Ultratech CNT

Controlling smoothness of thin platinum ALD films

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Outline

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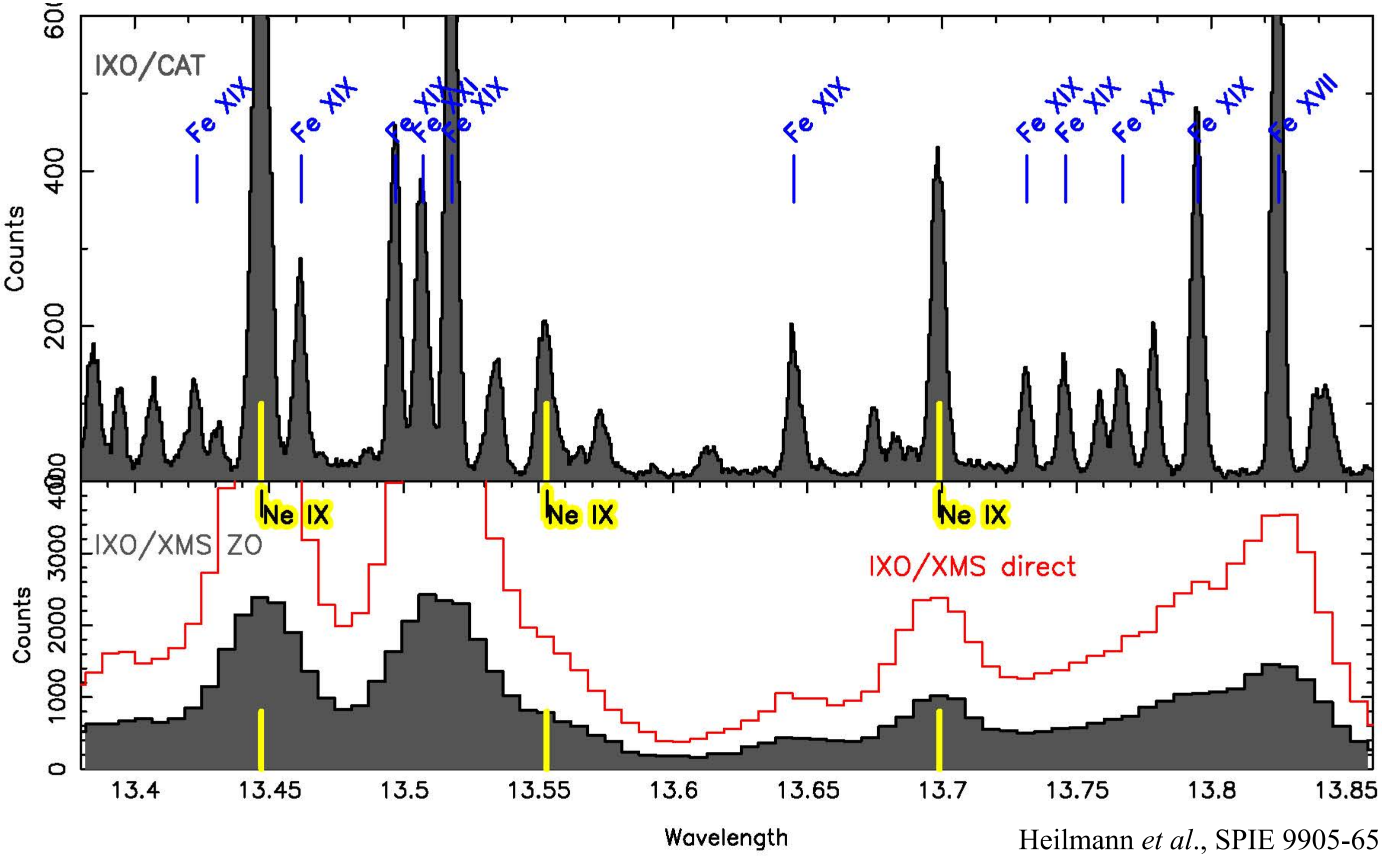
- Motivation: X-Ray Diffraction Gratings
  - Improvement in grating performance
- Making the Pt thinner
  - Methods:
    - Deposition
    - Metrology
  - Data
- Summary

- Important questions in cosmology are addressed by analysis of the soft x-ray spectrum
  - Role of Active Galactic Nuclei in galaxy formation
  - Characterization of the Warm-Hot Intergalactic Medium and the missing baryon problem



Simulated Spectra of Capella (from IXO studies; assuming ~ 5" PSF)

IXO/CAT: Grating readout spectrum

IXO/XMS Z0: Zeroth order transmitted to microcalorimeter (XMS)

IXO/XMS direct: Not intercepted by gratings

Courtesy of N. Schulz (MIT)

Heilmann *et al.*, SPIE 9905-65 High Resolution CAT XGS

Critical Angle Transmission Gratings

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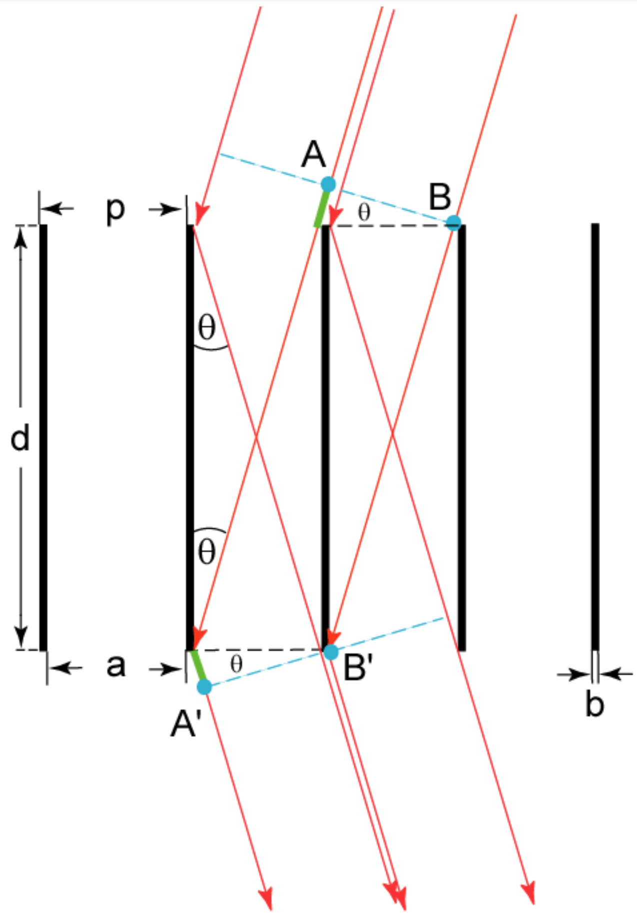

Grating equation:

$m\,\lambda = p\,(\sin(\theta) + \sin(\beta_m))$,
m = diffraction order

Blazing: $\beta_m \sim \theta$

High reflectivity:
$\theta < \theta_c$ = critical angle of total external reflection

Strawman:
Silicon grating, $\theta = 1.5^{\circ}$
p = 200 nm
b = 40 nm
d = 6 μm
aspect ratio d/b = 150

Total external reflection $\theta < \theta_c$

$\theta_c \uparrow \;\Rightarrow\; \theta \uparrow$

- m ↑ (higher order peaks i.e. greater resolving power)
- Higher energy

θ_c depends on (material, λ)

- $\theta_c \sim 1.7^{o}$ for (Si,1nm)
- $\theta_c \sim 2.4^{o}$ for (Pt,1nm)

Case for Pt ALD: increase θ_c by conformally coating Si grating with Pt

Heilmann *et al.*, SPIE 9905-65 High Resolution CAT XGS

Manufacturing CAT Grating

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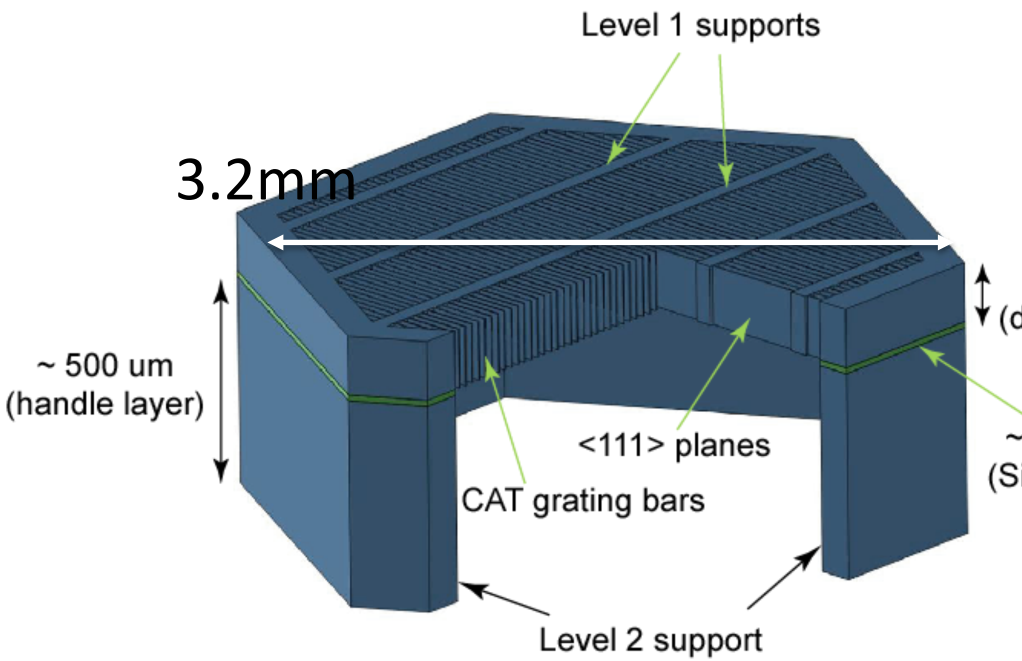

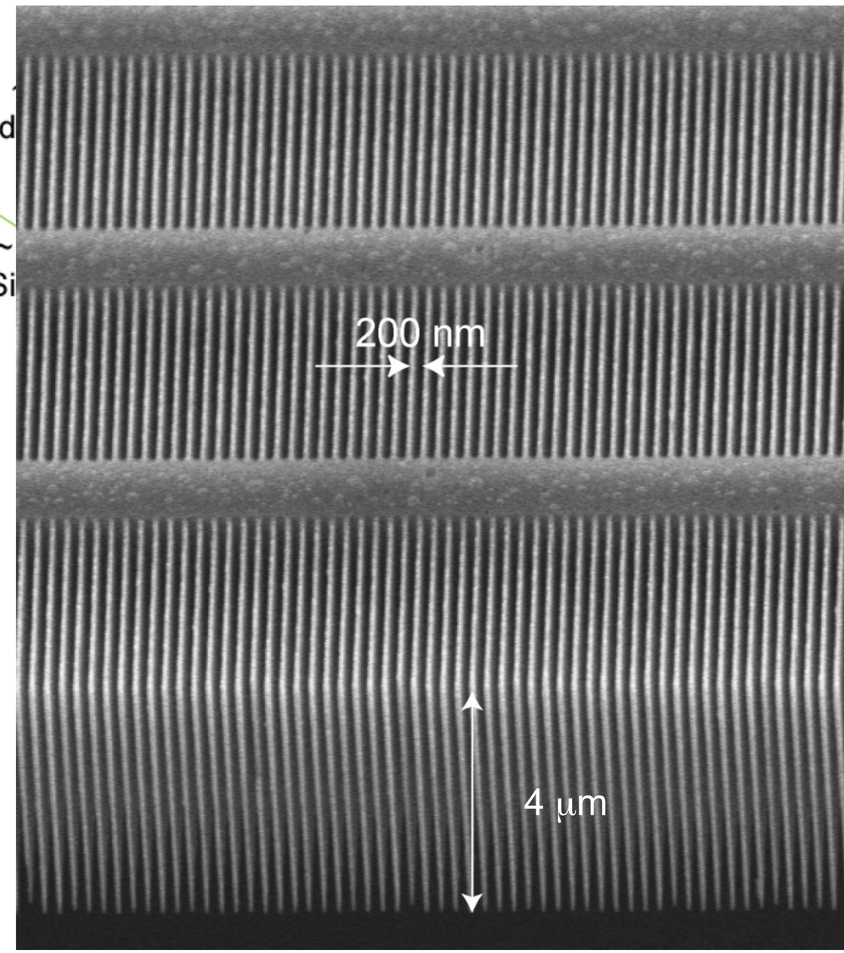

Period = 200nm
Opening ~ 130nm
Depth ~ 4micron (open both sides)
Aspect Ratio = 2000/130 ≈ 15:1
Future AR ~ 50

