2012 NNIN ALD Symposium
ALD Staff Review

Atomic Layer Deposition
at
Harvard CNS

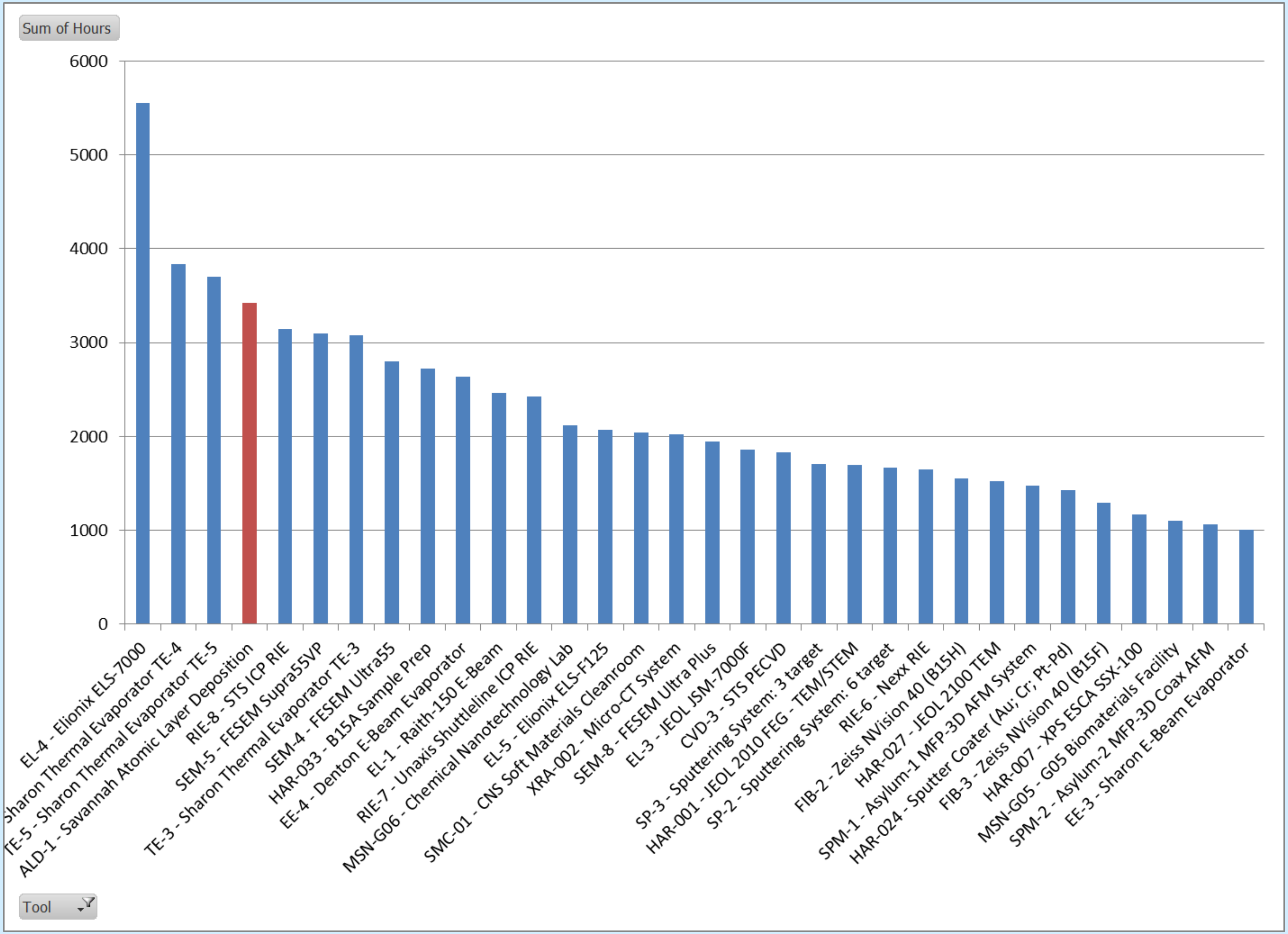
Mac Hathaway

Nov. 29, 2012

The CNS Cambridge Nanotech Savannah 200

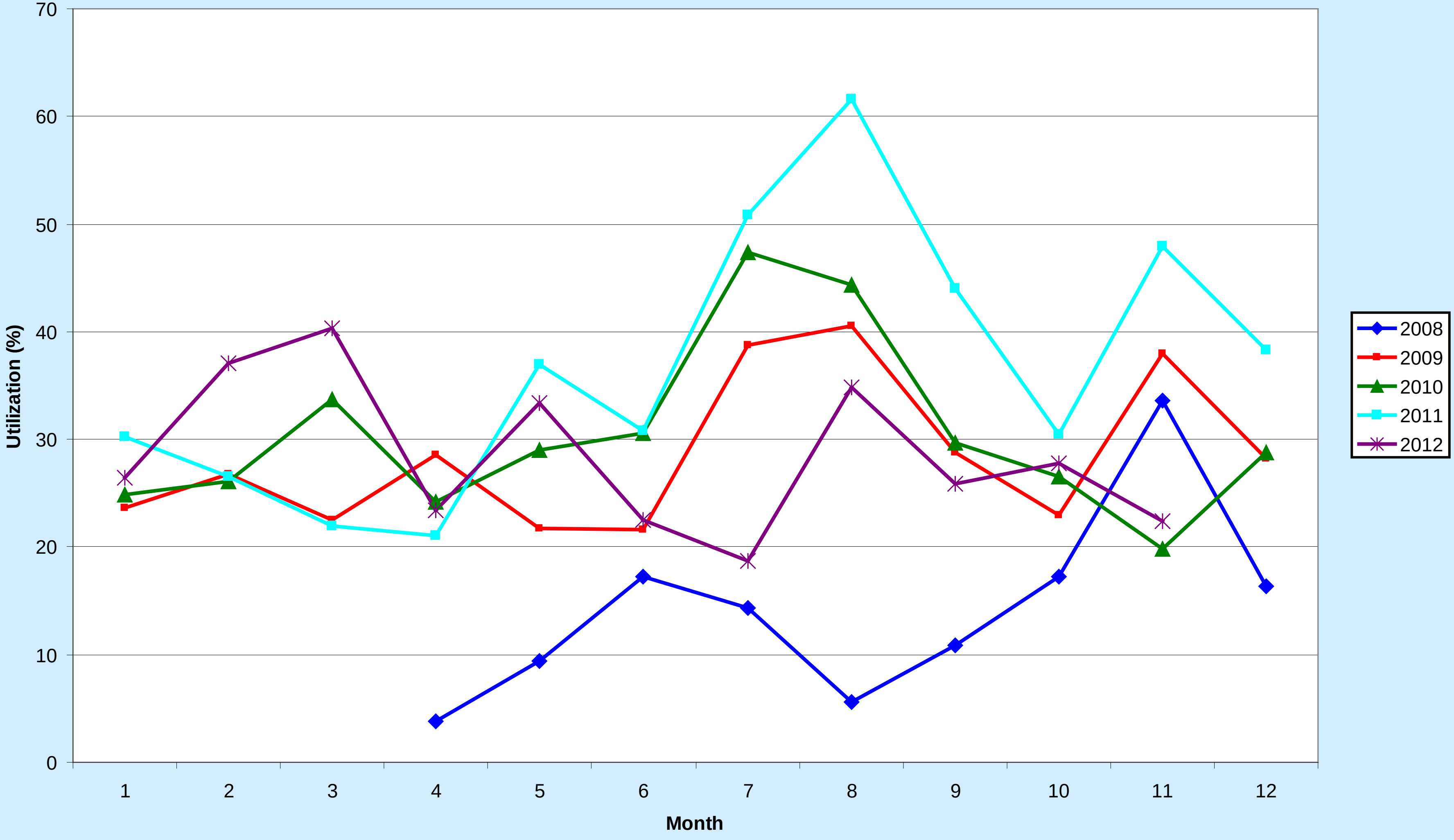
CNS ALD System Review

- Cambridge Nanotech Savannah 200 thermal ALD
- New in 2008
- 6-port configuration, 8” wafer capacity
- Available films –
  - Al_2O_3, HfO2, SiO2, TiO2, ZnO, Pt
- System Utilization – 31.3% (24/7 availability) –
  - For reference – our busiest tool – Elionix E-Beam writer – 46.6 %
- Rates – Academic
  - Regular - $18/hr; Assisted use - $55/hr; Remote Assisted - $165
- Rates – Non-academic
  - Regular - $120/hr; Assisted use - $165/hr; Remote Assisted - $220



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
EL-5 - Elionix ELS-F125
SMC-01 - CNS Soft Materials Cleanroom
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

Harvard CNS ALD Utilization (%)



Maintenance Schedule

- Oil Change – 6-12 months
- Pump Change – 1-2 years
- 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

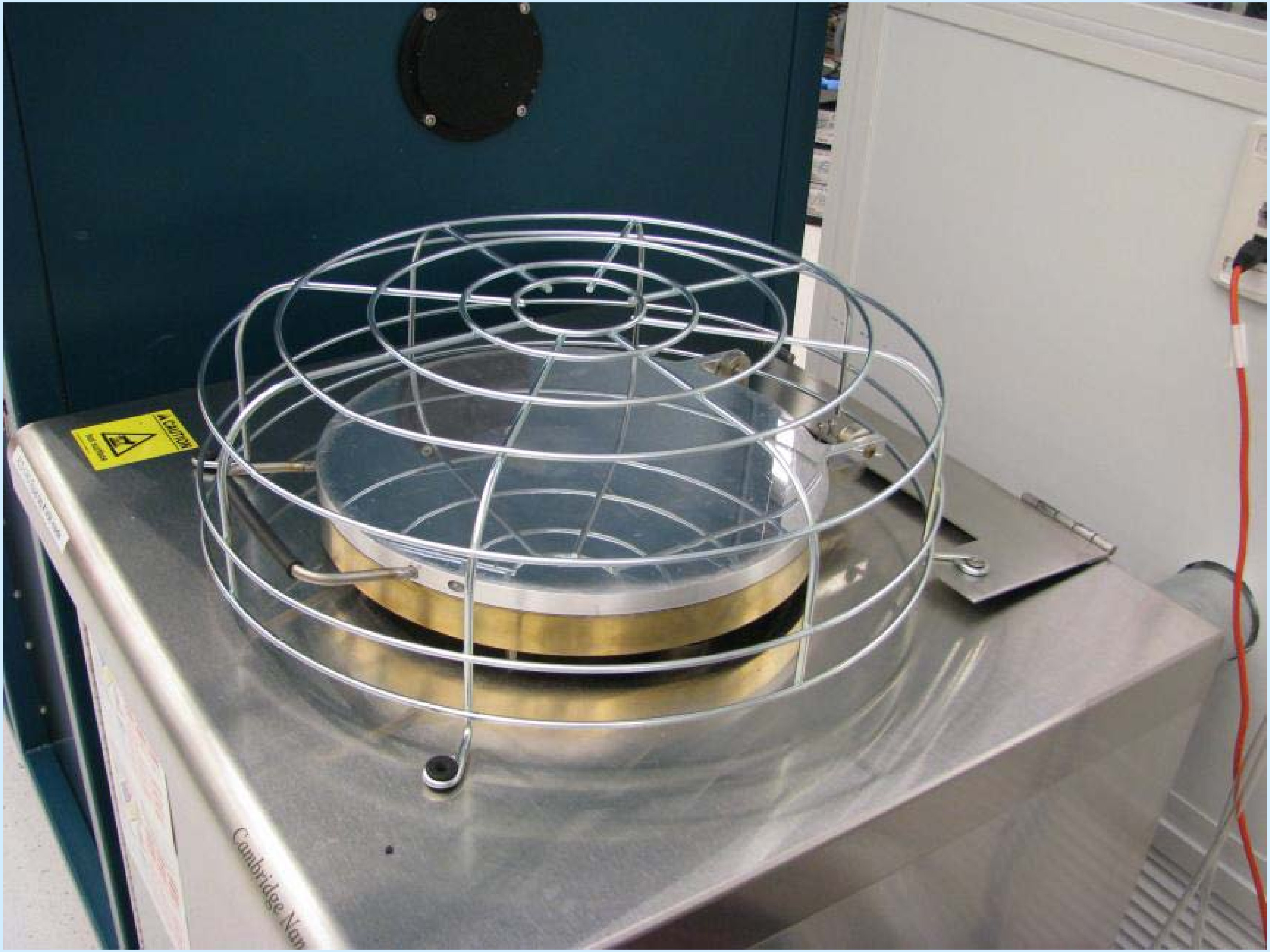
- Gauge Drift – due to coating up of pirani gauge
  - Added manometer gauge – doesn't drift, but hard to integrate into existing software
  - Tee for manometer gauge – added enough "ballast", or dead space, to prevent pirani from crudding up.
- Kalrez oring – Very expensive. $300+
  - Replaced with Viton, change more often (2-4 months), costs $8. 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.

