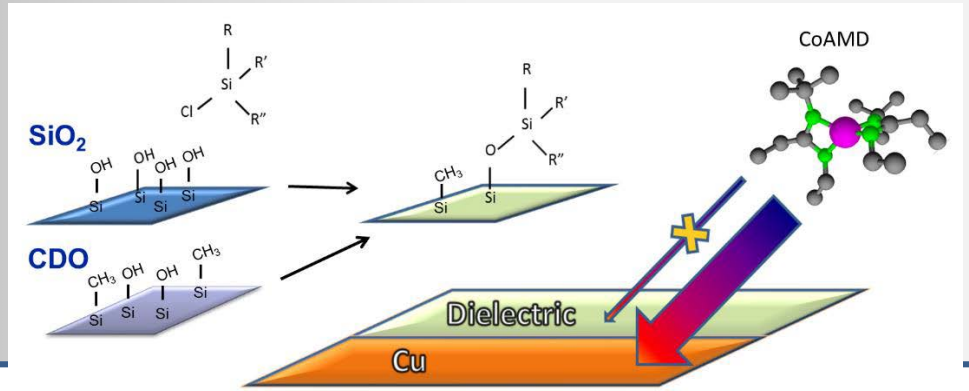
- **(Above):** Co 2*p* XP spectra from 3×2s CoAMD ALD cycles on respective substrates
- Shakeup peaks from Co 2*p* signals indicate Co(II).
- **(Left):** Schematic of likely initial CoAMD chemisorption events on respective BEOL substrates.

Elko-Hansen, T.D, Ekerdt, J.G.. *Chem. Mater.* **26,** 2642–2646 (2014)

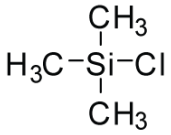
AS-ALD (or not) of Co

(Below): Passivation scheme and selected (OH) targeting passivants

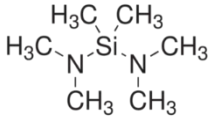
(Right): 250 cyc Co ALD at 265 °C after passivation at 50 °C

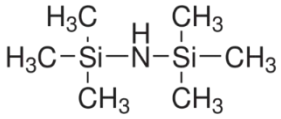


Trimethylchlorosilane (TMCS)



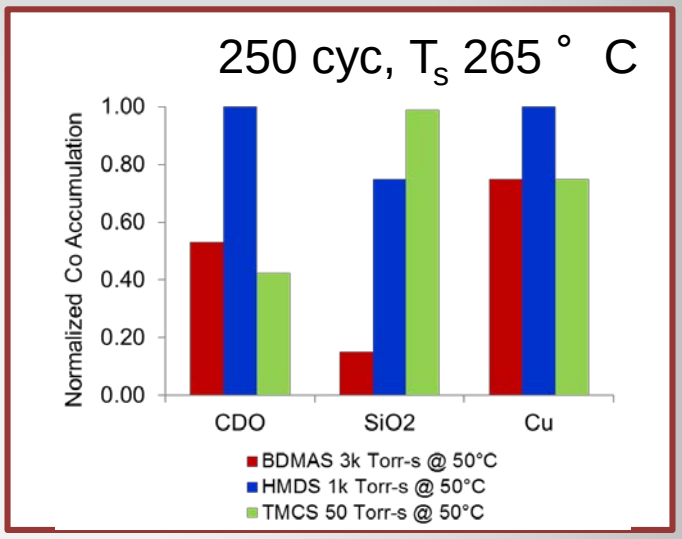
Bis-dimethyl amino dimethyl silane (BDMAS)





Hexamethyl disilazane (HMDS)

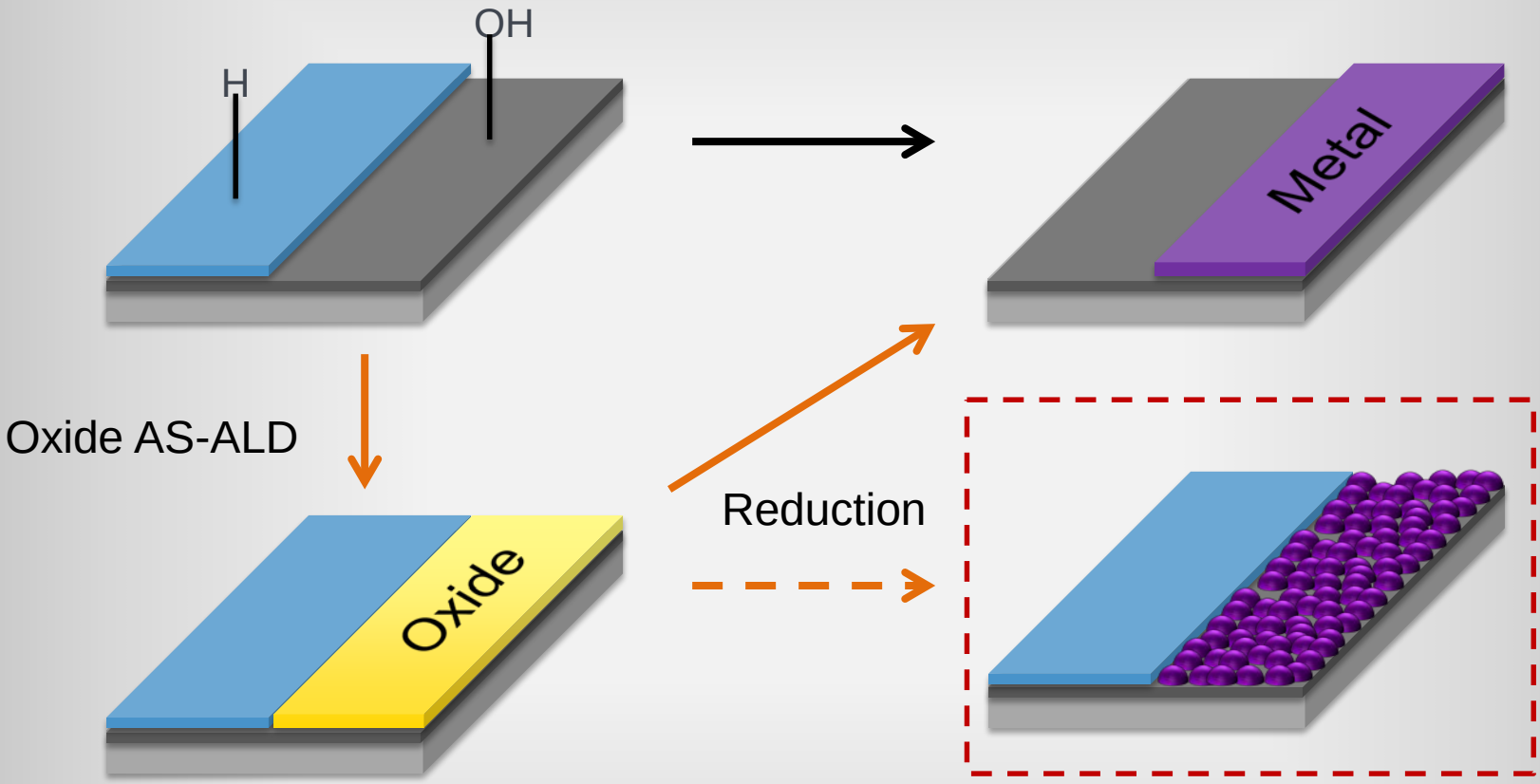
Precursor reactivity – precursor designed for surfaces



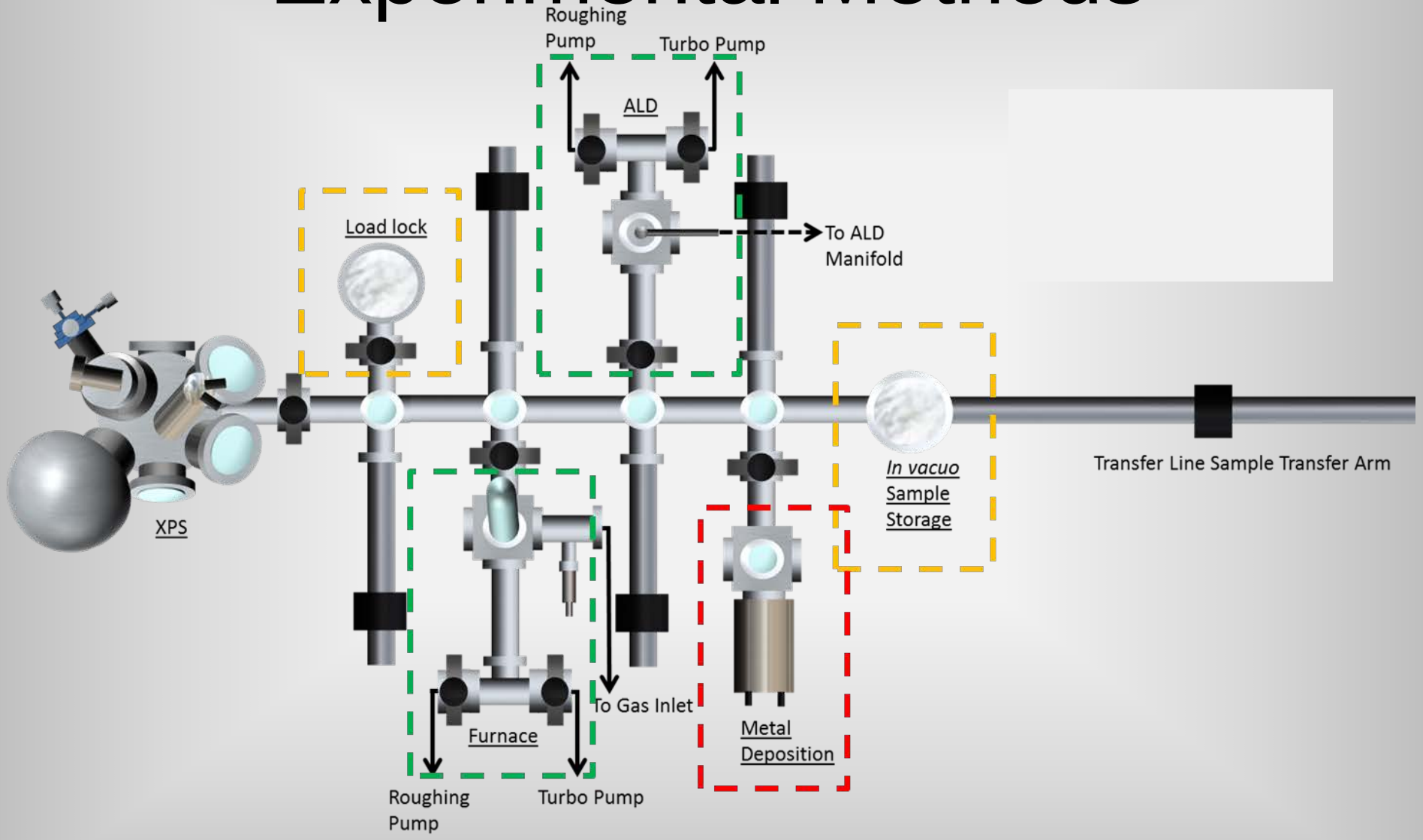
- TMCS – best candidate for Cu/CDO selectivity

- 250 cycle deposition on Teflon and Kapton indicate Co accumulation at 265 °C, need to lower temperature to eliminate thermal decomposition of CoAMD at surface → improve selectivity