Heilmann *et al.*, SPIE 9905-65 High Resolution CAT XGS

ALD Pt Coated CAT Grating

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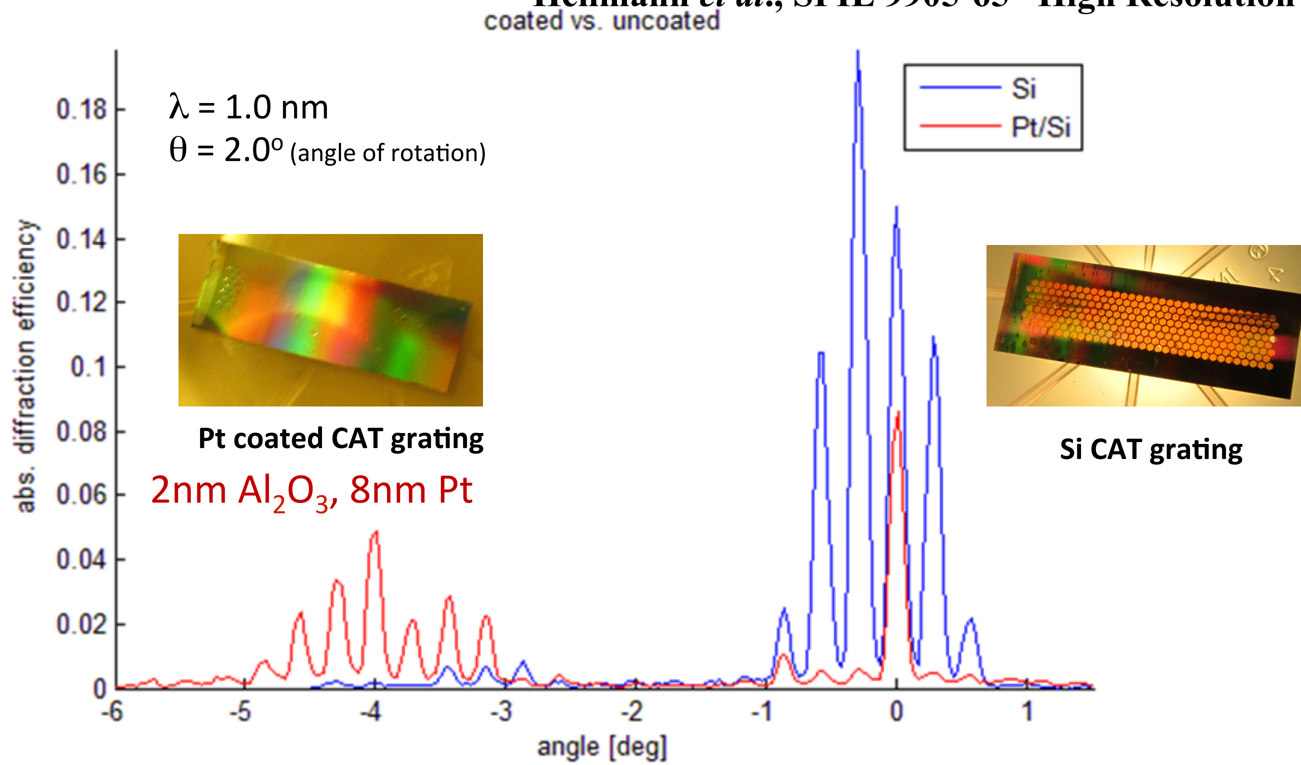

$\Theta < \Theta_c(Pt)$:
higher order fringes
$\approx 2\Theta$

$\Theta > \Theta_c(Si)$:
low order fringes

Heilmann *et al.*, SPIE 9905-65 High Resolution CAT XGS

Higher order diffraction peaks => greater resolving power
Access to higher energy (shorter wavelength)

Goal

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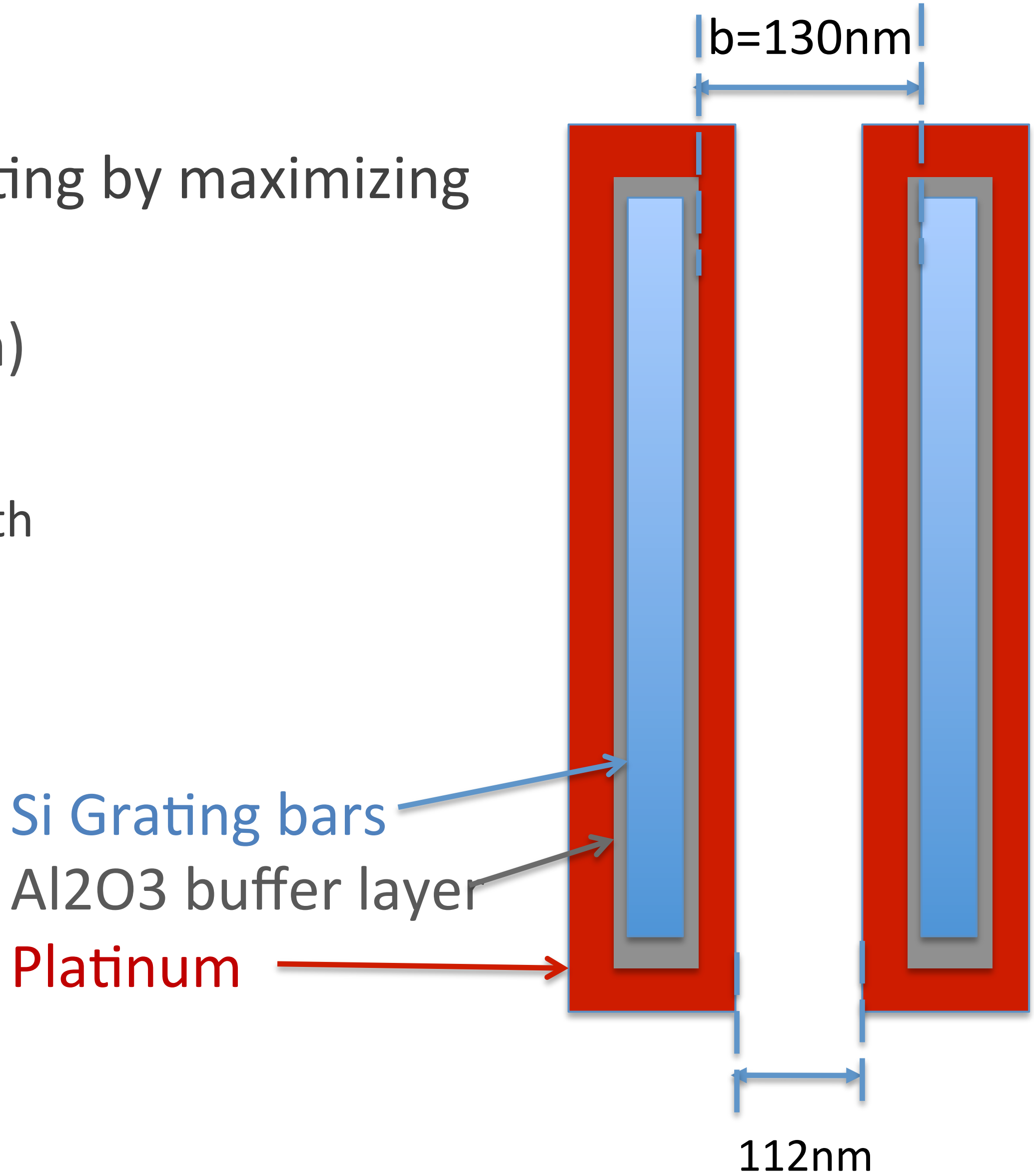
- Increase efficiency of grating by maximizing open area
  - Thinner film Pt (~ 5nm)
  - High X-Ray reflectivity
    - continuous and smooth
    - high density
    - low impurity



