2019 NNCI ALD/MOCVD/MBE Symposium Staff Review

Atomic Layer Deposition at Harvard CNS

Mac Hathaway

Oct. 3, 2019

The CNS Cambridge Nanotech Savannah 200

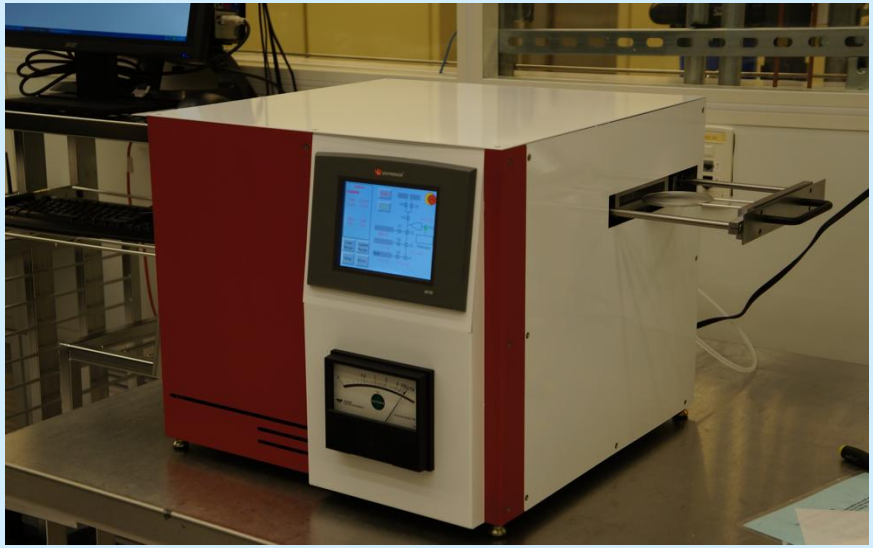
CNS ALD System Review

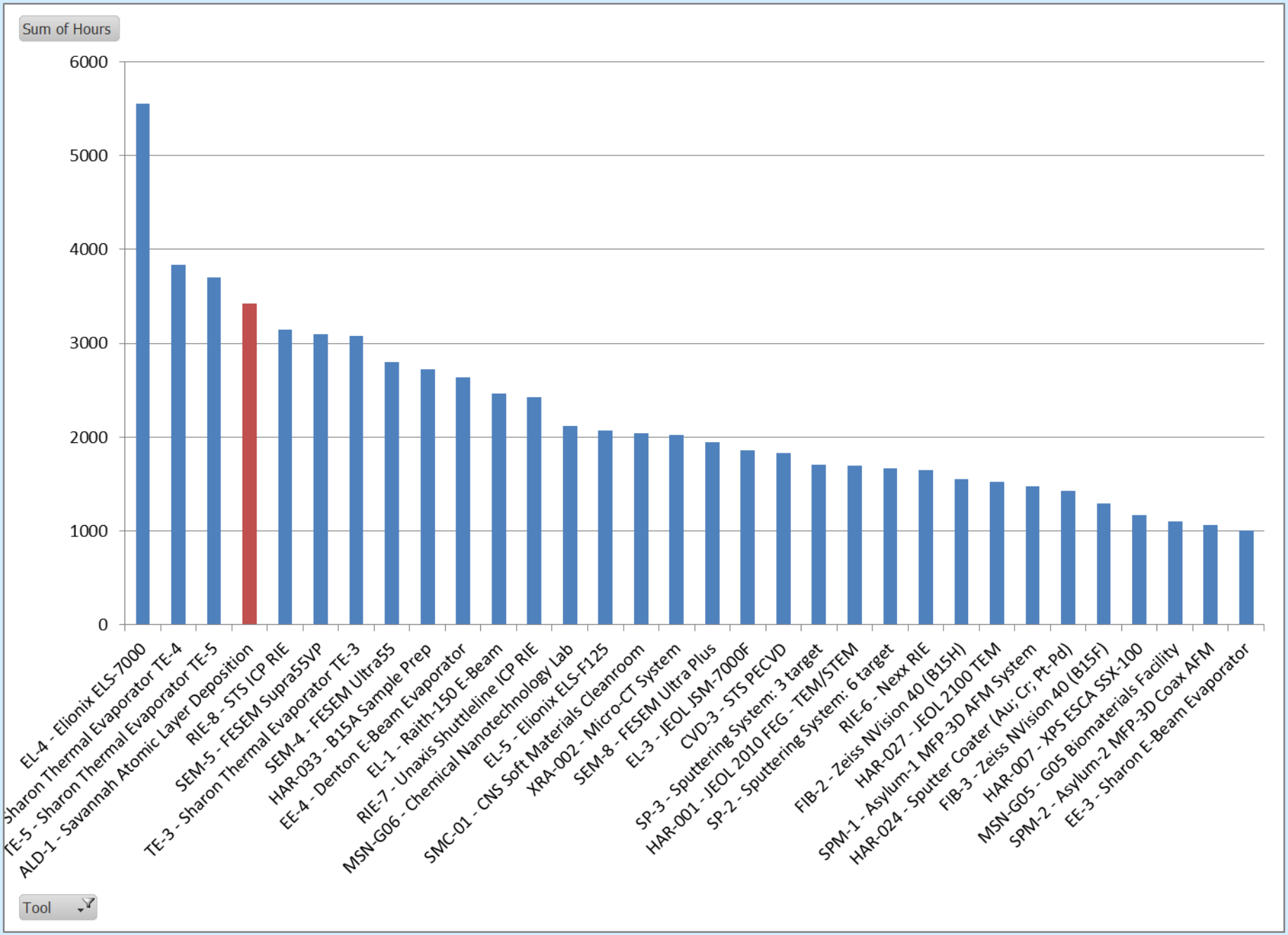
- Cambridge Nanotech Savannah 200 thermal ALD x2
- New in 2008
- 6-port configuration, 8” wafer capacity
- Available films on the Savannah –
  - Al_2O_3, HfO2, ZrO2, SiO2, TiO2, ZnO, AZO, Pt
- System Utilization – 31.3% (24/7 availability) –
  - For reference – our busiest tool – Elionix E-Beam writer – 46.6 %
- Rates – Academic
  - Regular - $29/hr; Assisted use - $75/hr; Remote Assisted - $125
- Rates – Non-academic
  - Regular - $120/hr; Assisted use - $165/hr; Remote Assisted - $220

The GEMStar™ Benchtop ALD System

- Arradiance GEMStar
  - Tabletop unit, thermal ALD
  - 8 precursor ports
  - Excellent temperature control
  - Very flexible
  - Currently configured for WiN, NiN, for anneal down to pure metal

- Lab Built unit
  - Tabletop unit, thermal ALD
  - 4 precursor ports
  - Excellent temperature control
  - Low Cost
  - Now commercialized as the Anric AT-4




Sum of Hours
6000
5000
4000
3000
2000
1000
0
EL-4 - Elionix ELS-7000
Sharon Thermal Evaporator TE-4
TE-5 - Sharon Thermal Evaporator TE-5
ALD-1 - Savannah Atomic Layer Deposition
RIE-8 - STS ICP RIE
SEM-5 - FESEM Supra55VP
TE-3 - Sharon Thermal Evaporator TE-3
SEM-4 - FESEM Ultra55
HAR-033 - B15A Sample Prep
EE-4 - Denton E-Beam Evaporator
EL-1 - Raith-150 E-Beam
RIE-7 - Unaxis Shuttleline ICP RIE
MSN-G06 - Chemical Nanotechnology Lab
SMC-01 - CNS Soft Materials Cleanroom
EL-5 - Elionix ELS-F125
XRA-002 - Micro-CT System
SEM-8 - FESEM Ultra Plus
EL-3 - JEOL JSM-7000F
CVD-3 - STS PECVD
SP-3 - Sputtering System: 3 target
HAR-001 - JEOL 2010 FEG - TEM/STEM
SP-2 - Sputtering System: 6 target
RIE-6 - Nexx RIE
FIB-2 - Zeiss NVision 40 (B15H)
HAR-027 - JEOL 2100 TEM
SPM-1 - Asylum-1 MFP-3D AFM System
HAR-024 - Sputter Coater (Au; Cr; Pt-Pd)
FIB-3 - Zeiss NVision 40 (B15F)
HAR-007 - XPS ESCA SSX-100
MSN-G05 - G05 Biomaterials Facility
SPM-2 - Asylum-2 MFP-3D Coax AFM
EE-3 - Sharon E-Beam Evaporator
Tool

Maintenance Schedule

- Oil Change – 12-18 months
- Pump Change – ~18-24 months
- O-rings: Lid – Every 2-4 months
- O-rings: Pump line – 12 months, as indicated by drifting up of pressure
- O-ring: Pump Valve – 12 months, as indicated by "leaking of vacuum" into chamber, slowing venting
- Chamber clean: ~2-4 months
- Lid changed out to facilitate cleaning

Problems

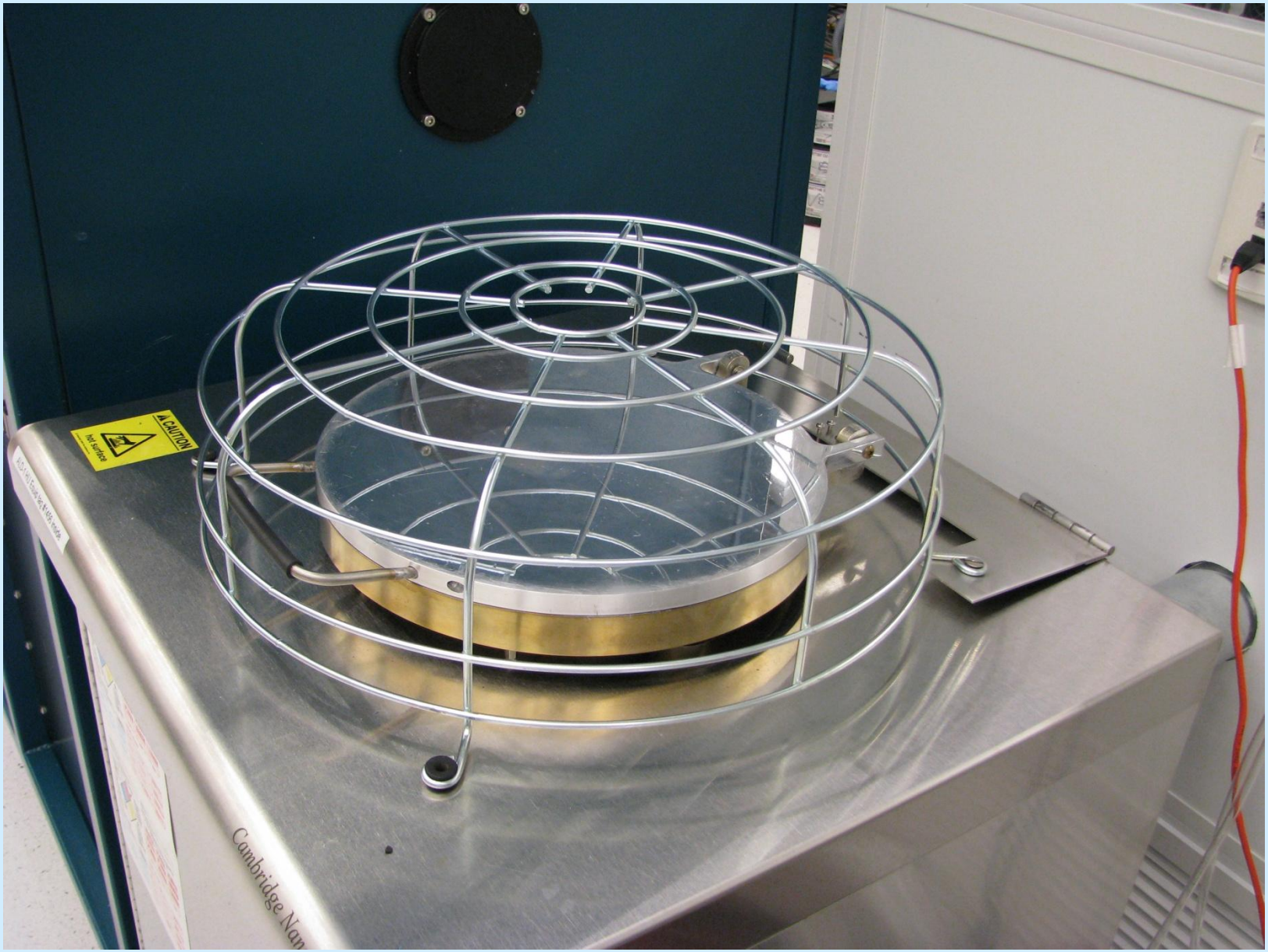
- Gauge Drift – due to coating up of pirani gauge
  - Added manometer gauge – doesn't drift, but hard to integrate into existing software
  - Tee for manometer gauge – added enough "ballast", or dead space, to prevent pirani from crudding up.
- Kalrez oring – Very expensive. $300+
  - Replaced with Viton, change more often (2-4 months), costs $4. Keep outer heater at 150C for most processing.
- Pump filling with Al2O3 powder, makes nasty stinky sludge. And pump efficiency goes down, base pressure goes up.
  - Added "in-line secondary reactor" (mist filter)
  - Now pumps regular last at least a year before oil changes.

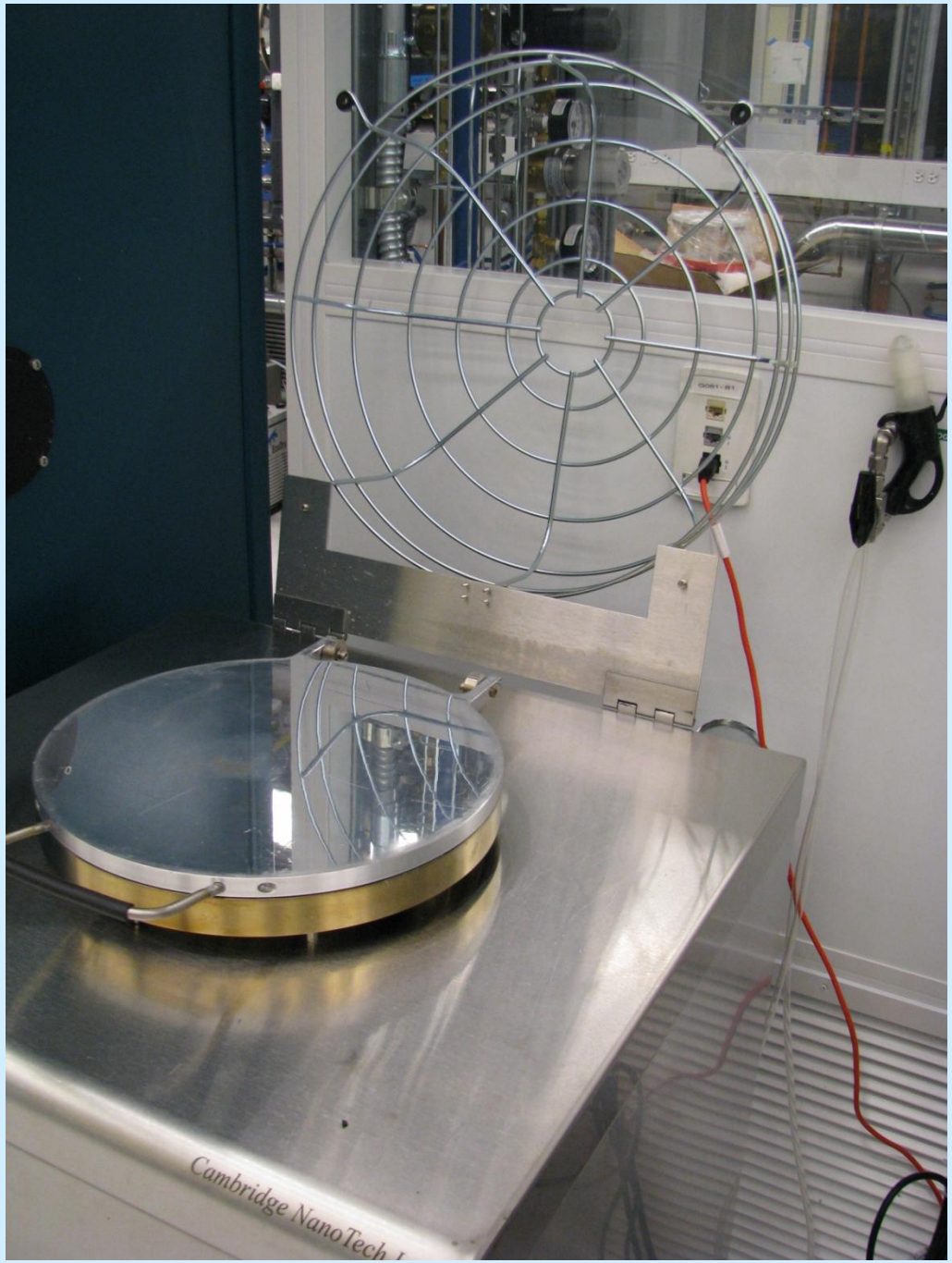
In-line Secondary Reaction Unit

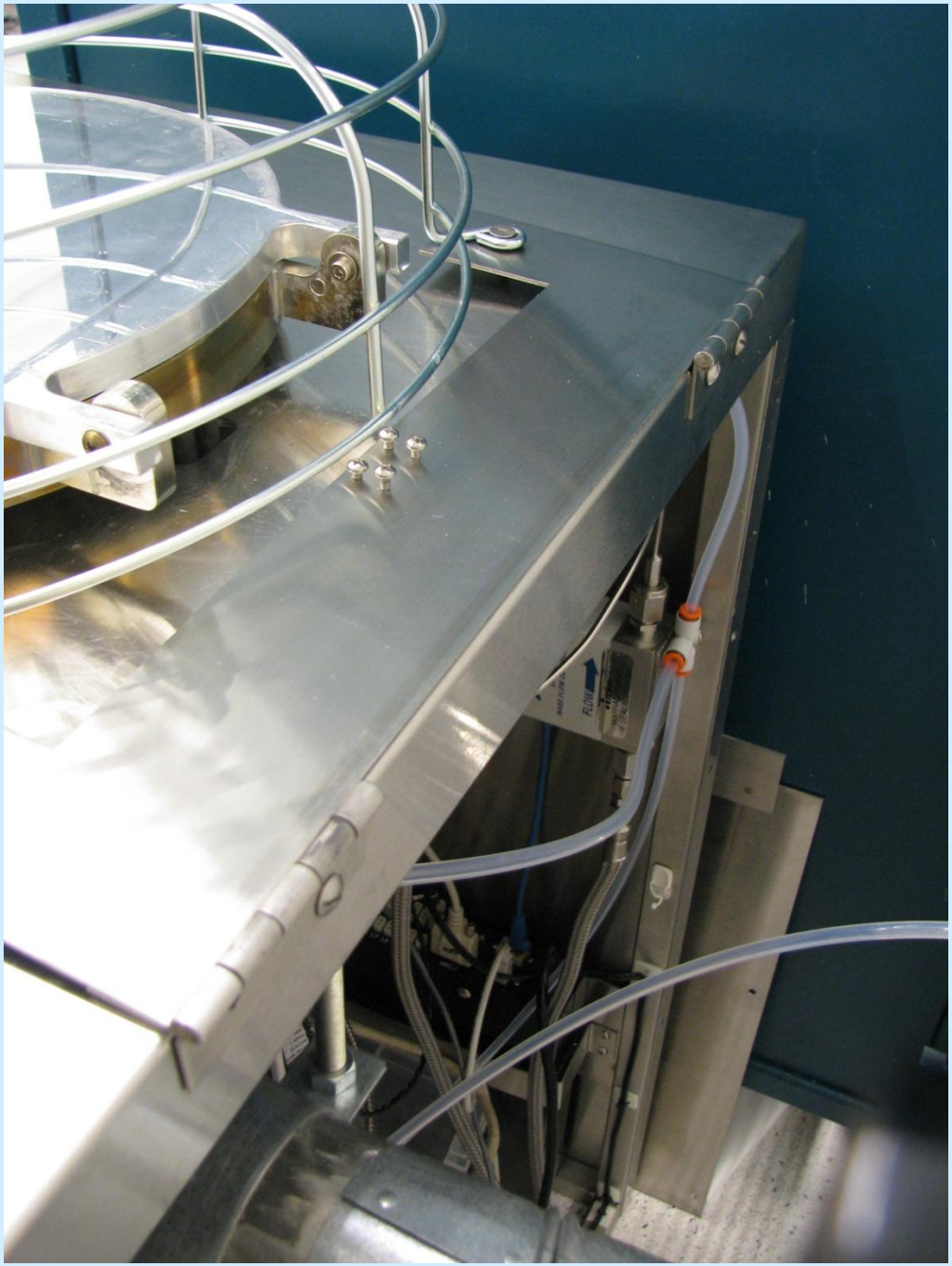
Problems (cont.)