Method

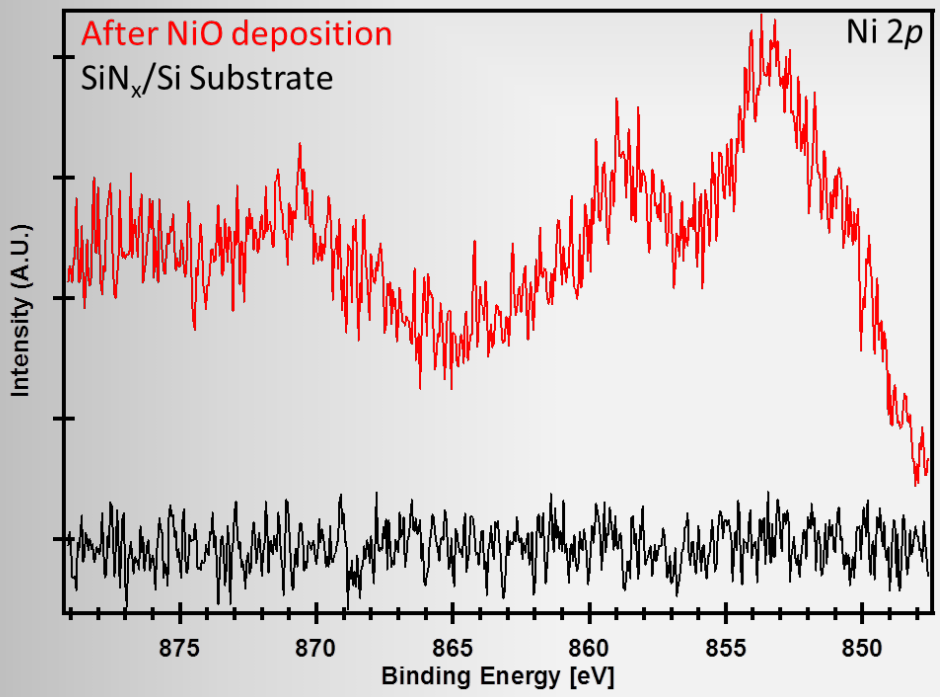


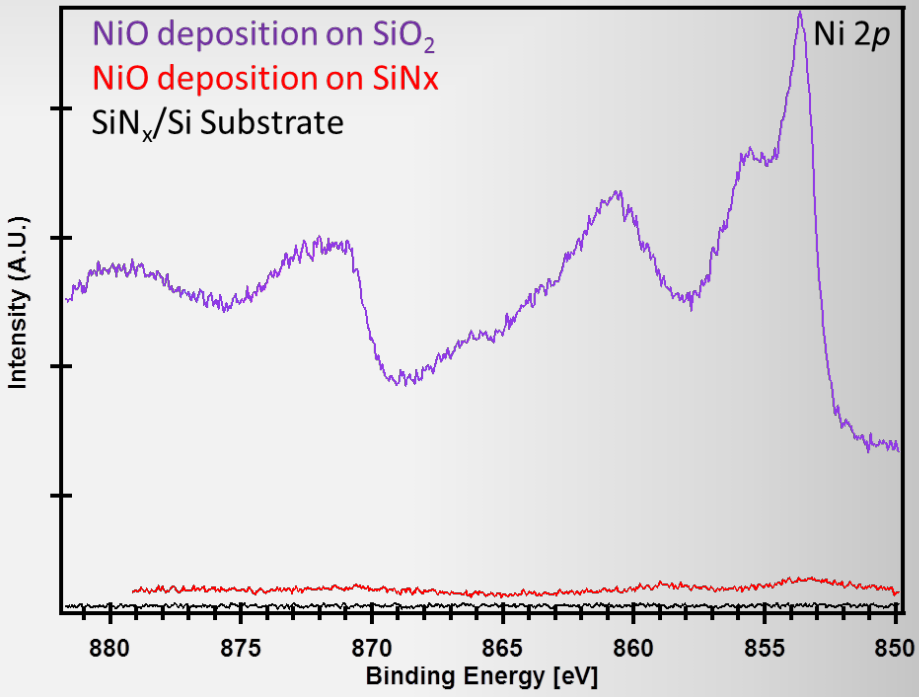
Experimental Methods



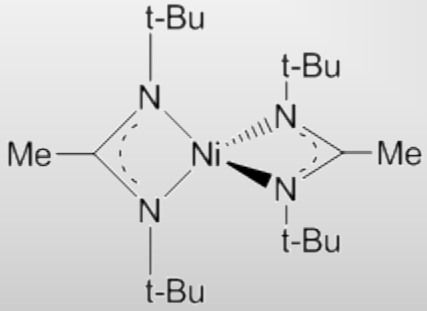
UNPATTERNED SUBSTRATES

Results – NiO on SiN_x





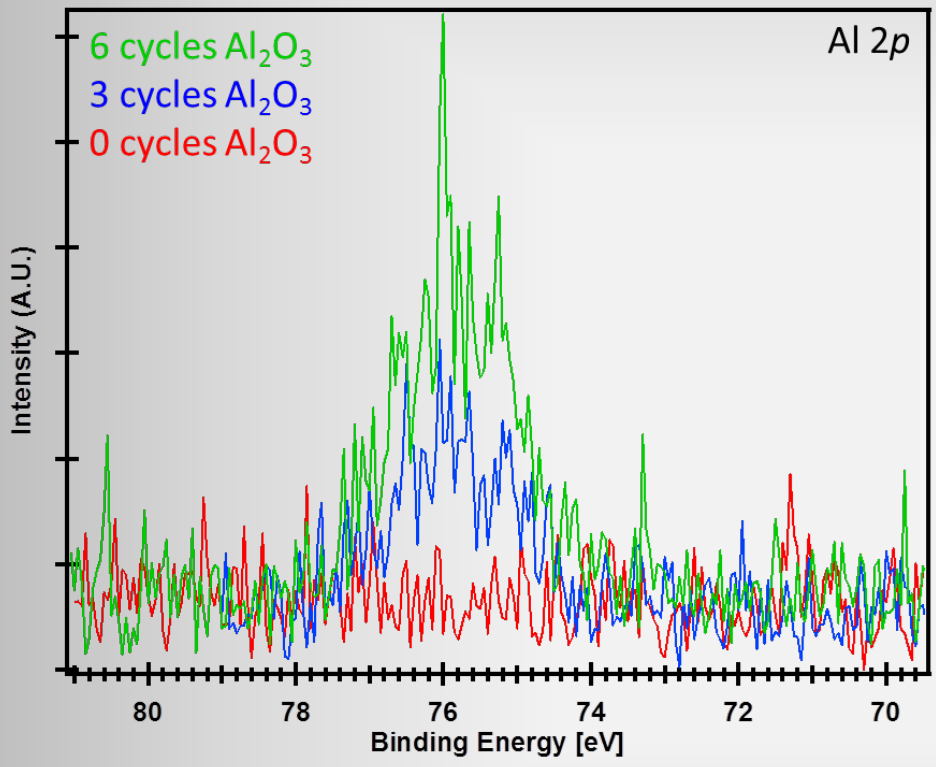
No color change observed on sample after deposition
Weak Ni 2*p* signal on SiN_x/Si – poor growth
Nucleation difficulty
Surface treatment required: buffer layer/oxygen plasma

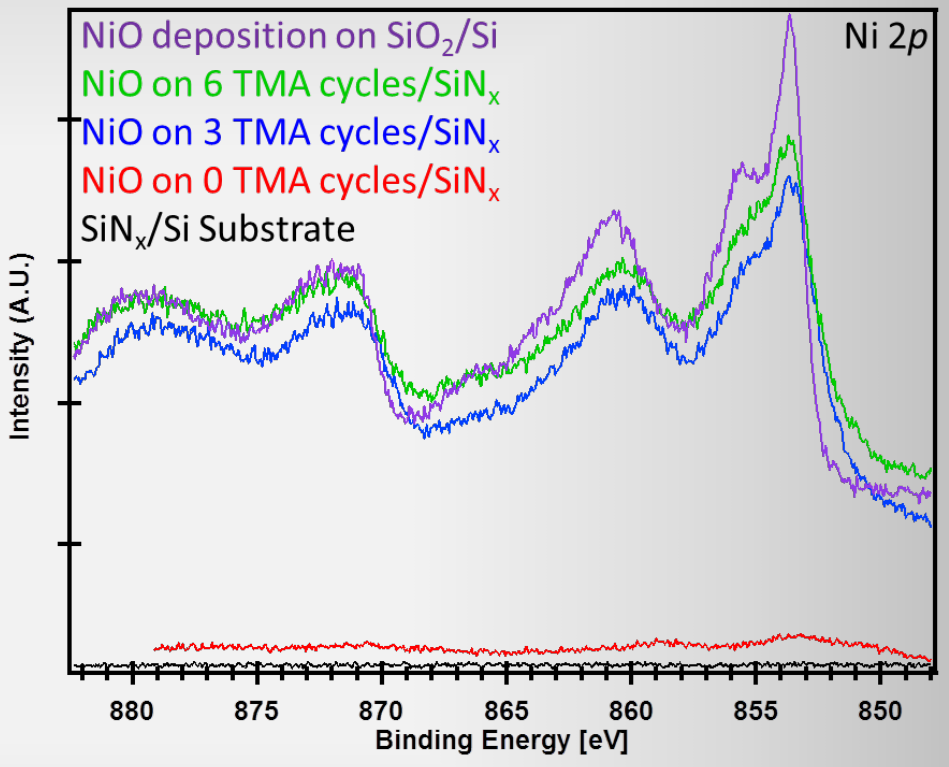


+ H_2O

200 °C

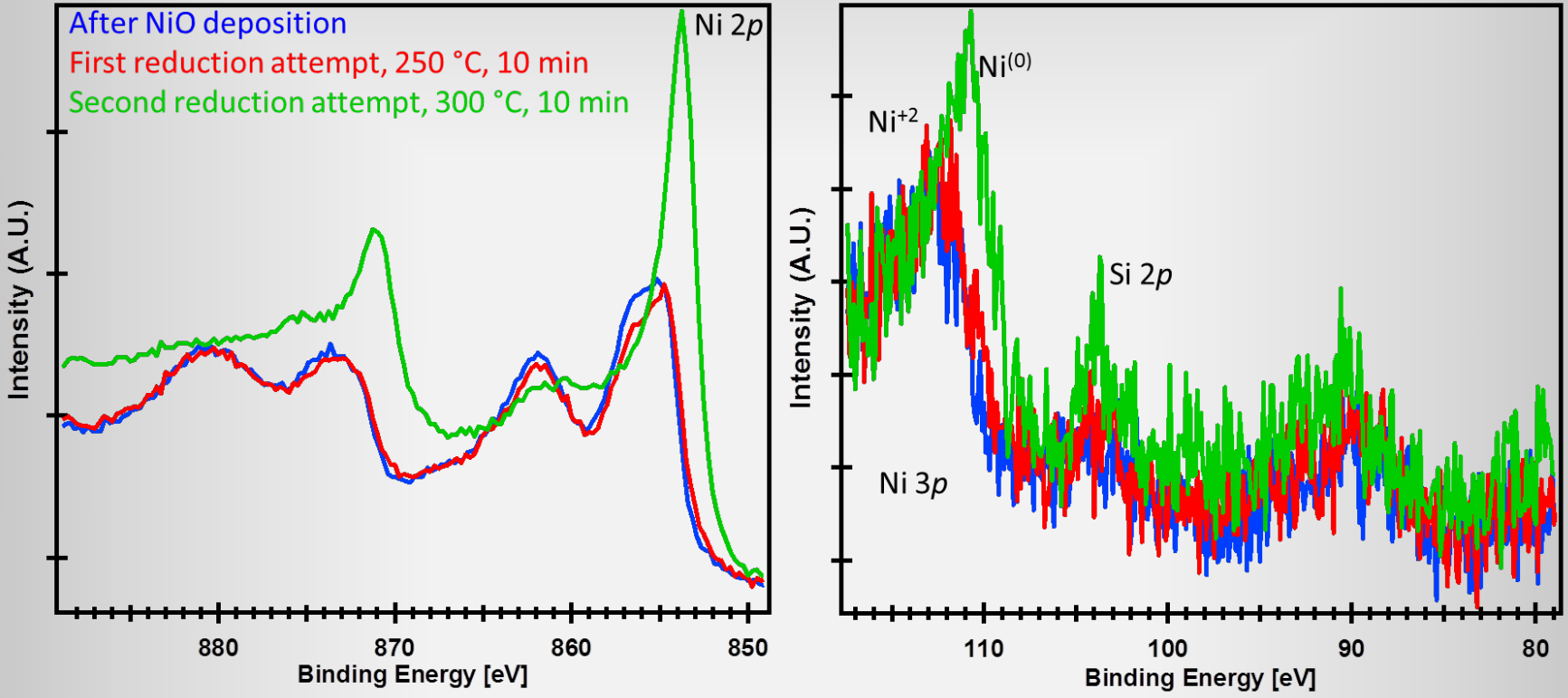
Al_2O_3 Buffer Layer





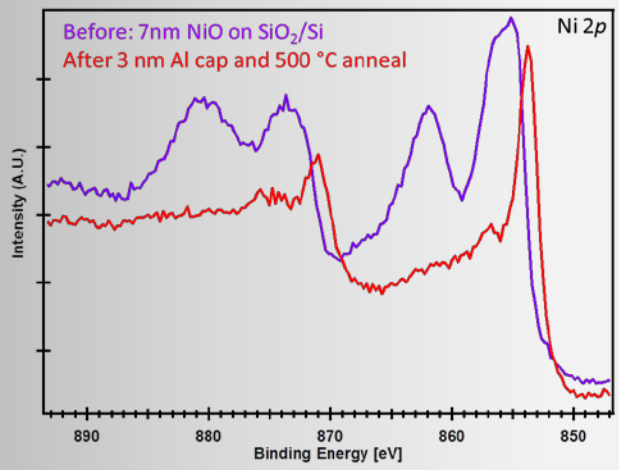
- Al_2O_3 was grown at 175 °C and NiO at 200 °C
- Al_2O_3 growth rate on SiO_2 is ~0.1 nm/cycle
- Assuming no nucleation delay, **buffer layers are at most 0.3-0.6 nm.**
- 300 ALD cycles of NiO - growth on buffered SiN_x comparable to growth on SiO_2.