Experimental

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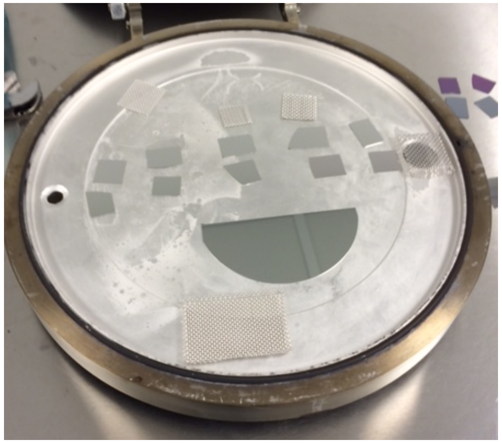
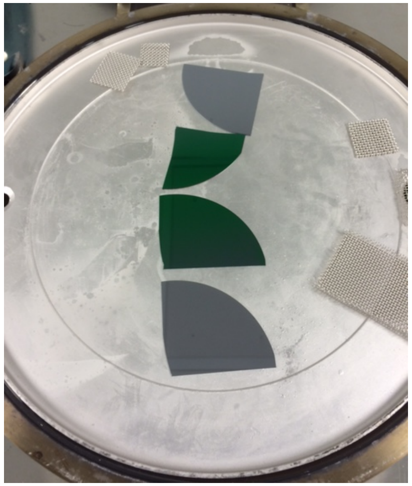
- Deposition:
  - Savannah 200 (200mm dia reactor)
  - 2” substrates of Si and Si-TOX at reactor center
  - 120sec UV-O3 pre-clean
  - $Me_3PtCpMe+O2$ (270°C), Me3PtCpMe +O3 (150°C)
  - Ozone 120mg/liter
- Measurement:
  - Ellipsometry – thickness
  - 4-point probe – resistivity/macroscopic continuity
  - XRR – thickness, density, roughness
  - AFM - roughness





Ellipsometry Validation

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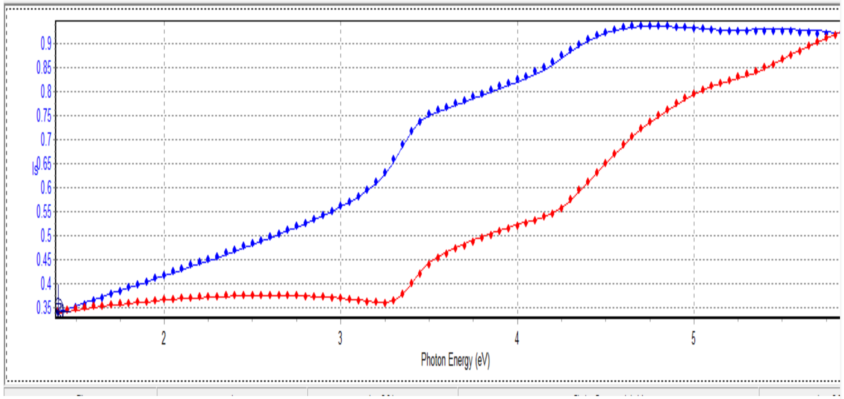


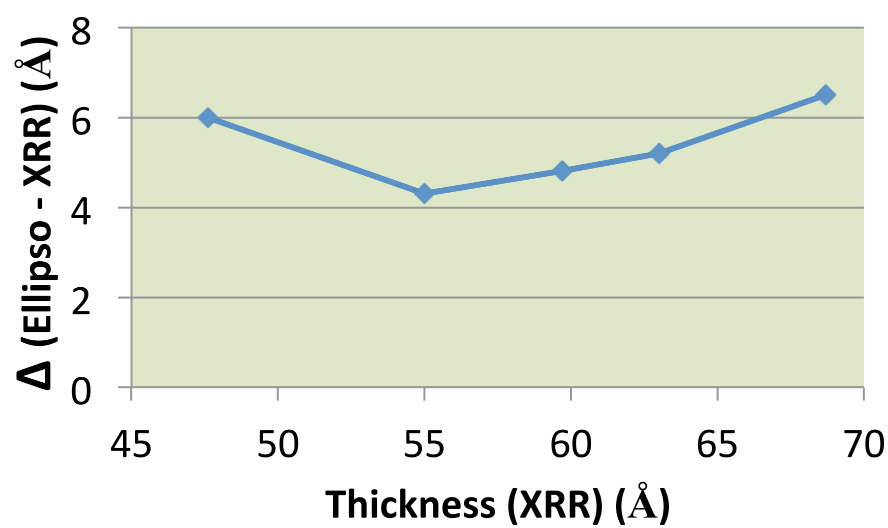
Parameters

1) L3 Thickness [Å] = 73.631 ± 0.537
2) Pt_Drude ε∞ = 3.3044650 ± 0.0535246
3) Pt_Drude εs = 36.1400500 ± 7.9889070
4) Pt_Drude ωt = 2.2627190 ± 0.2327800
5) Pt_Drude ωp = 8.9502930 ± 0.3585669
6) Pt_Drude Γ₀ = 6.7027850 ± 0.3149613
7) Pt_Drude Γd = 0.8551500 ± 0.0815929

Correlation matrix

=1=	=2=	=3=	=4=	=5=	=6=	=7=
1.000	0.227	0.006	0.018	-0.259	-0.516	-0.415
	1.000	0.019	-0.021	-0.094	-0.428	-0.330
		1.000	-0.996	-0.955	-0.562	-0.837
			1.000	0.952	0.592	0.834
				1.000	0.741	0.944
					1.000	0.857
						1.000

- Good quality fit over wide spectral range (1.4-5.9eV)
- Fit parameters tightly bound
- Correlation between optical parameters and thickness is low
- Thickness from ellipsometry is about 4-6Å more than XRR