- Hot lid…melts things.
  - Put heat shield on hinge (custom - drawing available)

Heat Shield Hinge




Cambridge NanoTech


FLOW

Problems (cont.)

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- Pnuematic fittings feeding ALD valves get leaky
  - Changed “push” fittings to barb fittings.


MAC
WIXOM, MI USA
LIEGE, BELGIUM
TAIPEI, TAIWAN
MODIF
MODEL
34C-AAA-GDFC-1KT
ELECTRICAL
24 VDC
WATTS
4.0
VAC TO
120 PSI
MAC

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  - Supposedly, new control box is better. Part was ordered.

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- Venting can be difficult, due to buildup on Pump Valve sealing surfaces.

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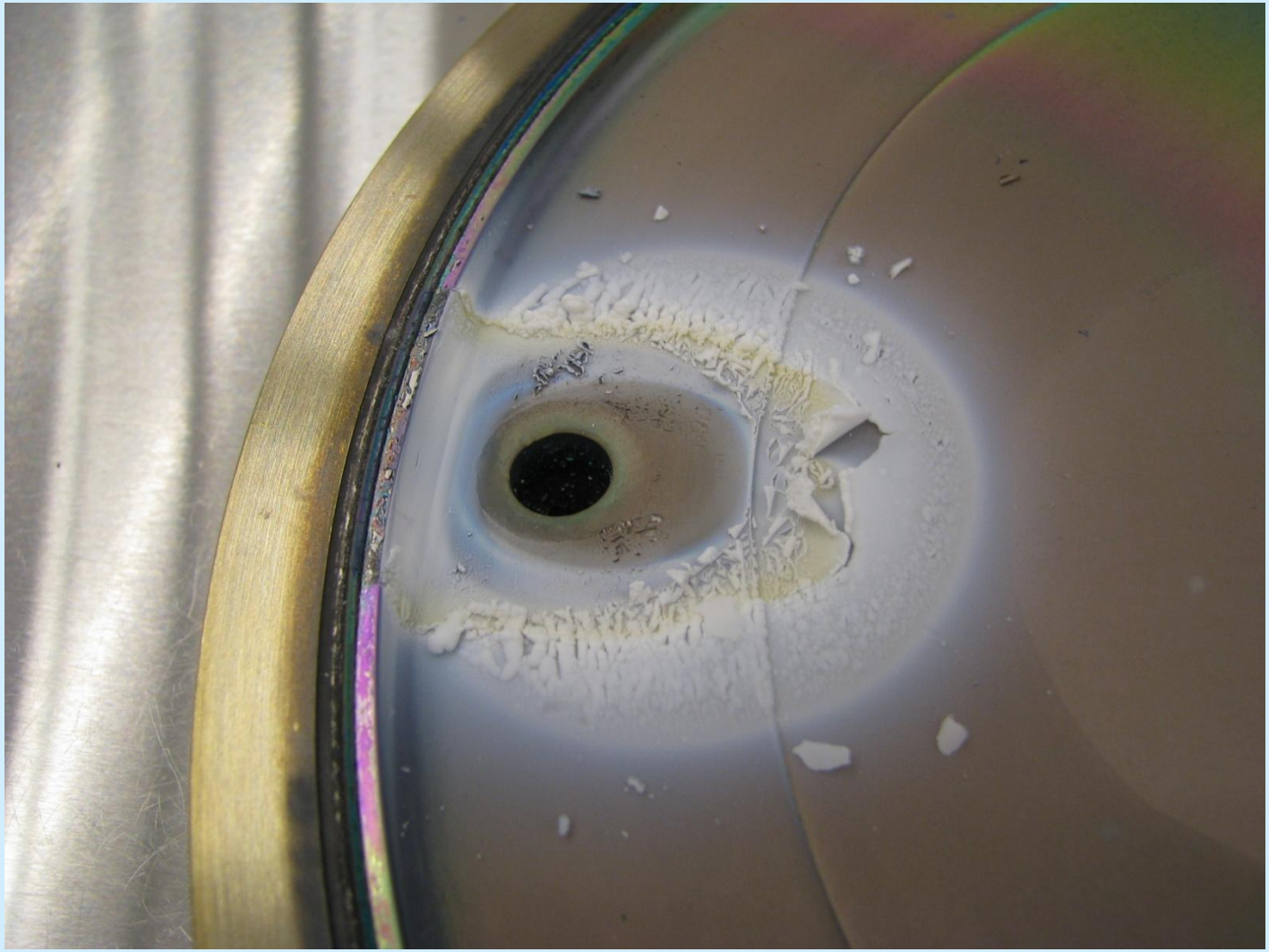
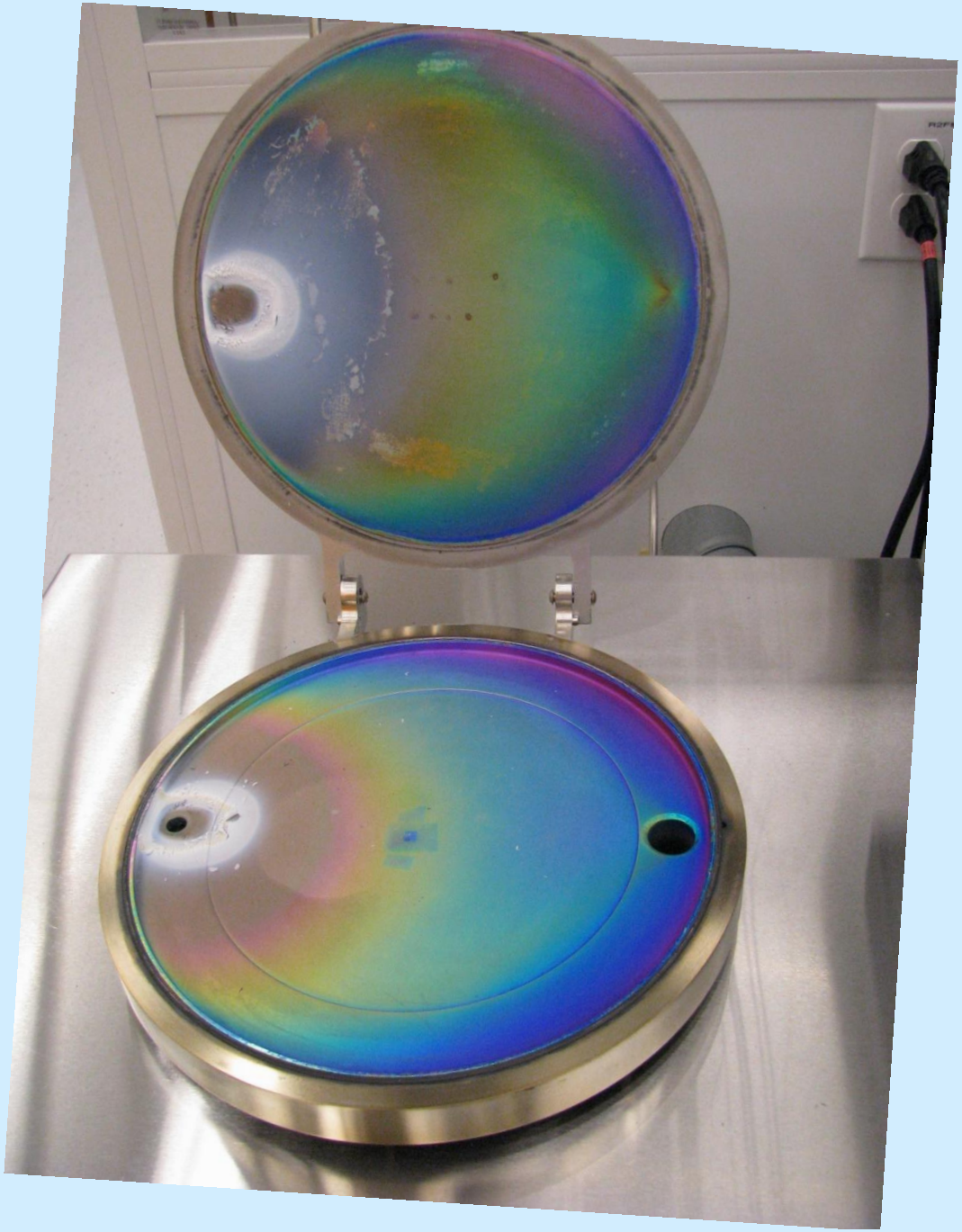
- Venting can be difficult.
  - Put Pump Valve directly on top of pump (a’ la Beneq!)
    - Initial sealing of lid during pump-down might be problematic, we’ll see…

Problems can occur.



Condensation of precursor causes distinctly non-monolayer deposition

HfO_2 deposition at below 80C.
Precursor is maintained at 85C

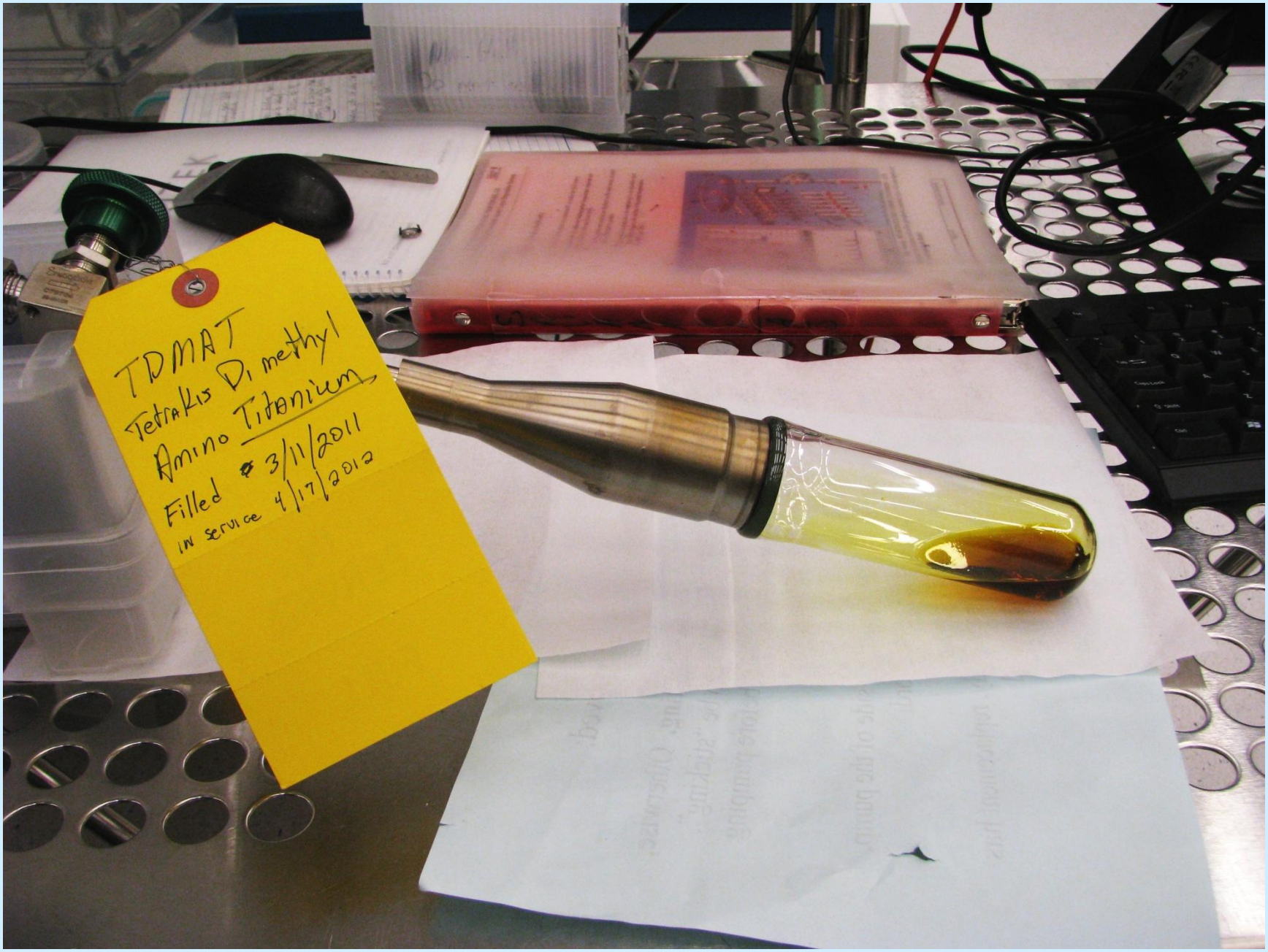


Special Modifications

- Large bore glass precursor cylinders
  - Easier to fill, visual monitoring of precursor, bigger vapor reservoir.
  - Existing bellows heater jacket fits quite nicely.

CNS Custom Precursor Cylinder

CNS Custom Precursor Cylinder


TDMAT
Tetrakis Dimethyl
Amino Titanium
Filled 3/11/2011
in service 4/17/2012

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- 7-port manifold – With slelector switch – switches between ZrO2 and SiO2

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- 7-port manifold – With slelector switch – switches between ZrO2 and SiO2
- Moved pump valve to immediately above pump

ALD Materials available at CNS?

- Available at CNS? - Al_2O_3, HfO_2, ZrO2, SiO_2*, Pt, TiO2, and ZnO/AZO (transparent conductor),
- Also, WN, NiN (for reduction to W and Ni metal), Pt via ozone, and SiO2 via ozone (more pure, no AlO interlayers)

Being characterized – ZrO, HfO2/ZrO, various other nanolaminates

Coming someday – Ruthenium? Other stuff?

*SiO2 – not pure ALD, catalyzed silanol process, has lower density, Al2O3 catalytic layer could be considered a "impurity", ~5% Al

Process Windows for CNS ALD

ALD Film	Dep. Temp.	Second Precursor	Notes
Al_2O_3	20C to 300C	H_2O	Precursor (TMA) is pyrophoric-spontaneously burns (brightly) in air.
HfO_2	120-250C	H_2O	Precursor is water sensitive – explosive decomposition products
SiO_2	130-250C	TMA+ H_2O	Not "pure" ALD process, uses Al2O3 layer for catalysis of silanol
Pt	140-150C	O_3	Doesn't like polymer, Precusor Very Expensive
TiO2	~100C – 240C	H_2O	Isopropoxide – rather slow 0.17 A/cycle TDMAT – faster – 0.4-0.7 A/cycle
ZnO	20C - 300	H_2O	Sheet resistance variable
ZrO2	120-240C	H_2O	Looks good, rate ~1 A/cycle

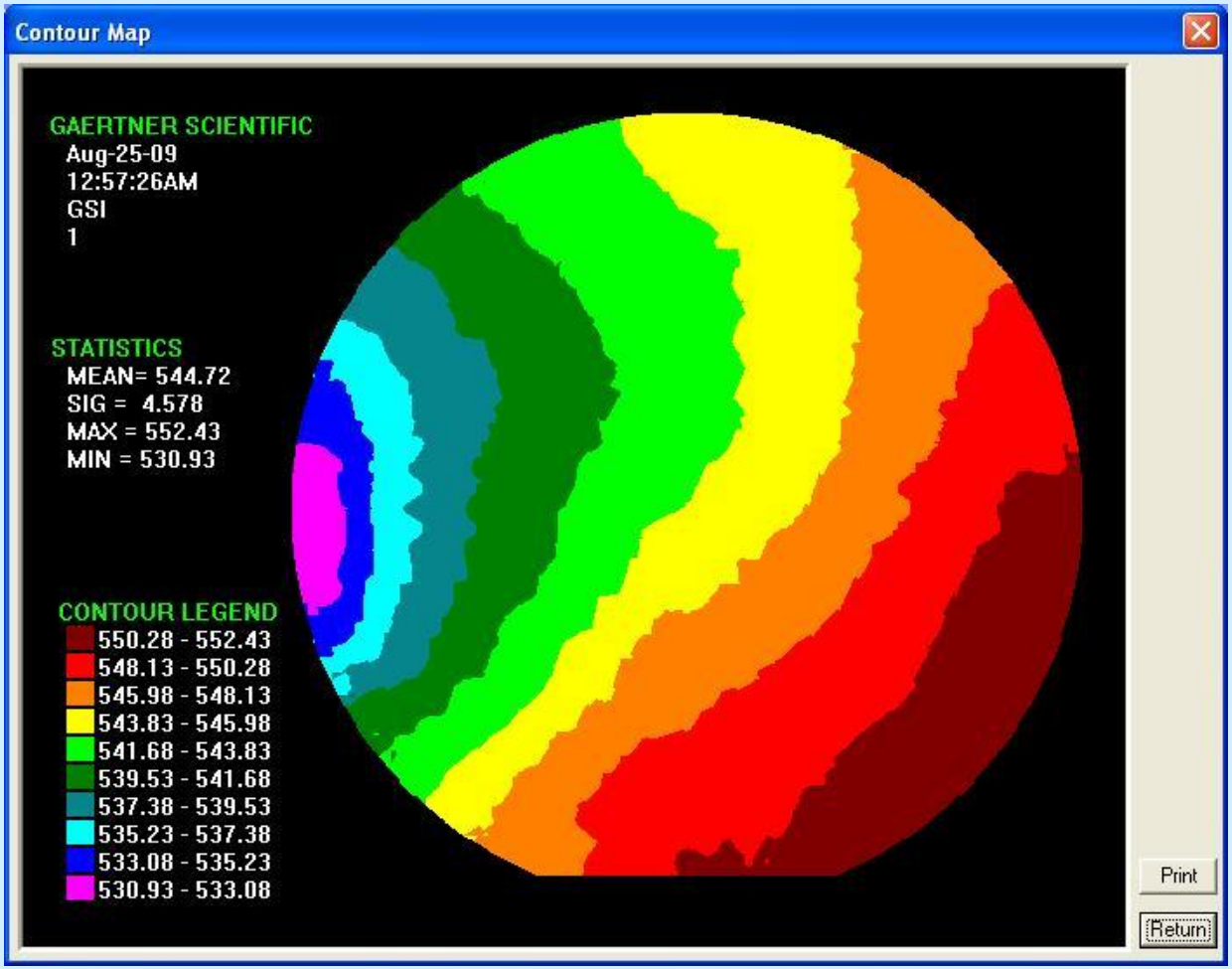
Film characterization for CNS ALD Films

ALD Film	Dep./ Cycle	Ref. Index	Dielectric Constant (ε)
Al_2O_3	1.1 Å	1.65	10.8
HfO_2	0.95 Å	2.05	18.0
SiO_2	15-20 Å	1.46	
TiO_2	0.17-0.5 Å	2.45	
ZnO	1.5-1.8 Å	1.95	
		Sheet resistivity	Bulk resistivity (for comparison)
Pt	0.48 Å	12.15 uΩ·cm	10.60 uΩ·cm