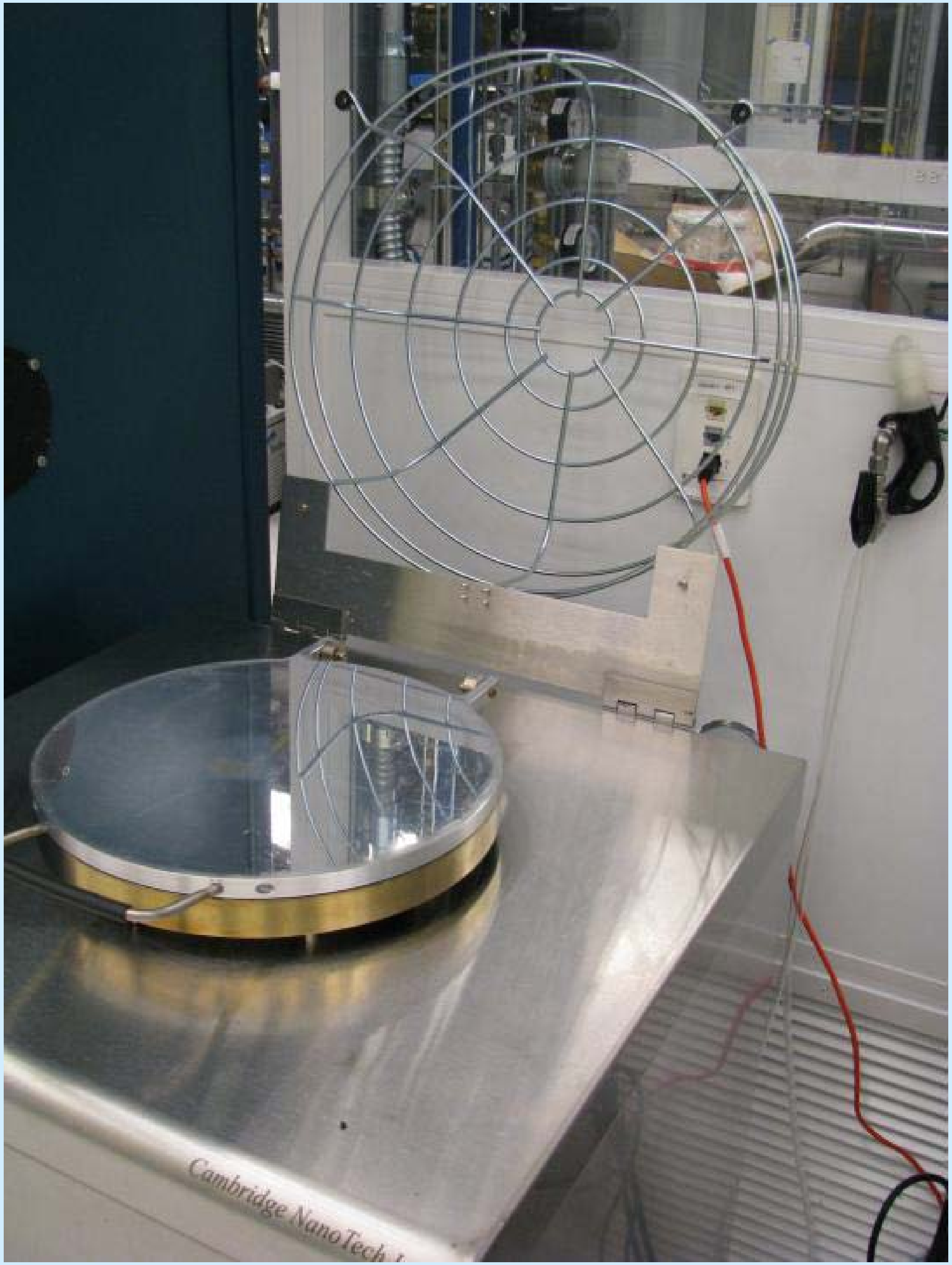
In-line Secondary Reaction Unit

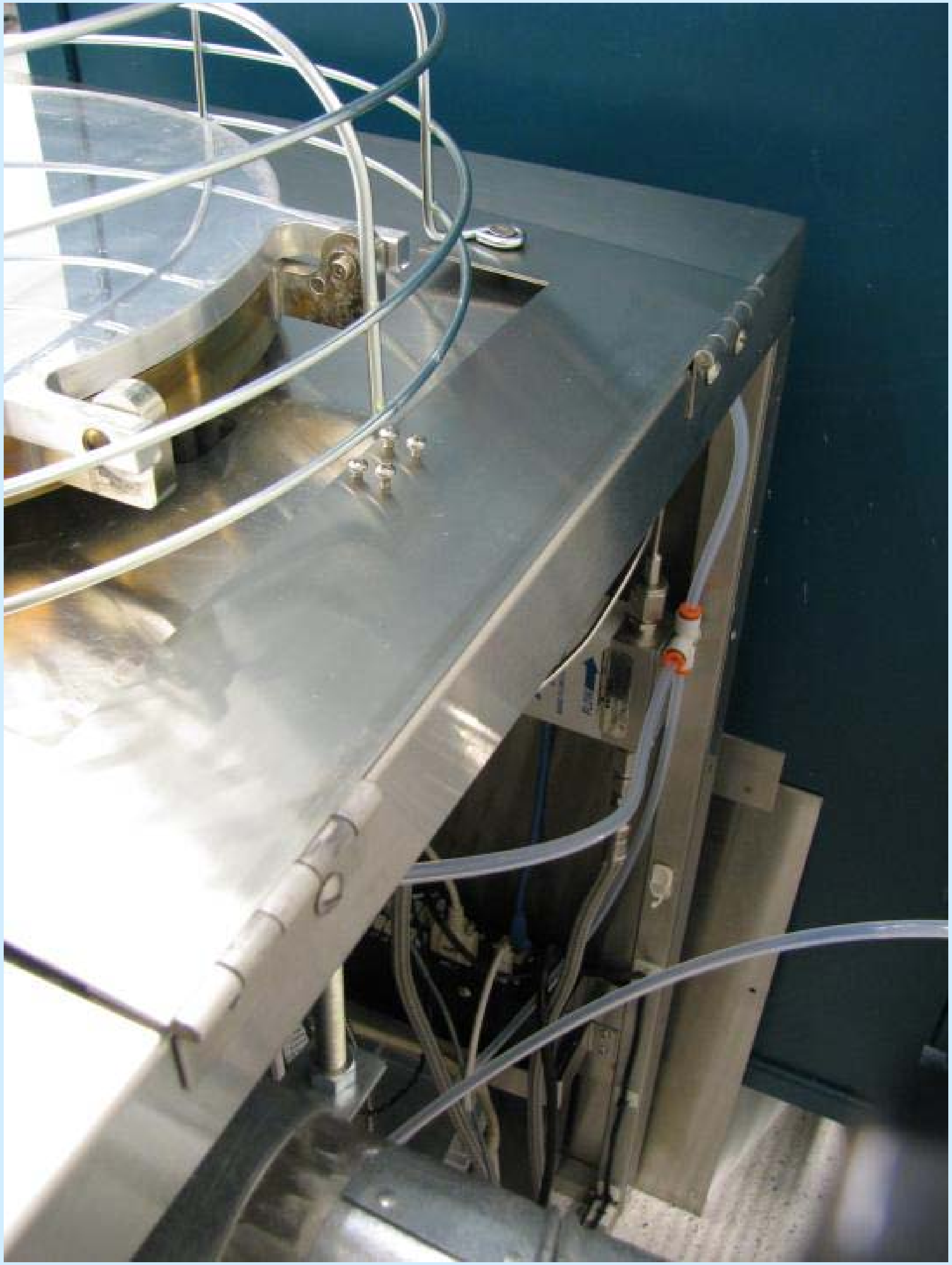
Problems (cont.)

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

Heat Shield Hinge




Cambridge NanoTech



Problems (cont.)

- Hot lid…melts things.
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- Pnuematic fittings feeding ALD valves get leaky
  - Changed “push” fittings to barb fittings.


MAC
VAC TO
120 PSI
24 VDC
4.0
34C-AAA-GDFC-1KT
MAC
5

Problems (cont.)

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- USB errors cause software to “lock up”, and heaters all turn off.
  - Supposedly, new control box is better. Part is “On order”.

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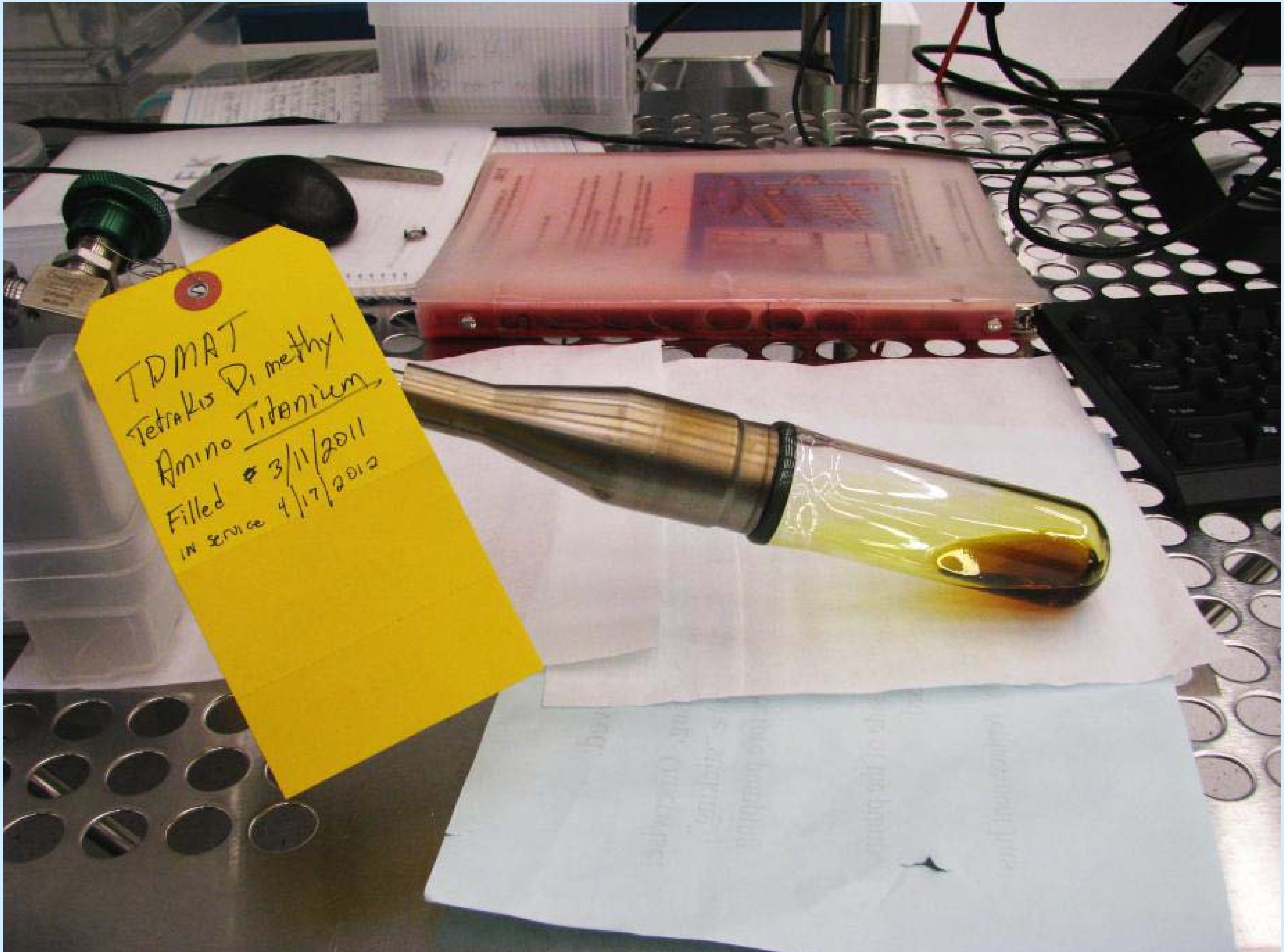
- USB errors cause software to “lock up”, and heaters all turn off.
  - Supposedly, new control box is better. On order.
- Vendor kaput.
  - Buy different system.

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

ALD Materials available at CNS?

- Available at CNS? - Al_2O_3, HfO_2, SiO_2*, Pt, and… TiO2 (new!)

Under Development – ZnO, AlZnO (AZO – better transparent conductor)

Coming someday - Cu, CoN, Strontium Titanate,

*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	270C	H_2	Doesn't like polymer, Precusor Very Expensive
TiO2	~100C – 240C	H_2O	Isopropoxide – rather slow 0. TDMAT – faster, more stable
ZnO	20C -	H_2O	Sheet resistance very variable