Physical considerations

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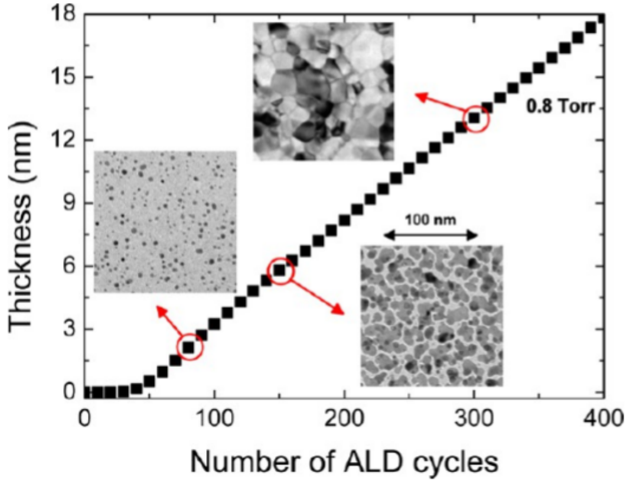
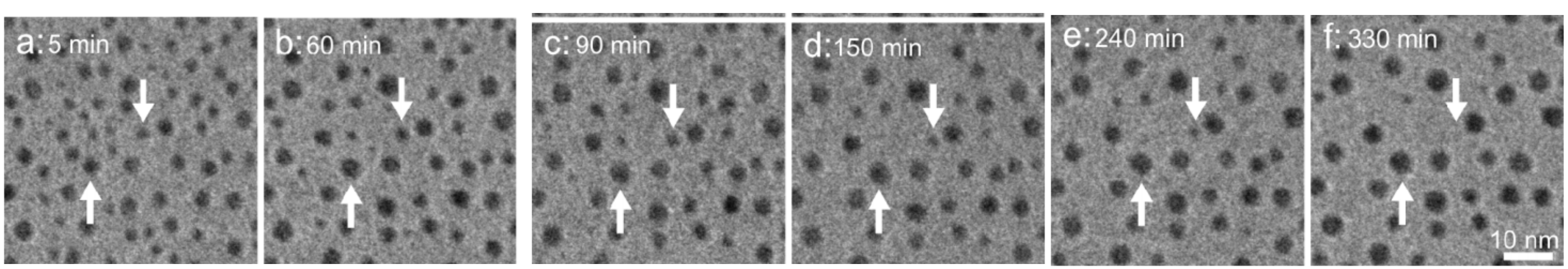
- Energetics:
  - Does Pt deposit on previously deposited Pt or on substrate?
  - Does deposited Pt tend to agglomerate into Pt particles vs remain as a film?

- Kinetics:
  - What is rate of surface diffusion/ agglomeration?
  - How does it compare to rate of deposition?



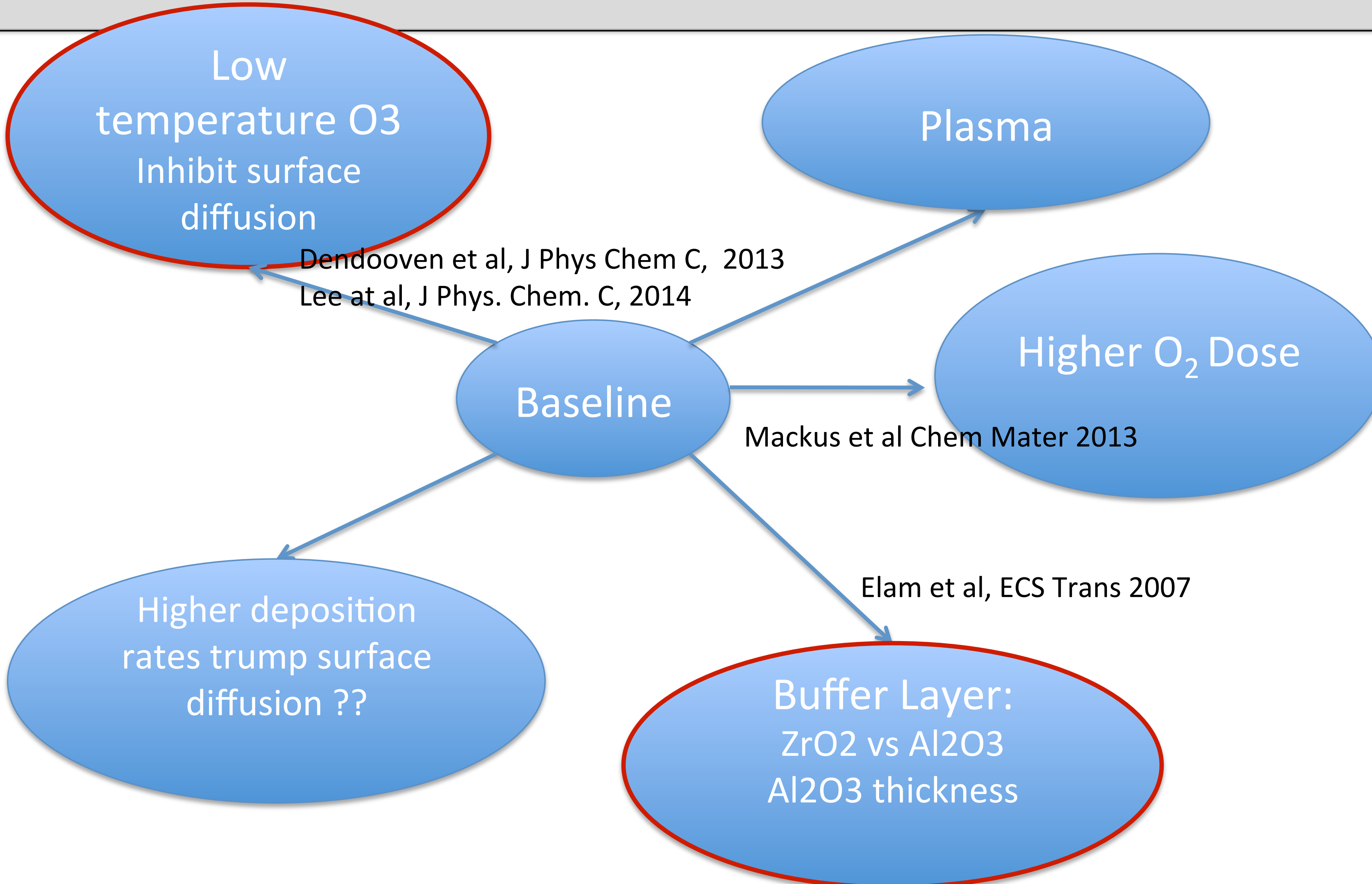
Mackus et al (2013). dx.doi.org/10.1021/cm400562u