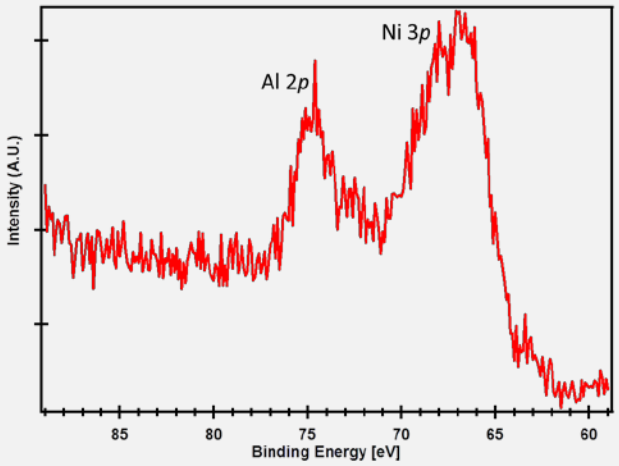
Thermal Reduction Using H_2

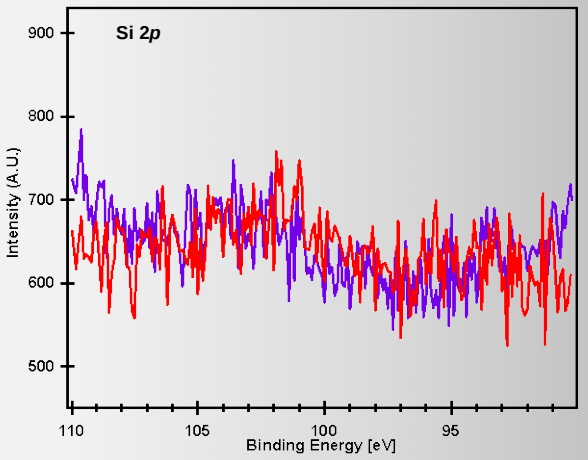


- **Reduction causes a change in film volume and Ni has a tendency to dewet – this potentially creates voids within the film.**

Reduction – Oxygen Scavenging Layer – 3 nm of Al

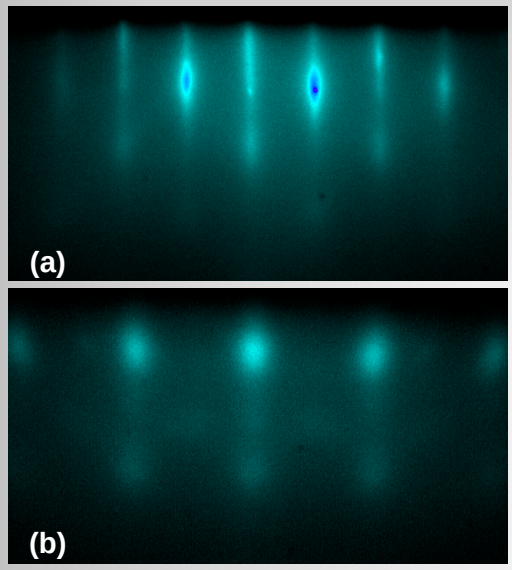




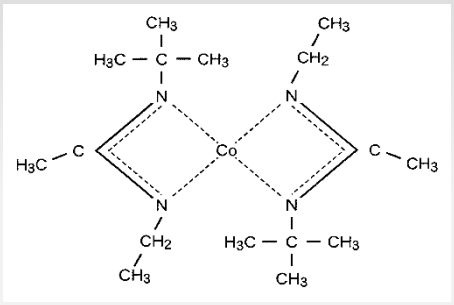


- 3 nm of MBE delivered Al on 150 ALD cycles (~7 nm) NiO grown on SiO_2.
- 30 minute vacuum anneal at 500 °C was performed after deposition to ensure the reaction was driven to completion.

Epitaxial CoO on $SrTiO_3$–buffered Si(001)



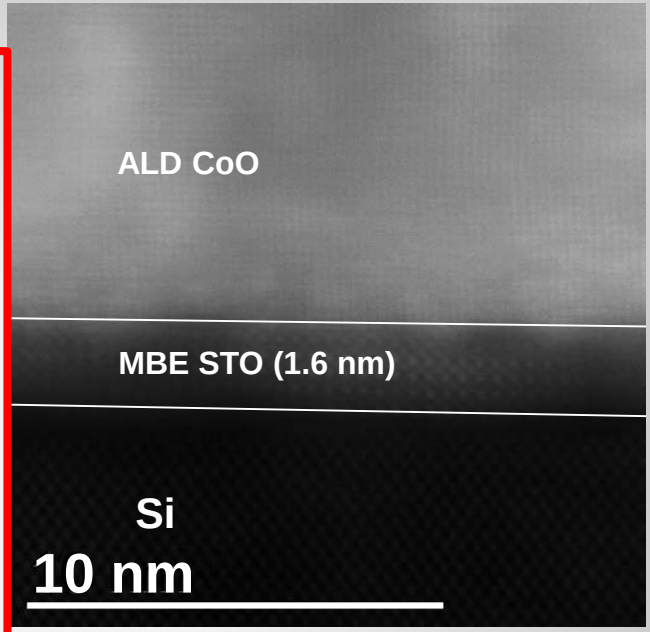
RHEED images of: (a) a four-unit-cell STO-buffered Si(001) grown by MBE, (b) a 2-nm thick ALD-grown CoO on four-unit-cell STO-buffered Si(001). All RHEED patterns were taken along <100> direction of STO



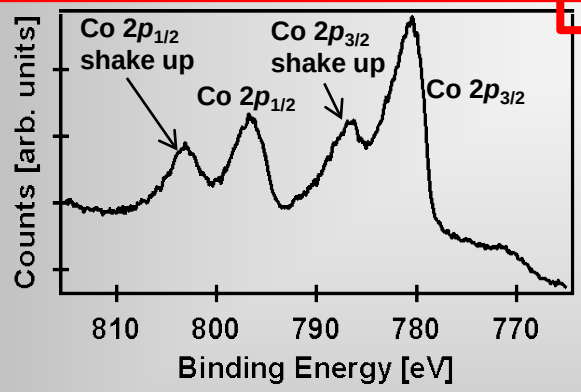
T = 170-180 ºC P = 1 Torr

(A) $CoOH^* + Co(Amd)_2 \rightarrow CoOCo(Amd)^*$

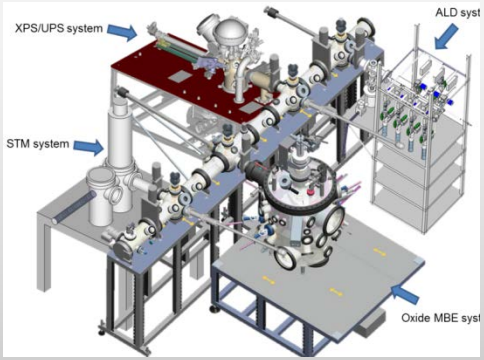
(B) $Co(Amd)^* + H_2O \rightarrow CoOH^* + Amd$

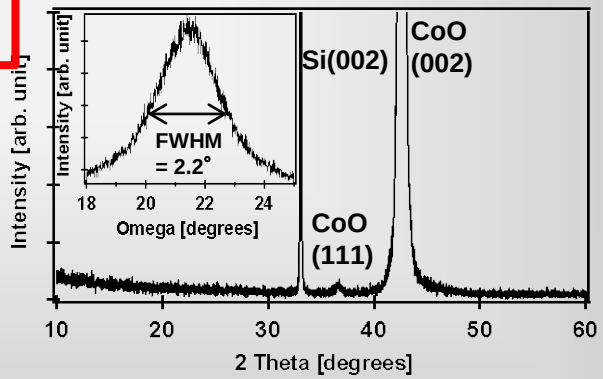


TEM image of a 24-nm thick ALD-grown CoO film on a four-unit-cell STO-buffered Si(001)



Core level Co 2*p* XP-spectra of an 8-nm ALD CoO film grown on a four-unit-cell STO-buffered Si(001)

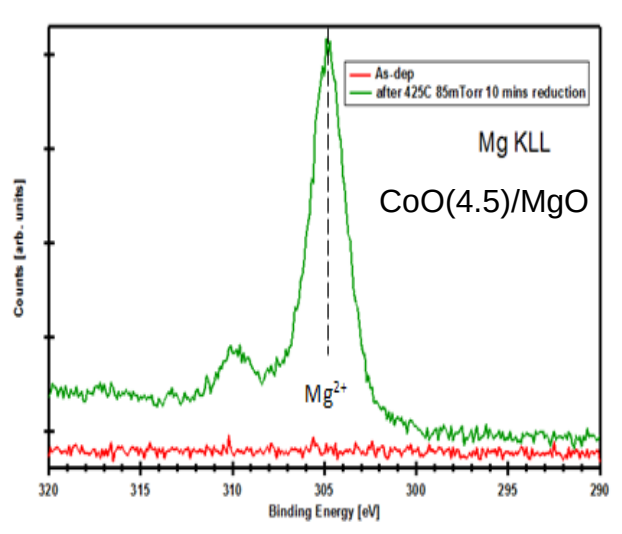


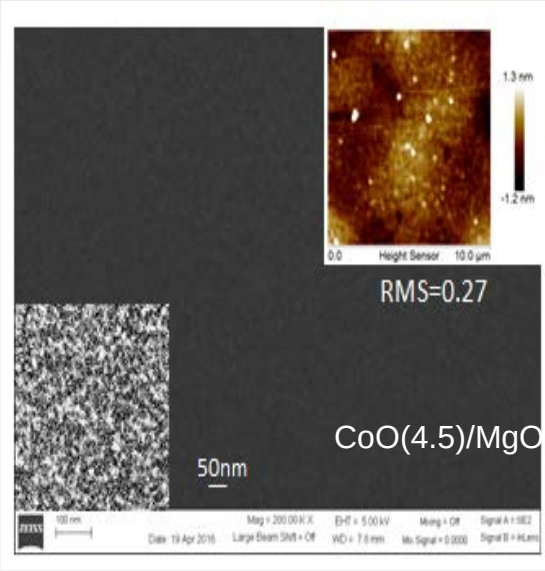


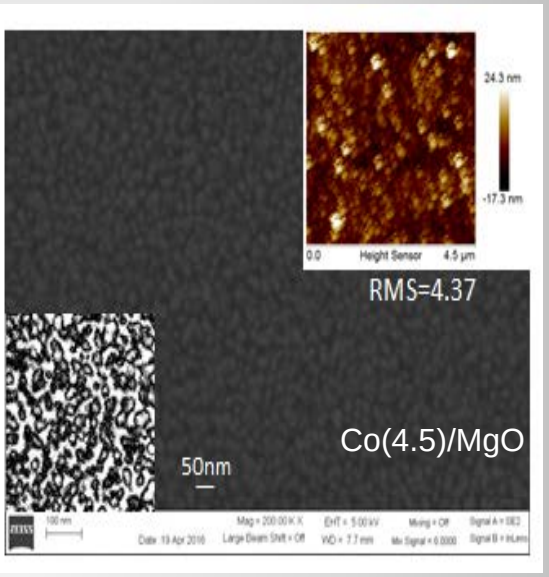
XRD patterns of a 24-nm ALD CoO film grown on a four-unit-cell STO-buffered Si(001)

T. Ngo, *et al*., J. Appl. Phys.. 104, 084901 (2013)

Dewetting During Thermal Reduction (Uncapped)