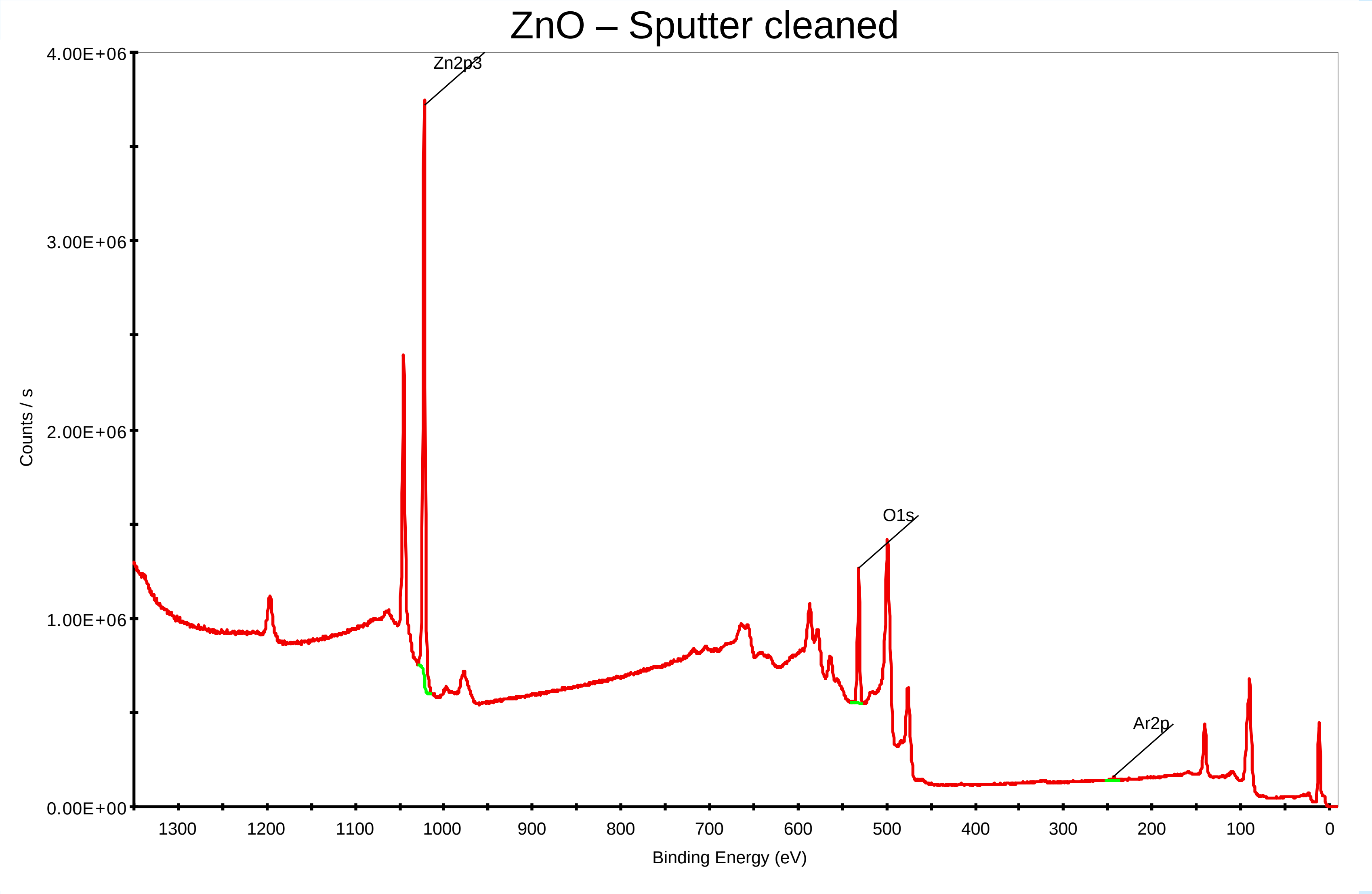
Film characterization for CNS ALD Films

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

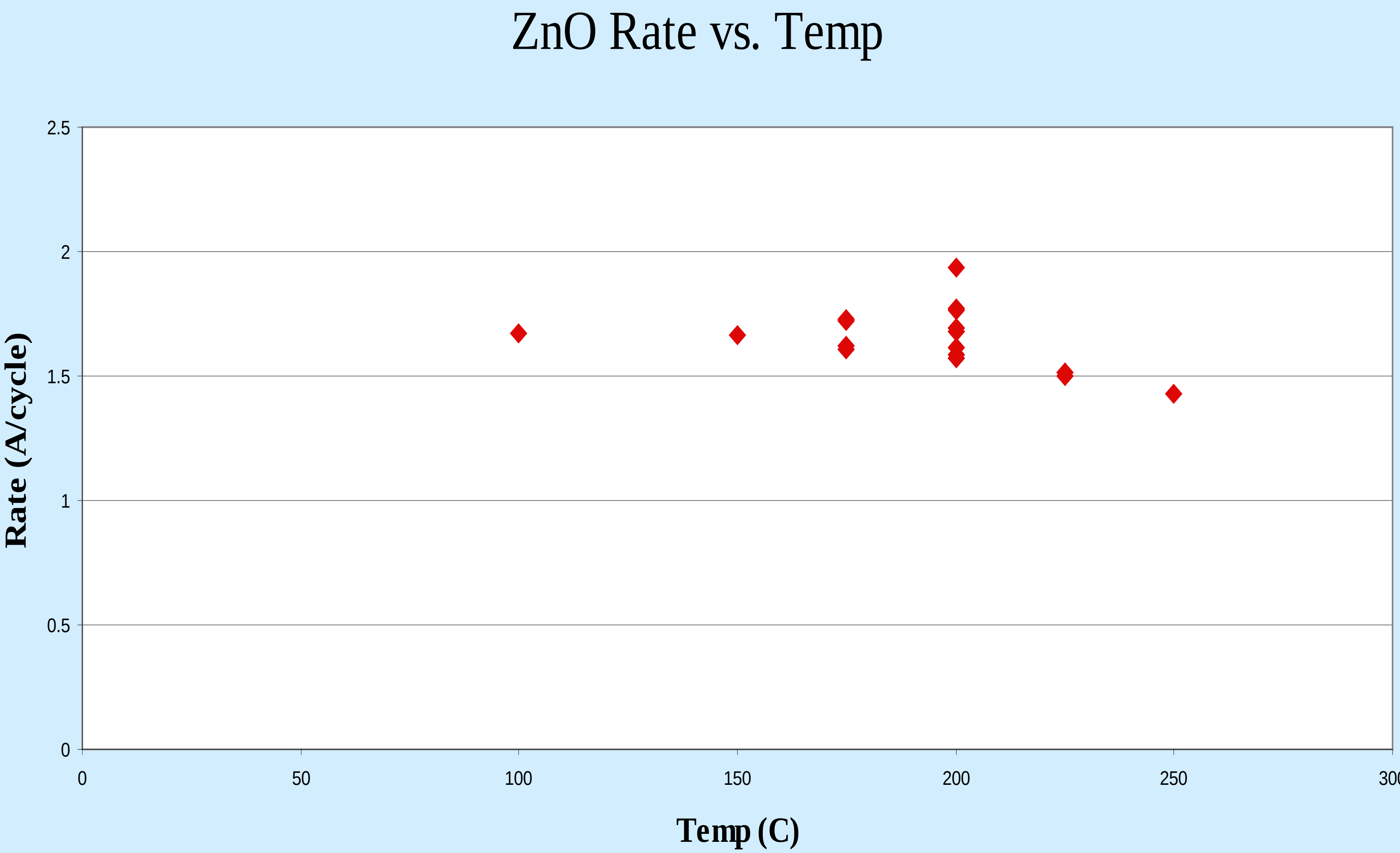
Film Characterization

- Al_2O_3

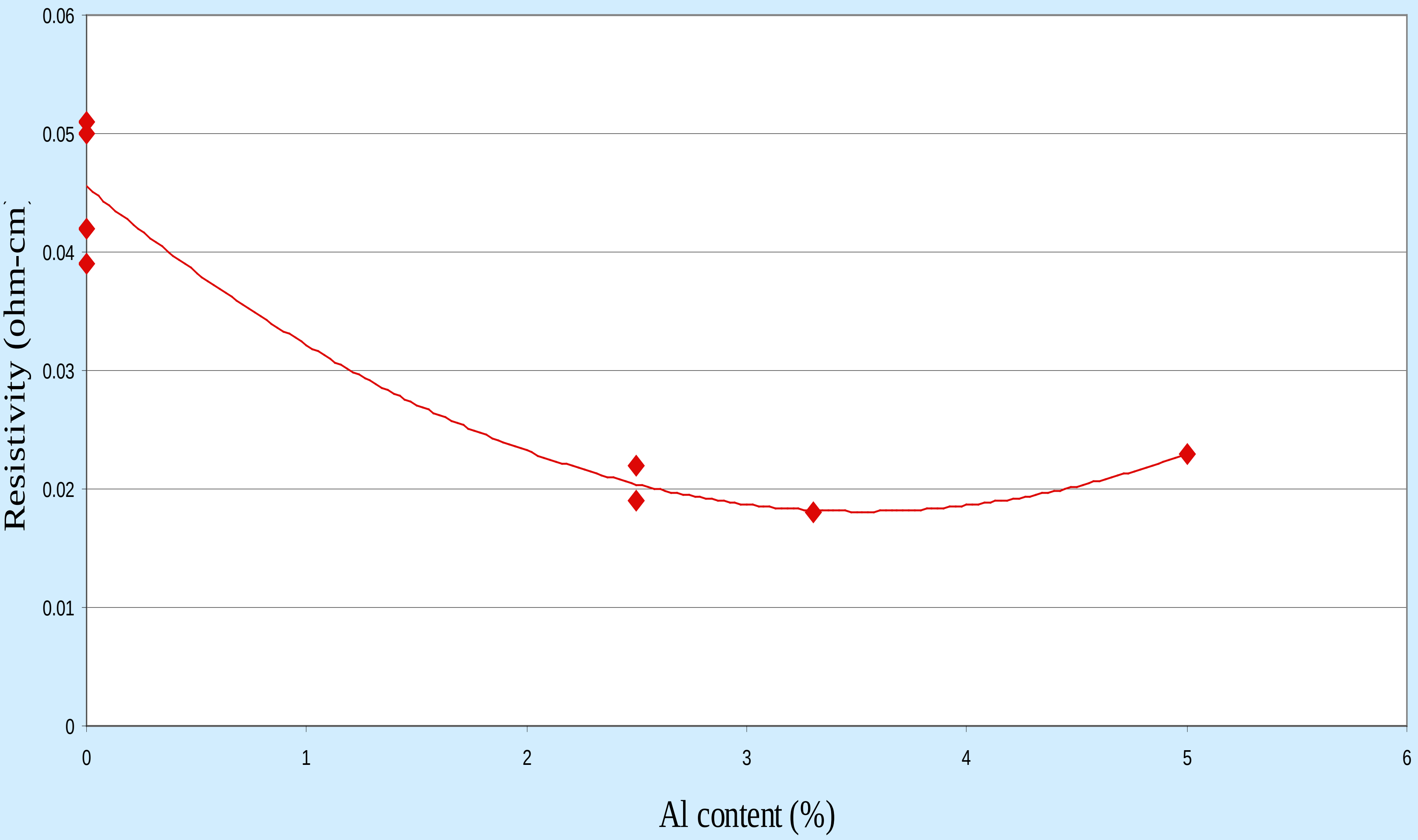
Film Characterization - ZnO



AZO – ZnO with Al laminates



AZO Resistivity vs. Al %



Process Challenges

ZnO – Need to characterize doping/conductivity behavior

Pt - Need to characterize nucleation

TiO_2 – Need to characterize anatase catalytic behavior

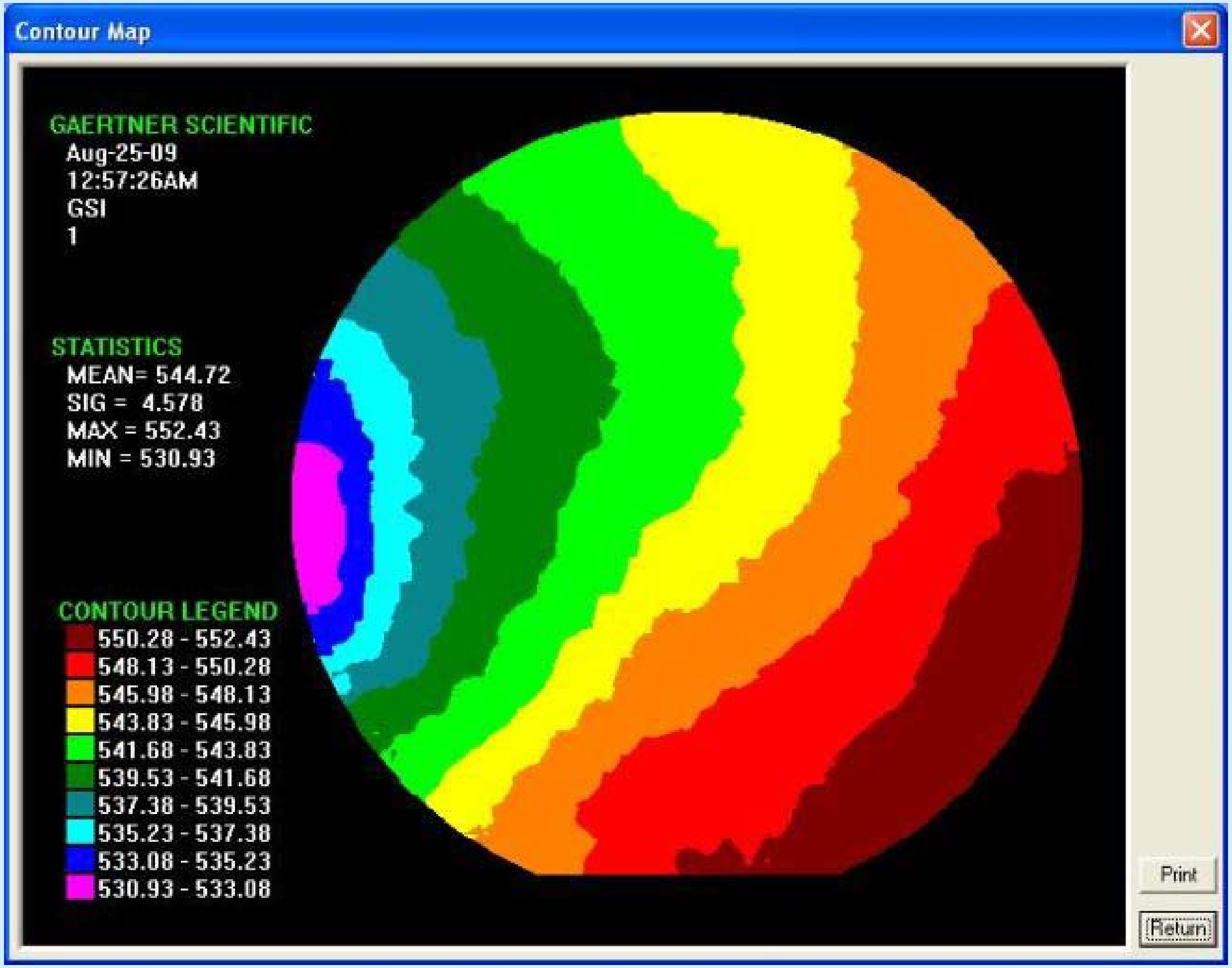
Explore Nitrogen doping and effects on conductivity, photo-catalysis, wave-guiding

What can ALD do for YOU?

- Due to exceedingly high conformality, very high aspect ratio structures can be coated, including the insides of microfluidic devices and micro-porous structures

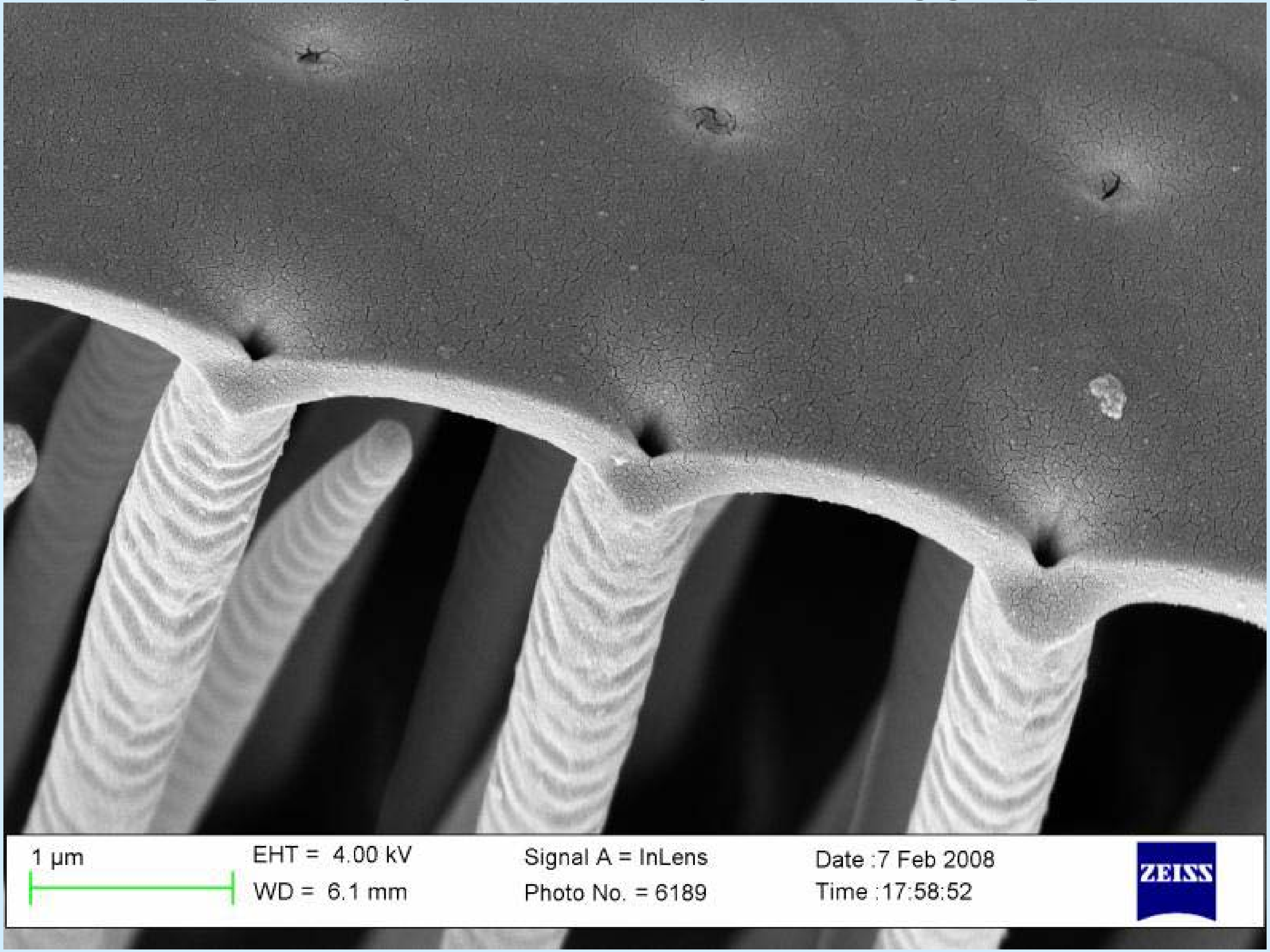
ALD Al_2O_3 – 450 cycles 6" wafer on Gaertner Laser Ellipsometer