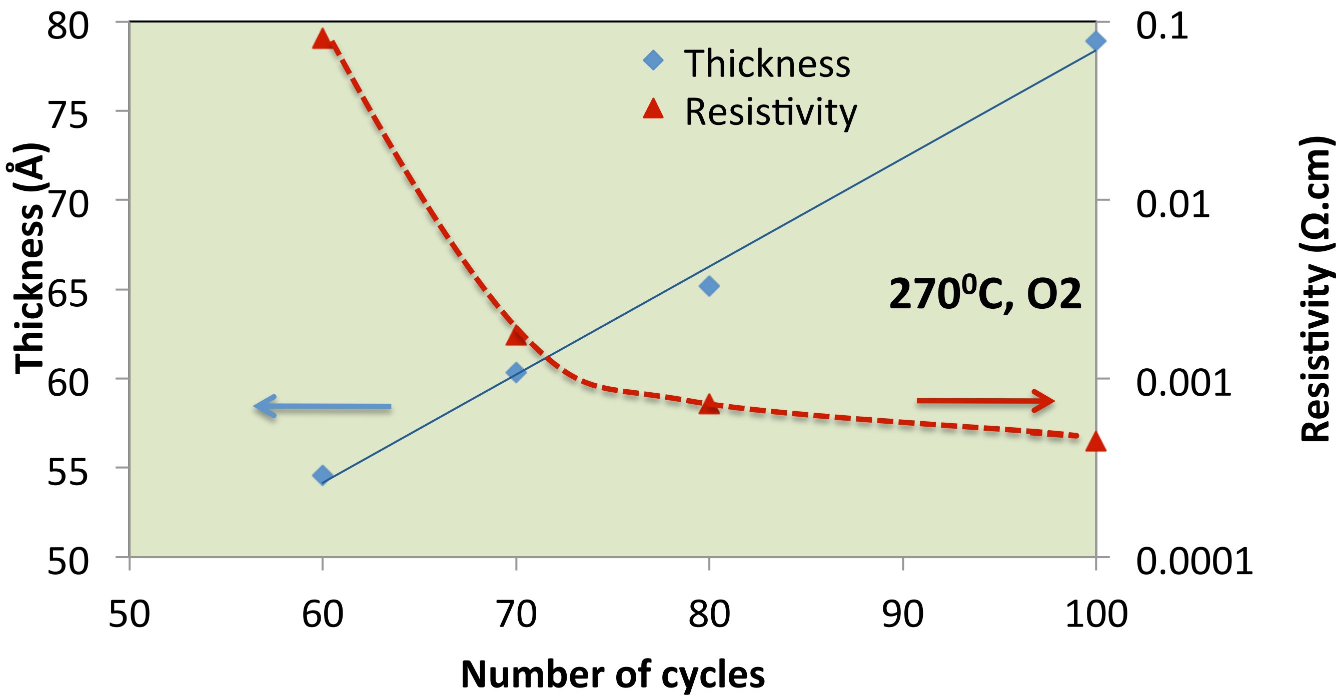
Simonsen et al (2011). DOI: 10.1016/j.jcat.2011.04.011

In-situ TEM at **650ºC,** 10mbar "air"

Routes to smoother, thinner films

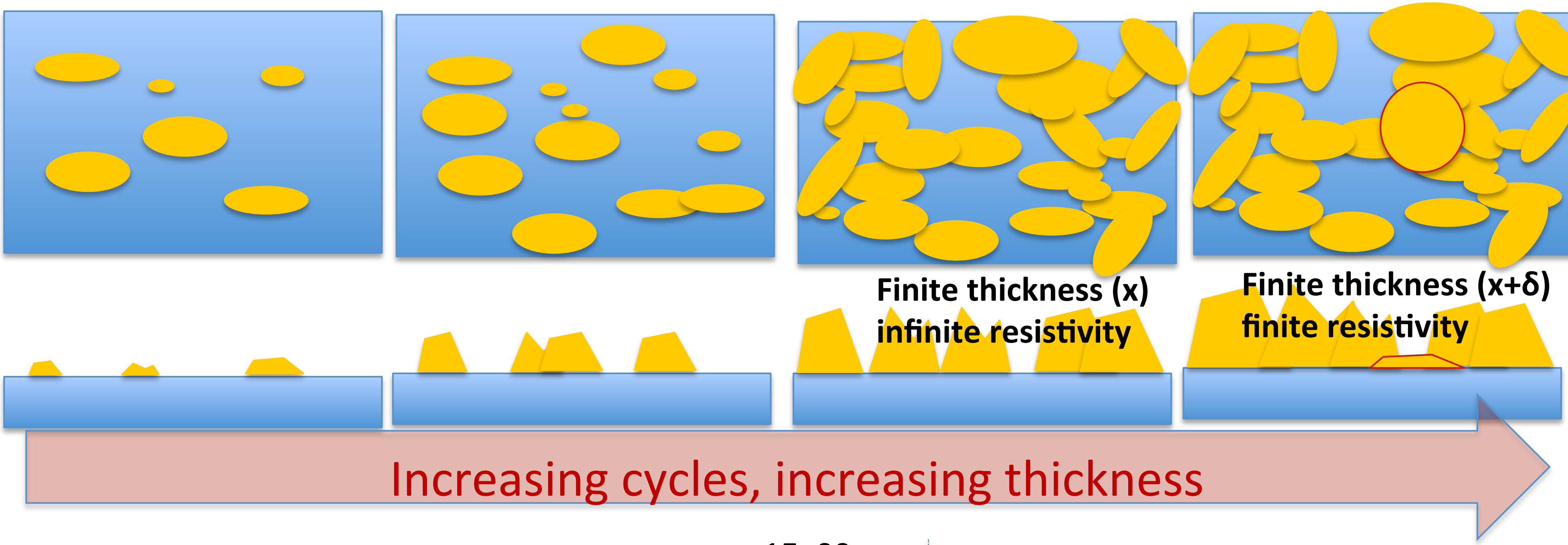


“Standard” (270ºC, O_2 process) Ultratech CNT



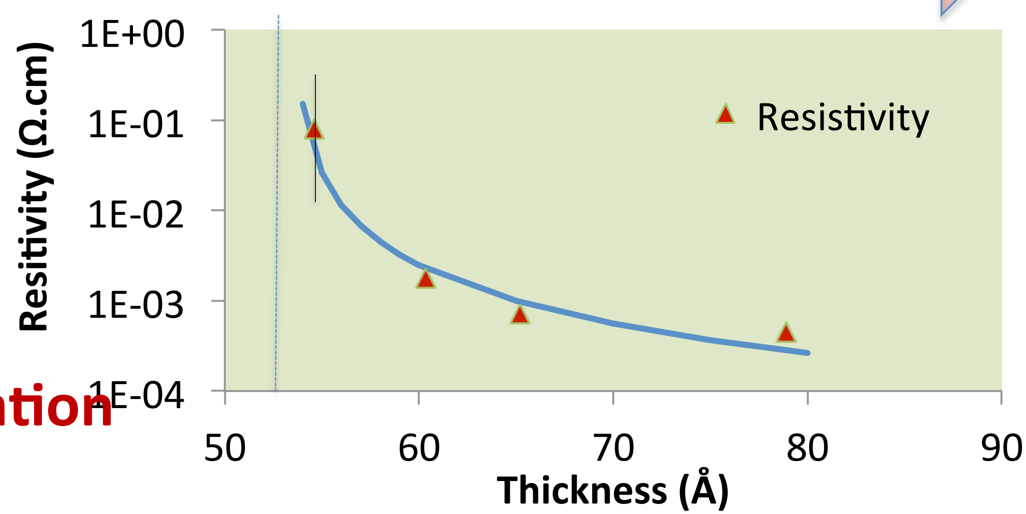
Thickness increases linearly with number of cycles
Resistivity increases super-exponentially → percolation?