Al_2O_3
Film Characterization and Results

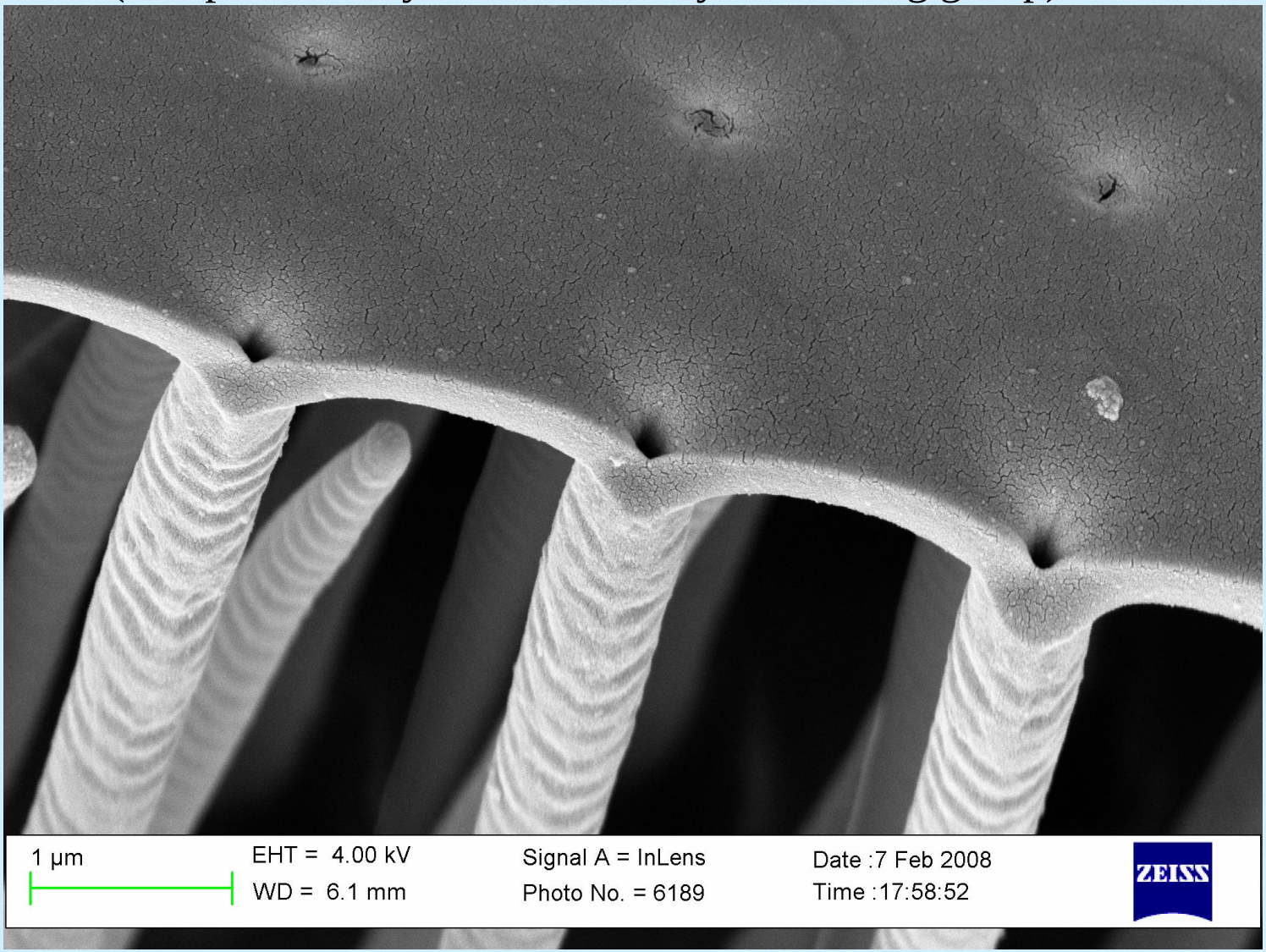
ALD Al_2O_3 – 450 cycles 6" wafer on Gaertner Laser Ellipsometer

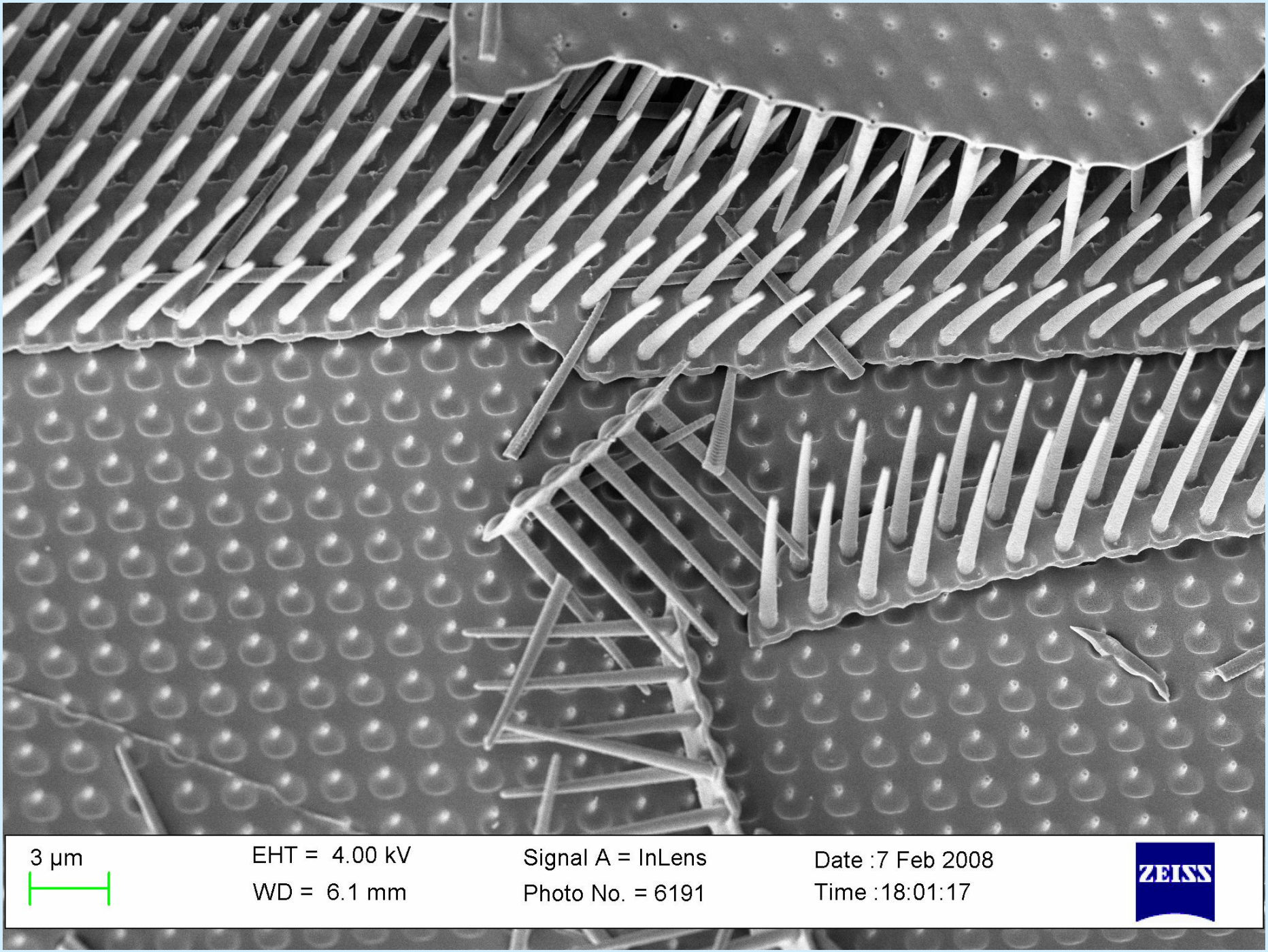
- Thickness Unif. – 0.84 %

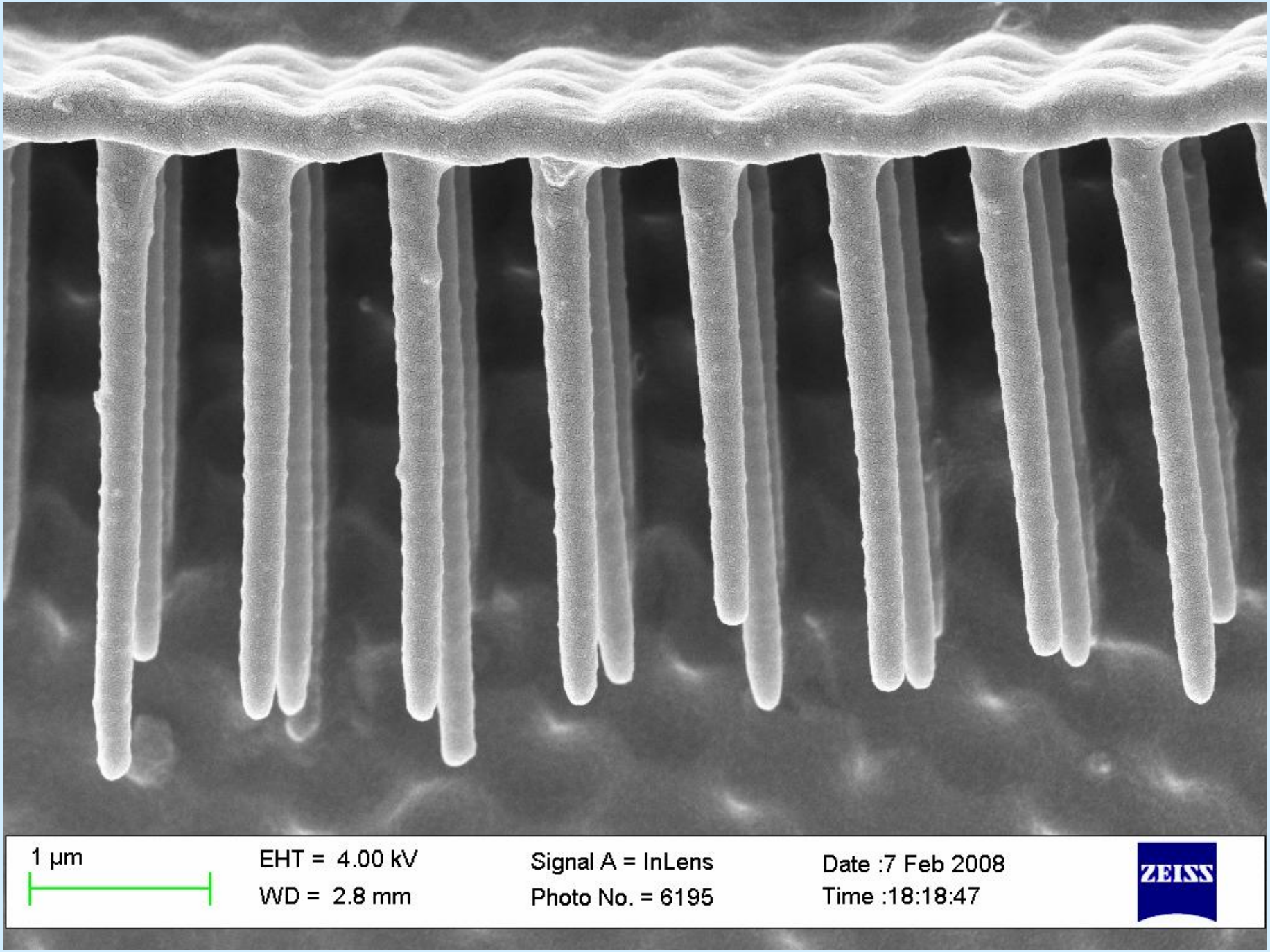


Al_2O_3 fill in PDMS holes imprinted by 10 x 2 um Si pillars, PDMS removed.

(Sample courtesy of Boaz Pokroy, Aizenberg group)




3 µm
EHT = 4.00 kV
WD = 6.1 mm
Signal A = InLens
Photo No. = 6191
Date :7 Feb 2008
Time :18:01:17
ZEISS


1 µm
EHT = 4.00 kV
WD = 2.8 mm
Signal A = InLens
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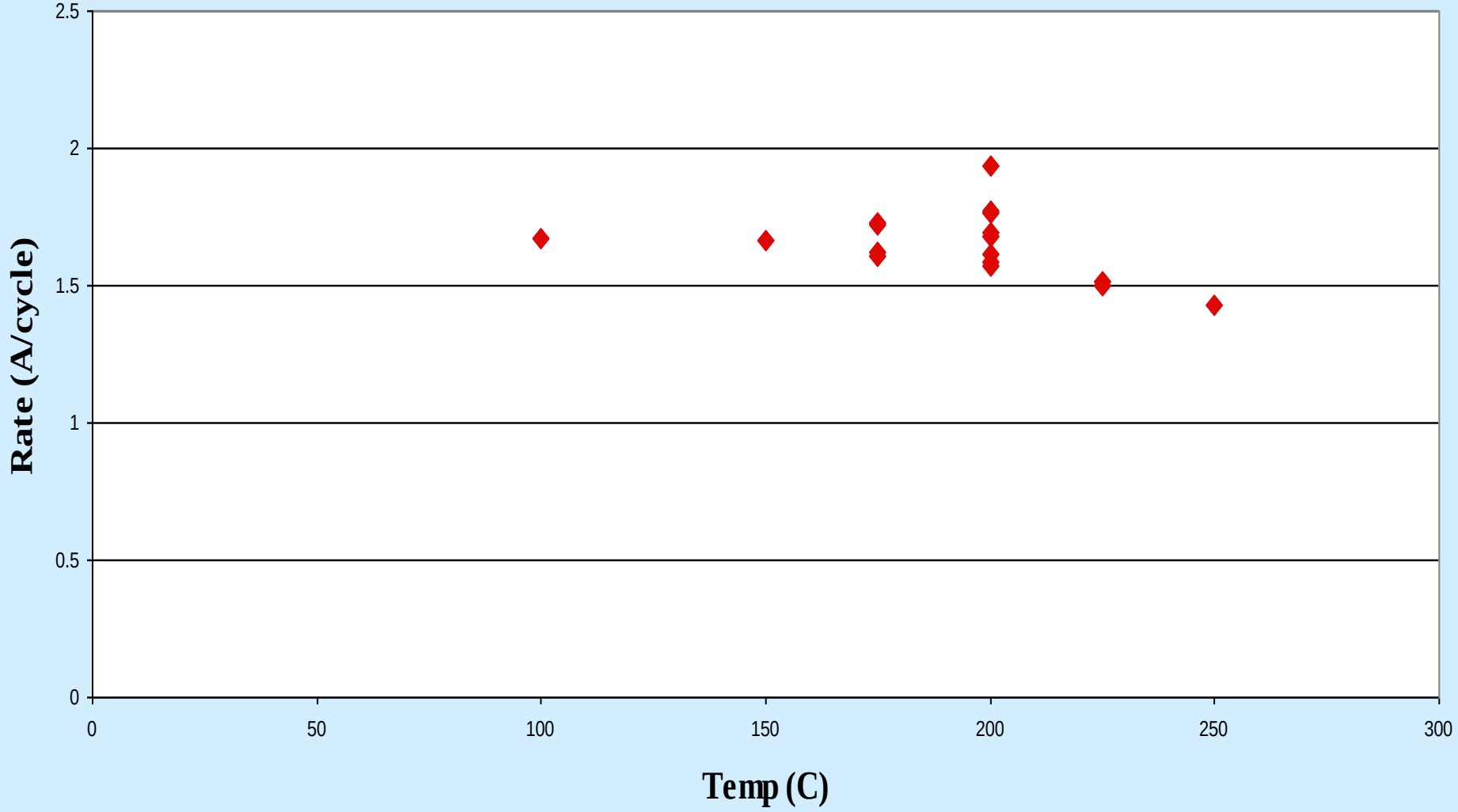
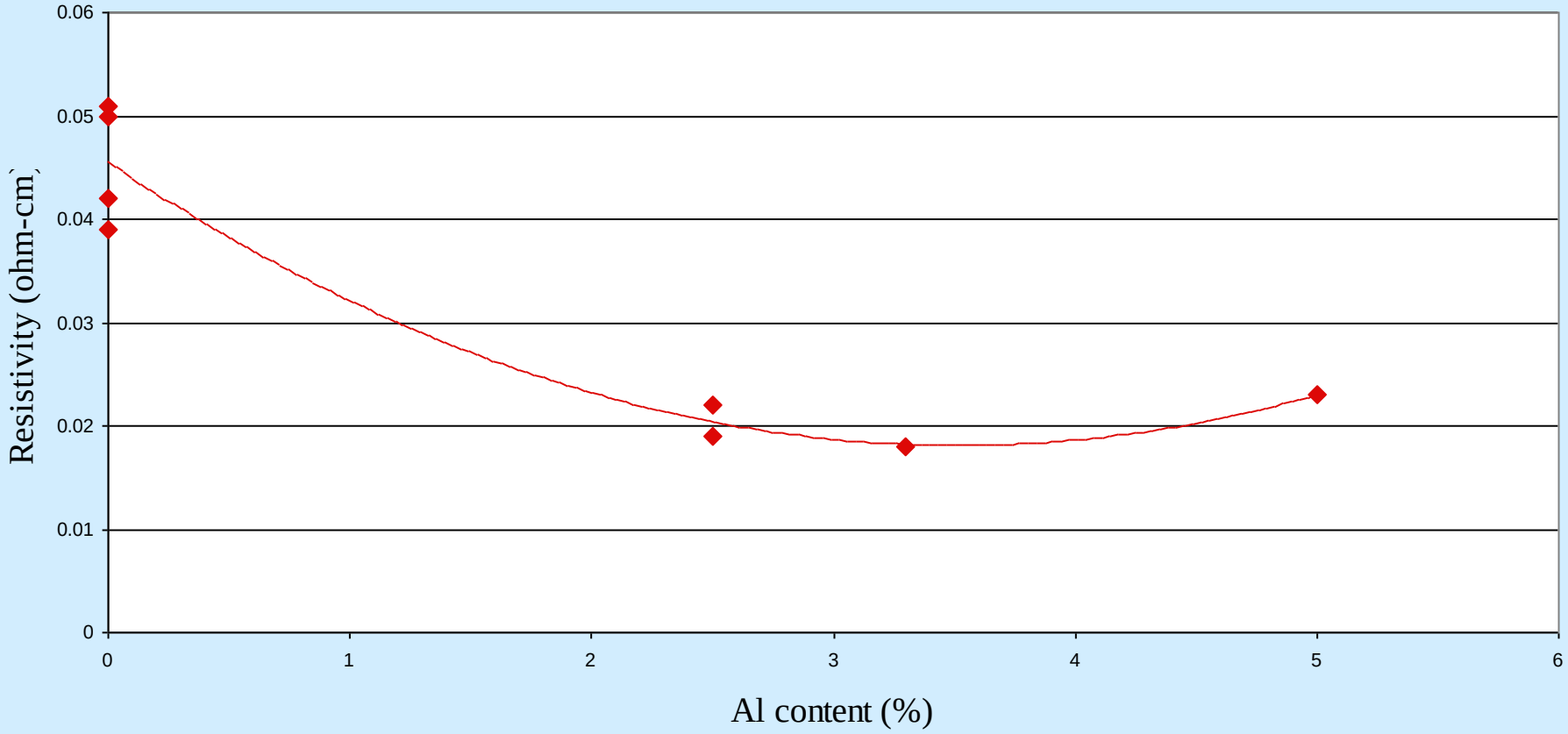
Date :7 Feb 2008
Time :18:18:47
ZEISS