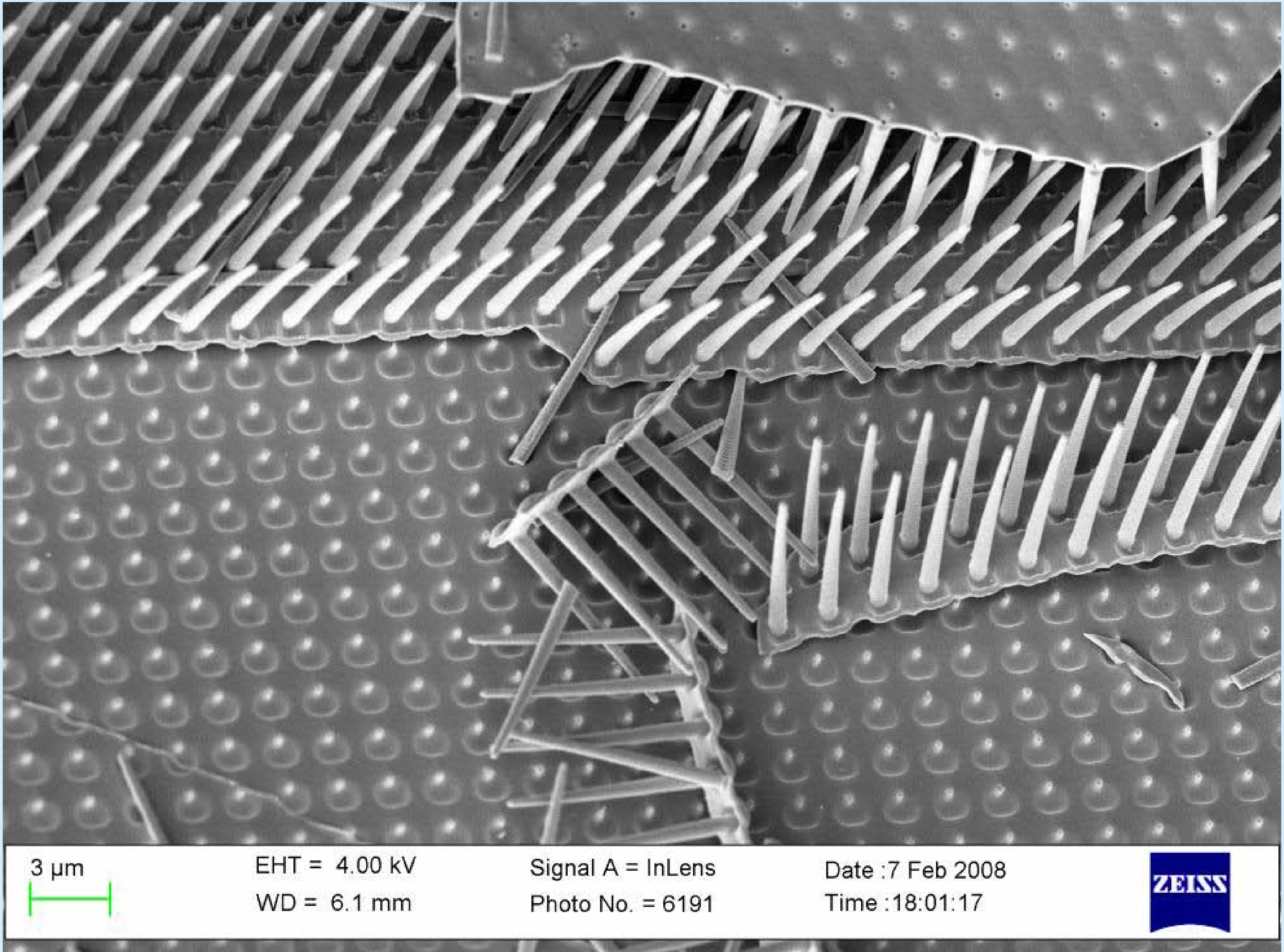
- Thickness Unif. – 0.84 %

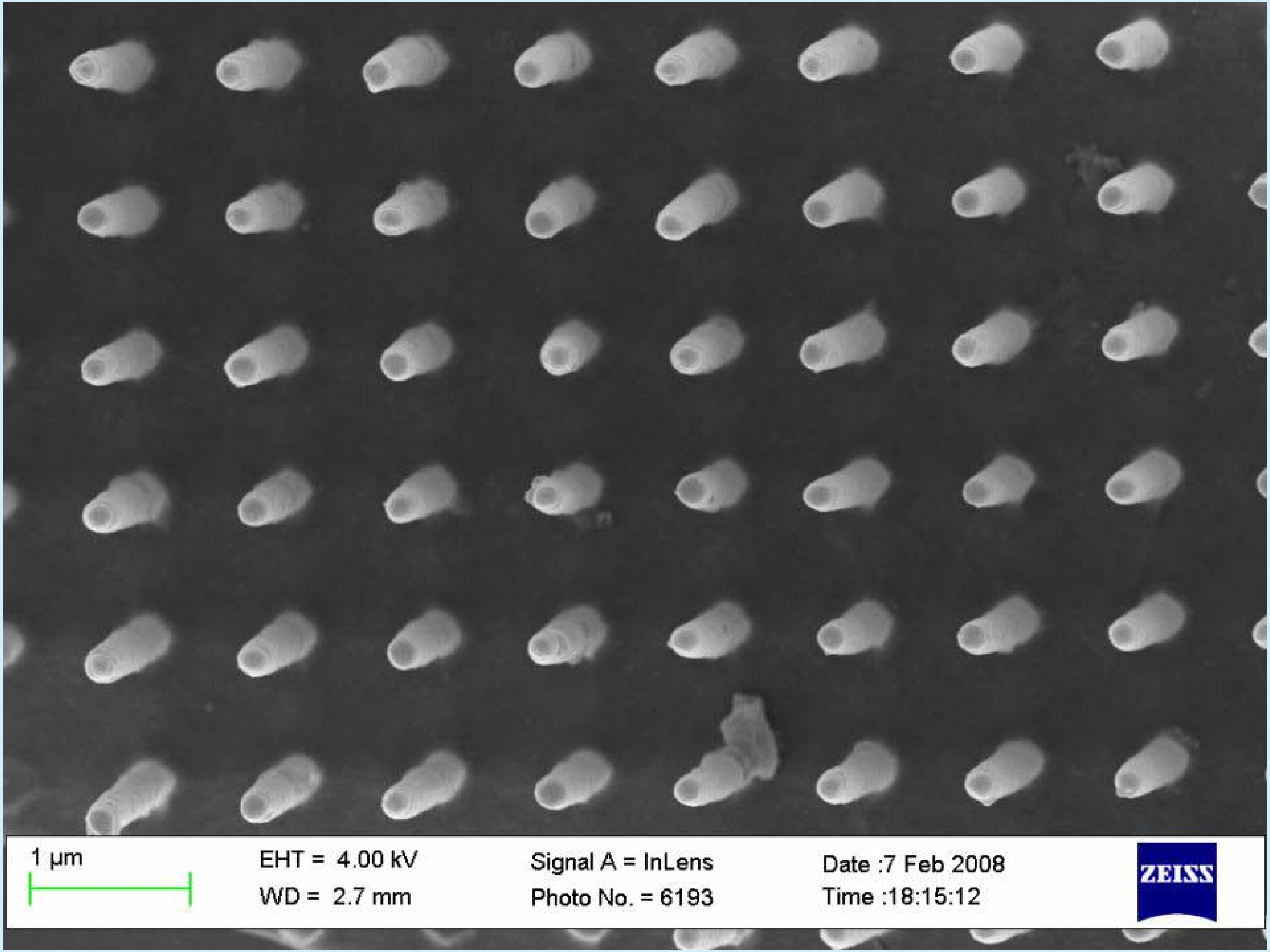


Al_2O_3 fill in PDMS holes imprinted by 10 x 2 um Si pillars, PDMS removed.

(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 = 2.7 mm
Signal A = InLens
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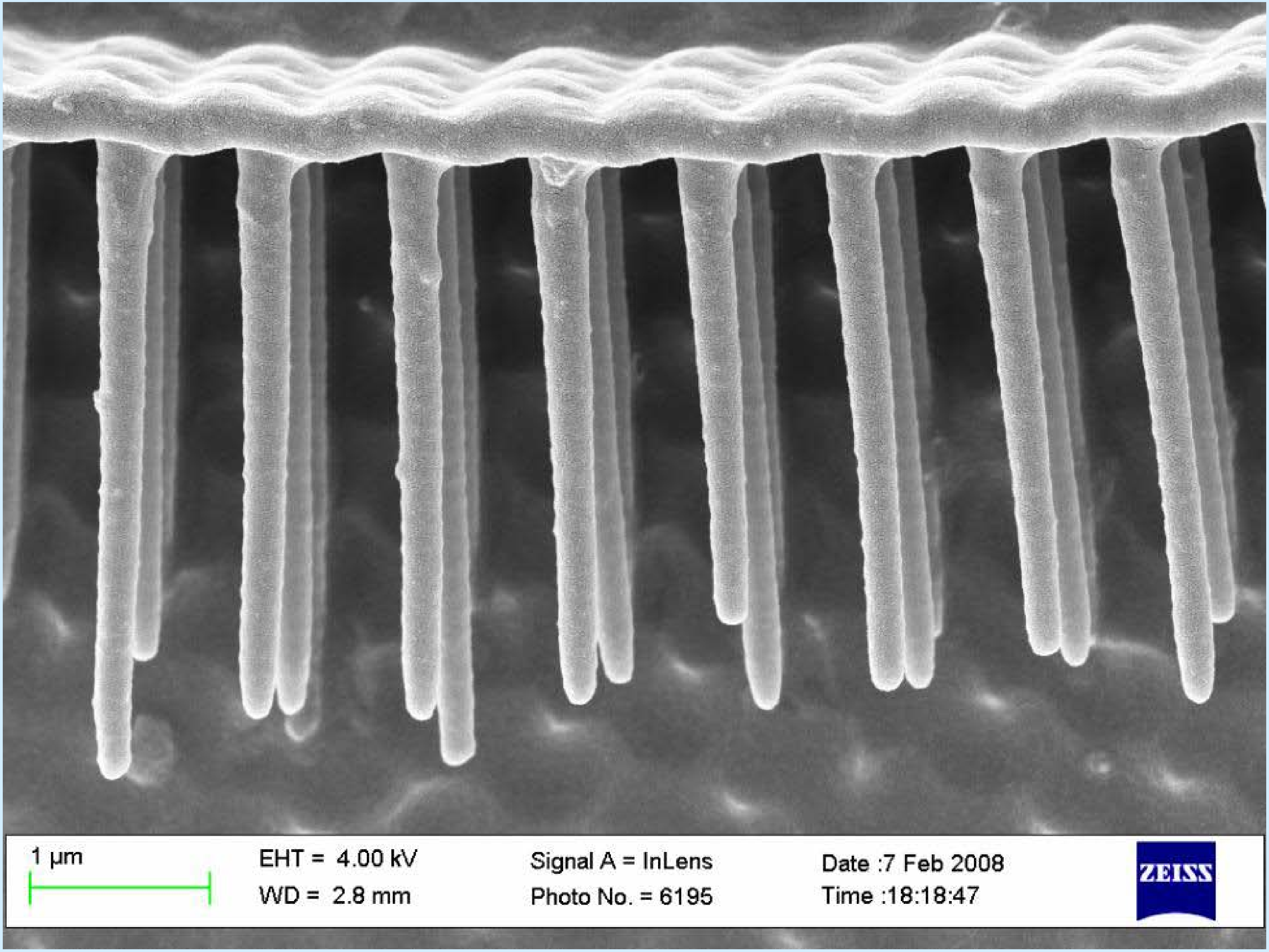
Date :7 Feb 2008
Time :18:15:12
ZEISS


1 µm
EHT = 4.00 kV
WD = 2.8 mm
Signal A = InLens
Photo No. = 6195
Date :7 Feb 2008
Time :18:18:47
ZEISS

ALD Deposition Disadvantages

- Slow
- High conformality means even back-side of sample gets deposition – sometimes a problem.
- Masking not effective for all films
- Some films are quite substrate sensitive, and even "atmosphere" sensitive.
- Lift-off processing possible, but not optimal due to high conformality.

- Very Slow

Notable Materials NOT generally available using ALD

- Au,
- Ag

- C, graphene, nanotubes – requires extremely high temperatures.

Substrate issues using ALD?

- Carbon Nano-tubes and graphene are problematic.
  - Nucleation achieved using surface functionalization with:

    NO_2 , carboxylated perylene, DNA, IPA?
- Pt deposition on/near polymeric materials not possible
- Pt dep on HF cleaned Si is slower to nucleate
- Cu dep on many materials is slow to nucleate, prefers CoN, other seed layers.
- No current material restrictions on CNS system

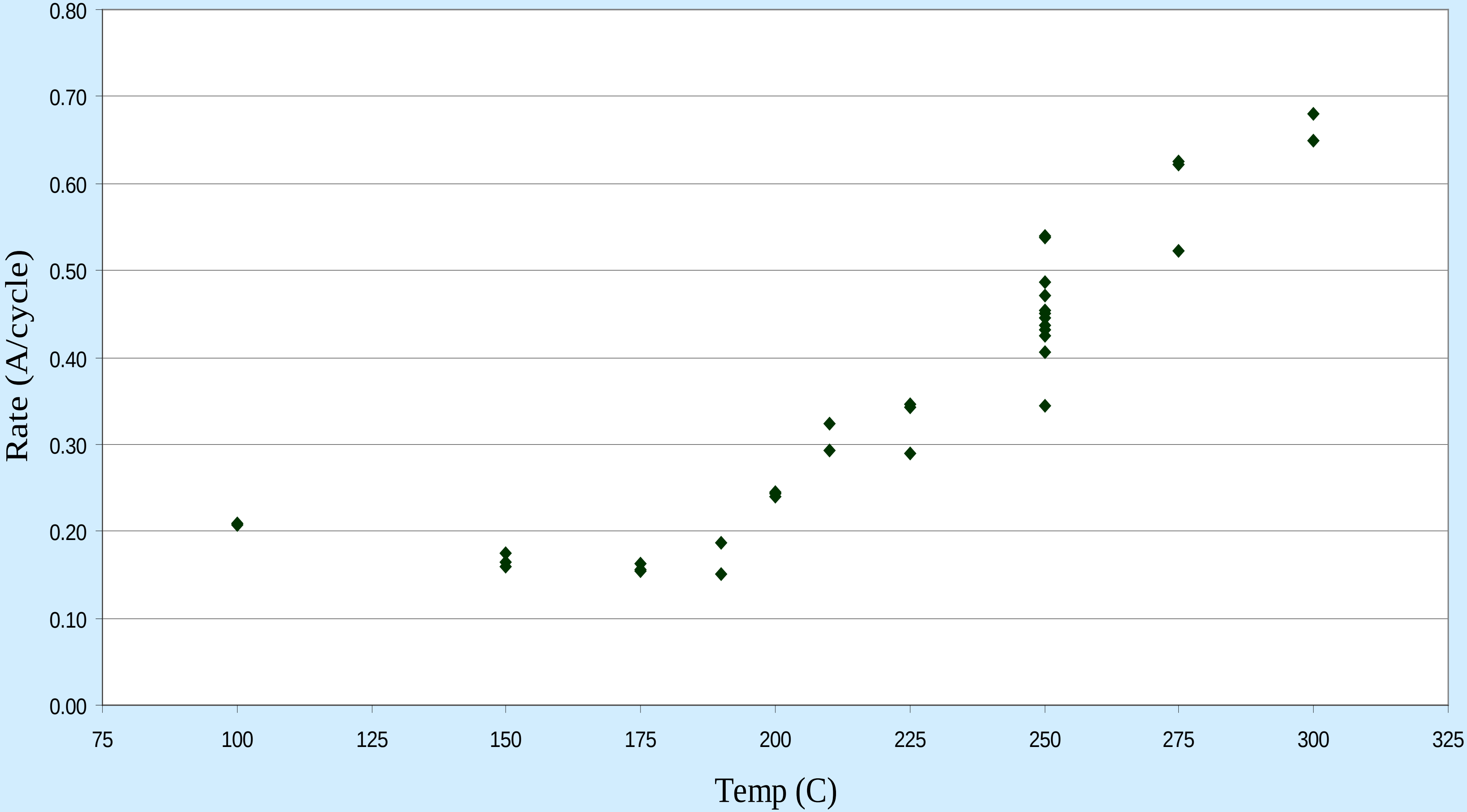
ALD Oxide Characterization

- Best suited to ellipsometry
- Initial process qualification using Woollam spectroscopic ellipsometer - Slow, very precise
- Sustaining characterization can use laser ellipsometer – single wavelength, fast, requires some knowledge of film.

TiO2 News

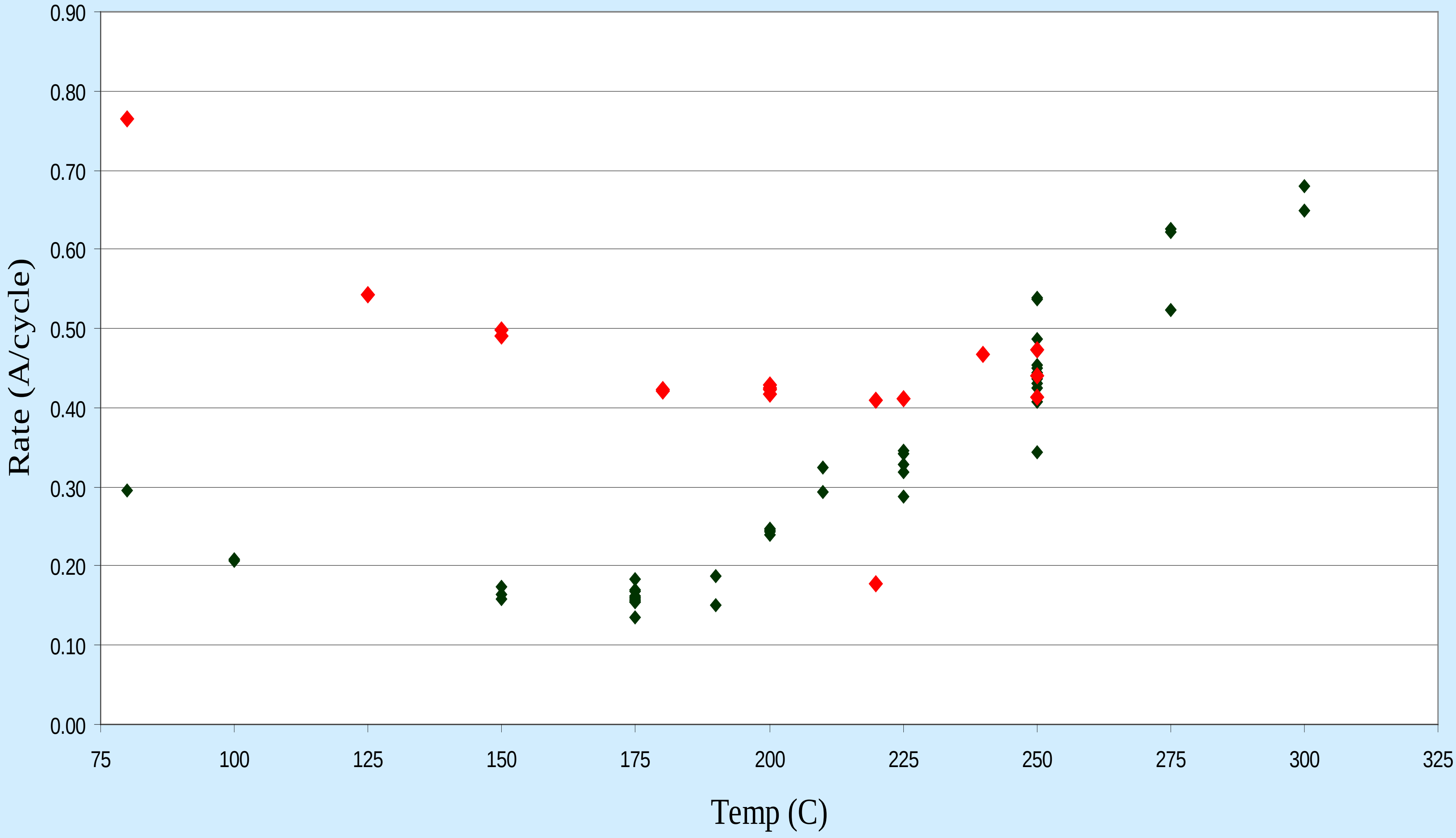
- ALD TiO_2 process using water and Ti-isopropoxide precursors has been explored.
- Above ~200C, rougher anatase predominates
- Below ~200C, structure is smoother, amorphous, with some rutile (?) microstructure.
- Further testing will include higher precursor temp., dep on gold, sputtered XPS, and possibly exporing TDMAT precursor –Preliminary results below….