Percolation



$$\rho \propto \frac{1}{(t-t_c)^{\gamma}} \quad t \rightarrow t_c, t > t_c$$

$$\rho = \infty \quad t < t_c$$



"Baseline" process has percolation threshold at ~50Å

Ozone at 150°C

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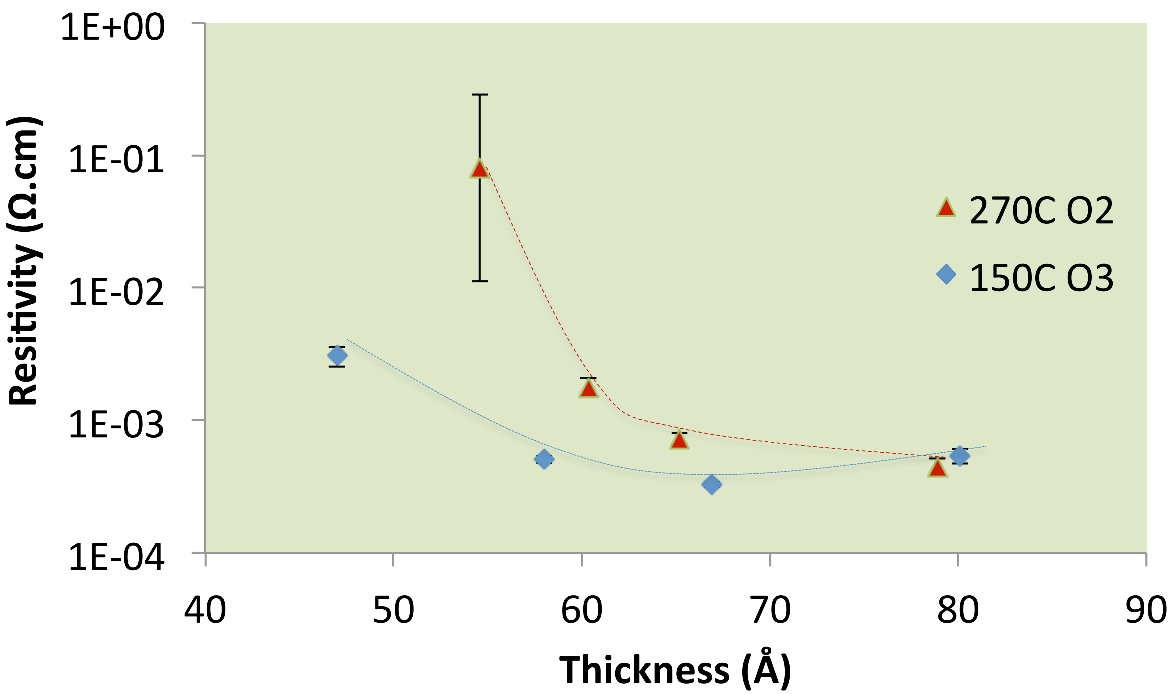

- O_3 film is continuous at lower thicknesses
- No sign of percolation threshold
- However, ~ 80Å resistivity suggests film quality is poorer
  - Xray Reflectivity is low
  - Residual carbon?

Ozone dose

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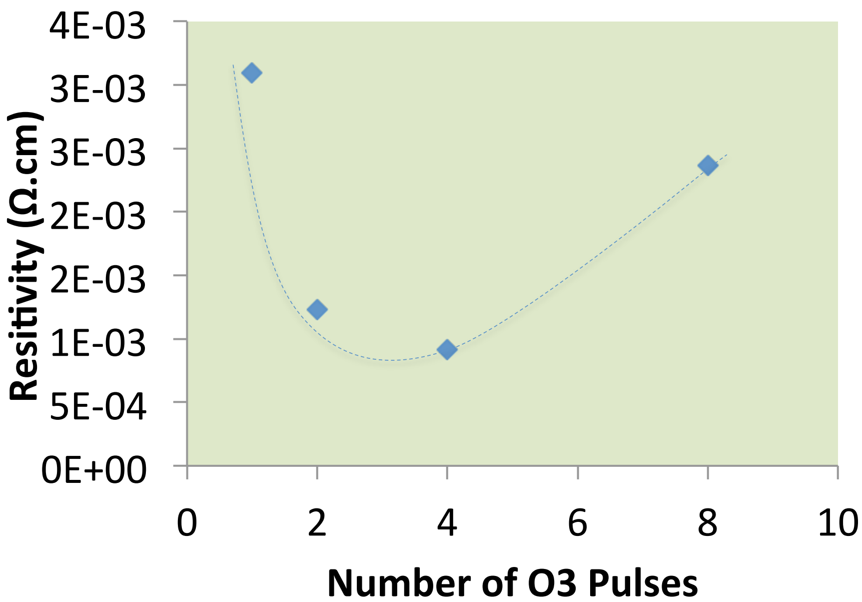
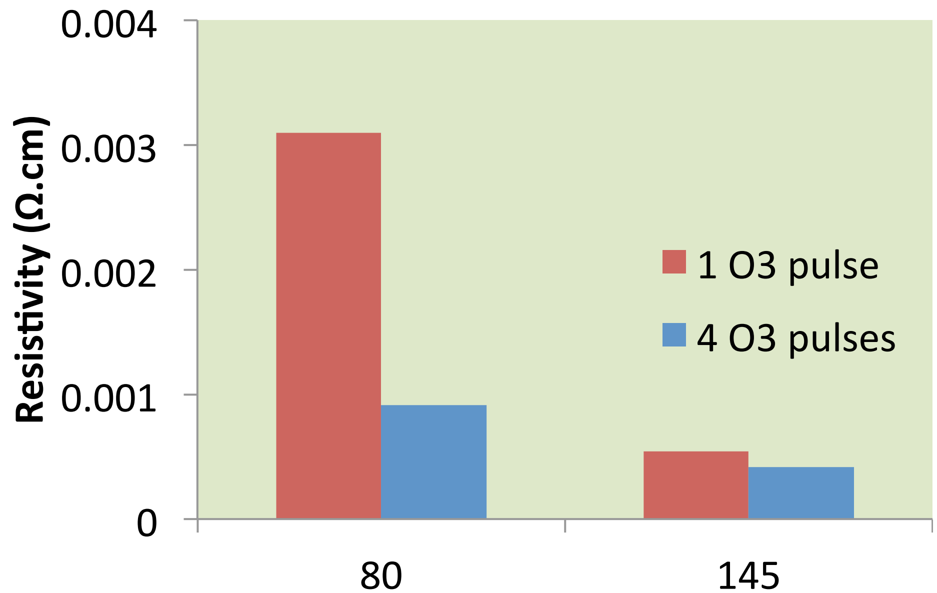
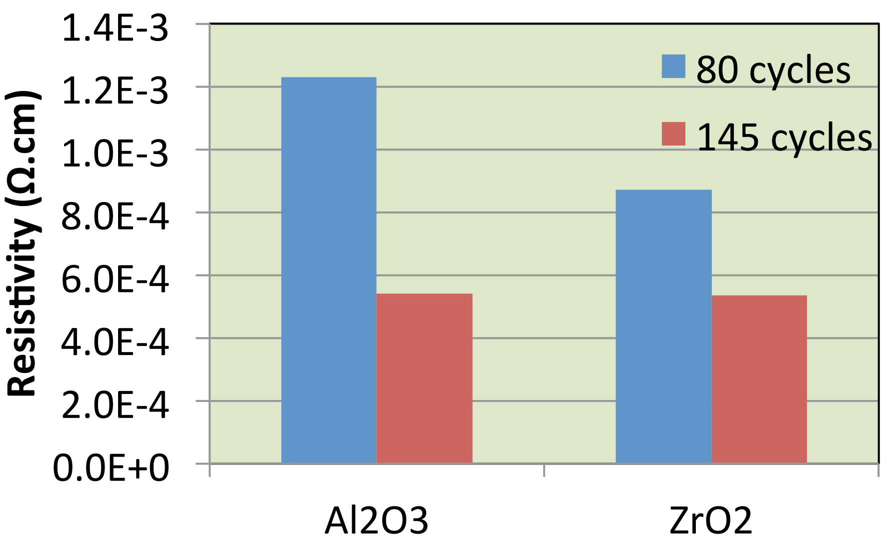
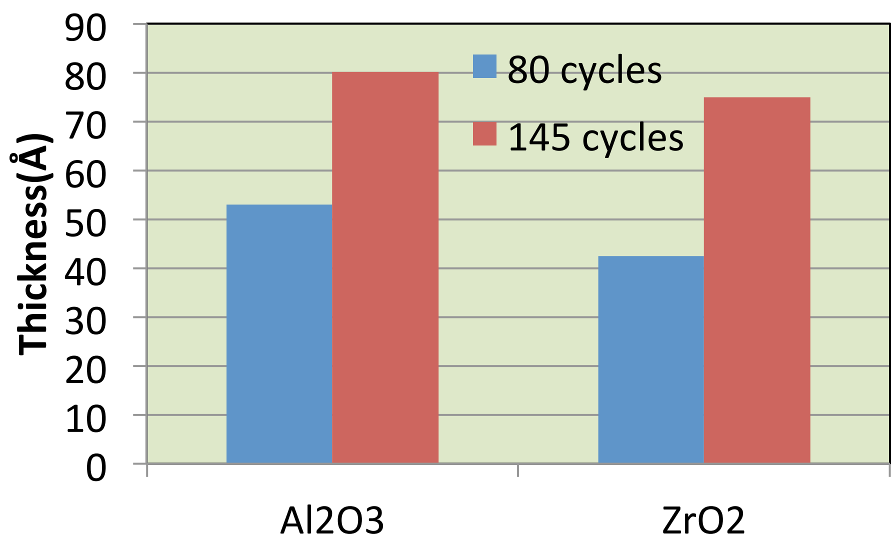