ZnO
Film Characterization and Results

ZnO Rate vs. Temp



AZO Resistivity vs. Al % - 200C

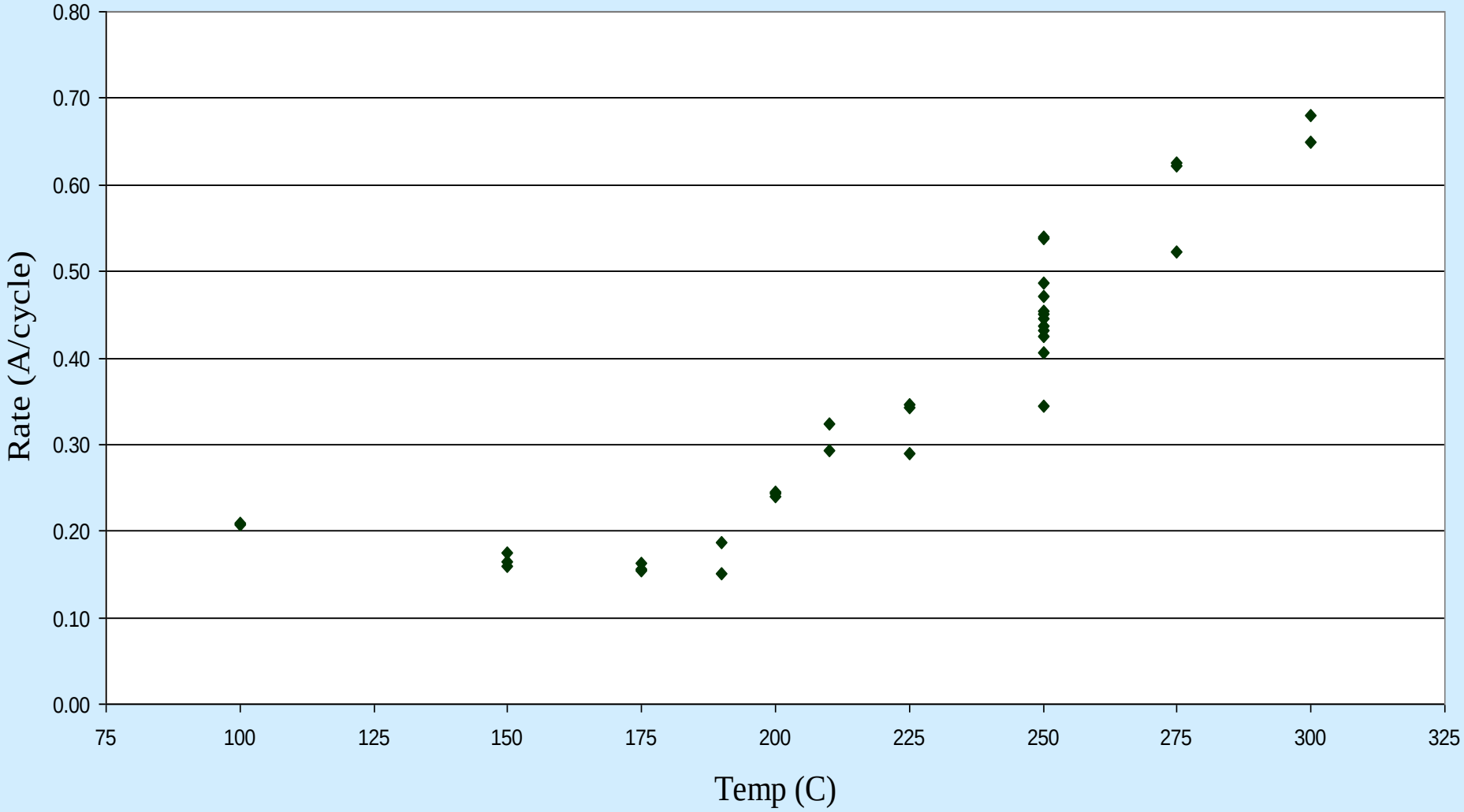


TiO_2
Film Characterization and Results

TiO2 News

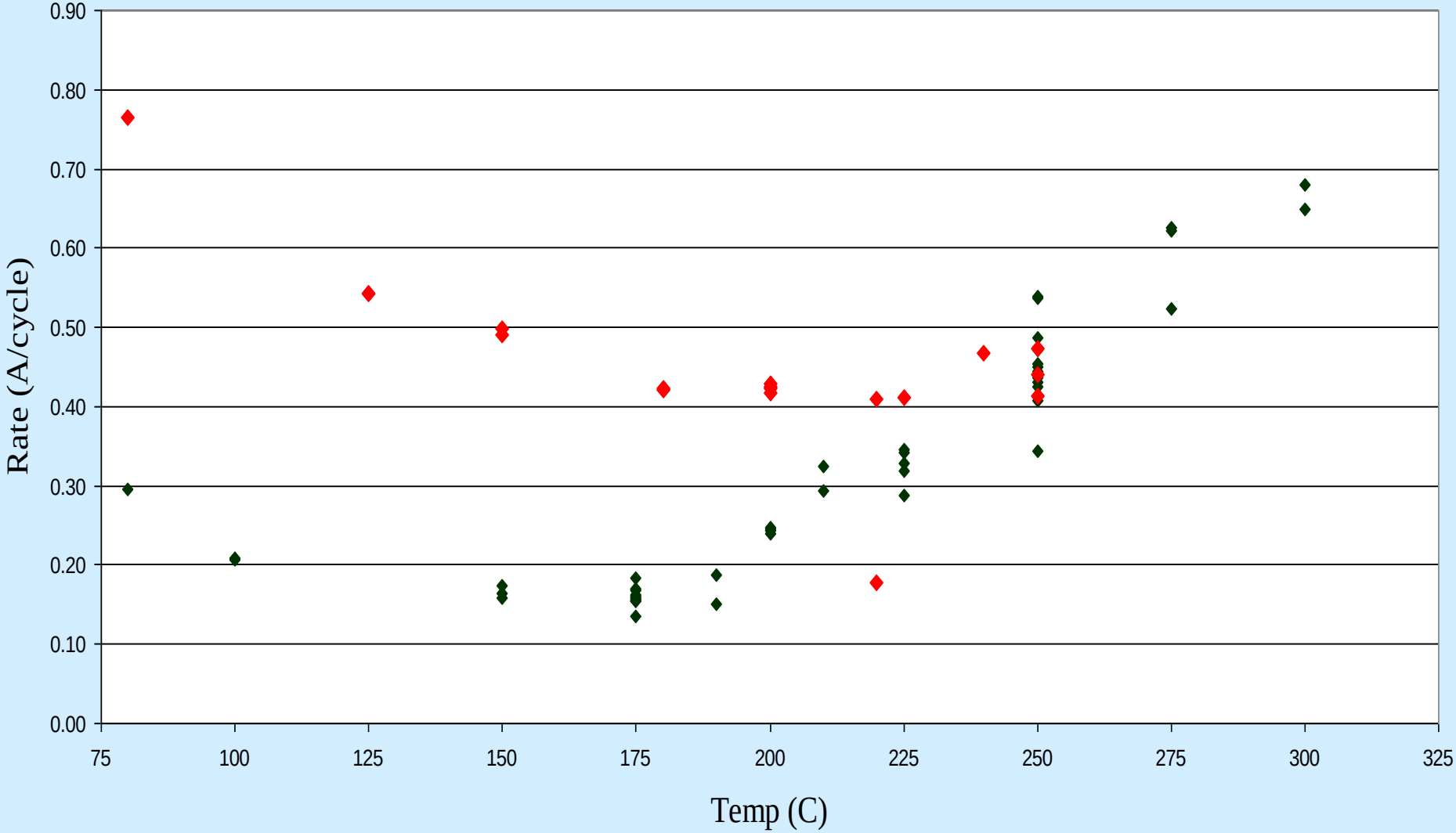
- ALD TiO2 process using water and Ti-isopropoxide and TDMAT precursors has been explored.
- Above ~200C, rougher anatase predominates
- Below ~200C, structure is smoother, amorphous, with some rutile (?) microstructure.
- Below 150C, XRD reveals no crystallinity at all.

ALD TiO2 Growth Rate Vs. Temperature
(using Ti isopropoxide)



ALD TiO2 Growth Rate Vs. Temperature

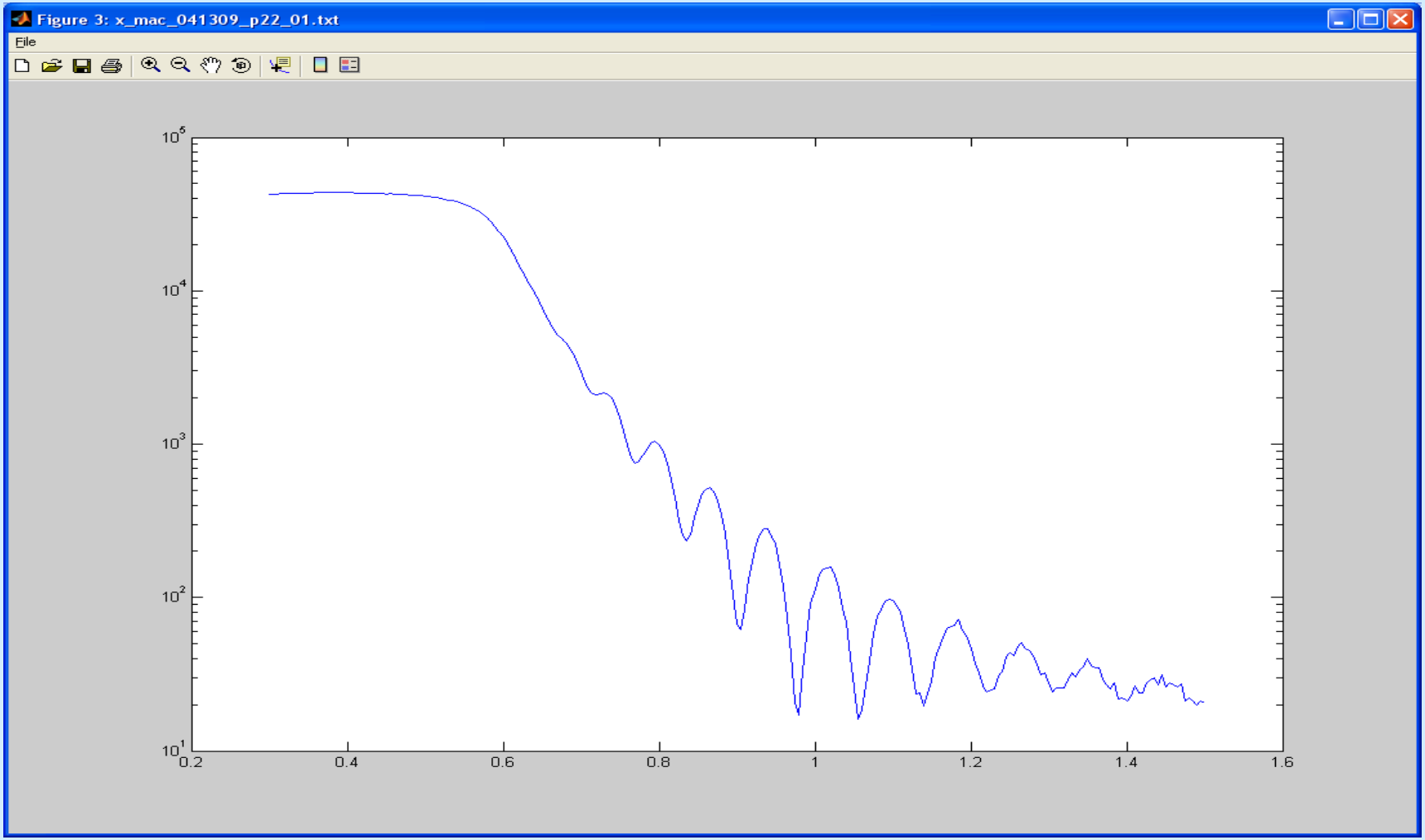
(using TDMAT - red, Ti-isopropoxide - dark green)



Pt characterization

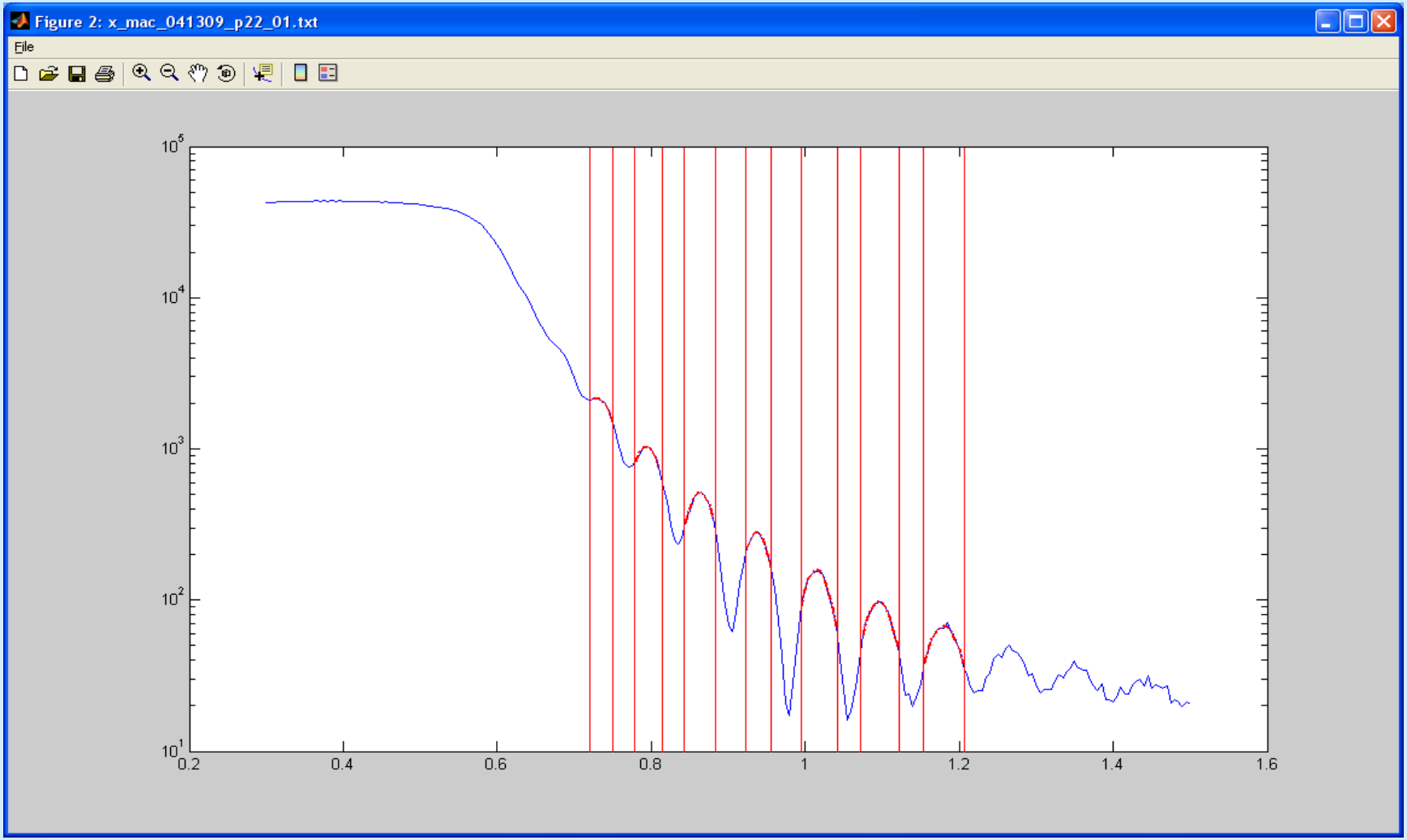
- Too thin for profilometer
- Too tricky on the spectroscopic ellipsometer due to semi-transparent nature
- AFM problematic due to difficulty in creating sharp edges without complicated patterning
- SEM – insufficient resolution
- TEM – sample prep problematic
- **XRR – X-Ray Reflectometry**
  - Using Interference of X-ray beam, highly precise and repeatable measurement of thin films, (metals in particular) are possible.
- **Resistivity Mapper (RESmap)** – 4-pt probe for measuring sheet resistance

XRR trace of Pt film from Cintag XRD

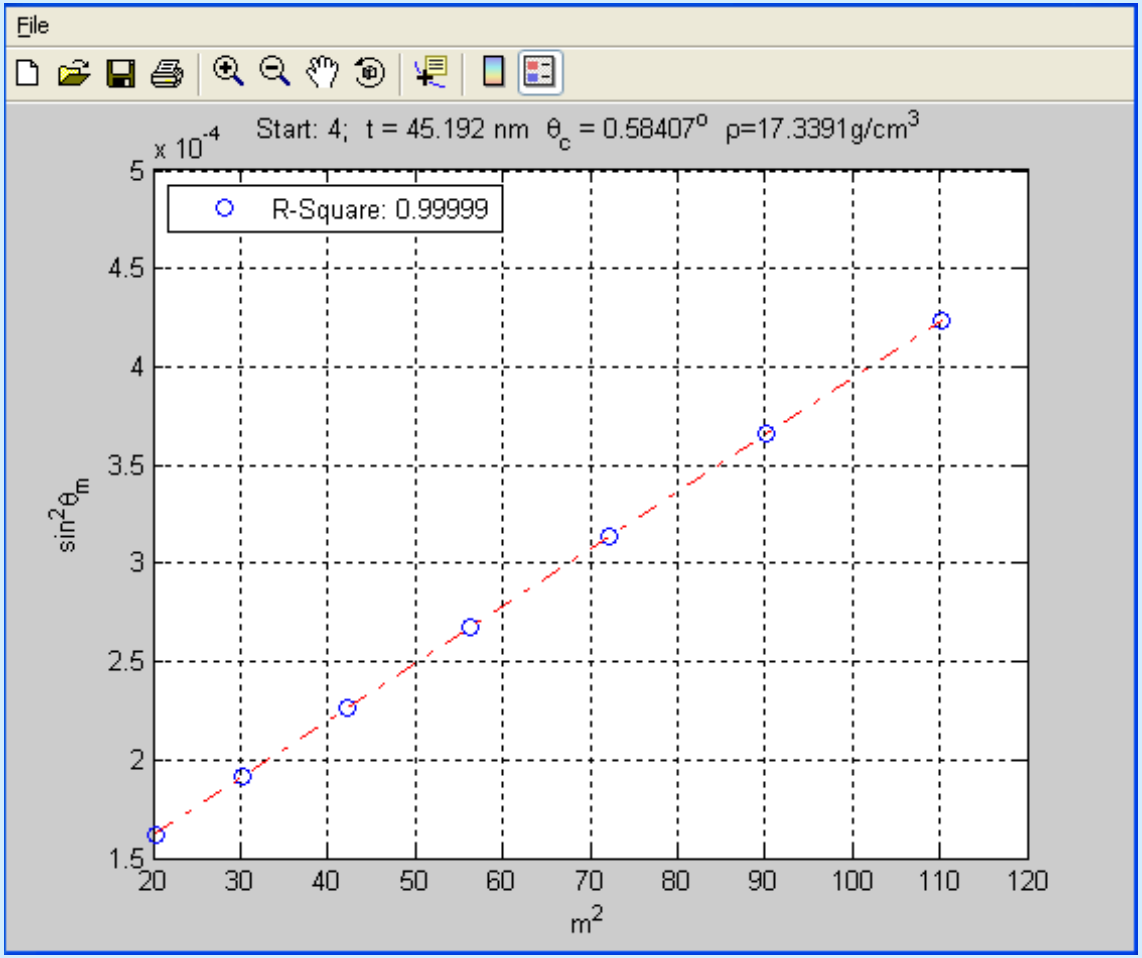


XRD expertise courtesy of Dr. Bill Croft, Harvard University
XRR analytical software courtesy of Hongtao Wang – Gordon Group – Harvard University