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

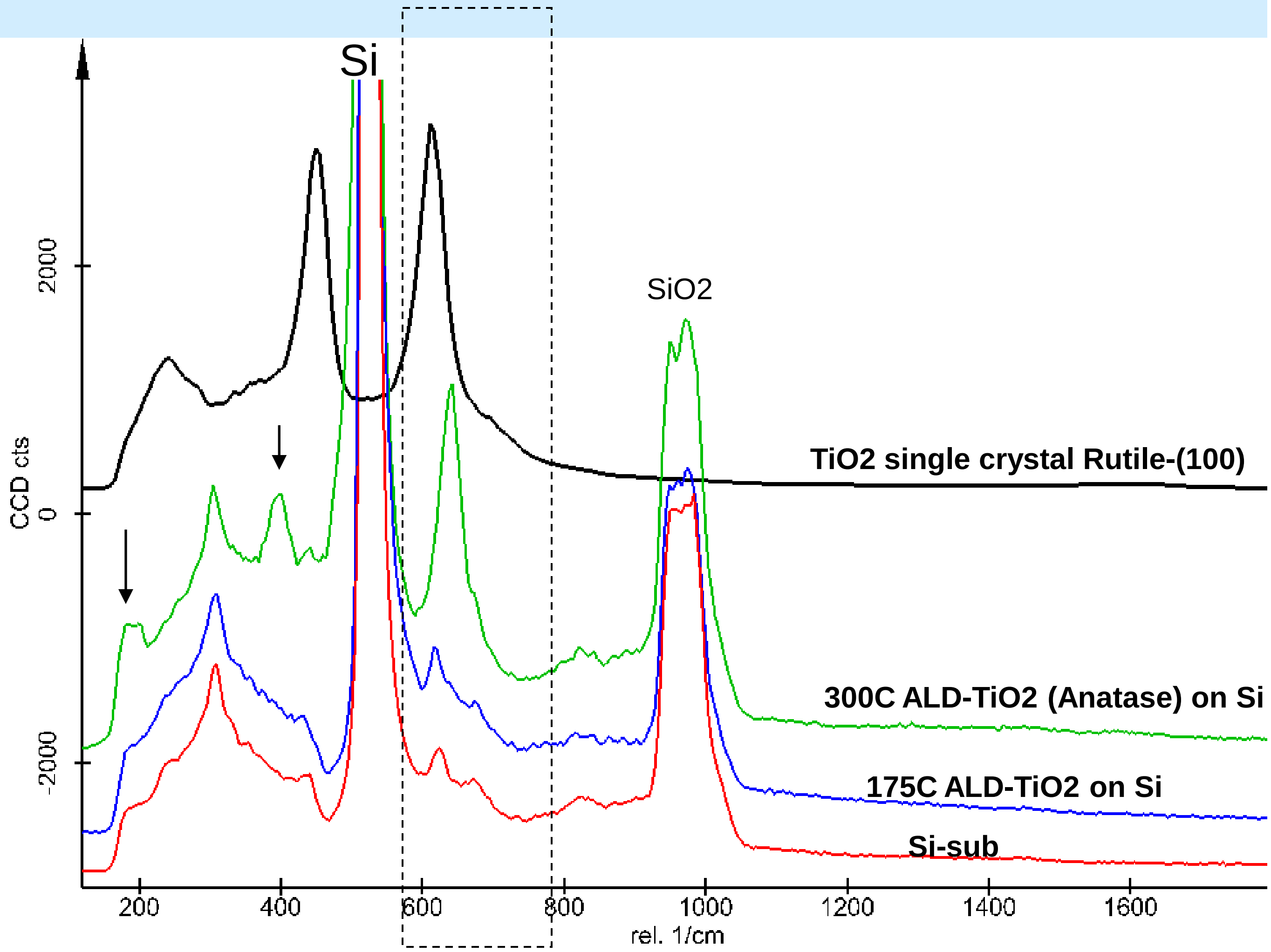


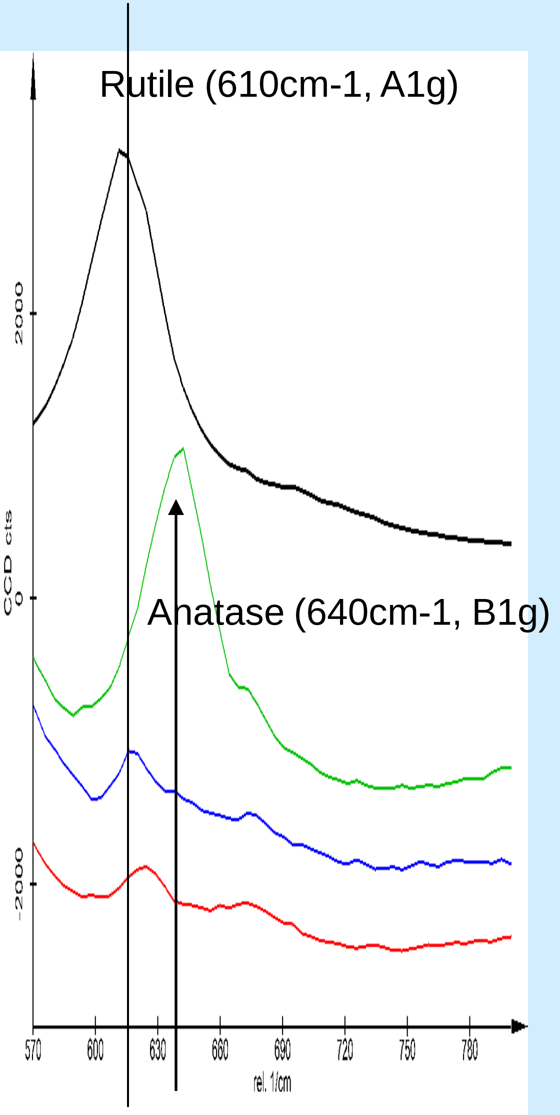
ALD TiO2 Growth Rate Vs. Temperature

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



ALD-TiO2 film Raman Spectrum

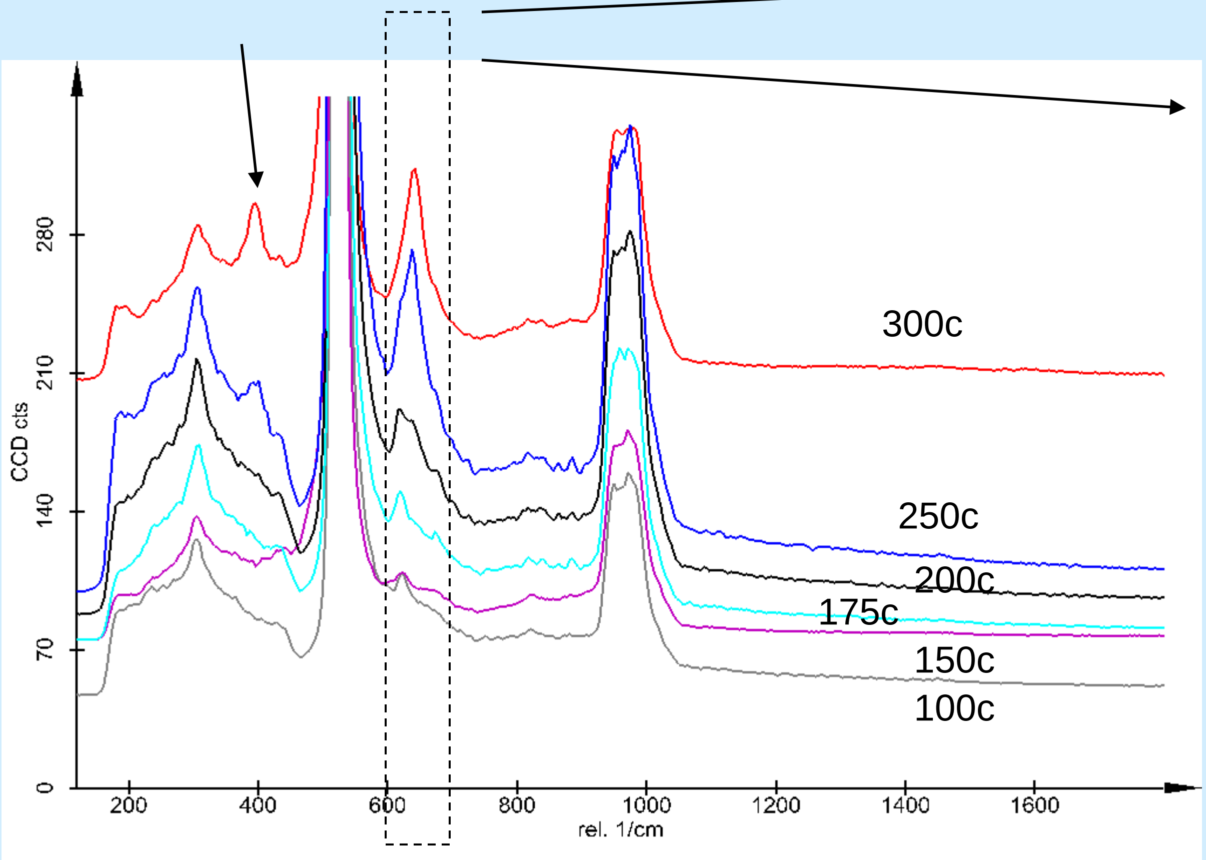


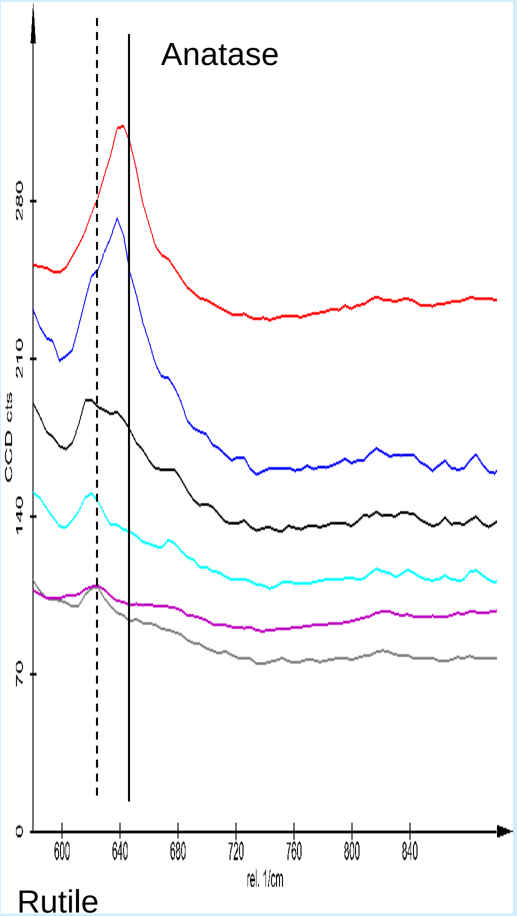


300C ALD TiO2, Anatase phase, very rough surface

175C ALD TiO2, more like Rutile phase, and smooth surface,

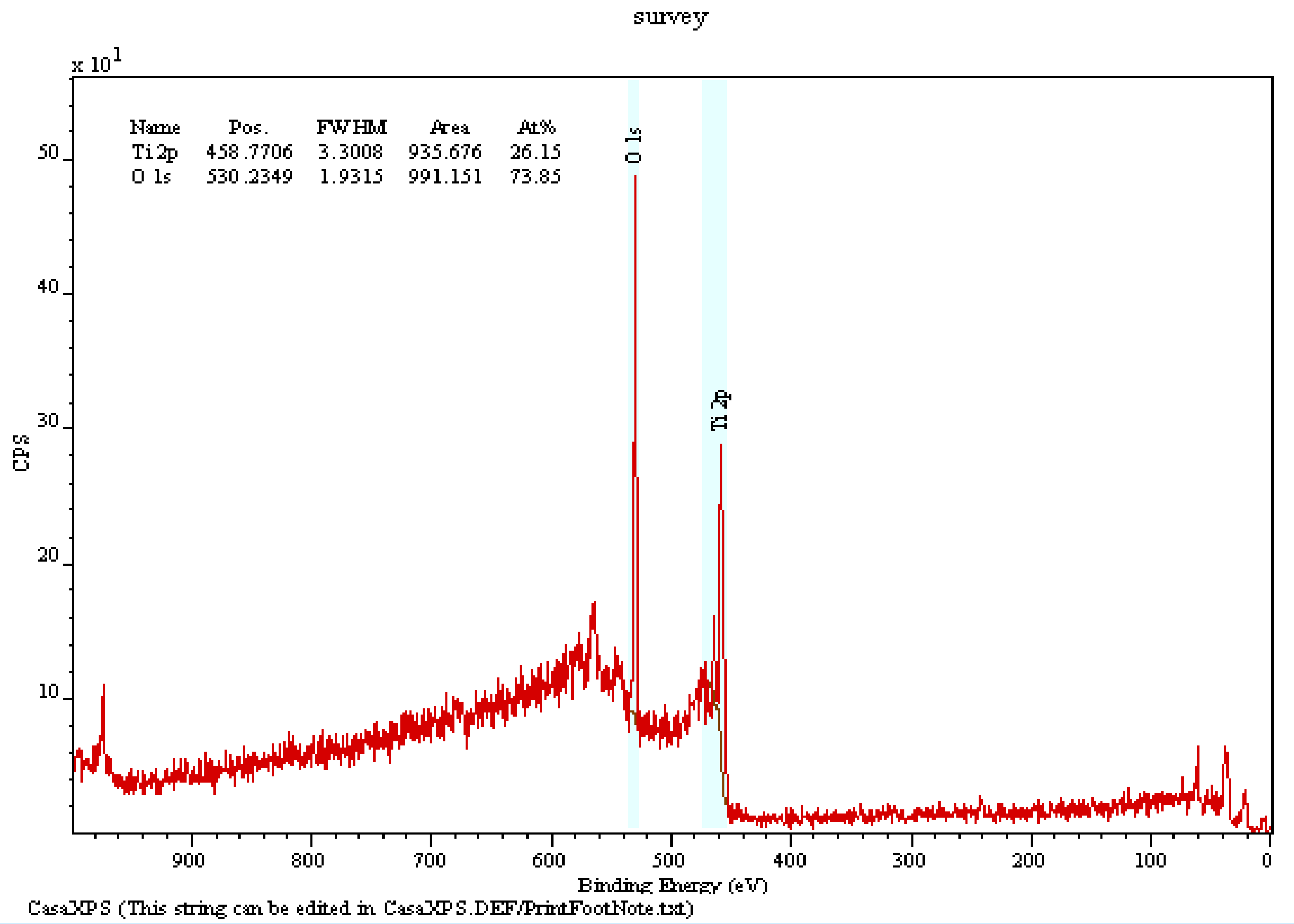
ALD-TiO2 film Raman Spectrum





- At lower temp, structure appears to contain some Rutile.
- At higher temp. (300C), Anatase phase is dominant