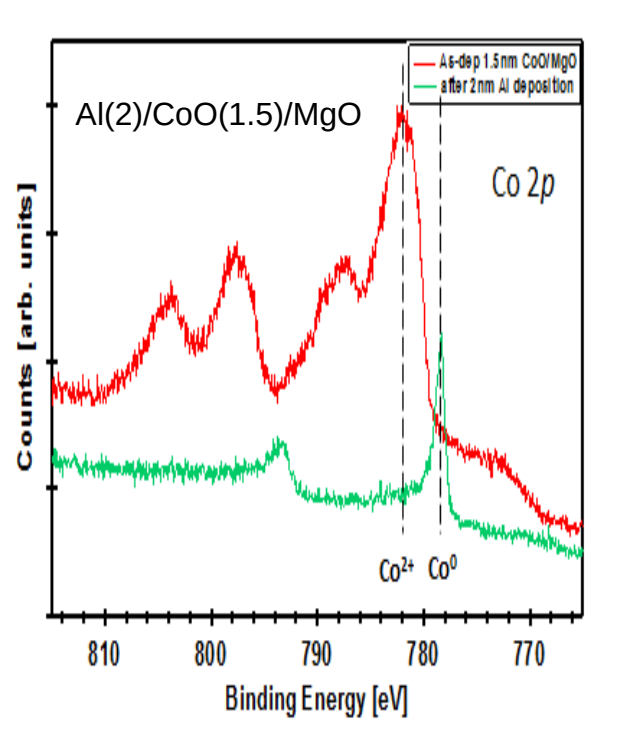


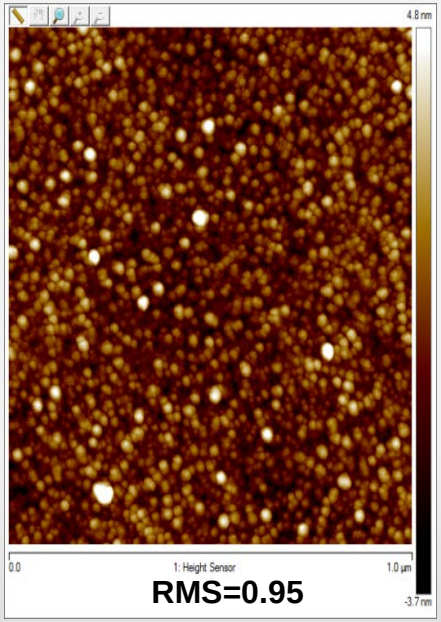


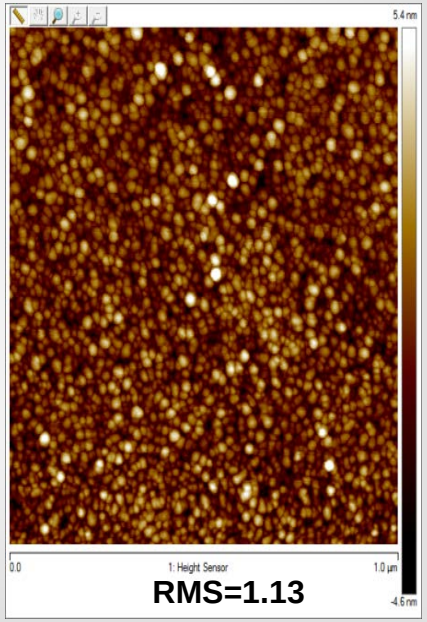
- There was no Mg peak for the CoO/MgO sample before reduction while the Mg peak showed up after reduction
  - –MgO substrate was completely buried by the continuous CoO film before reduction
  - –MgO substrate was exposed after the CoO film was reduced to Co film
- Dewetting of the Co film happened during thermal reduction
  - –Continuous CoO film became disconnected Co islands
  - –40% volume contraction

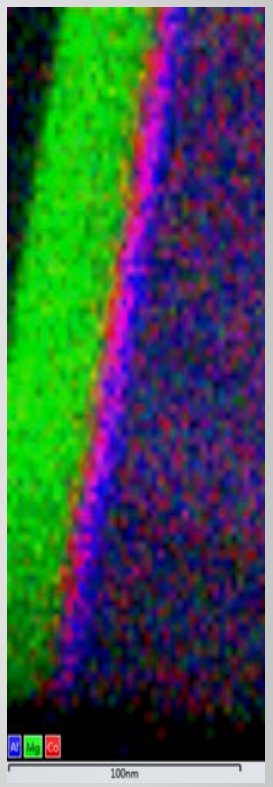
Reduction of CoO to Co at Lower Temperature

- Reduction of CoO to Co is achieved by using O scavenger
  - –Al metal was deposited on CoO by MBE at 200 °C
  - –Al was oxidized to Al_2O_3 **and acted** as a capping layer





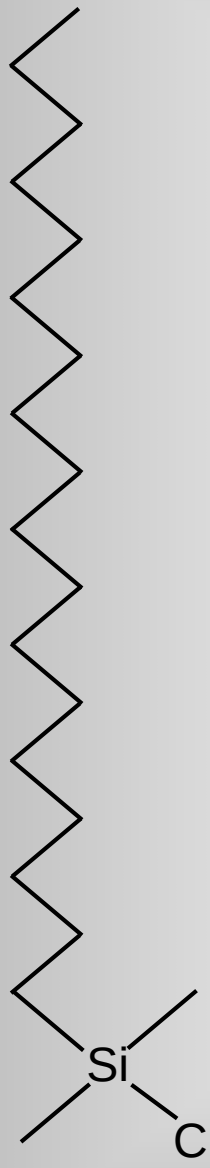


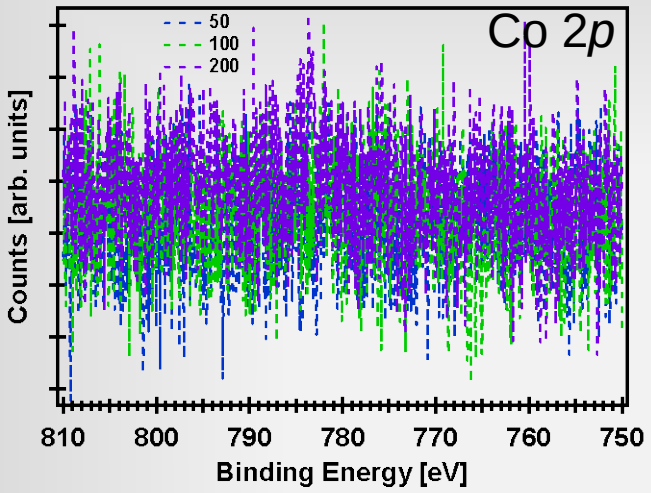


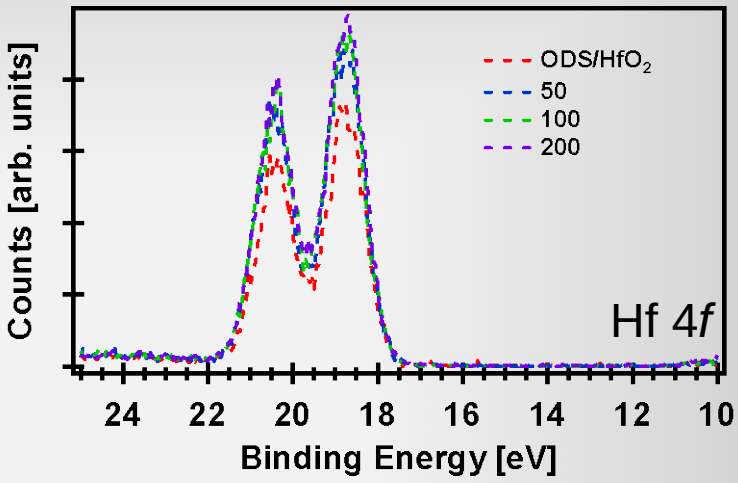
CoO(3nm)/MgO

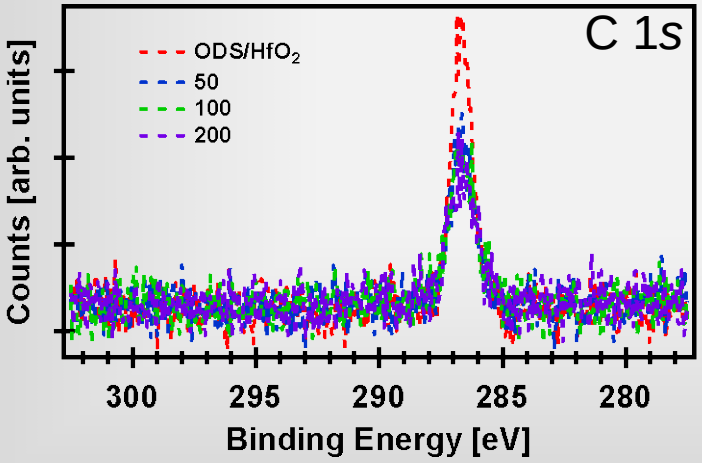
Al(3nm)/CoO(3nm)/MgO

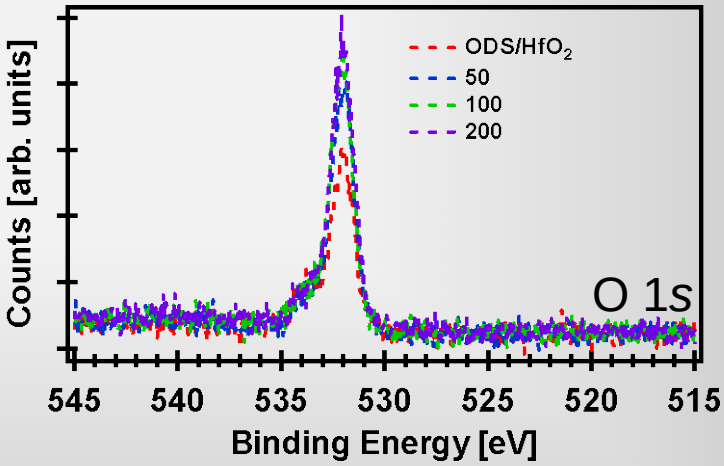
ODS Blocks CoO Nucleation











50, additional 100, additional 200 cycles of CoO

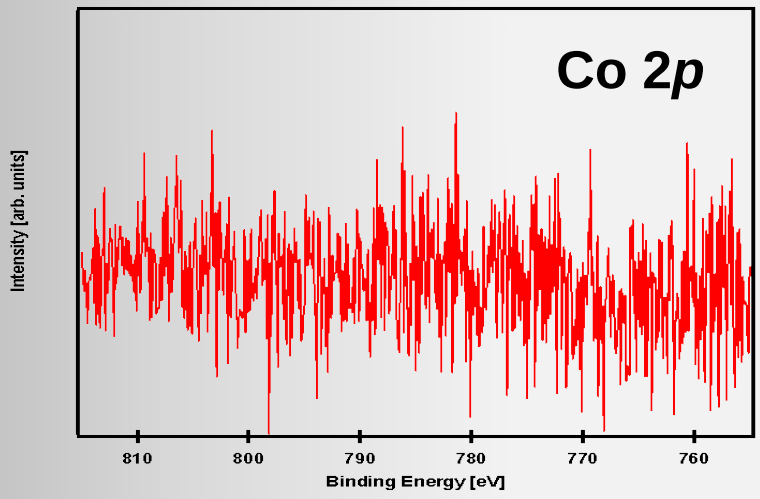
n-octadecyldimethylchlorosilane

T = 177 °C

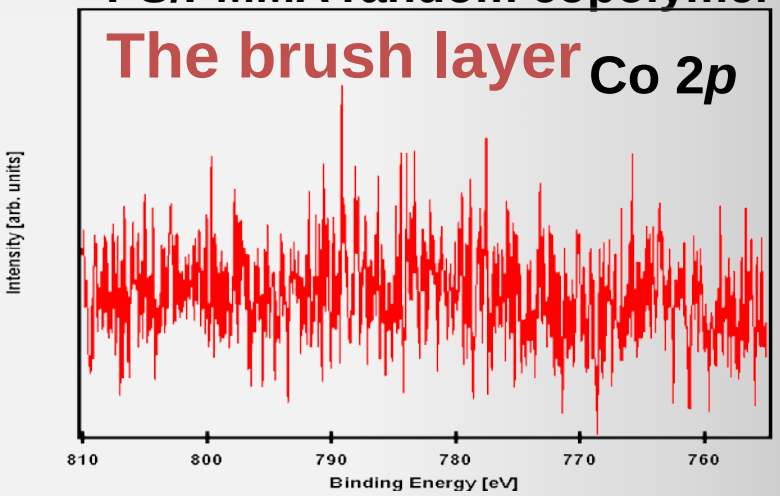
350 cycles on SiO_2 → 10.5 nm

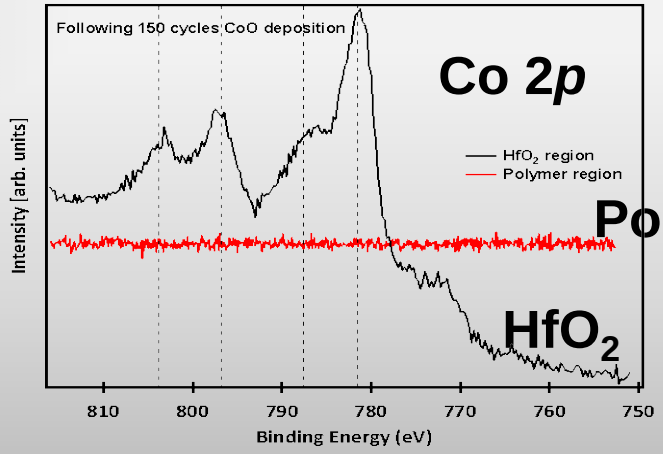
CoO ALD Blocked on PS/PMMA

150 CoO ALD cycles on PS



150 CoO ALD cycles on PS/PMMA random copolymer



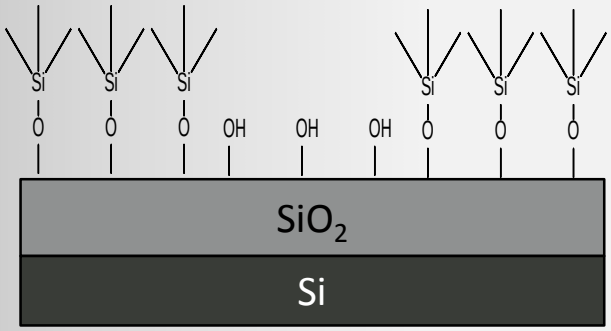


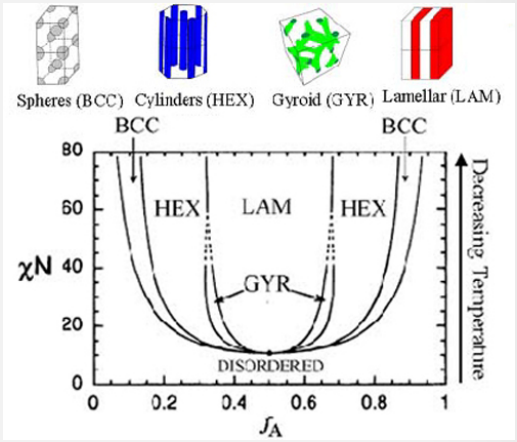
Poly(trimethylsilylstyrene)