- Increasing O_3 dose by 4X gives lowest resistivity
- Resistivity improvement is not as much for thicker film

Buffer Layer (Al_2O_3 vs ZrO_2)





150^{0}C O3 process

- At 80cycles:
  - Resistivity on ZrO2 is ~ 35% lower *with 10Å thinner film*
- At 145 cycles
  - Resistivity is similar for both surfaces

ZrO_2 surface encourages faster nucleation and continuity

Thickness of Al_2O_3 layer

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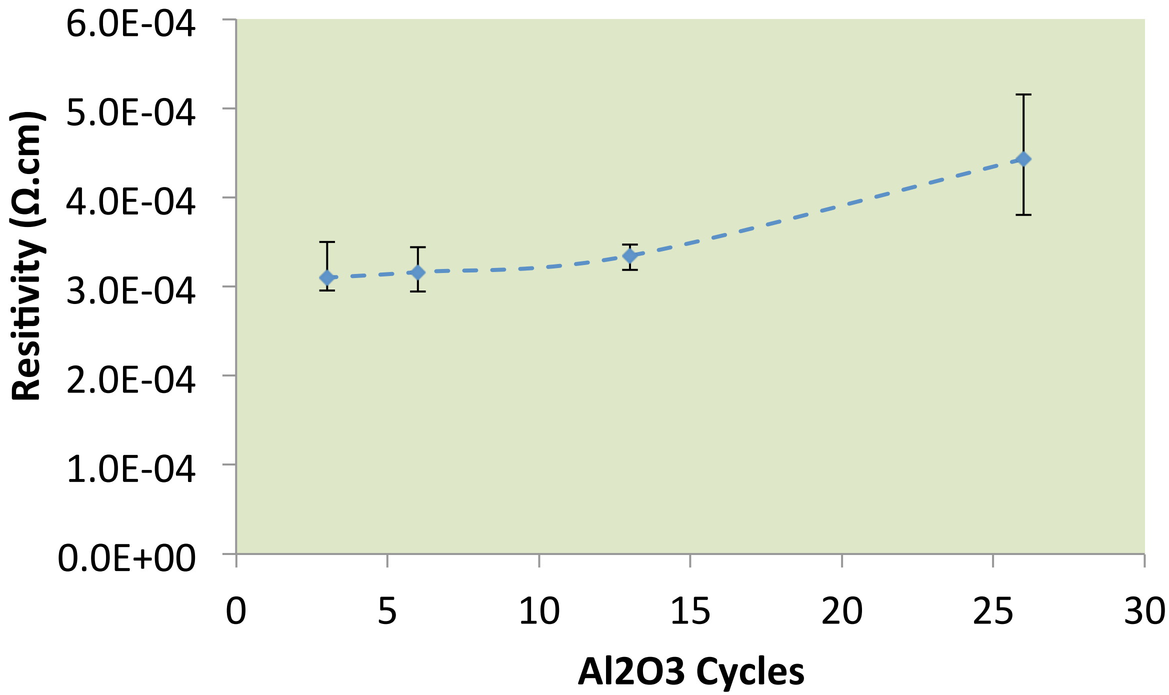

100 cycles Pt

270^{o}C, O_2

Pt nucleation enhancement on Al2O3 maintained to 3 cycles of Al2O3

Summary

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- Improvement in “device” performance – increase in critical angle for X-Ray CAT grating
- Percolation threshold reduced from ~ 5nm to less than 4nm for ozone process.
  - Film quality improvement required
- Thin (3cycles) Al2O3 is adequate for improved Pt coalasence