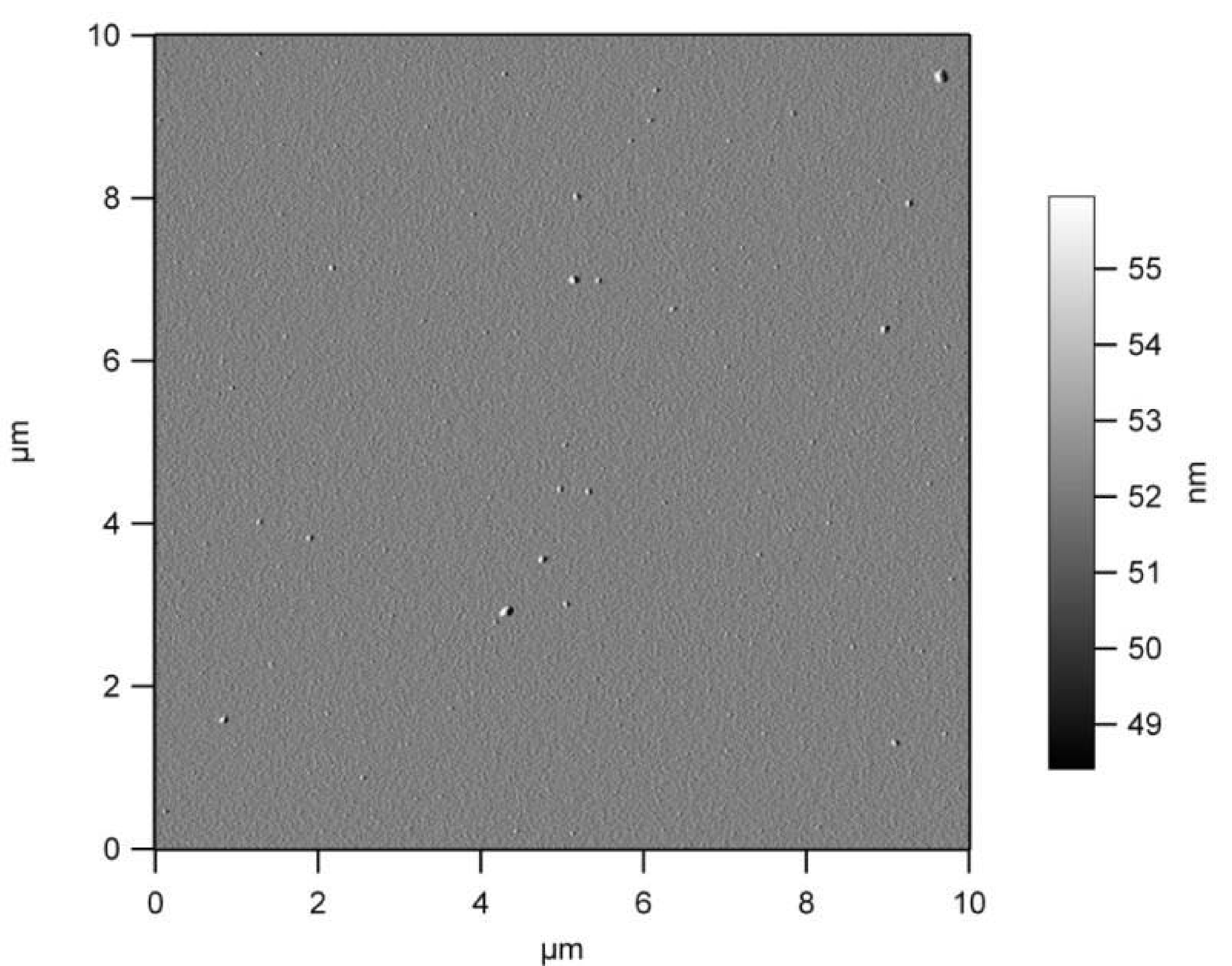
TiO2 – 250C - TDMAT



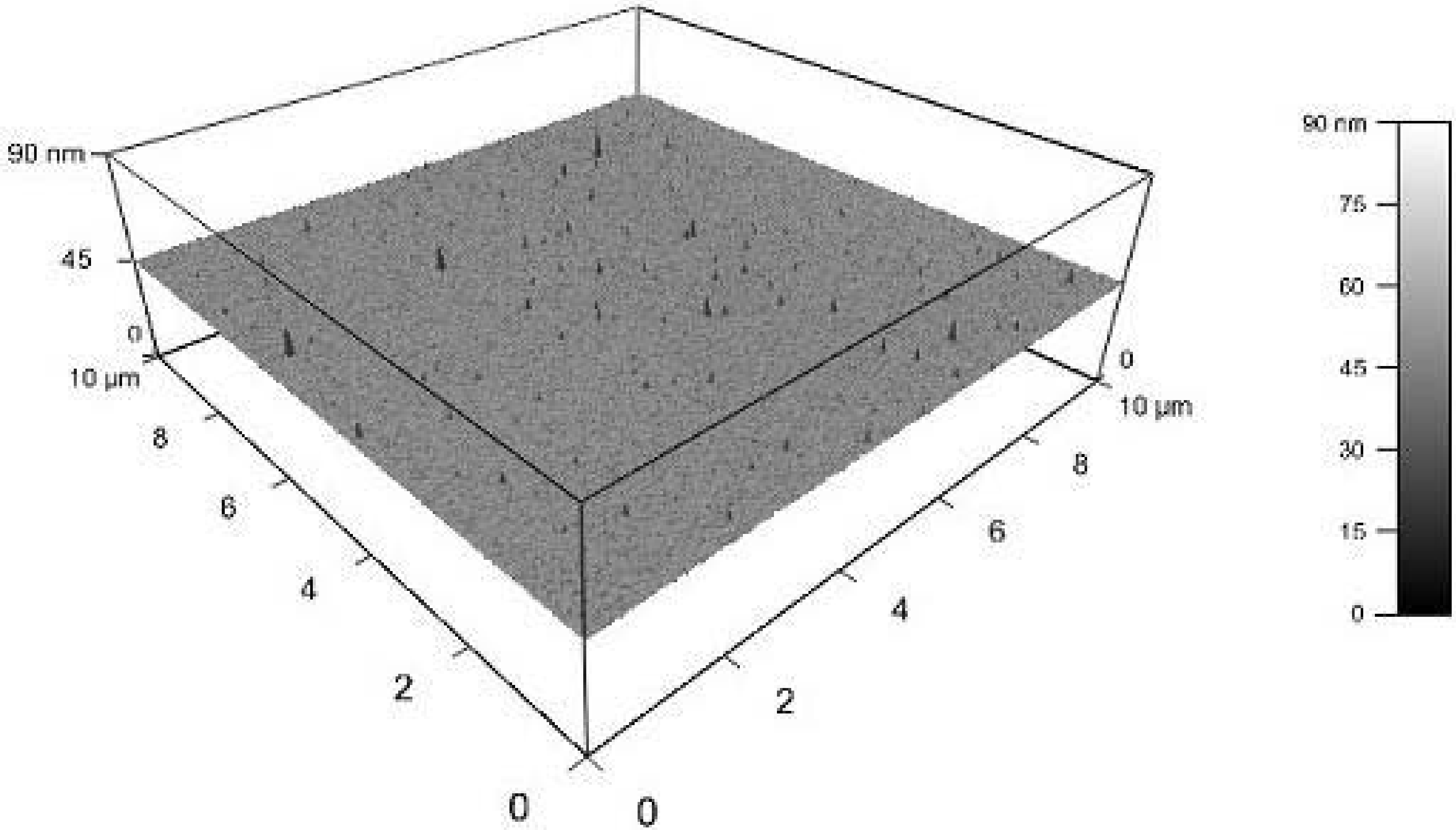
After 2 min Ar sputtering

TiO2 film – AFM scans – Ti-isopropoxide precursor

100° C/1500 cycles

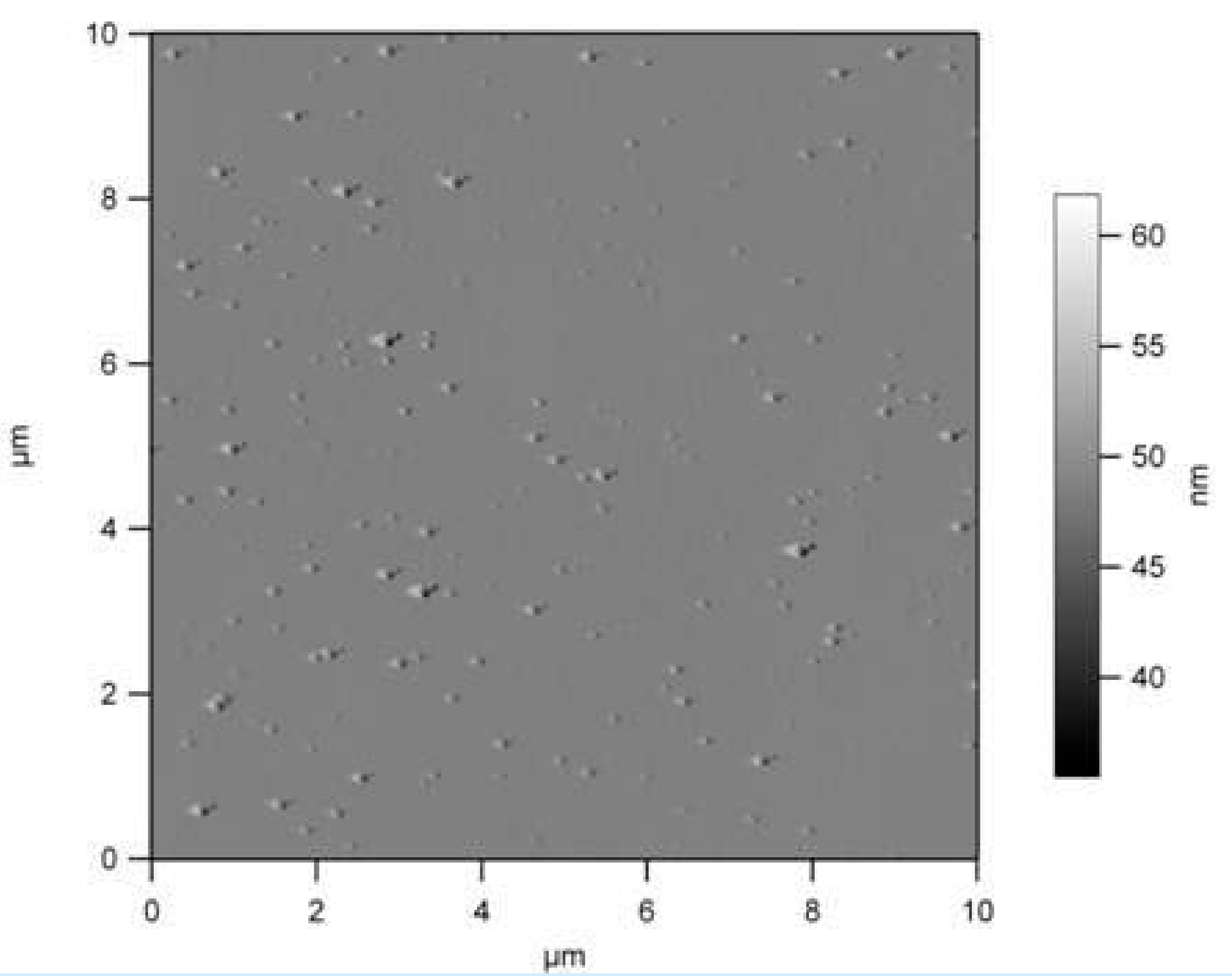


100° C/1500 cycles

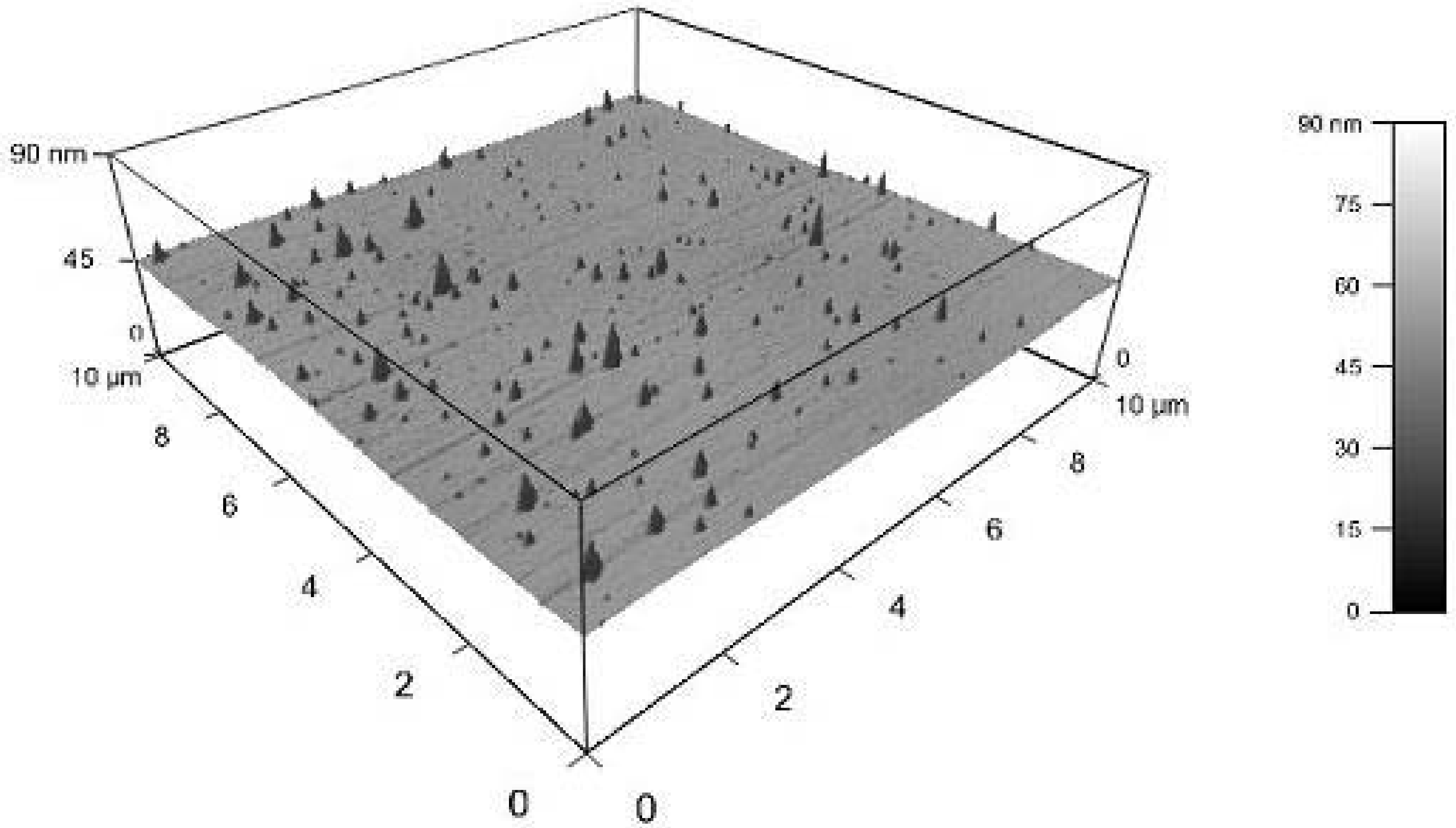


AFM scans of TiO2