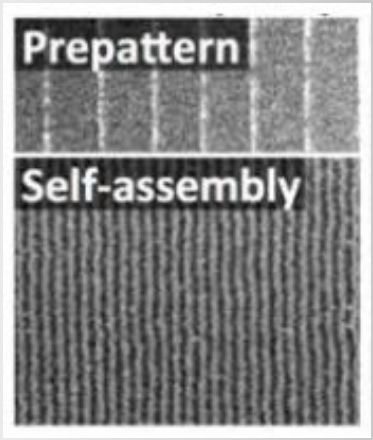
A component of designer BCP

PATTERNED SUBSTRATES

Patterned SAM or Diblock Self Assembly







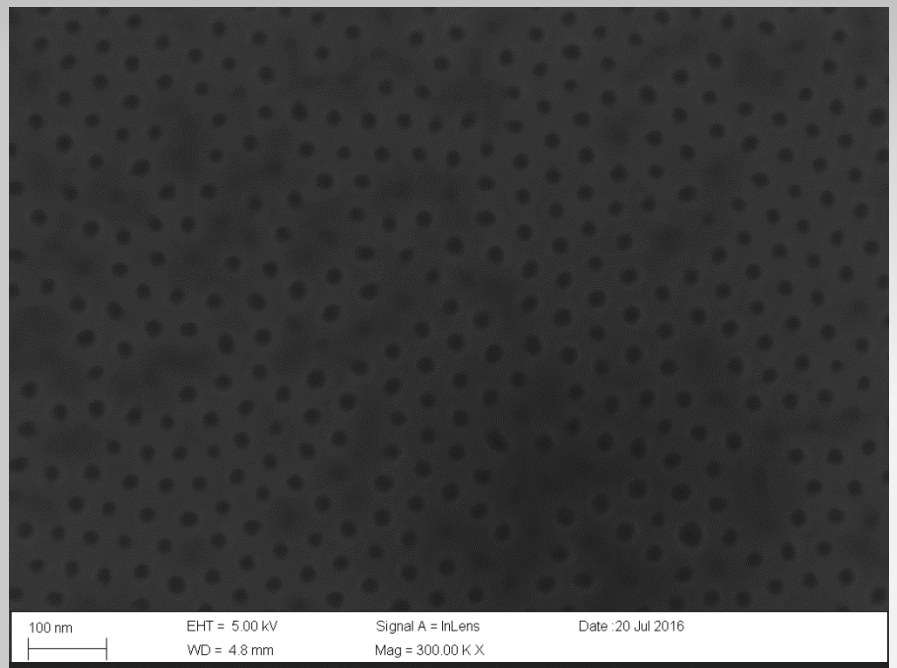
- Self-assembled monolayers patterned by
  - –Microcontact printing
  - –Photolithography
  - –Electron beam lithography

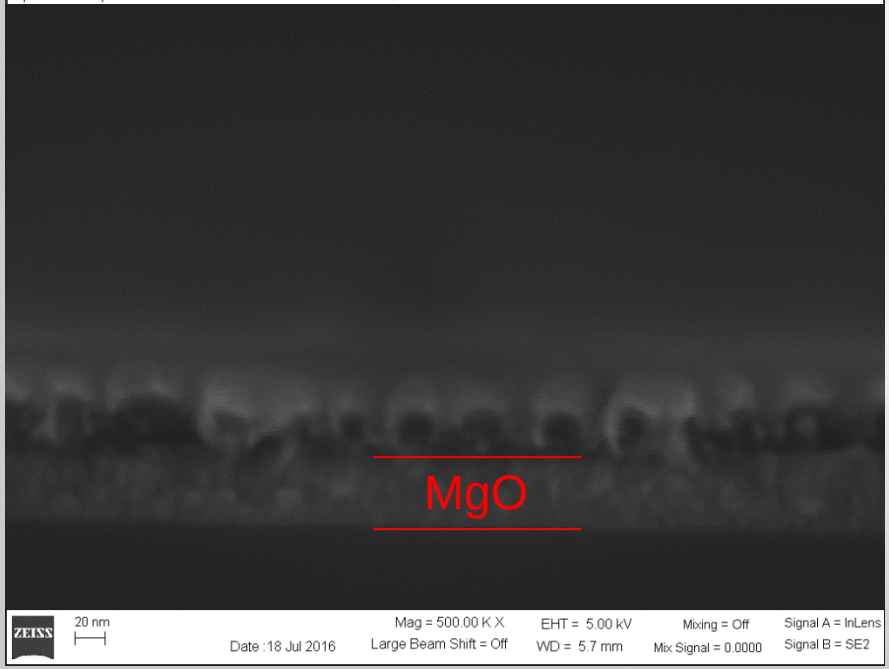
ACS Appl. Mater. Interfaces, 7, 13476, 2015

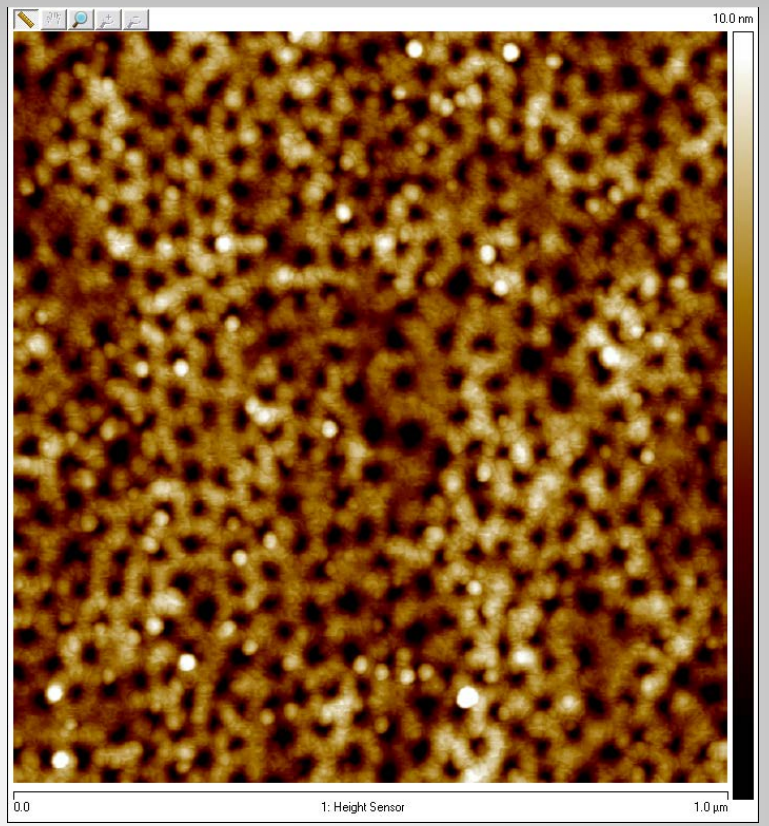
- Block copolymers patterned by
  - Directed self-assembly
  - Photolithography
  - Electron beam lithography

10 nm features realized

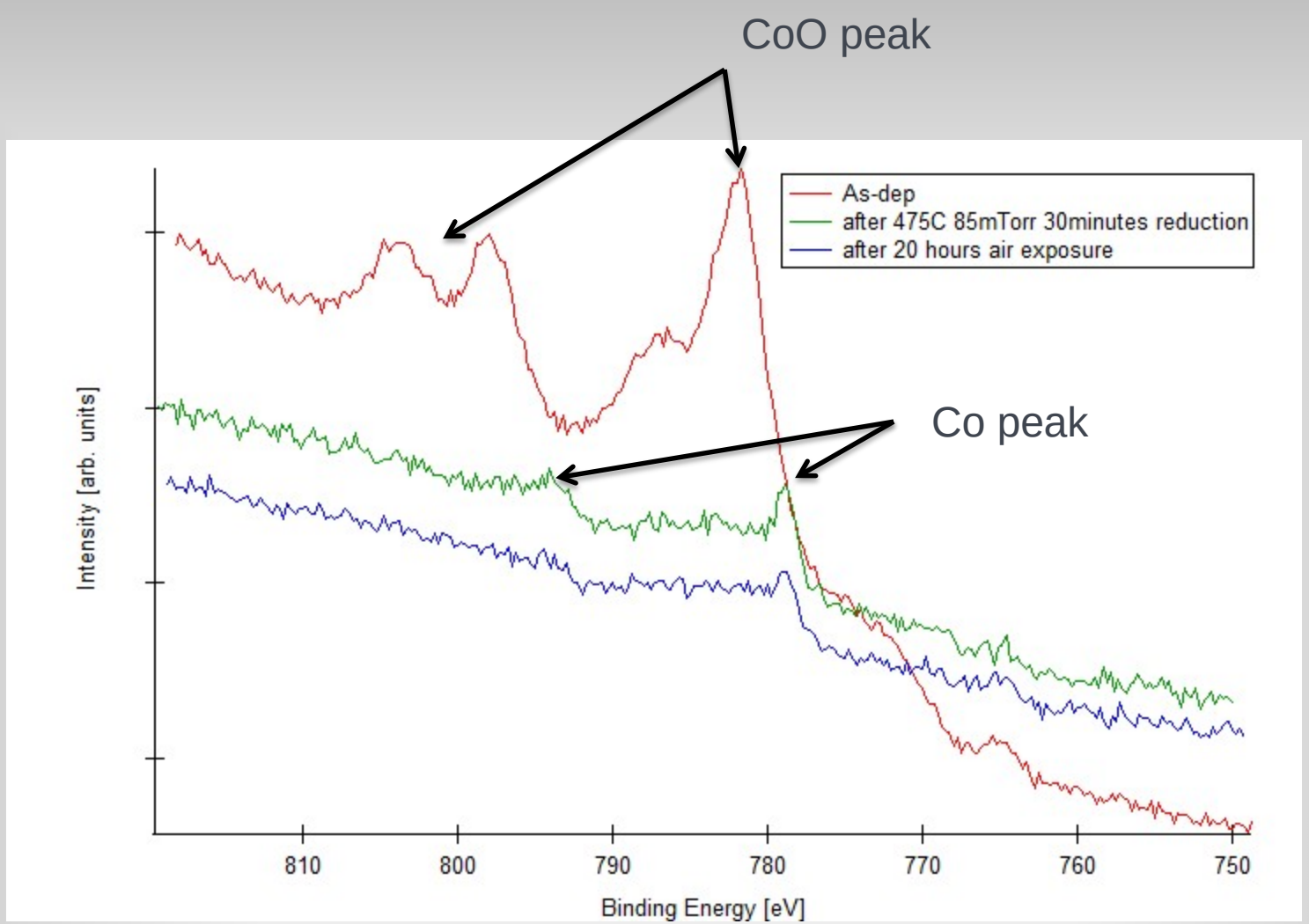
- **clearing the brush layer**
- **what remains after this etch?**







PS-PMMA pattern---Achieved

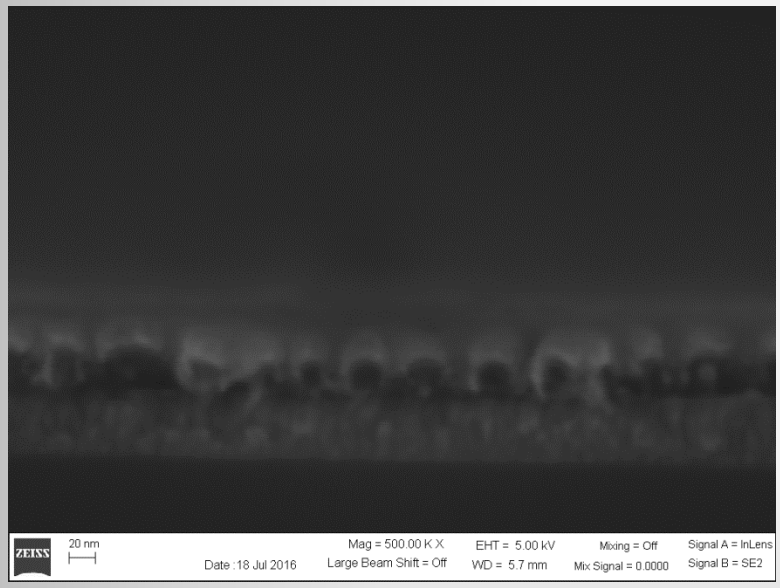


Al2O3 (1nm)/CoO (4.5nm)/MgO (30nm)

ALD of CoO on MgO substrate and reduction of CoO to Co with Al_2O_3 capping layer---Achieved