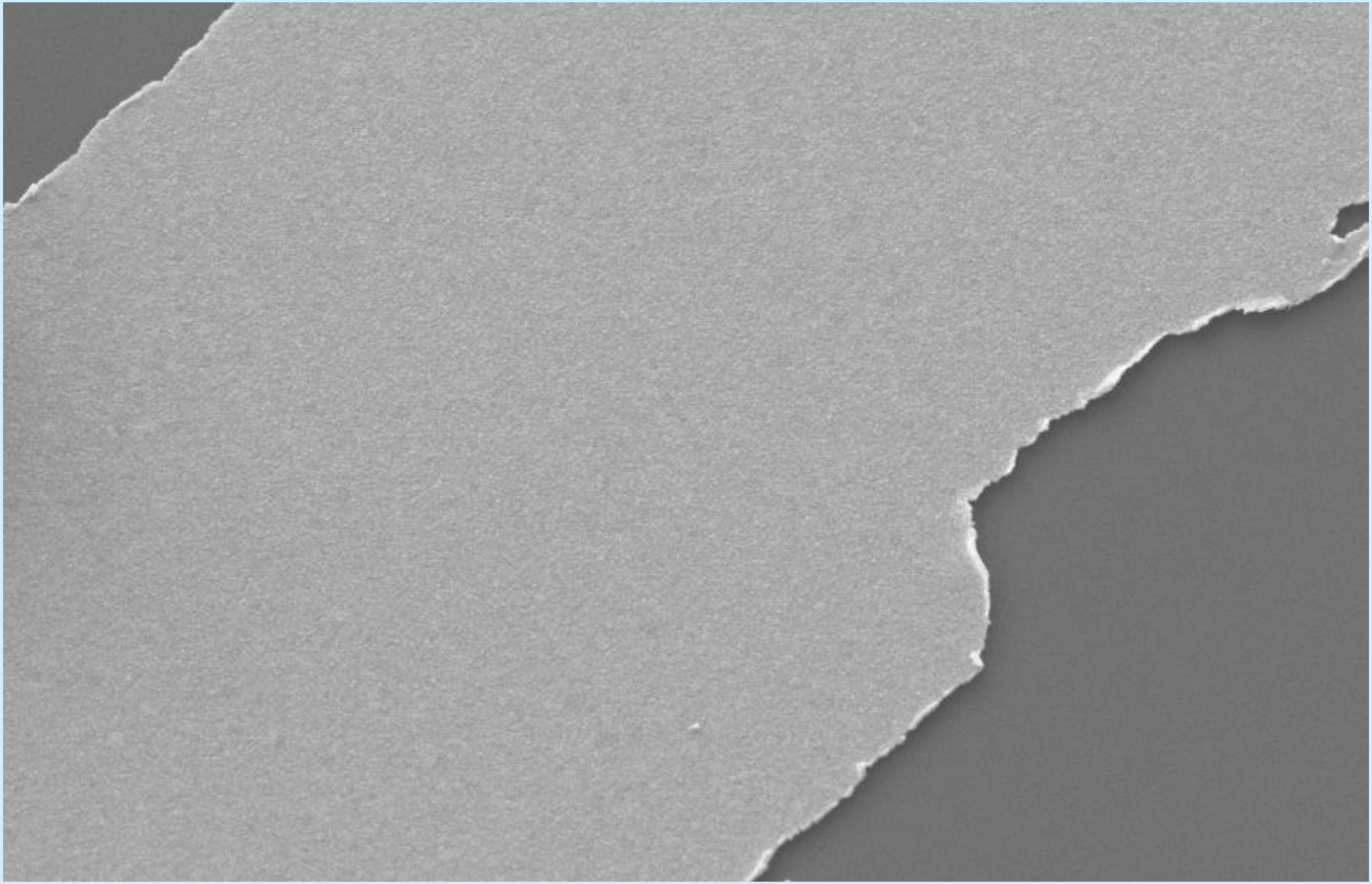
XRR trace – peaks selected



XRR Data – Thickness calculation

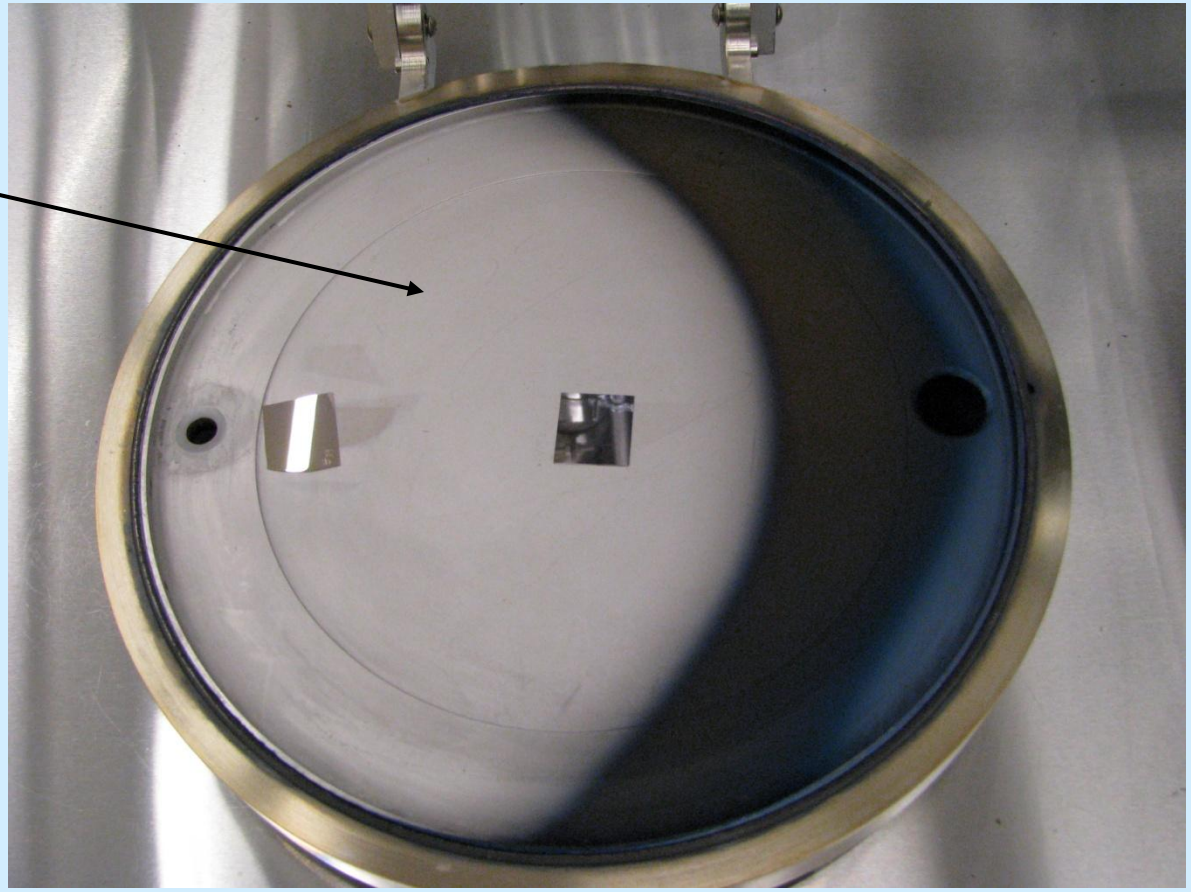


Platinum on Silicon (scratched to create step)

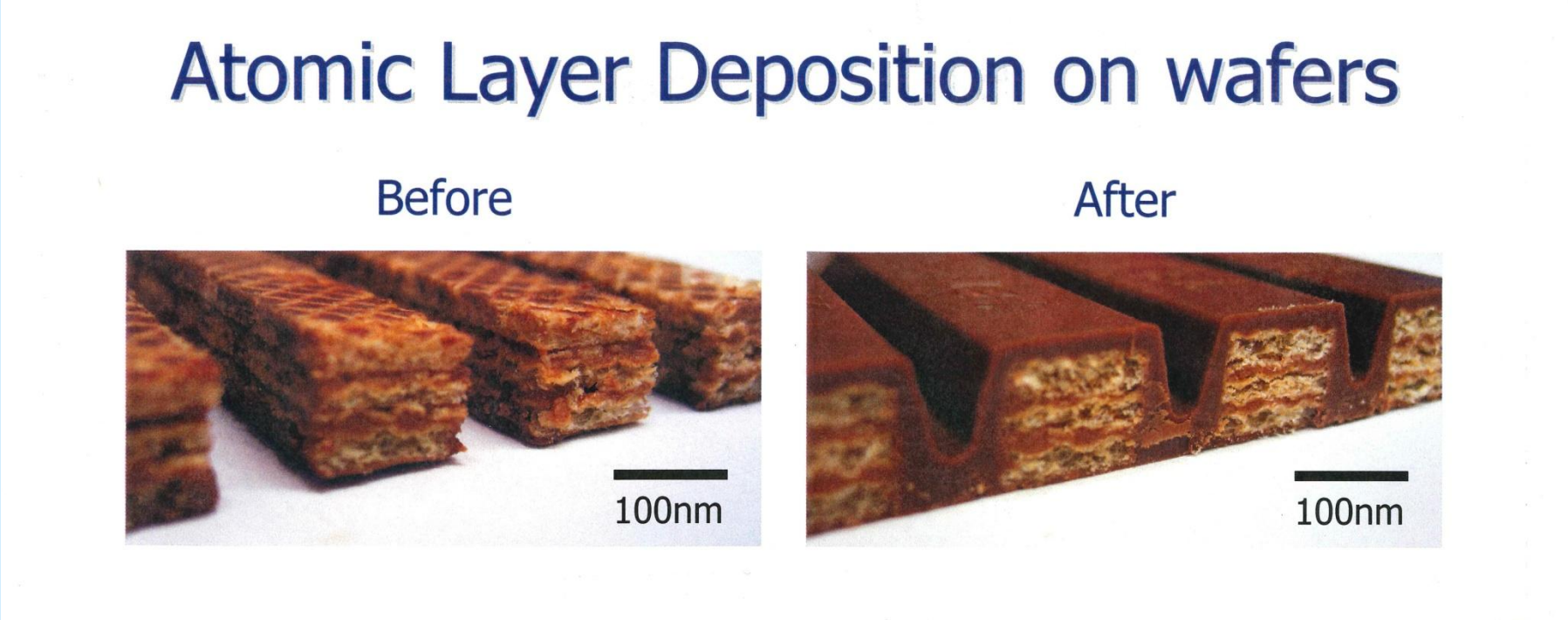


- "Too short" pulses can lead to insufficient area coverage.

Pt deposition within coverage zone is full thickness, due to self-limiting nature of reaction, (not subject to variations in vapor pressure)



Can be used to create a "virtual" reaction chamber of smaller size, conserving expensive precursor



- Major issue:

  Consumption of precursors and substrate before, during and after processing

Process Challenges

ZnO - Need to characterize doping/conductivity behavior before/after anneal

Pt - Need to reduce precursor consumption, stabilize precursor, check purity using O3 precursor

TiO_2 - Need to characterize anatase catalytic behavior, see if processing conditions have any effect.

Explore Nitrogen doping and effects on conductivity, photo-catalysis, wave-guiding

HfO_2 - Determine causes of leakage current variations

Silanol and TDMAH precursor “instability” over time

Substrate issues using ALD?

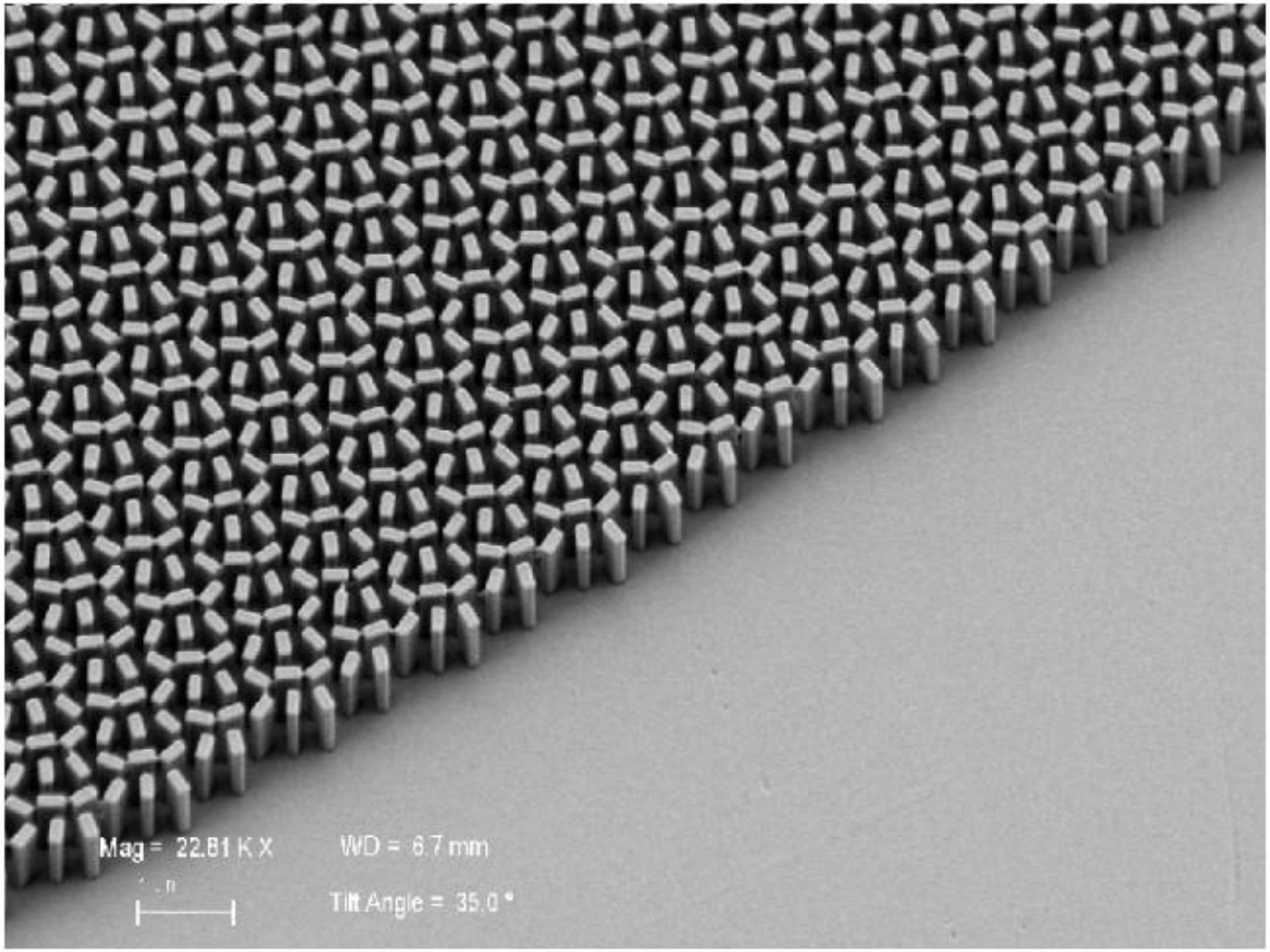
- CNTs/graphene and 2D materials are problematic.
  - Nucleation achieved using surface functionalization with:

    NO_2 , carboxylated perylene, DNA, IPA?
- Pt deposition on/<u>near</u> polymeric materials not possible, ozone may help
- **Nucleation of all oxides not immediate. Need earlier film "closure"**
- No current material restrictions on CNS system

CNS ALD in Action!

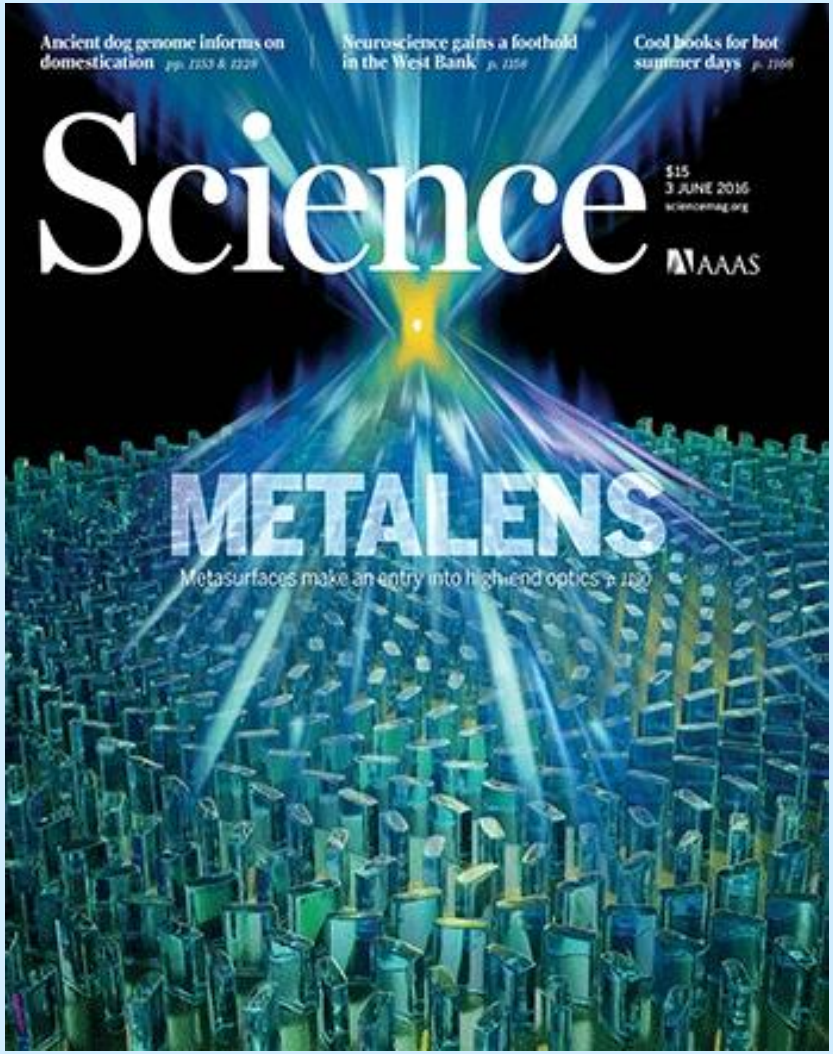
- TiO2 “Meta-lenses”
- Very thick deposition (400-600nm)
- 90C, to protect resist substrate, film completely amorphous
- Process “modified by user”

CNS ALD in Action!



Scanning electron microscope micrograph of the fabricated meta-lens. The lens consists of titanium dioxide nanofins on a glass substrate. Scale bar: 2 mm (Image courtesy of the Capasso Lab)

CNS ALD in Action!



CNS ALD in Action!