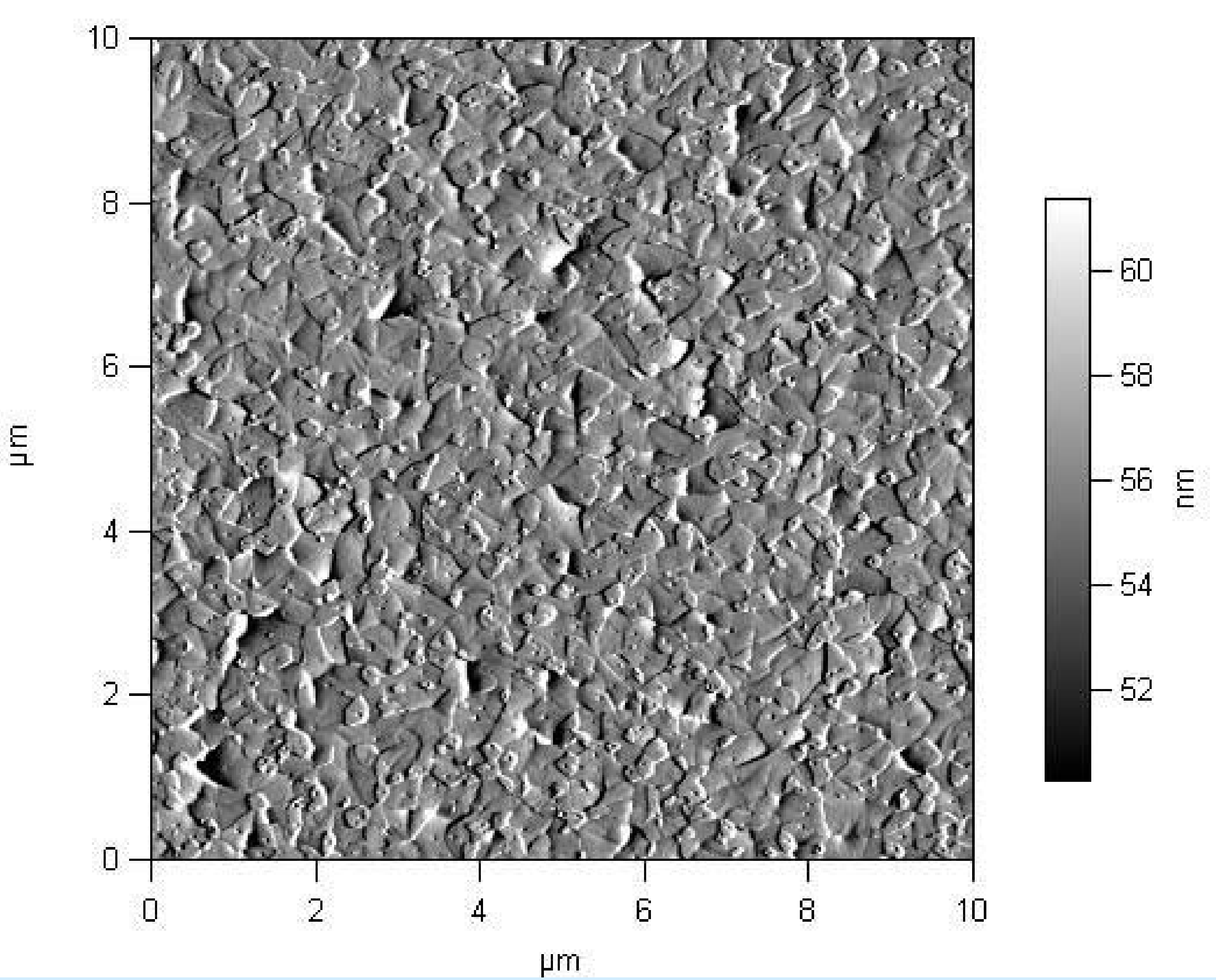
175° C/1500 cycles



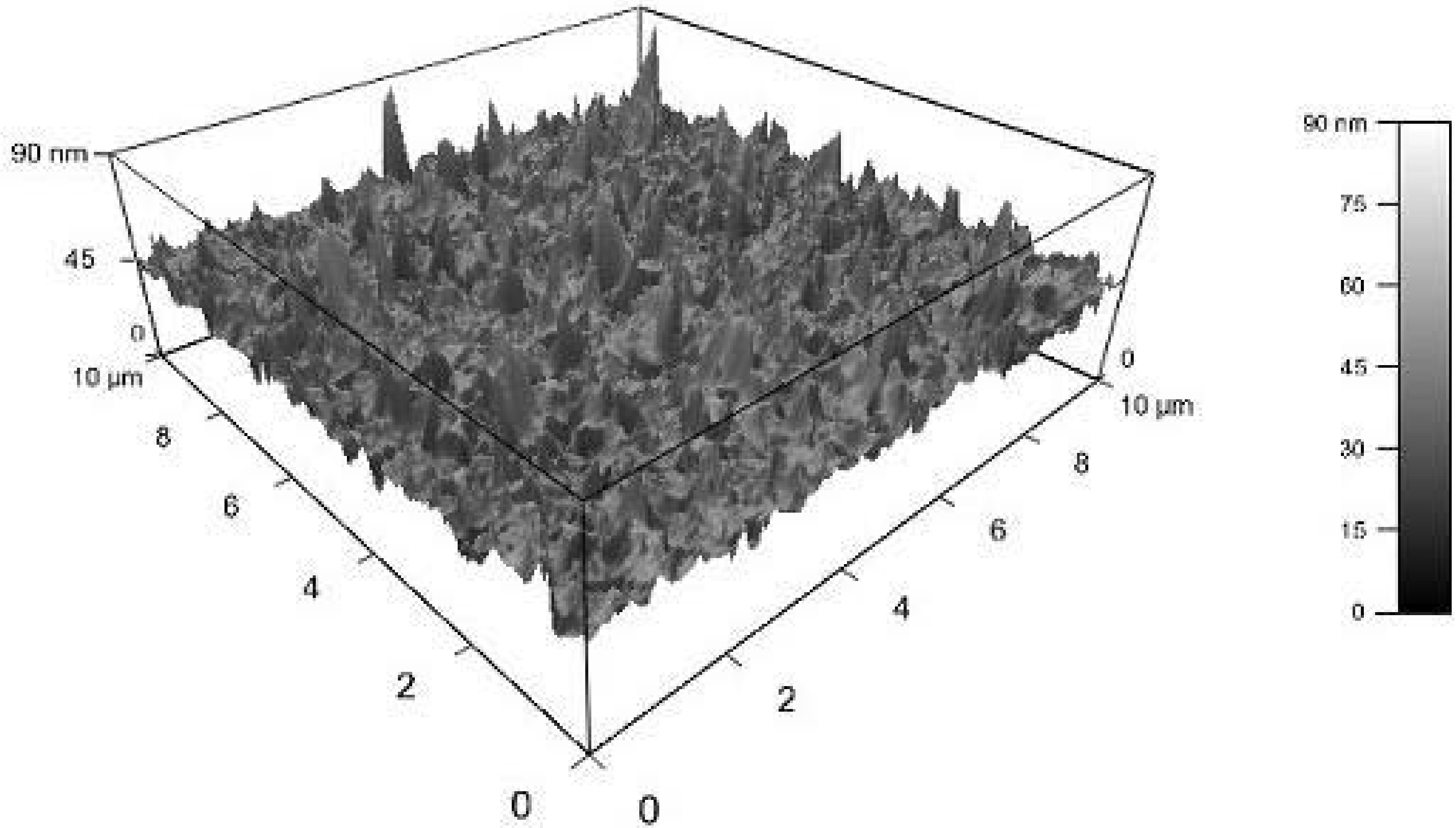
175° C/1500 cycles



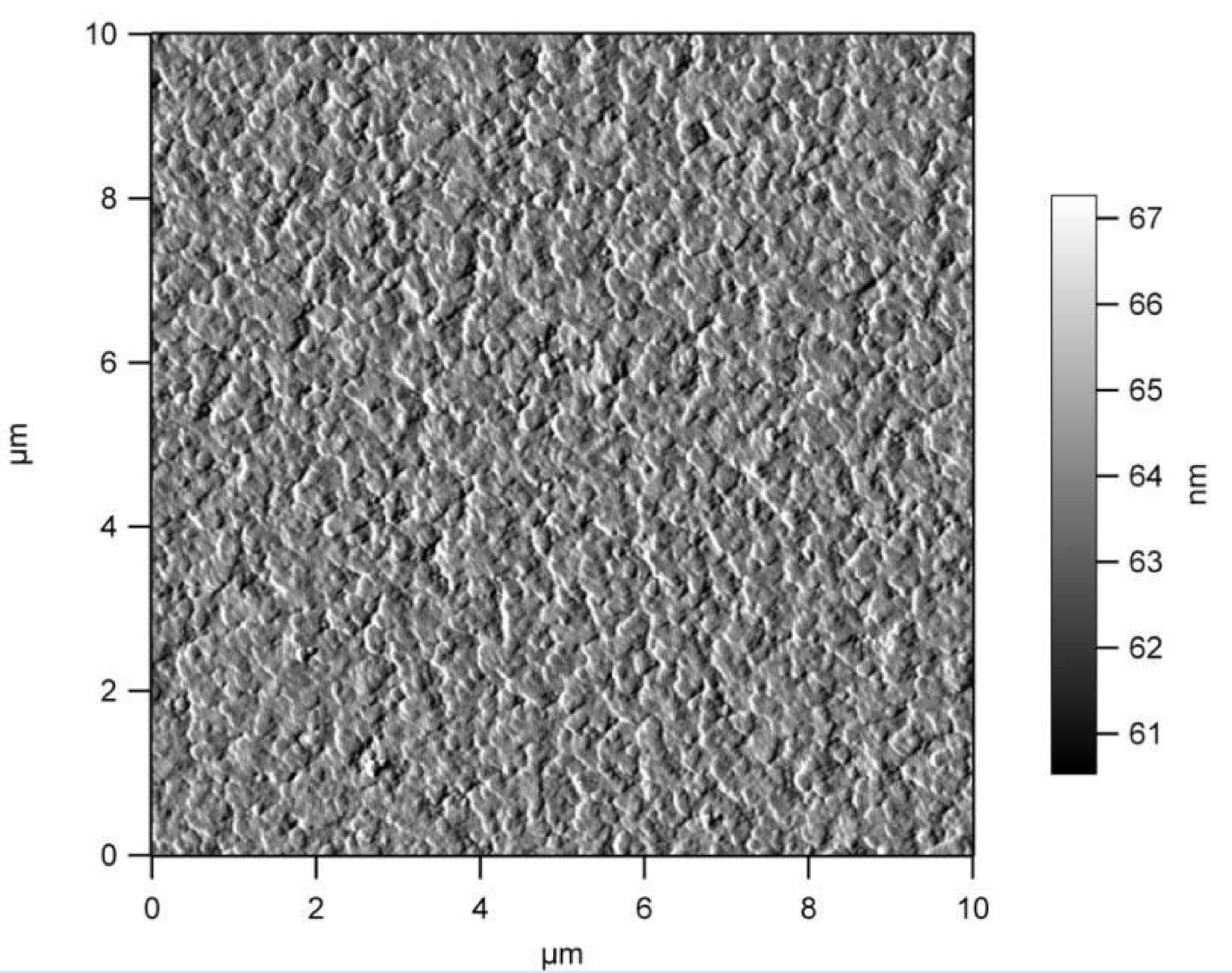
200° C/1500 cycles



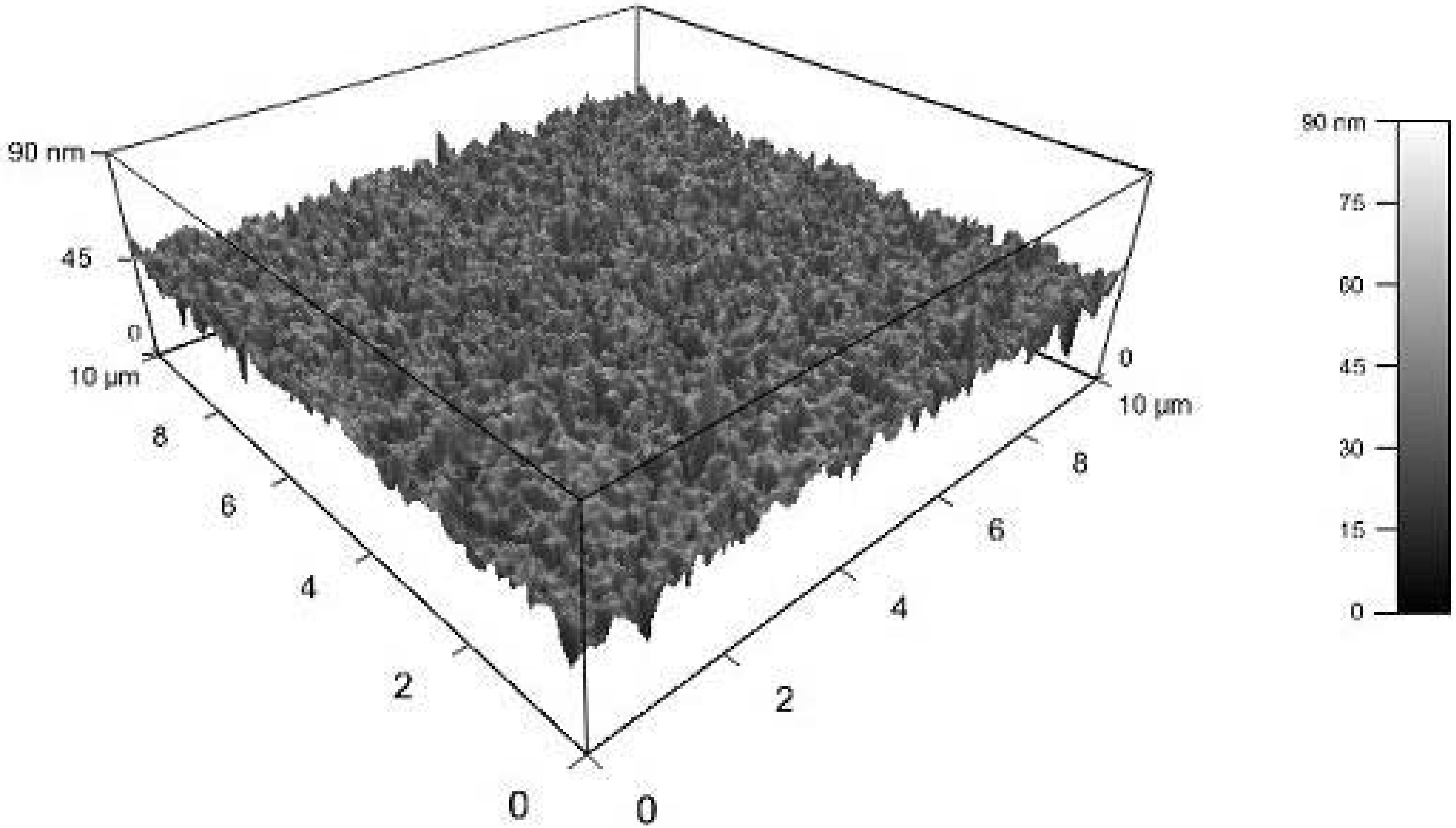
200° C/1500 cycles



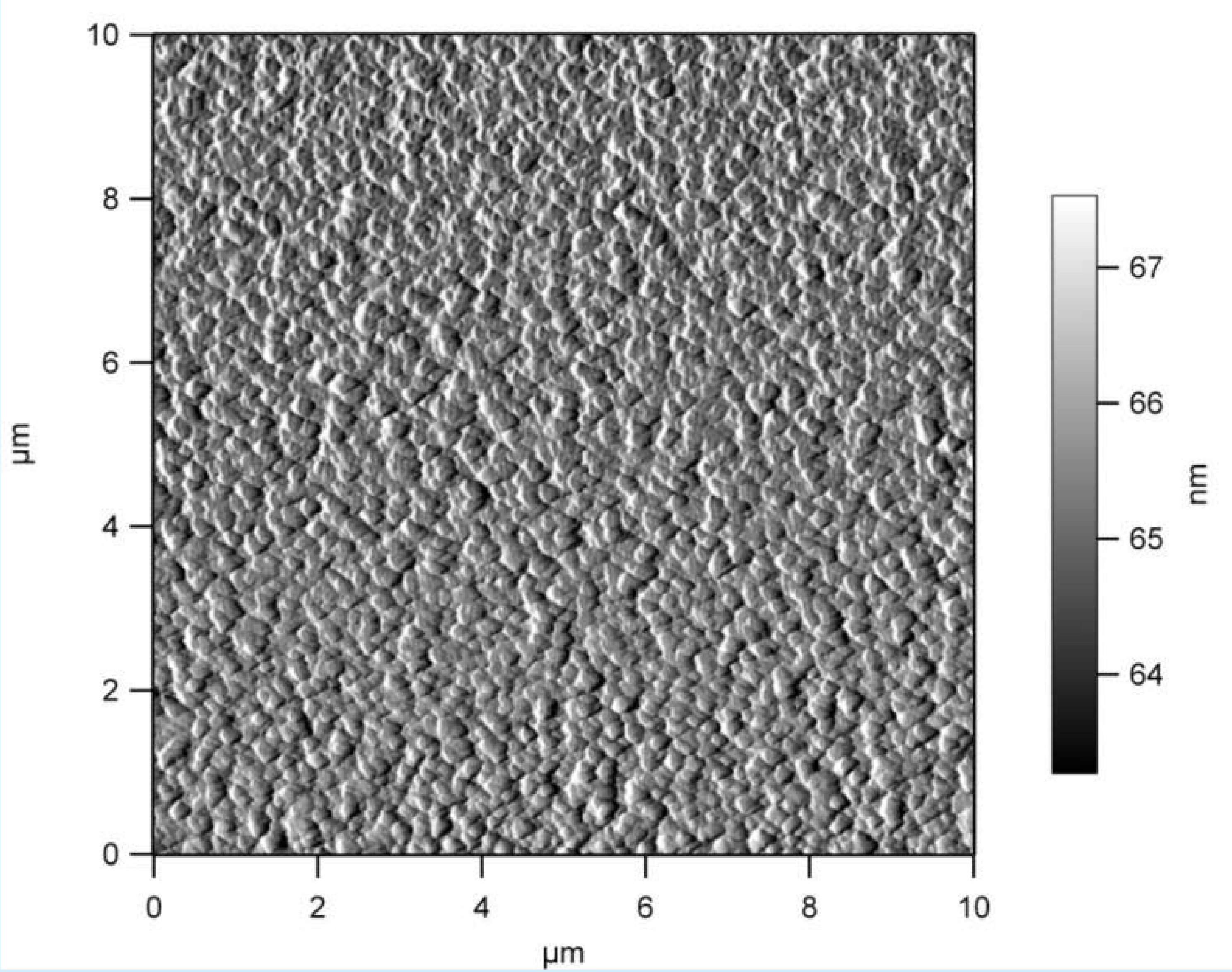
250° C/1500 cycles



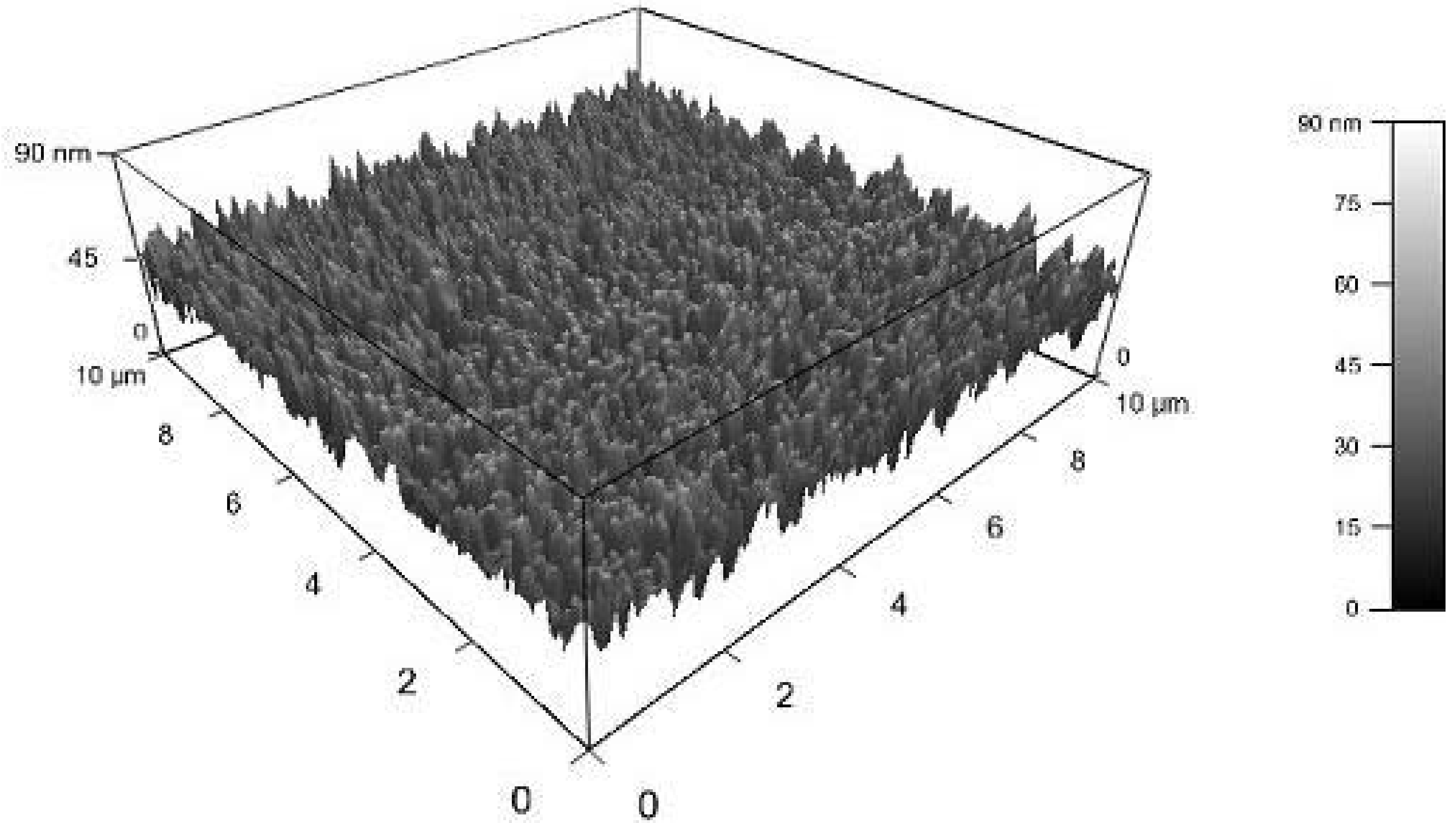