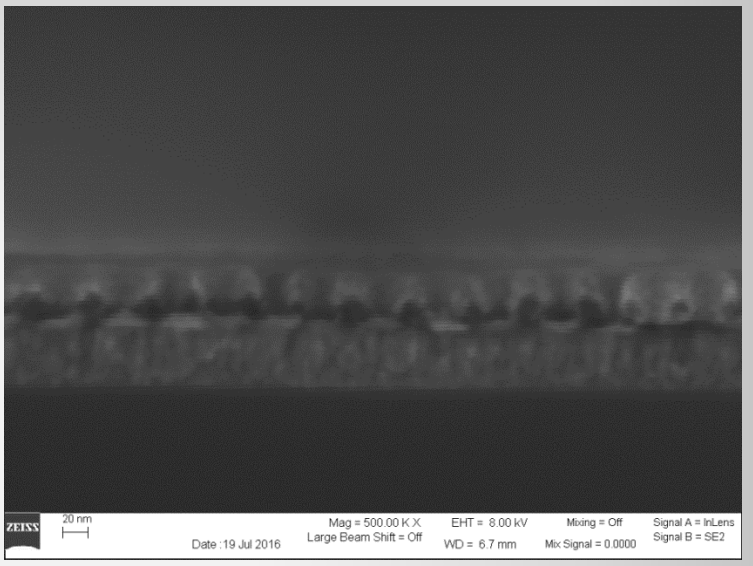
Our attempts on etching

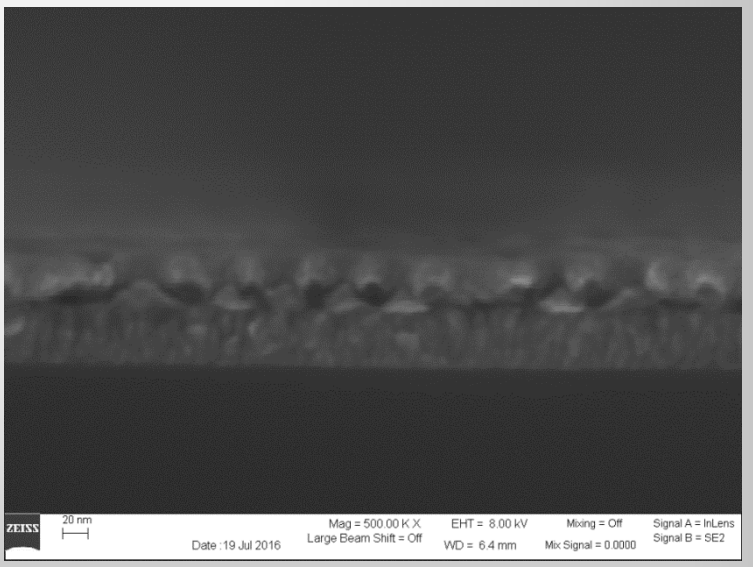
Low power and high anisotropic etch:
65W power, 15 mTorr pressure,
70 sccm Ar, 2 sccm O_2, 45s
(etch rate is about 15nm/min)



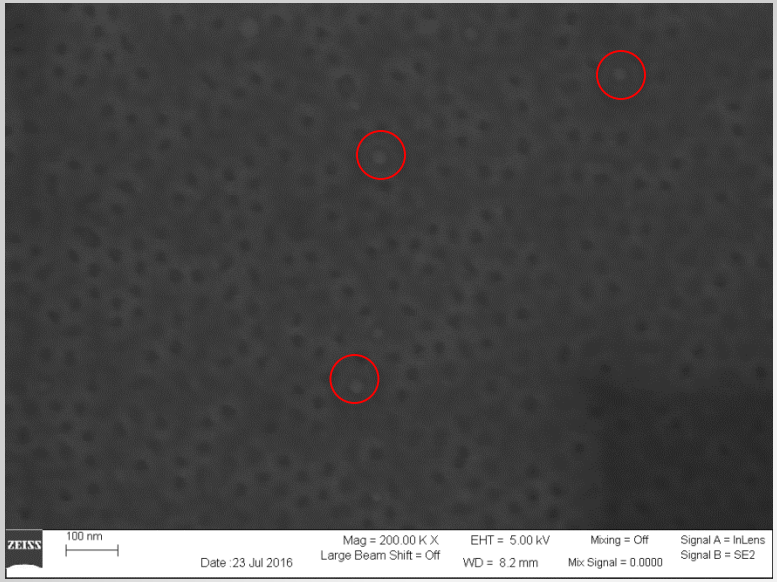
Less O_2

More O_2



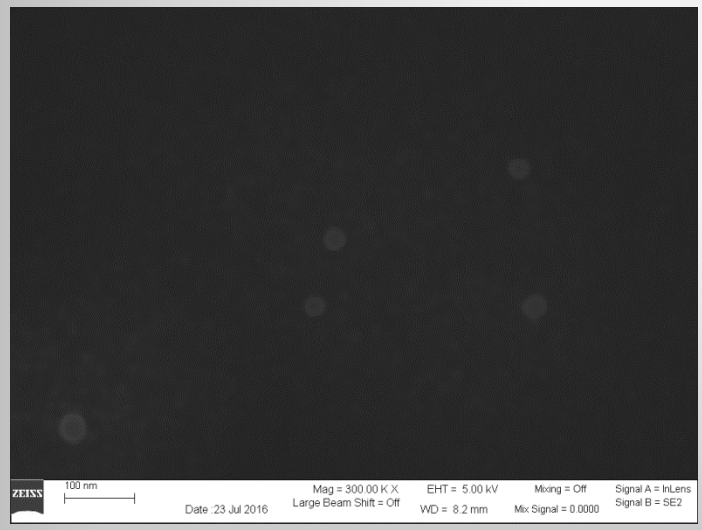


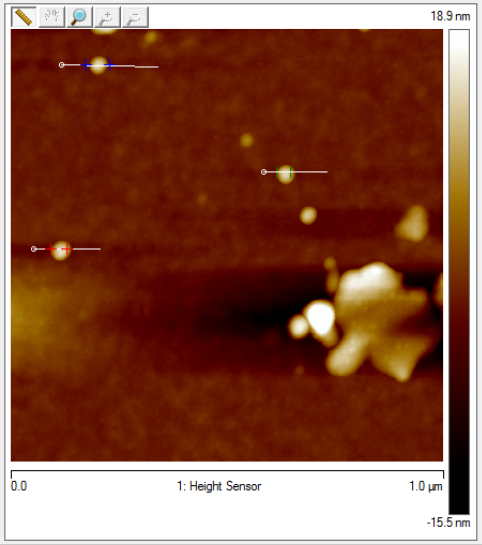
After ALD of CoO

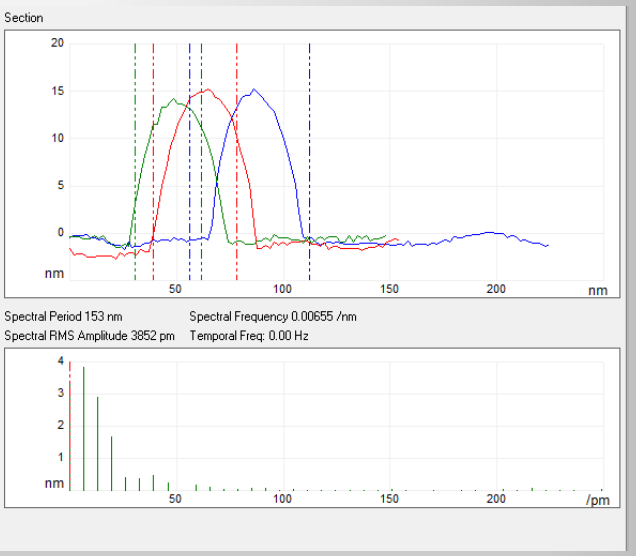


Sparse dots results due to uncomplete brush removal

After ALD and all polymers removal

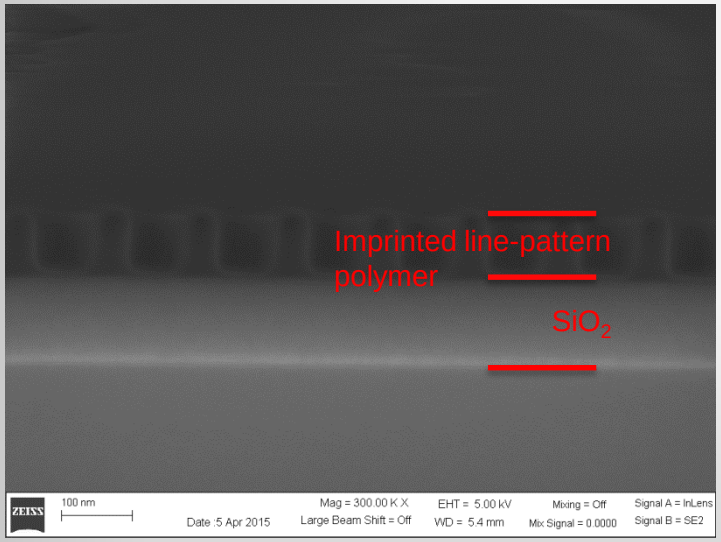




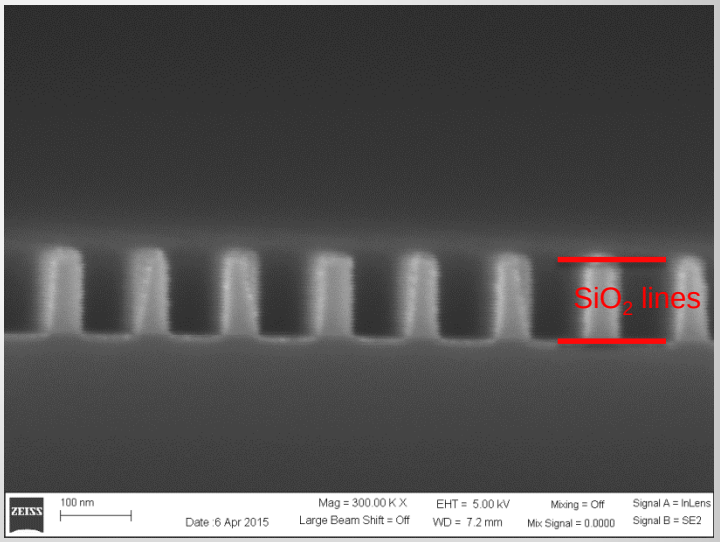


Nanoimprint Polymer

- Proprietary – does not contain Si and ‘may be similar to PMMA’; T_g ~180-200 °C
- A residual layer (~ 5 nm must be removed with an oxygen etch

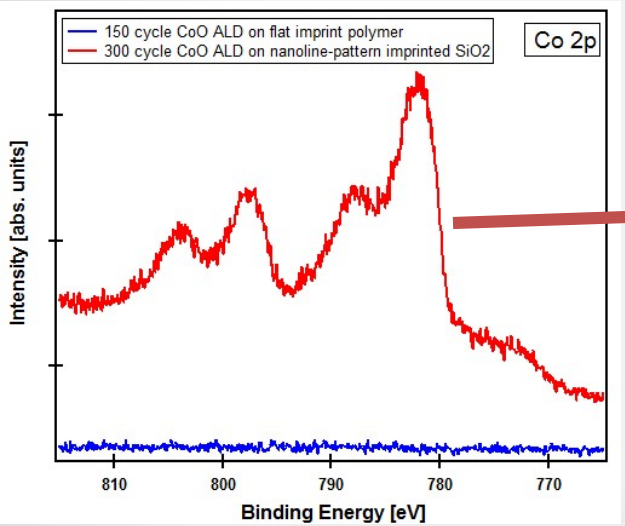


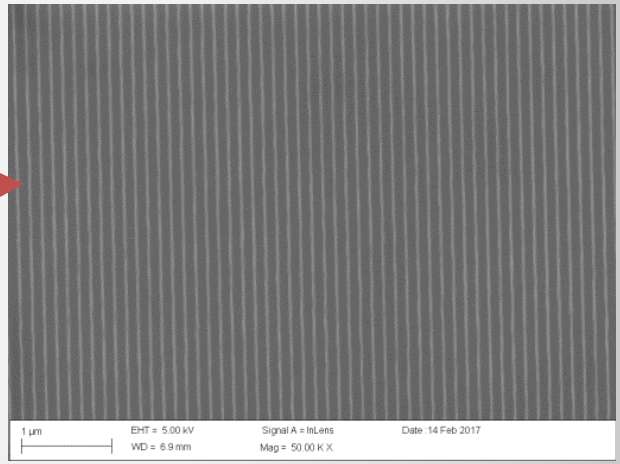
Pattern Transfer Etch



ALD of CoO on Nanolines

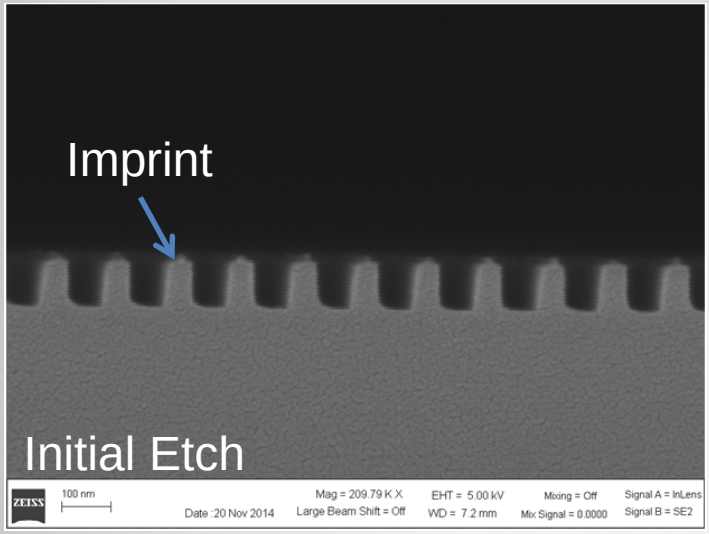
Nanoimprint → Residual layer removal (60 sec etch) → Metal oxide ALD