- Alumina-coated Diamond Anvil
- Used to create Metallic Hydrogen!
- PI forgot to credit us. Very Sad…

CNS ALD in Action!

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- Used to create Metallic Hydrogen!
- PI forgot to credit us. Very Sad…
- Still, ALD (sort of) got in the NYTimes!…

CNS ALD in Action!

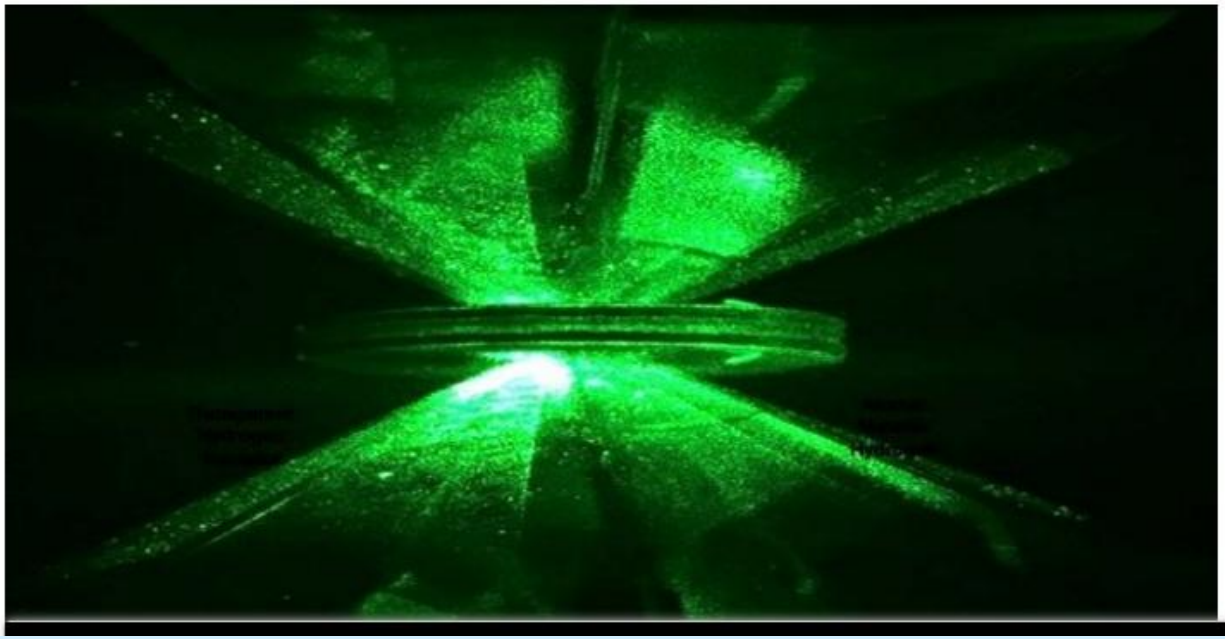
Secure | https://www.nytimes.com/2017/01/26/science/solid-metallic-hydrogen-harvard-physicists.html

pps Imported From Firefo Sheet Music For Pianc Google News Weather Interactive R Journals | Harvard Lib WEB MAIL Google

SCIENCE | Hydrogen Squeezed Into a Metal, Possibly Solid, Harvard Physicists Say

Hydrogen Squeezed Into a Metal, Possibly Solid, Harvard Physicists Say

By KENNETH CHANG JAN. 26, 2017



RELATED COVERAGE

The Big Squeeze DEC. 16, 2013

Research Review

- Tried to reproduce results using IPA as precursor. (Should wet graphene better) Didn’t work. Similar to Finnish group. Conclusion – Original paper flawed, had water in IPA

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- Considering other counter precursors to improve 2D nucleation.

Research Review

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- Considering other counter precursors to improve 2D nucleation.
- Used LEIS to characterize early nucleation.

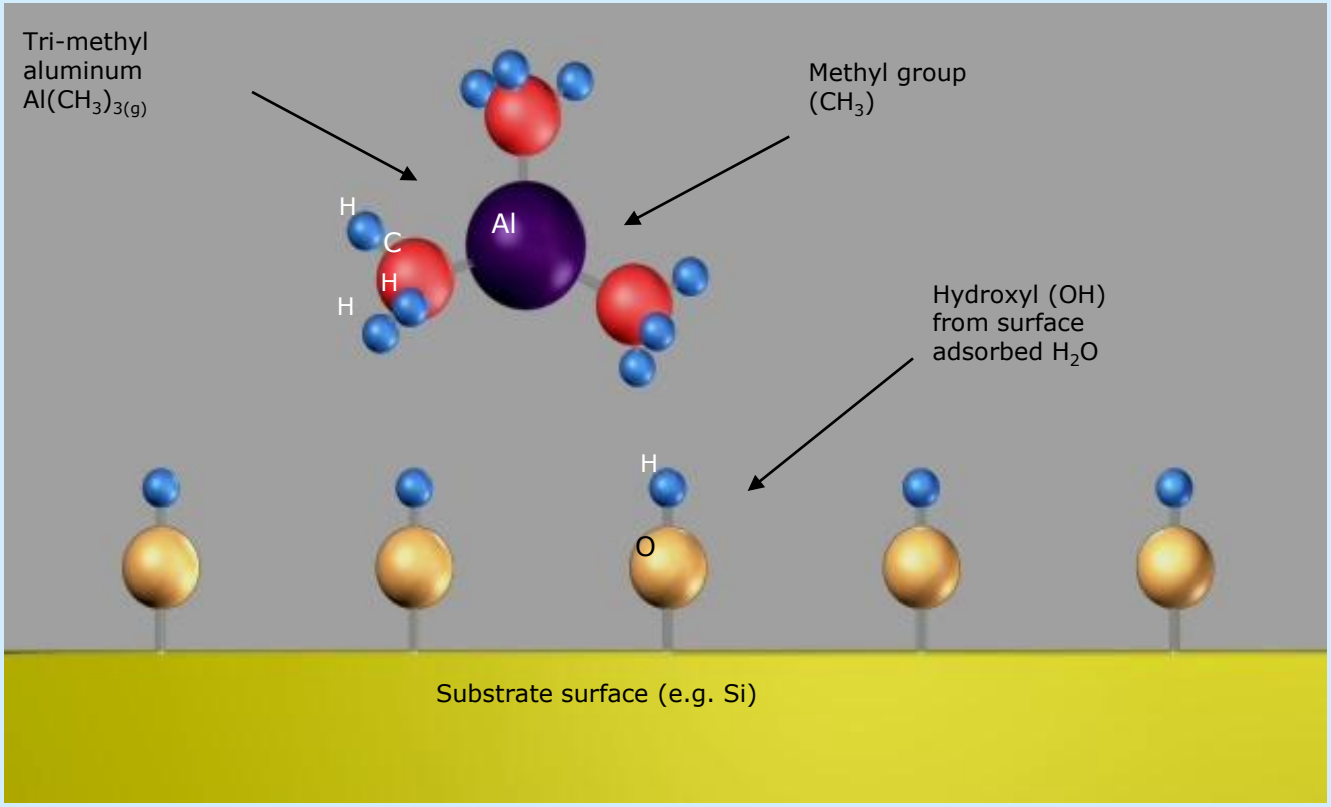
Investigation of Few-Layer ALD Films by Low Energy Ion Scattering (LEIS) Spectroscopy

Mac Hathaway; Harvard University Center for Nanoscale Systems***X***
Thomas Grehl; ***X*** Philipp Bruener; Hidde Brongersma;
ION-TOF GmbH, Germany
Michael Fartmann; Tascon GmbH, Germany

AVS 62 - San Jose, CA - Oct 23, 2015

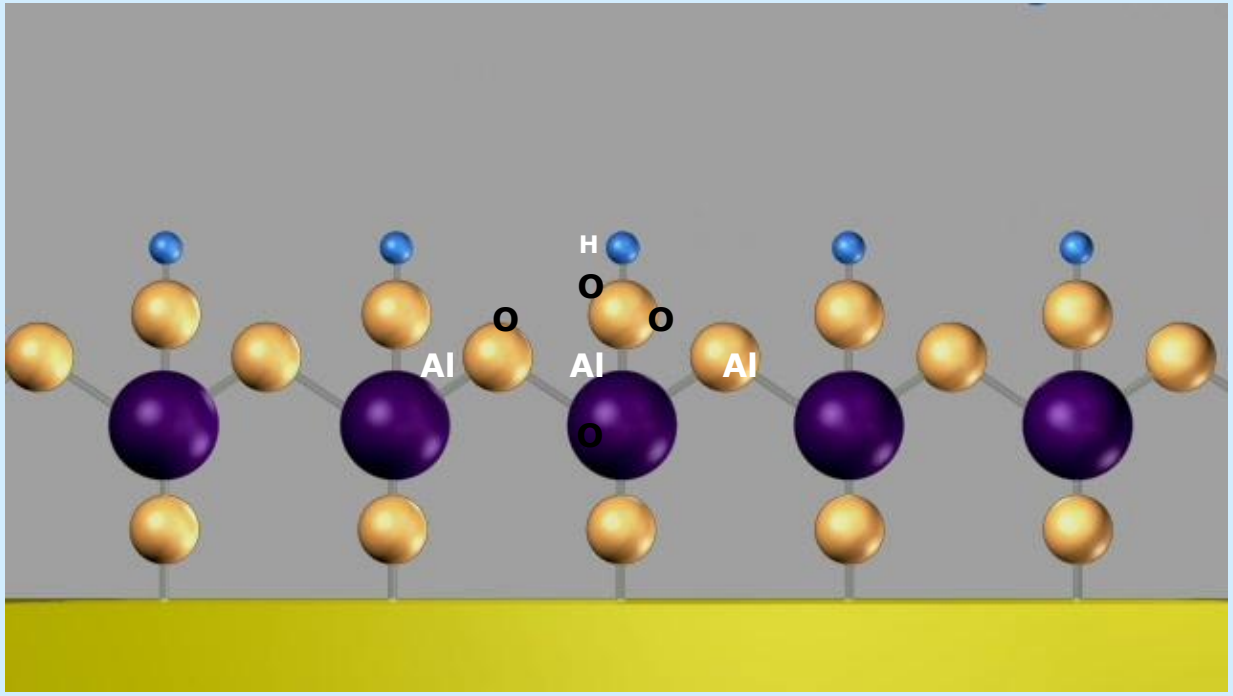
Center for Nanoscale Systems
Harvard University

ALD Cycle for Al_2O_3 Deposition



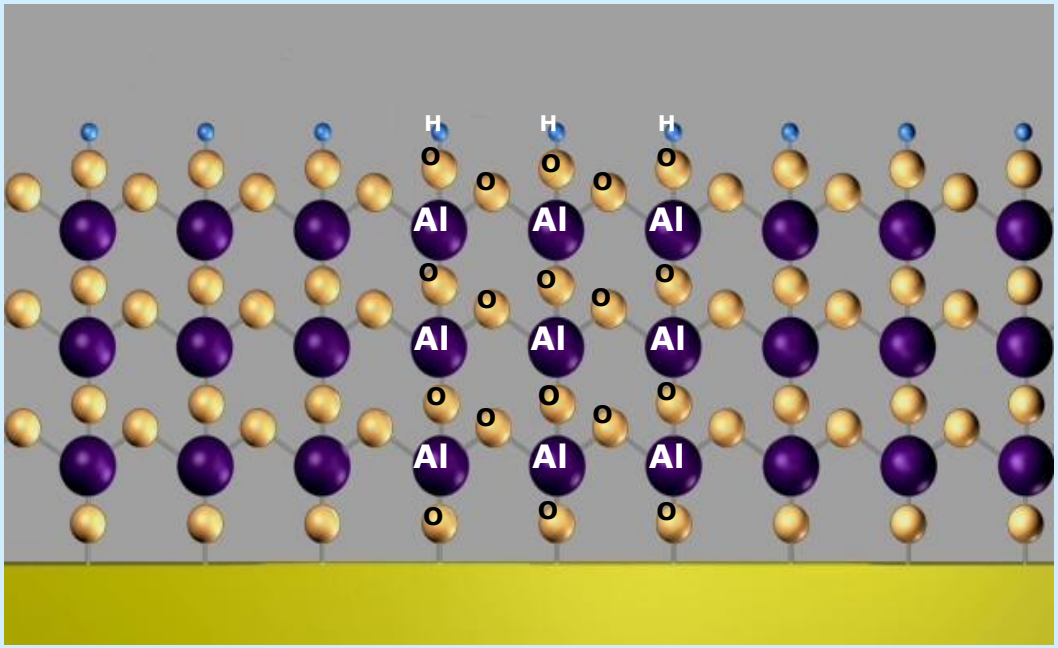
Trimethyl Aluminum (TMA) reacts with the adsorbed hydroxyl groups, producing methane as the reaction product.

ALD Cycle for Al_2O_3 Deposition



Reaction product methane is purged. Excess H_2O vapor does not react with the hydroxyl surface groups, reaction self-limits to one oxide layer.

ALD Cycle for Al_2O_3 Deposition



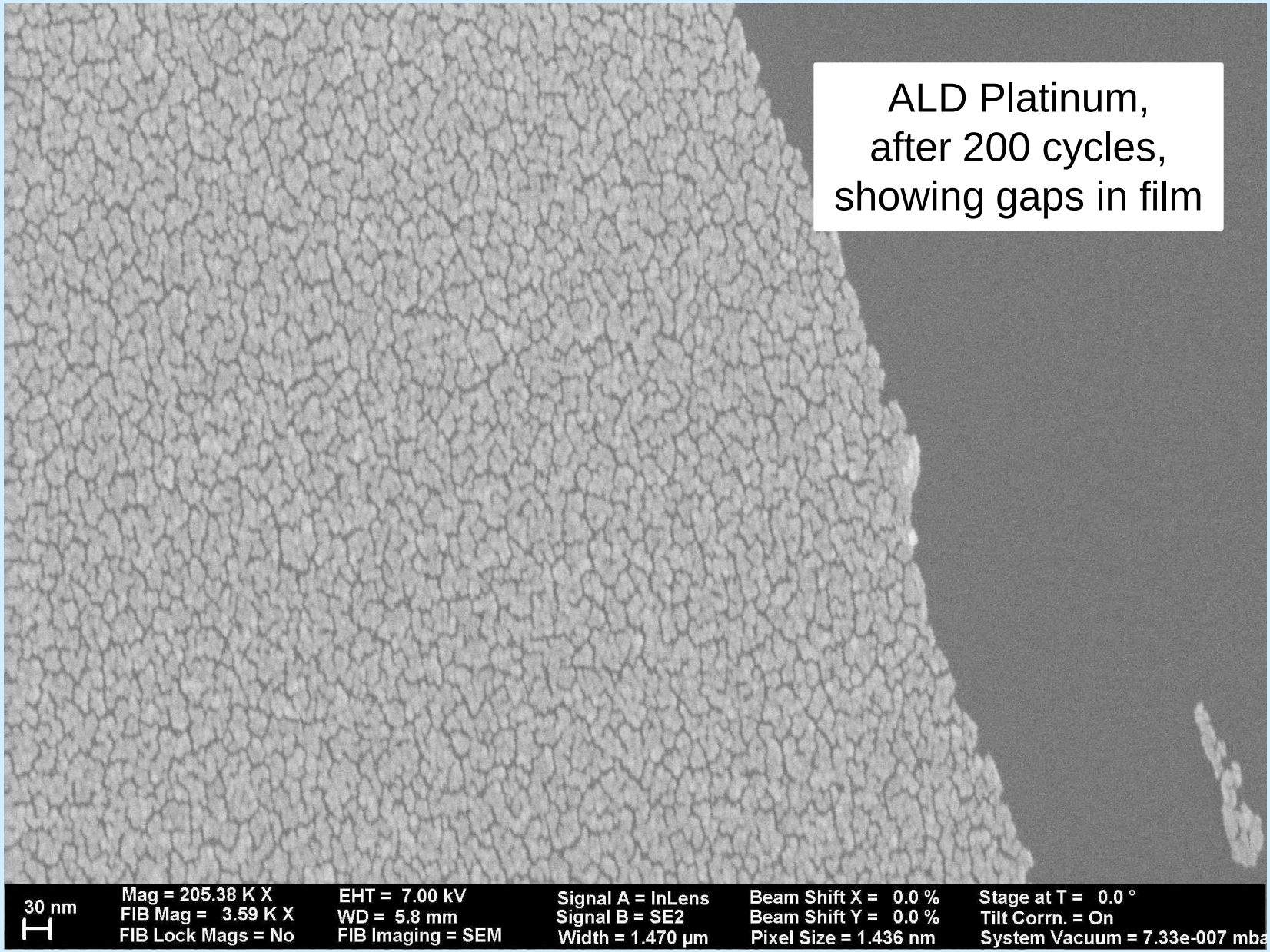
One TMA and one H_2O vapor pulse form one cycle.

~10-14 sec.

Film Closure?

- Film Closure - Growing film is completely filled, no gaps or pinholes
- Ideally, film closure occurs very early, 1st few layers
- Not always…

Film Closure?



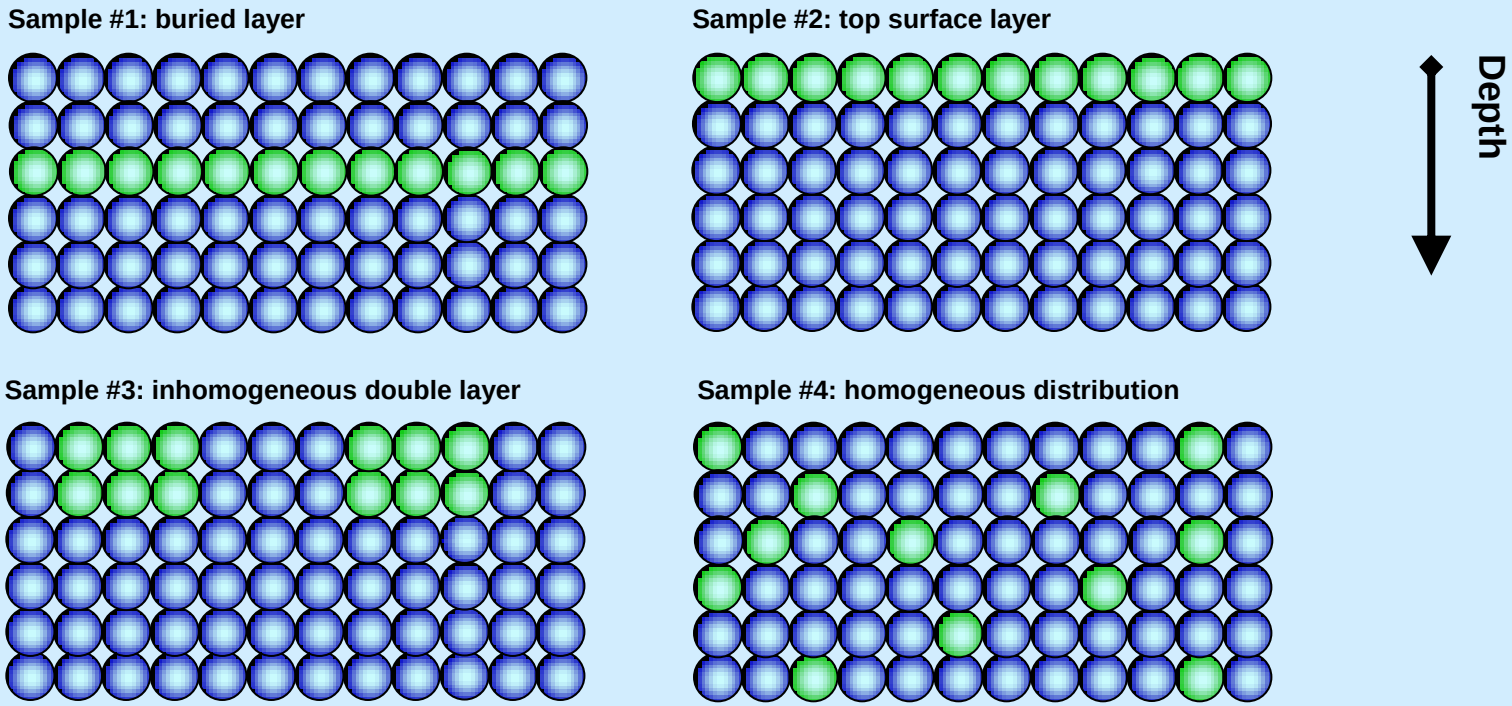
Characterization of "Few Monolayer" films

- To characterize ALD film "closure", you need to see just the top layer of atoms, or discern a clear difference between the top layer and the one immediately below – Difficult
- For best results, you need to see just an angstrom or two deep.
- Most techniques show information from too deep in the film

LEIS
Low Energy Ion Scattering Spectroscopy

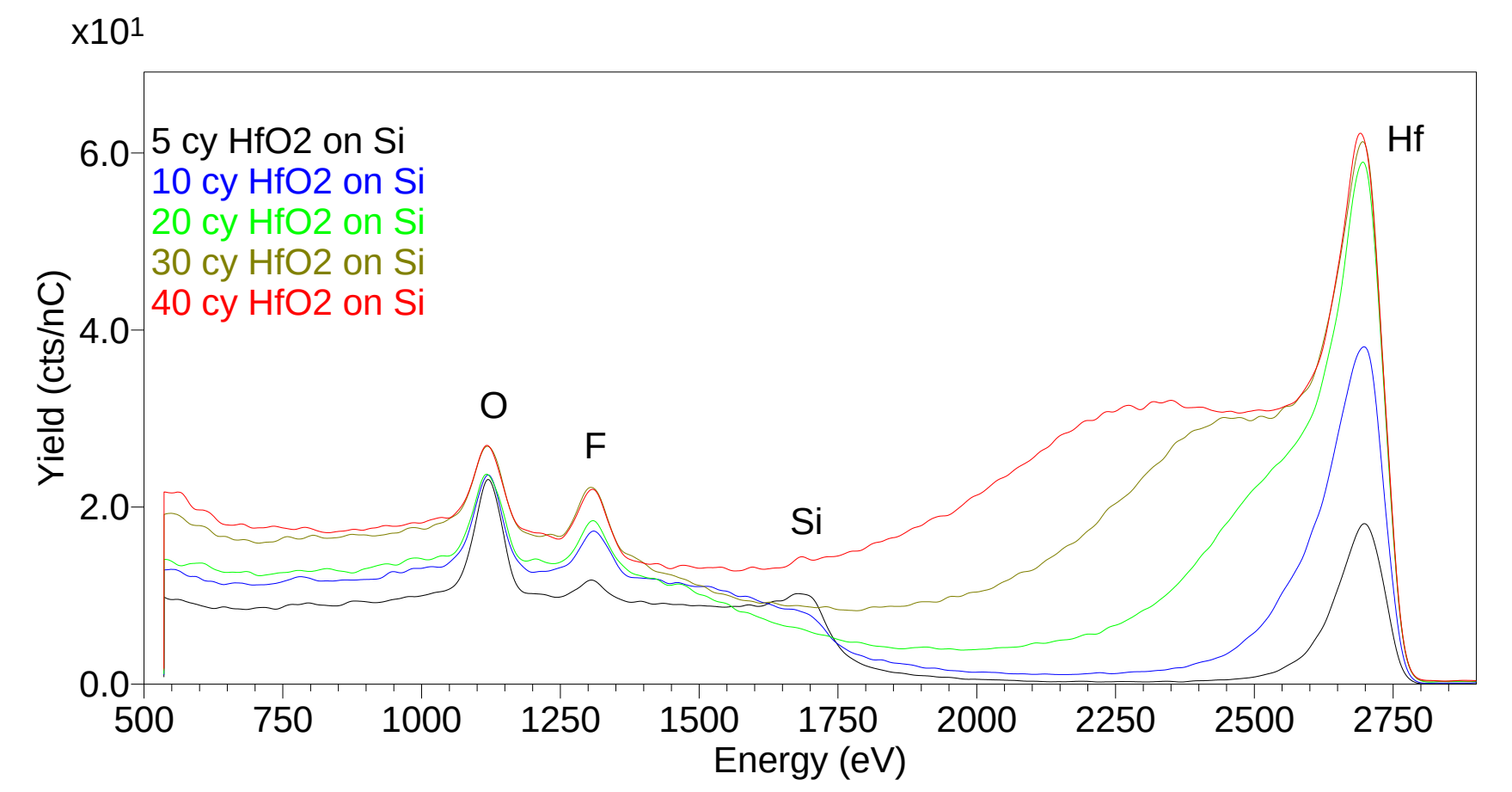
- Low Energy – Shallow penetration
  - Information is coming from the **first few atom layers**
  - Deeper scattered ions tend to be neutralized
- Atomic information from rebounding ions (He, Ne, etc)
- Energy signature of ions from “line-of-sight” outer surface atoms, distinctly different from that of ions back-scattering from deeper in sample.
- High Sensitivity
- Usually no matrix effects

Challenging Surfaces where LEIS shines

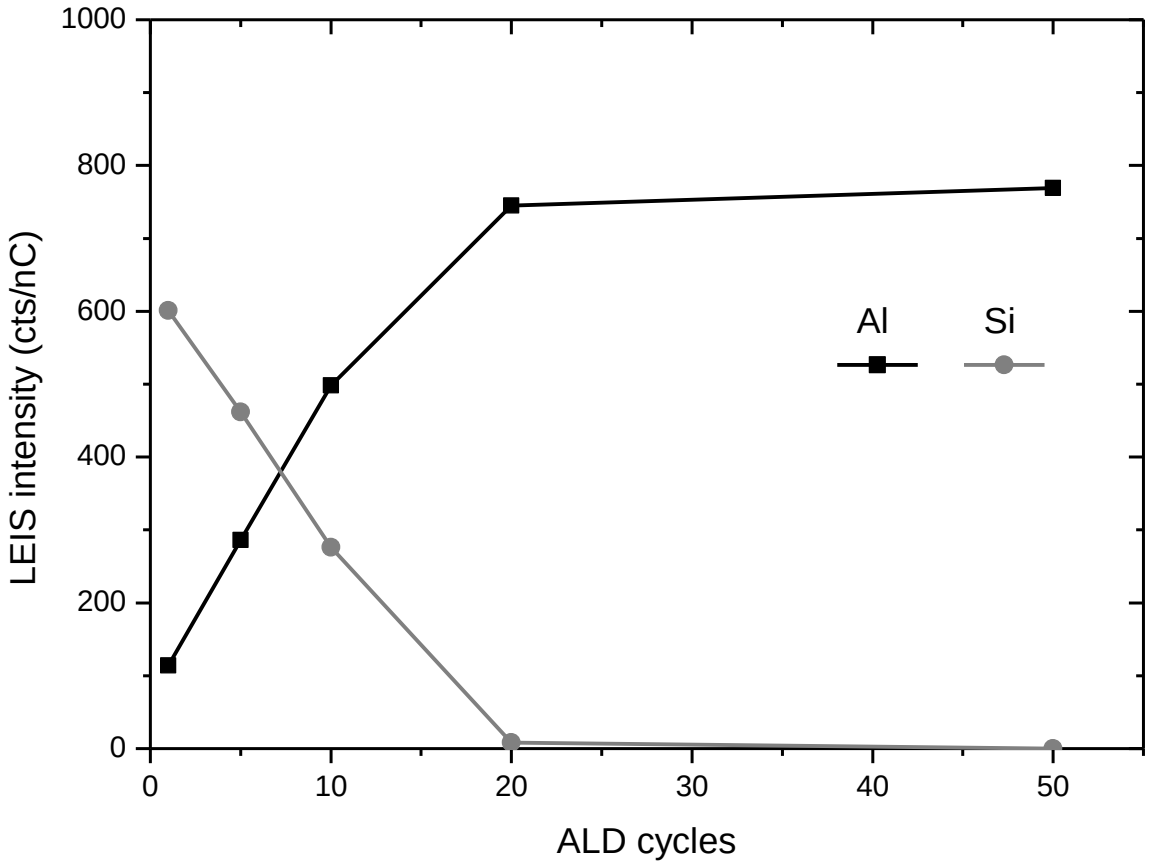


- Four samples with “identical” surface coverage (integrated over a few nm depth)
- XPS: All these will look the same
- LEIS: Clear differences, easily resolved, between different samples

LEIS – Backscattered Ion Energy Spectrum –HfO_2 Film Si

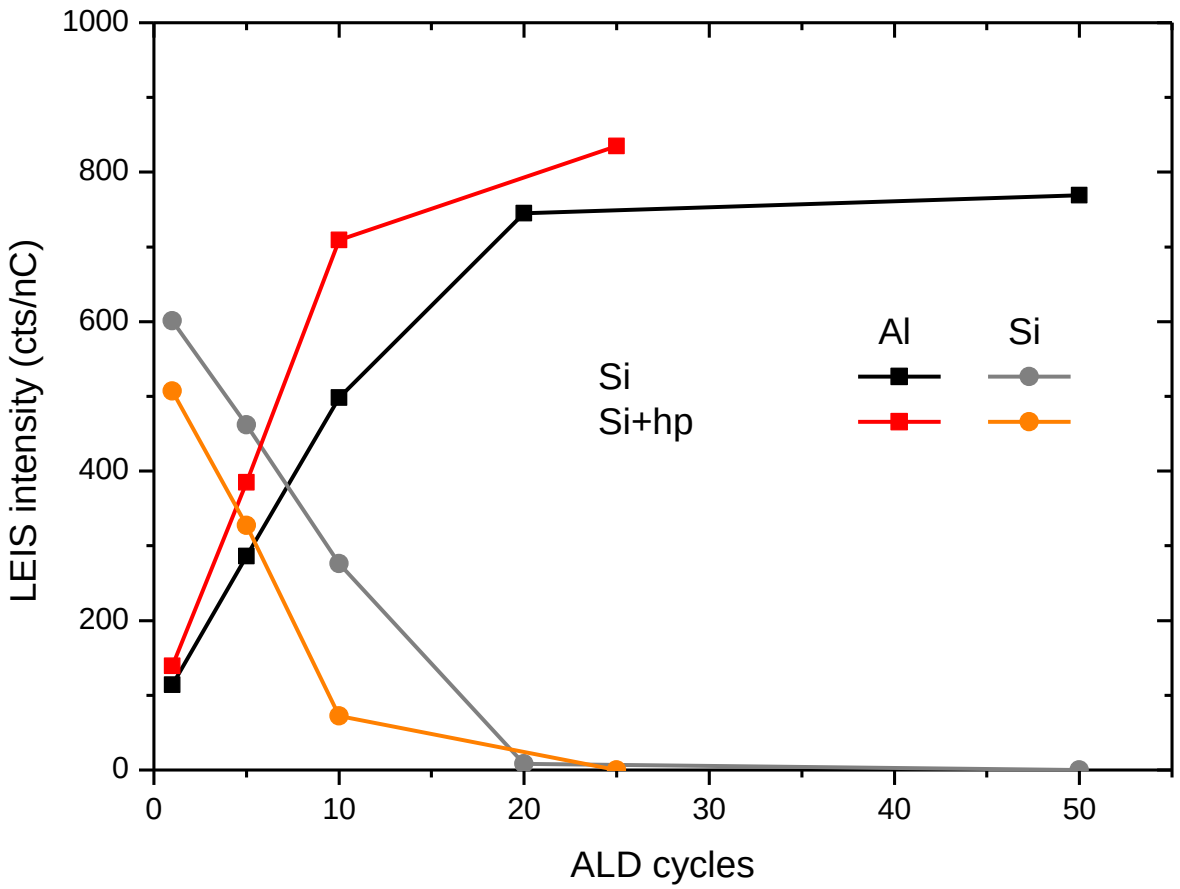


LEIS – Al_2O_3 Film Closure on Si



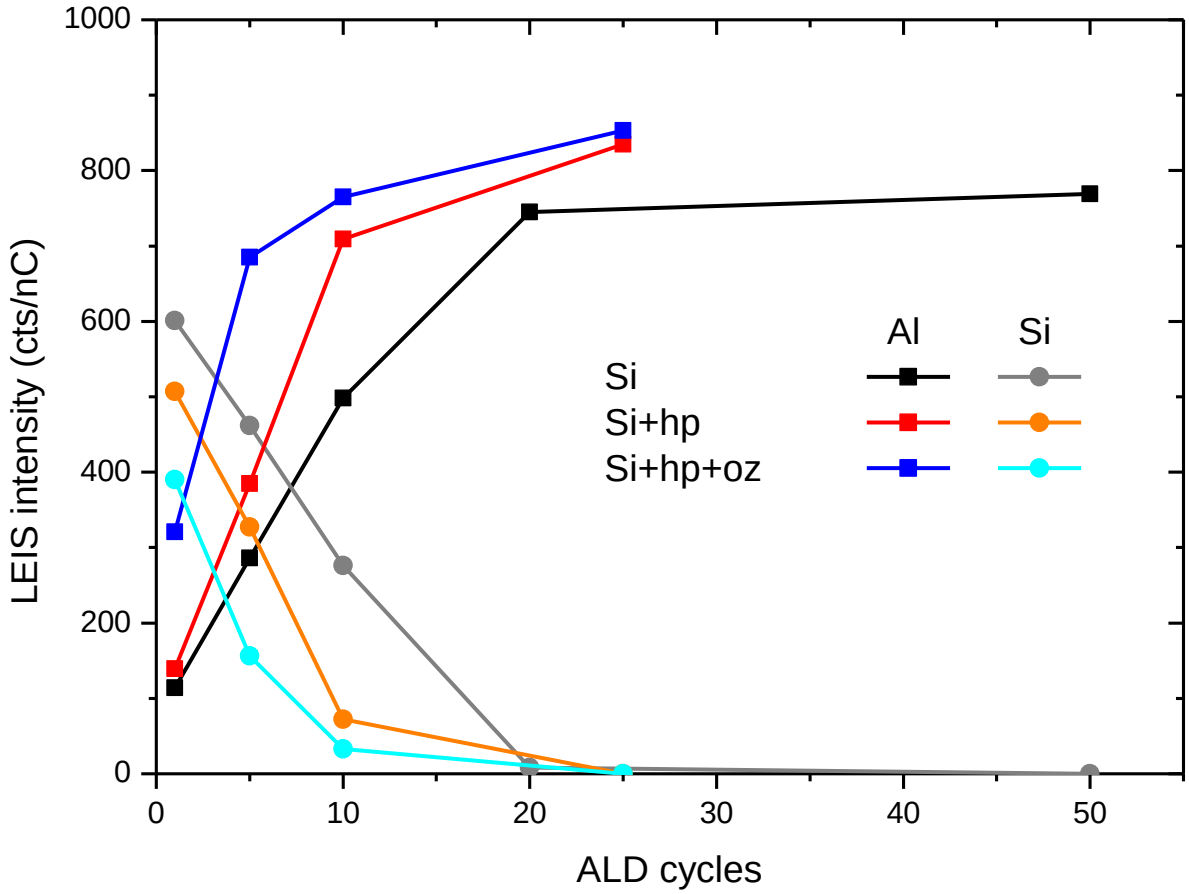
- Al_2O_3 doesn't close immediately. Takes 10-20 cycles

LEIS – Al_2O_3 Film Closure on Si



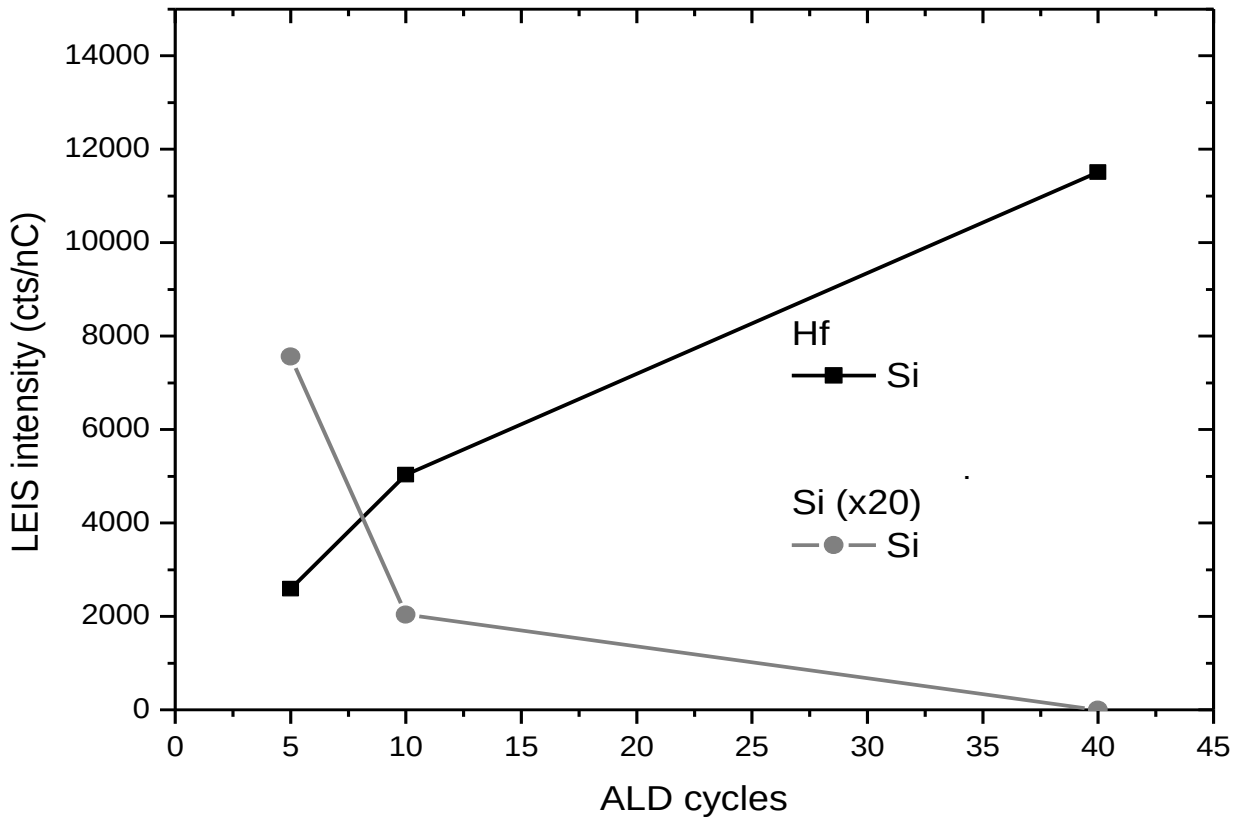
- Al_2O_3 closing up sooner. Still not immediate.