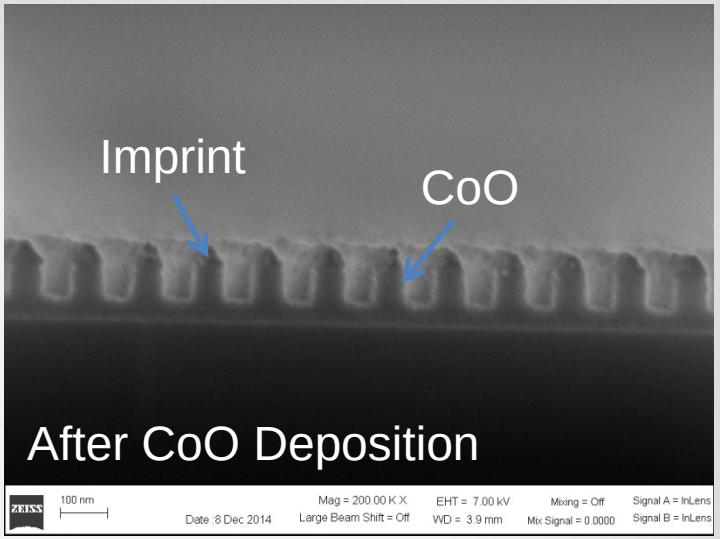




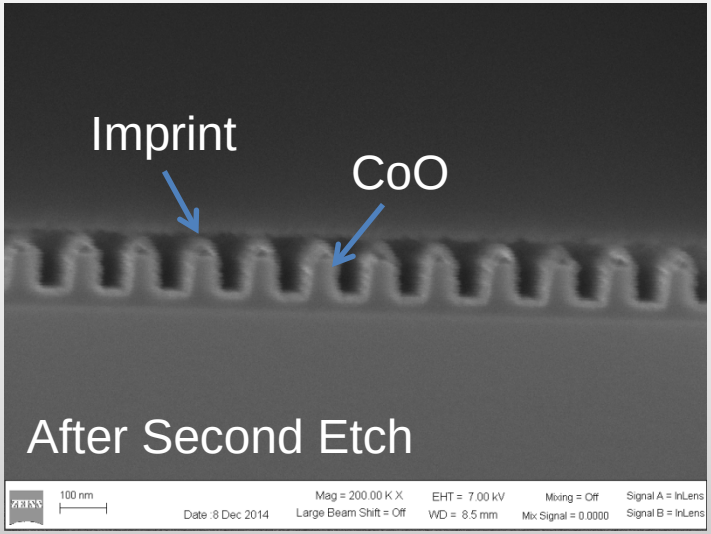
Line width can be tuned by O_2/Ar treatment of polymer patterns and line height can be tuned by number of ALD cycles

ALD of CoO on Nanoline Pattern – Not AS



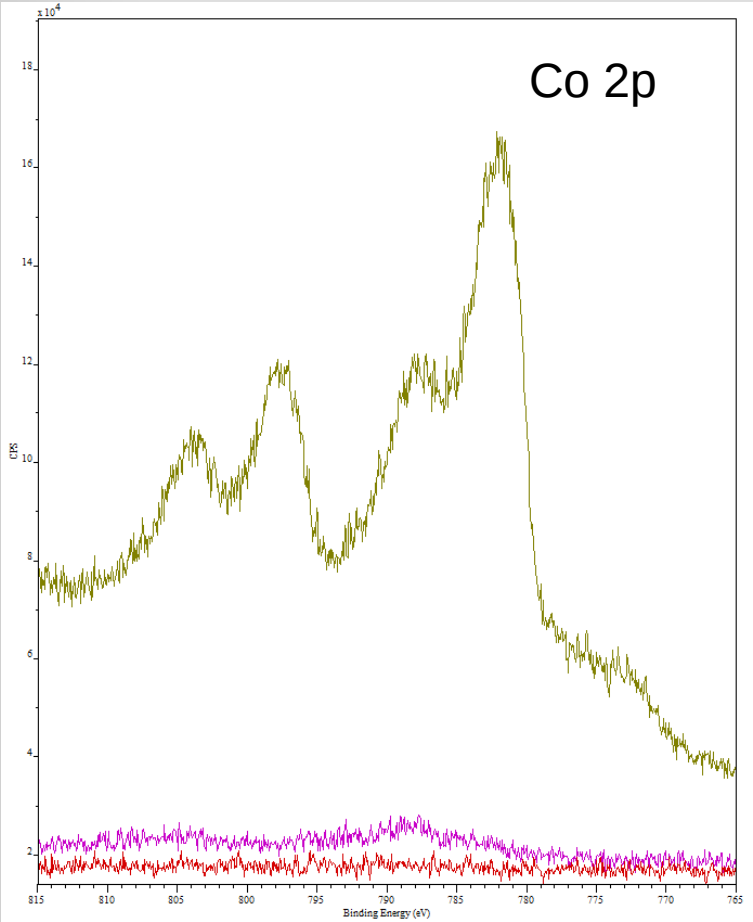


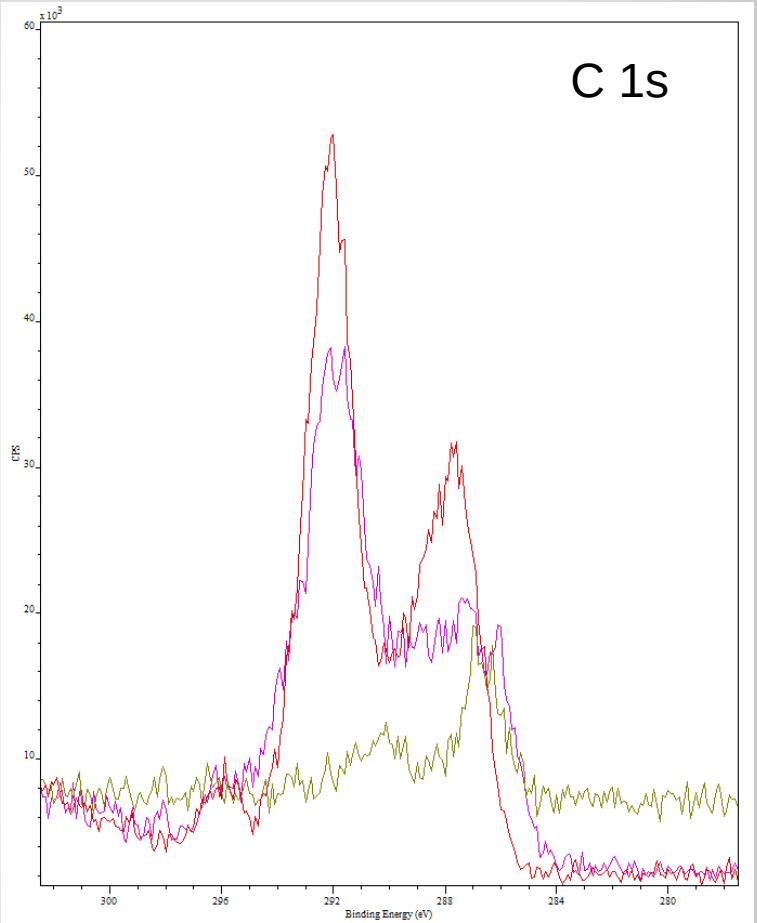
CoO appears to be depositing everywhere and is blocking final removal of imprint



Residual etch could be optimized to eliminate activating the imprint template?

Nanoimprint polymer





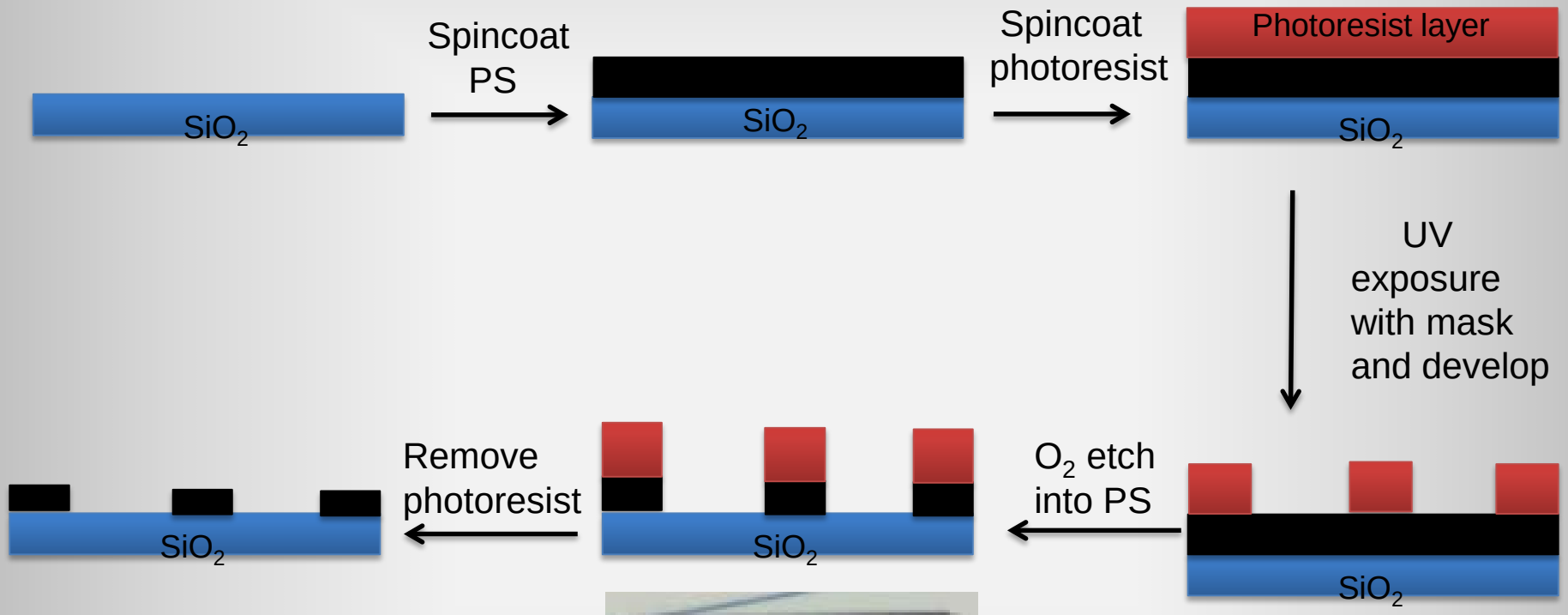
------- 150 cycle CoO on imprint polymer

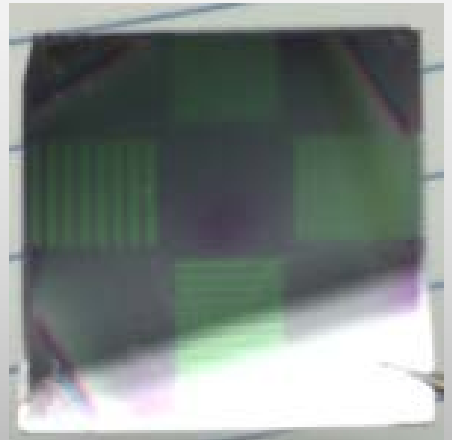
------- 150 cycle CoO on 10s O_2/Ar-treated imprint polymer