LEIS – Al_2O_3 Film Closure on Si



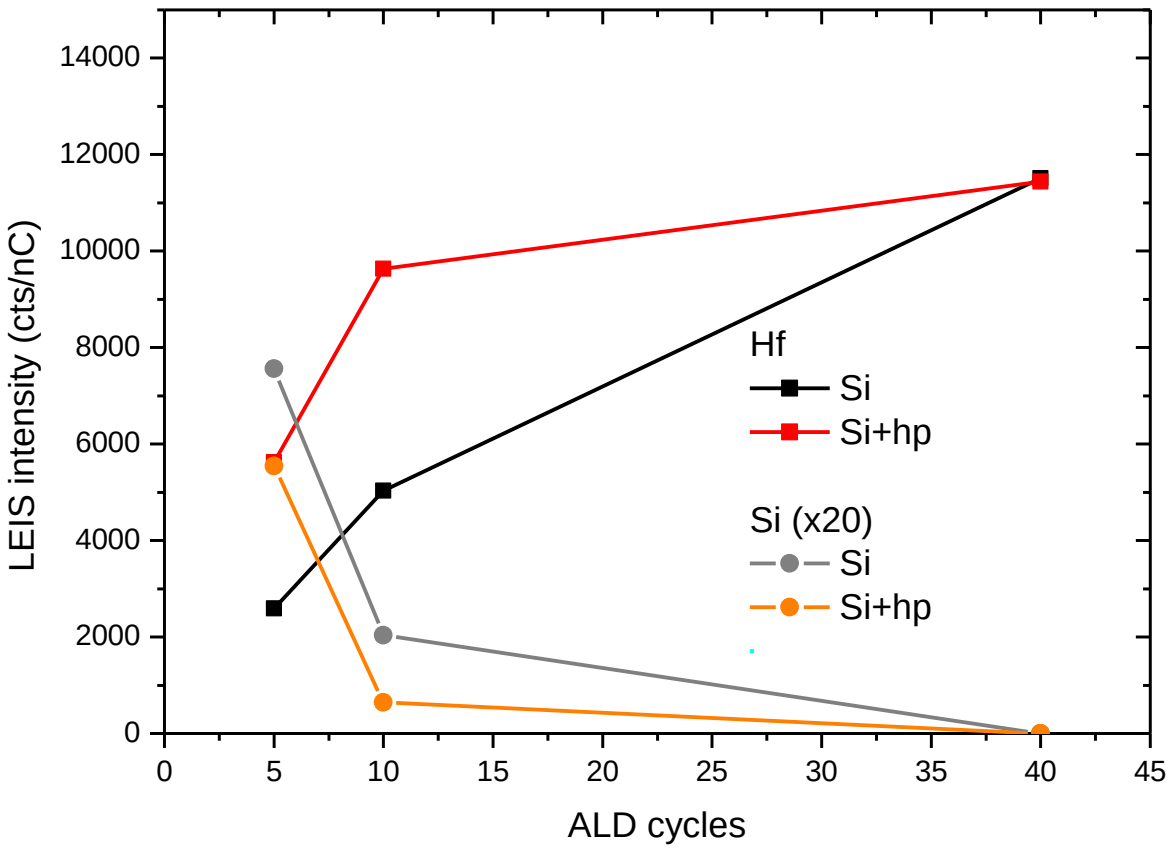
- Al_2O_3 closing up yet sooner. Still not immediate.

LEIS - HfO_2 Film Closure on Si



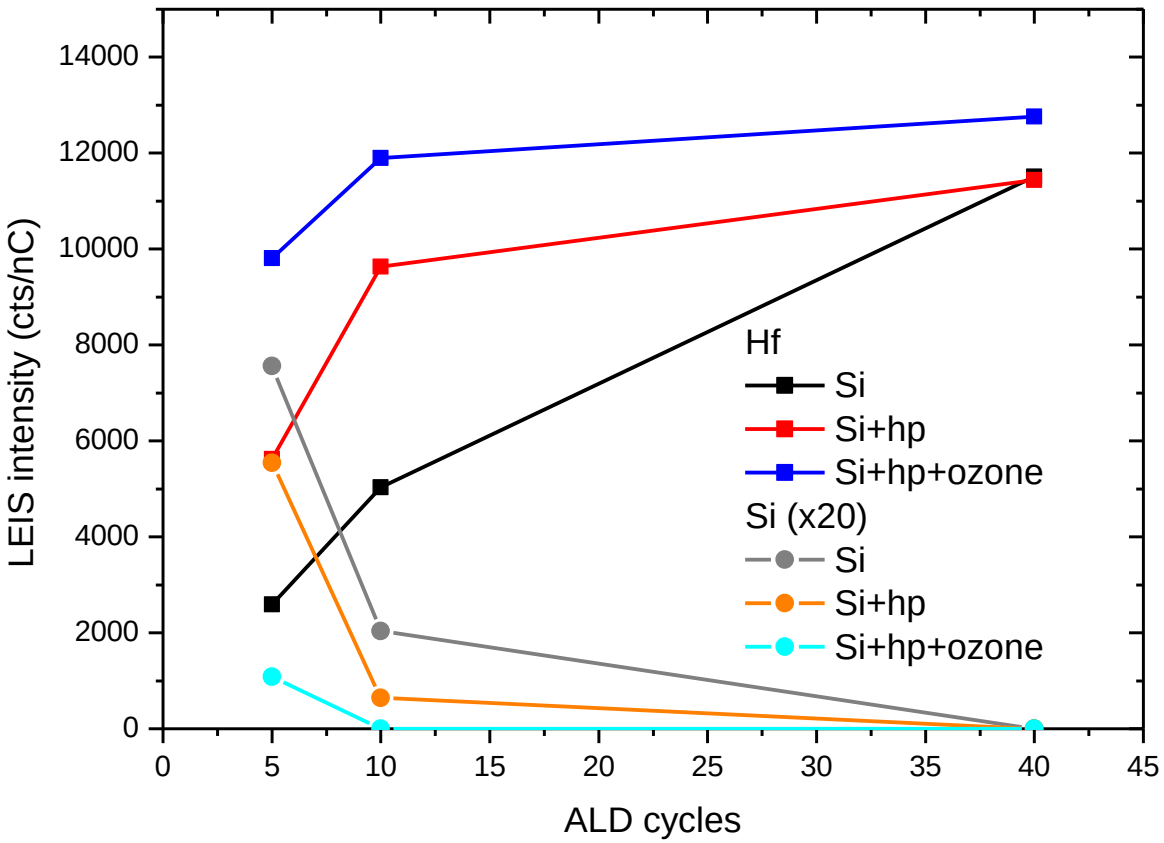
- HfO_2 closes even later, after 20-30 cycles

LEIS - HfO_2 Film Closure on Si



- HfO_2 film closure improved at 2-4 Torr

LEIS - HfO_2 Film Closure on Si



- HfO_2 film closure improved by combining elevated pressure + UV-Ozone.

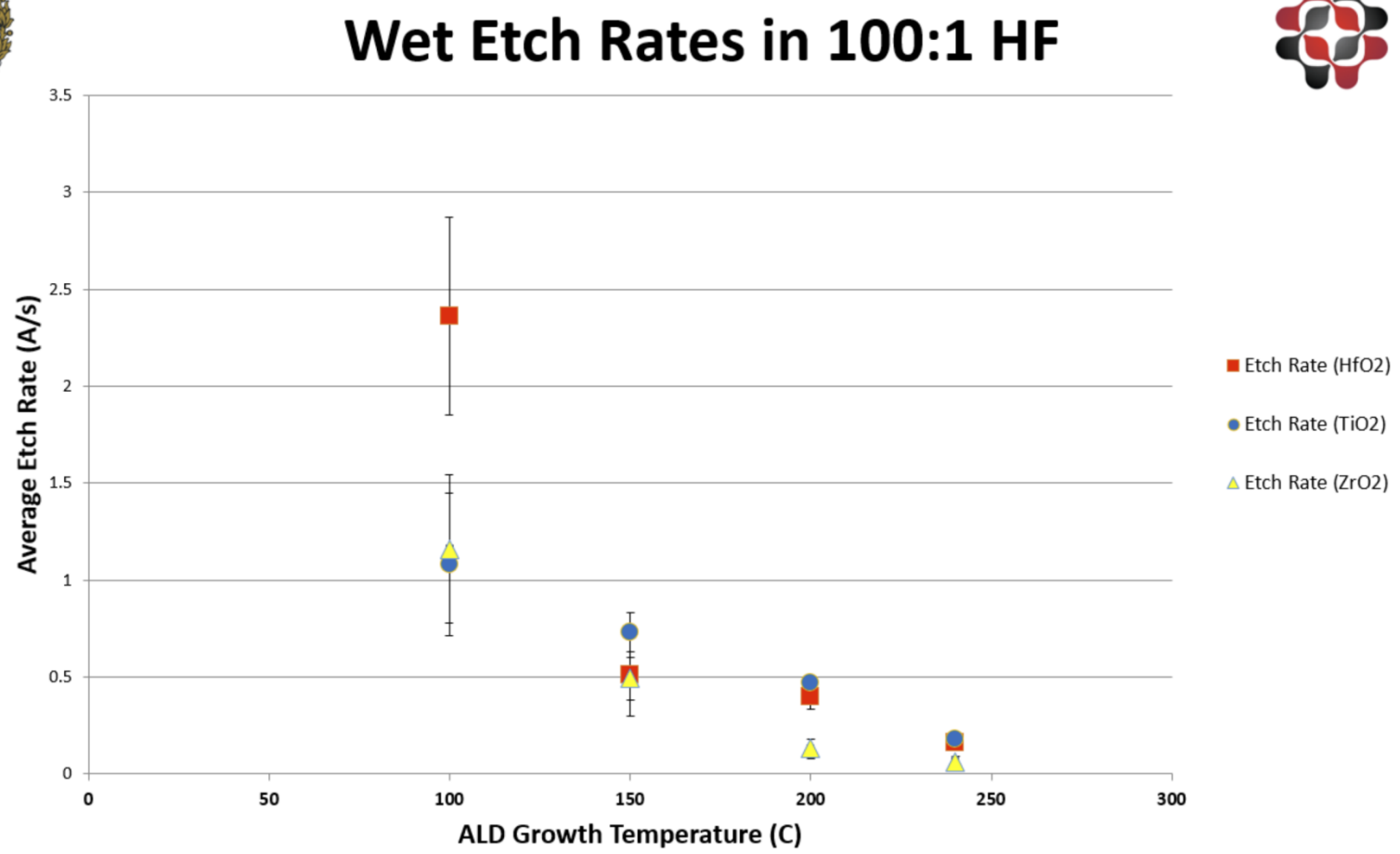
Conclusion

- Al_2O_3 and HfO_2 ALD films don't close as early as expected
- Higher pressure ALD process enables earlier film closure
- Increased pressure regime need re-examination for a "fully saturated" ALD process
- UV-Ozone clearly improves film closure
  - Due to better OH-termination, surface cleaning, oxidation
- Implications: Controlling film closure with these "knobs" could lead to improvements in gate oxide leakage, passivation, film permiability, and other characteristics
- LEIS is uniquely effective tool for examining ALD film closure during initial deposition

New Work since 2017…

- Tried to reproduce results using IPA as precursor. (Should wet graphene better) Didn't work. Similar to Finnish group. Conclusion – Original paper flawed, had water in IPA
- Considering other counter precursors to improve 2D nucleation.
- Used LEIS to characterize early nucleation.
- Etch Rate Characterization

Etch Rate Characterization



New Work since 2017...

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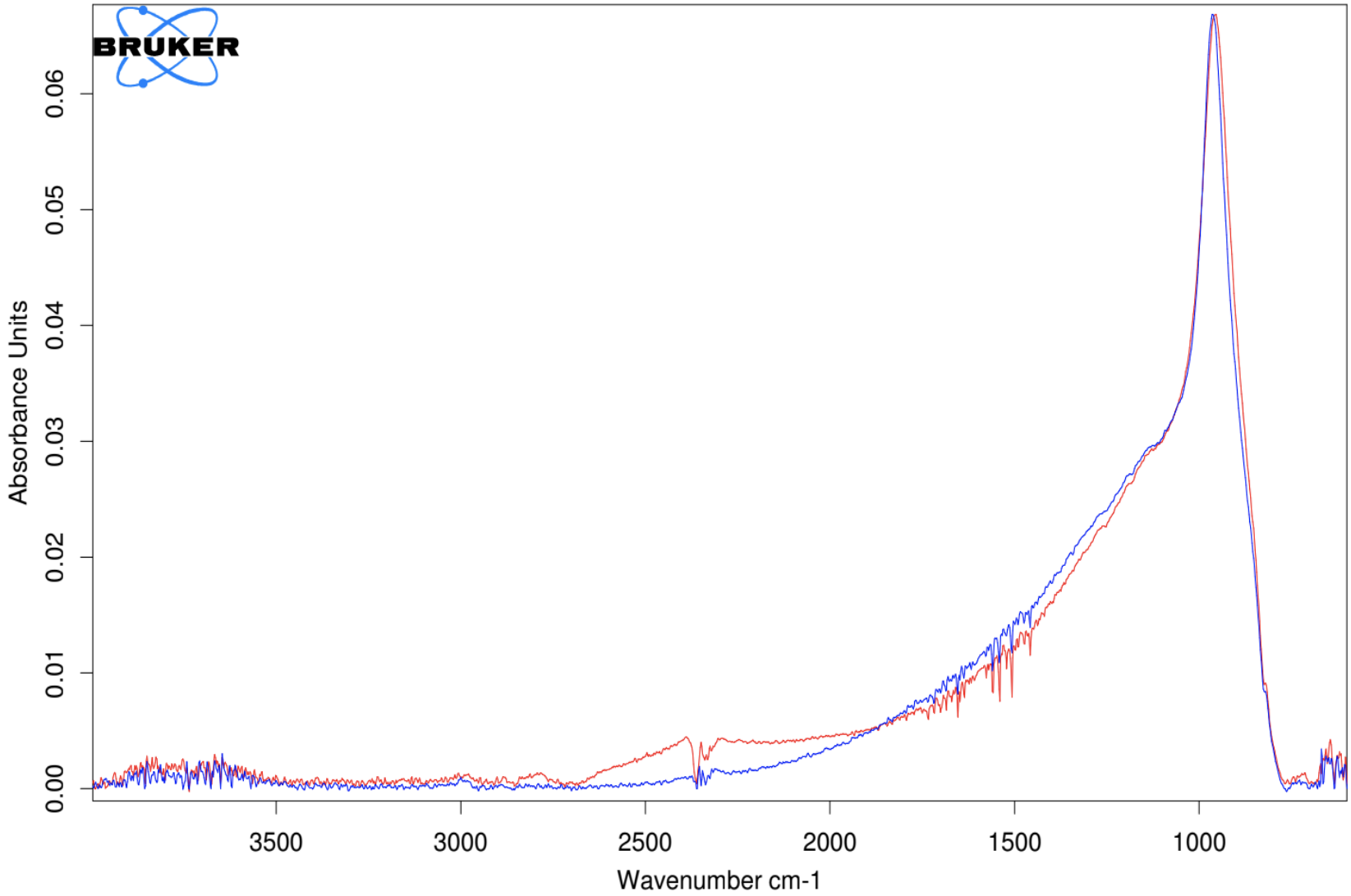
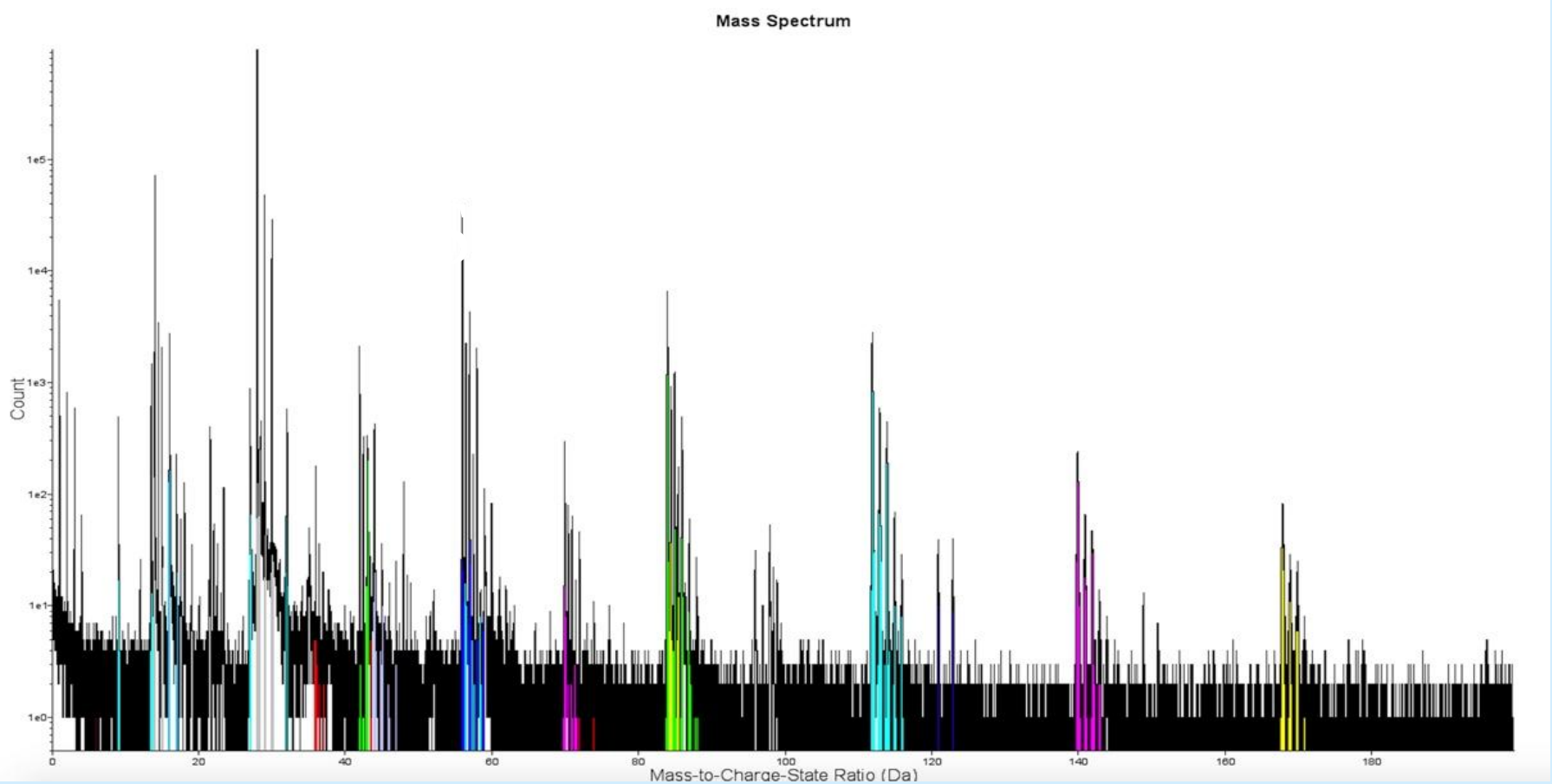
- Considering other counter precursors to improve 2D nucleation.
- Used LEIS to characterize early nucleation.
- Etch Rate Characterization
- OH concentration, in the form of D_2O



FTIR Spectrum - Al2O3 at 240C (blue), 120C (red)



HfO2 Dep. Temp. °C	Deuterium (% of deuterated atoms present)
240°C	**2.6%**
120°C	**5.6%**

Future Directions for ALD at CNS

- ZrO and ZrO-nanolaminates are next to be characterized.
- No Plasma ALD at Harvard.... yet….
- **Films of Interest** – 3D lithography + ALD...
- *Few Layer Deposition*
- ALD *EPITAXY?!...*

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- J.D.Deng - Raman, Hou Yu Lin - XPS, Jason Tresback - AFM
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- Boaz Pokroy, recently of Harvard University (Aizenberg group), for samples.
- Omair Saadat, MIT, for film characterization data.
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