------- 300 cycle CoO on imprinted pattern without residual layer

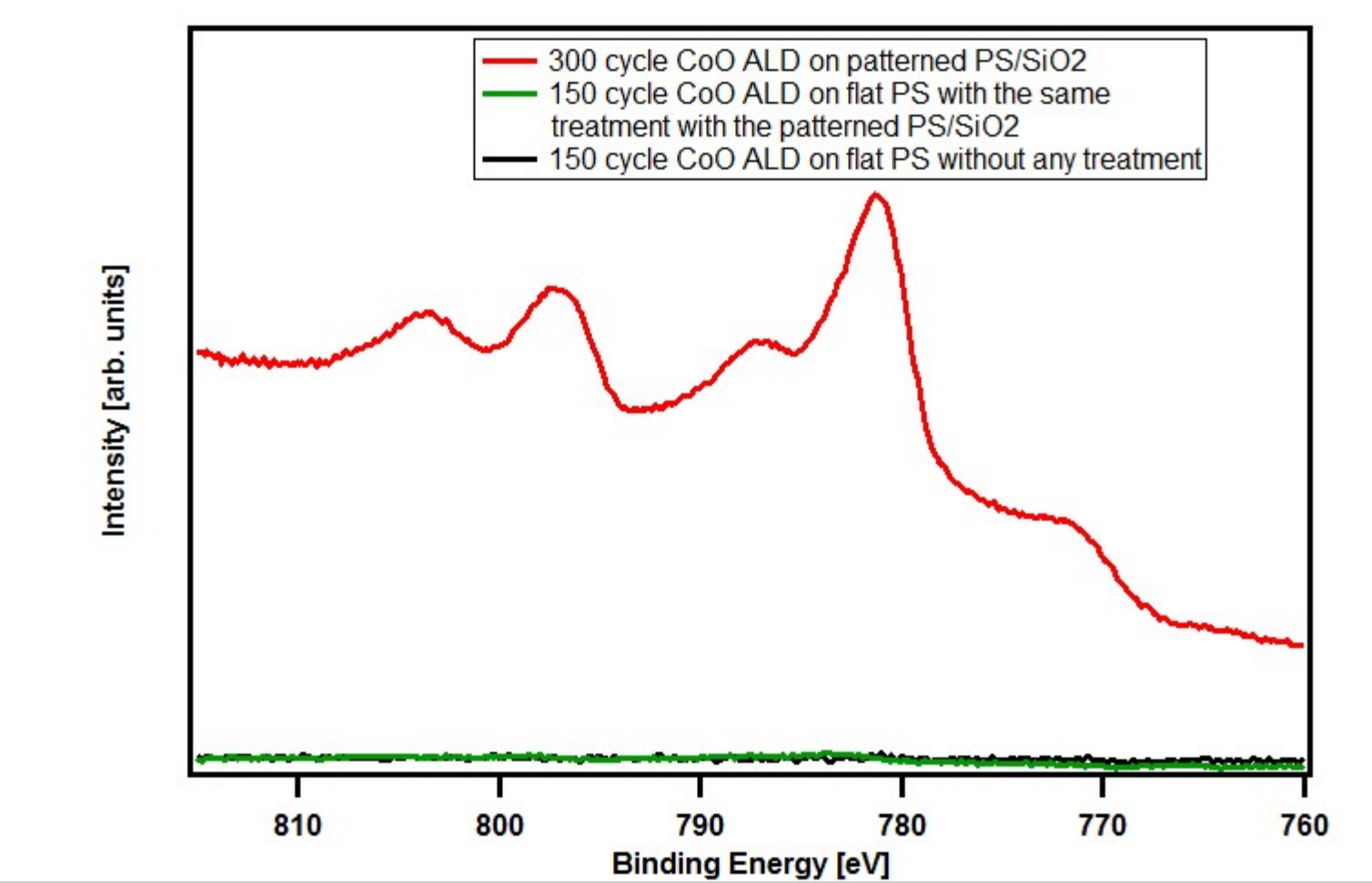
Patterned Polystyrene

- Use photolithography to pattern PS

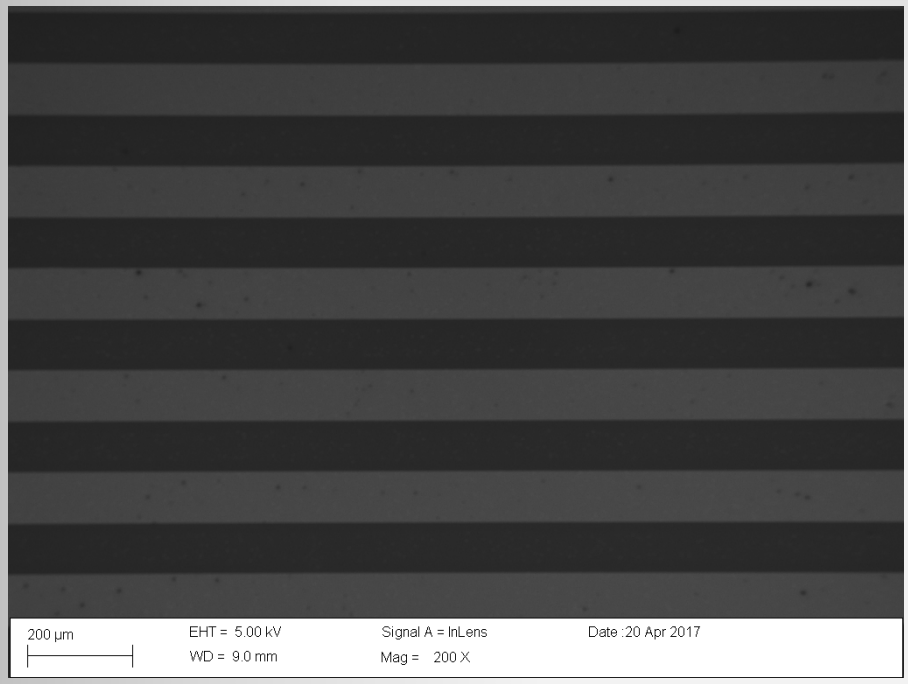




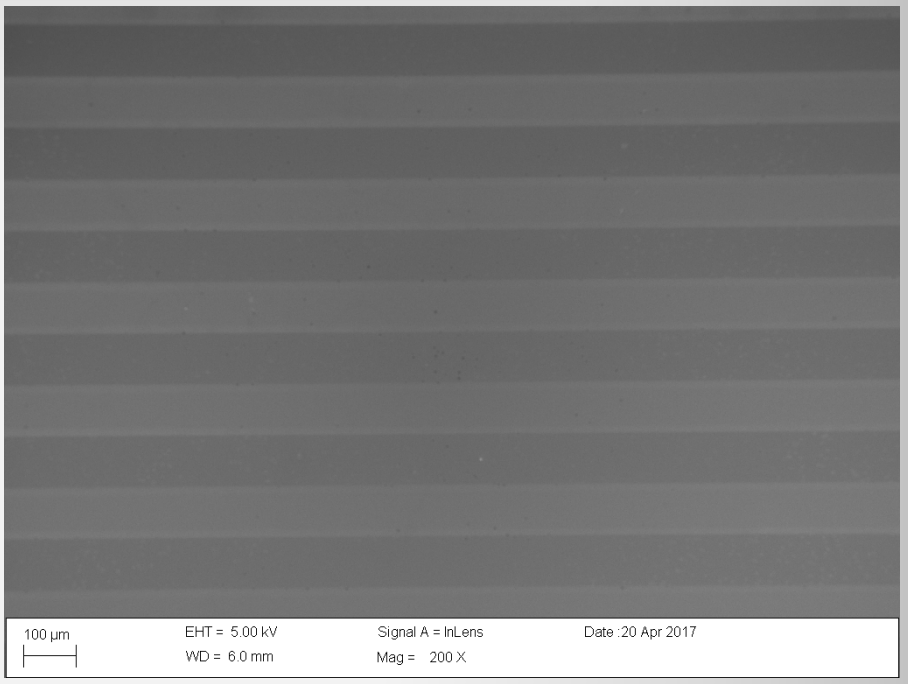
Polystyrene Subjected to the Full Treatment is Inactive



SEM data



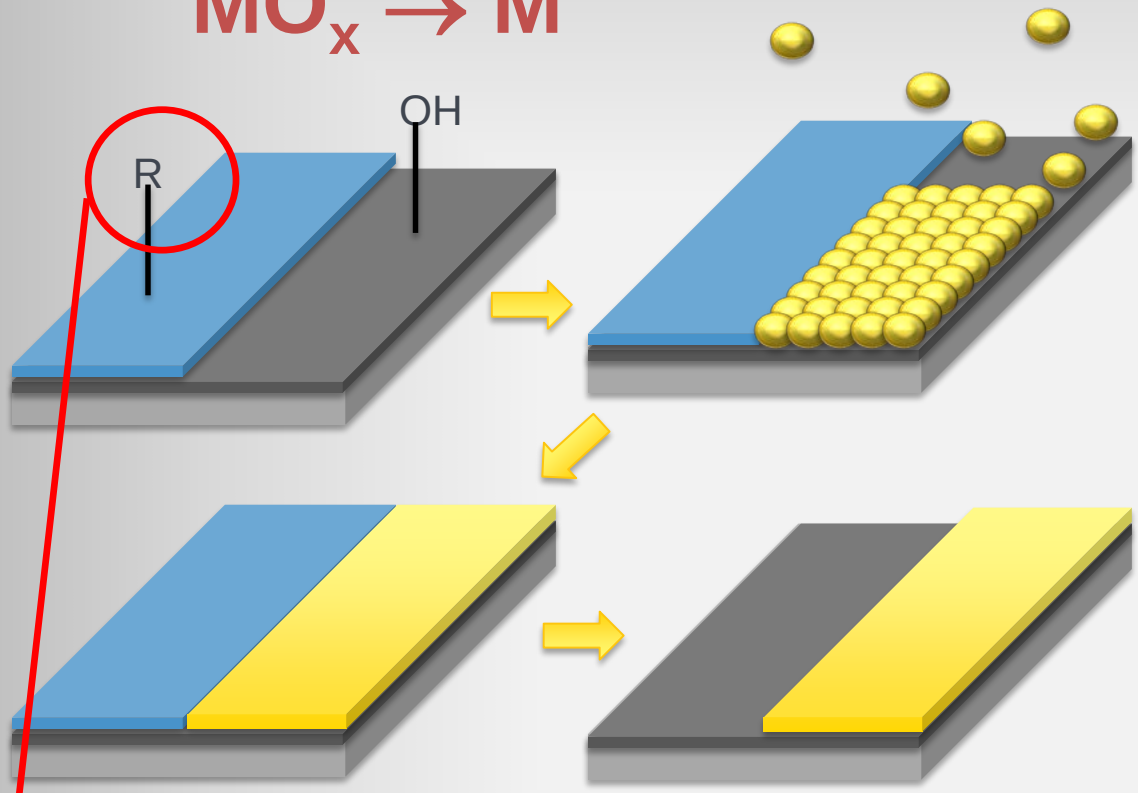
Patterned PS before ALD



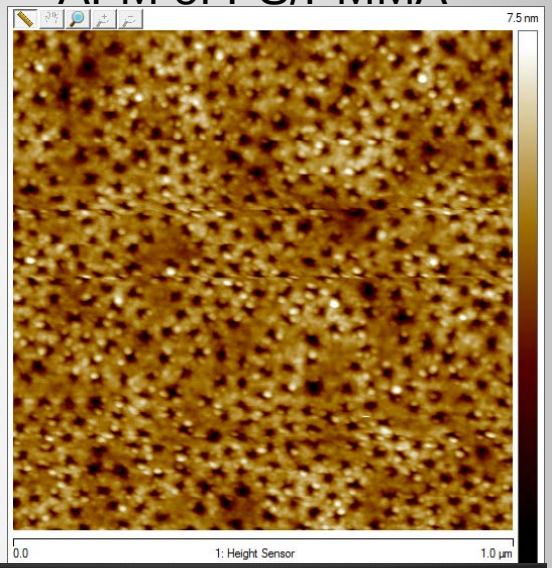
Patterns after 300 cycle CoO ALD (9nm CoO) and PS is removed by toluene

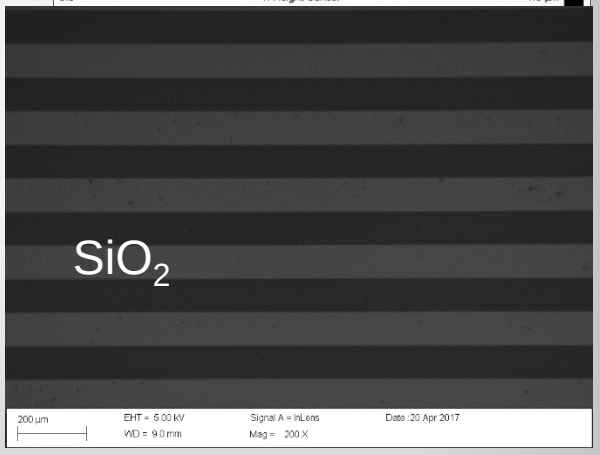
Area Selective ALD (AS-ALD)

$MO_x \rightarrow M$



AFM of PS/PMMA





Patterned PS on SiO_2 before ALD

- AS-ALD advantages
  - Eliminates post deposition etch step
  - Eliminates alignment

Every R-group studied blocked CoO and NiO ALD.

After extended O_2 RIE "PMMA" is active !

Lee, H; Bent, S (2012). Nanopatterning by Area-Selective Atomic Layer Deposition. In *Atomic Layer Deposition of Nanostructured Materials.* John Wiley & Sons.
George, Steven M. "Atomic Layer Deposition: An Overview." *Chemical Reviews* 110, no. 1 (2009): 111–31