250° C/1500 cycles



300° C/1500 cycles



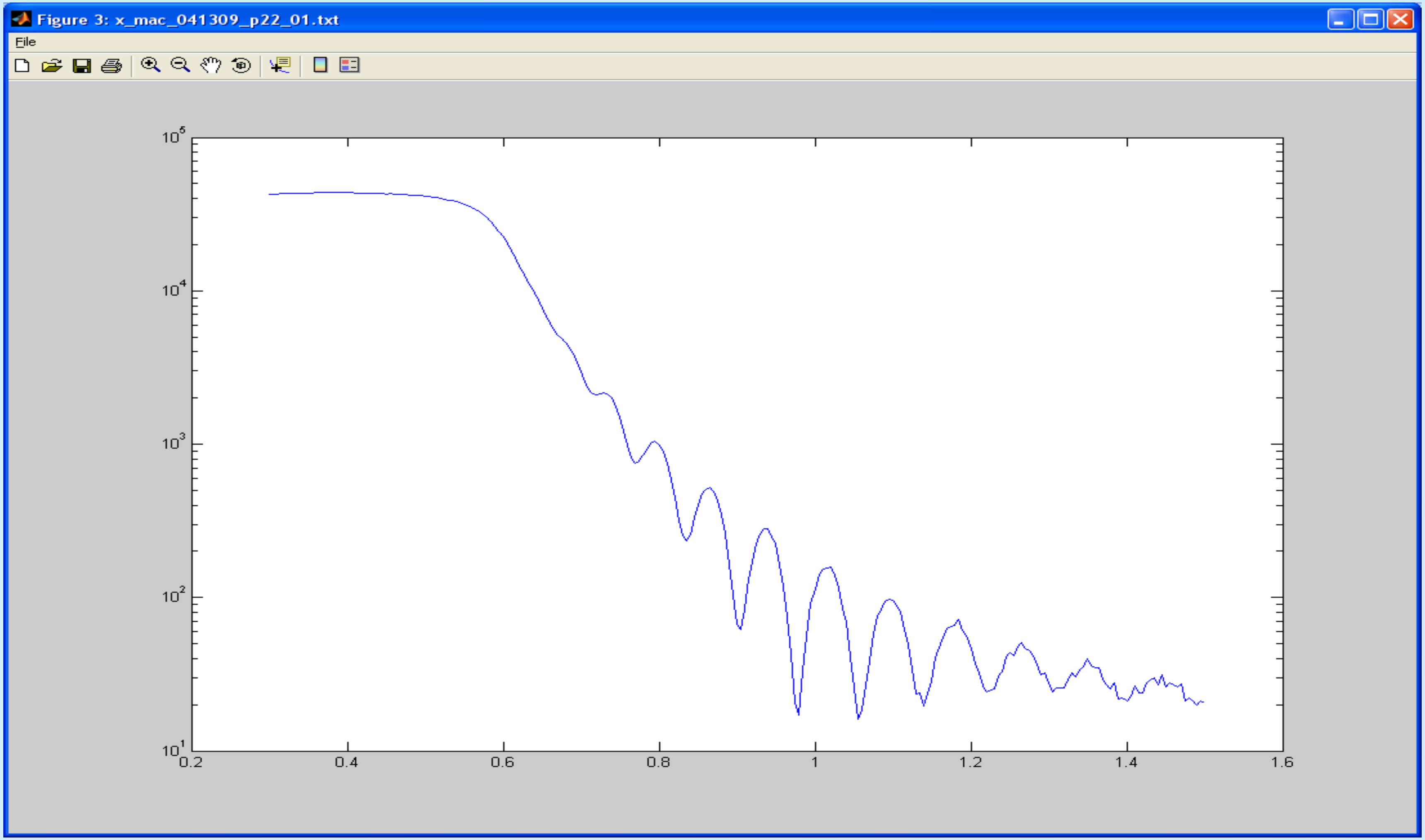
300° C/1500 cycles



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

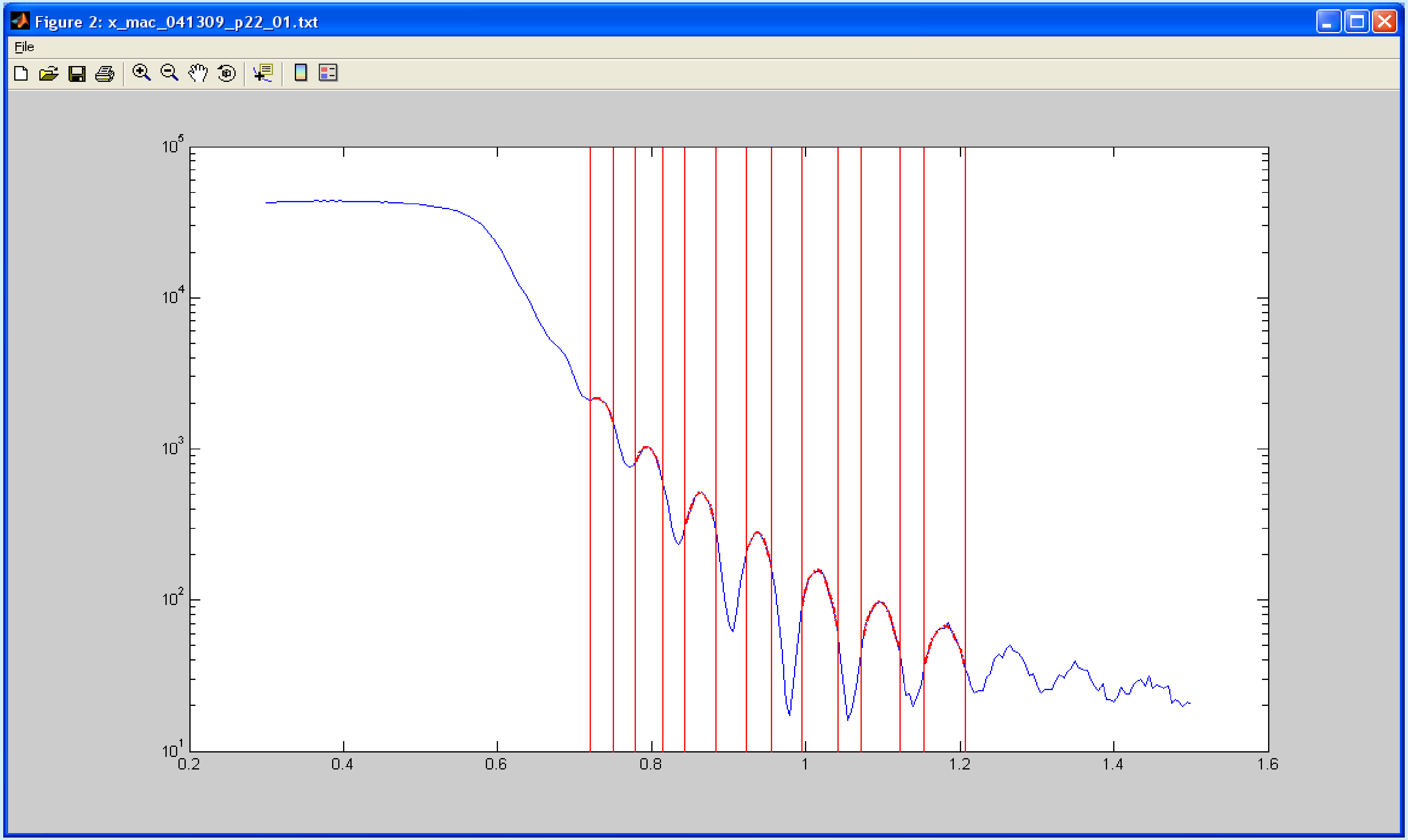
XRR trace of Pt film from Cintag XRD



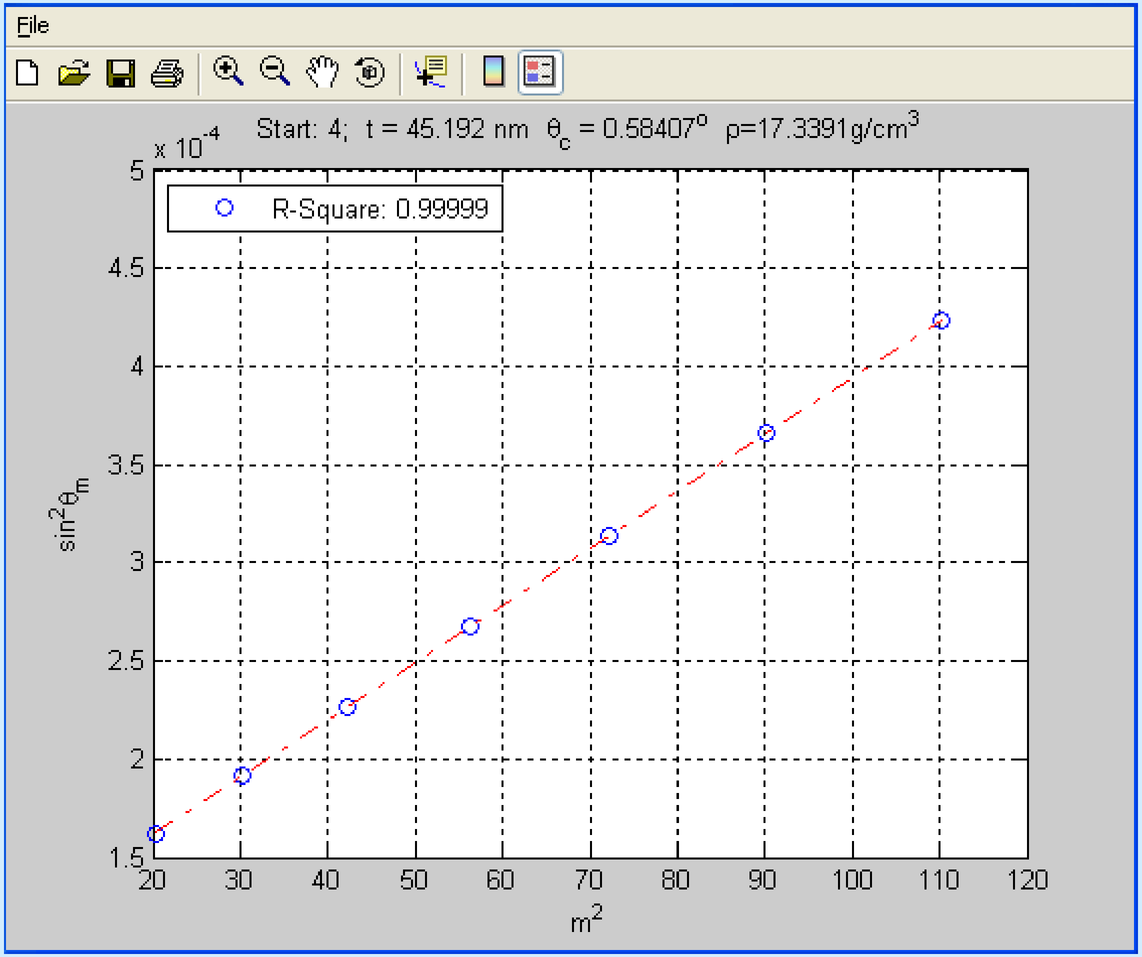
XRD expertise courtesy of Dr. Bill Croft, Harvard University

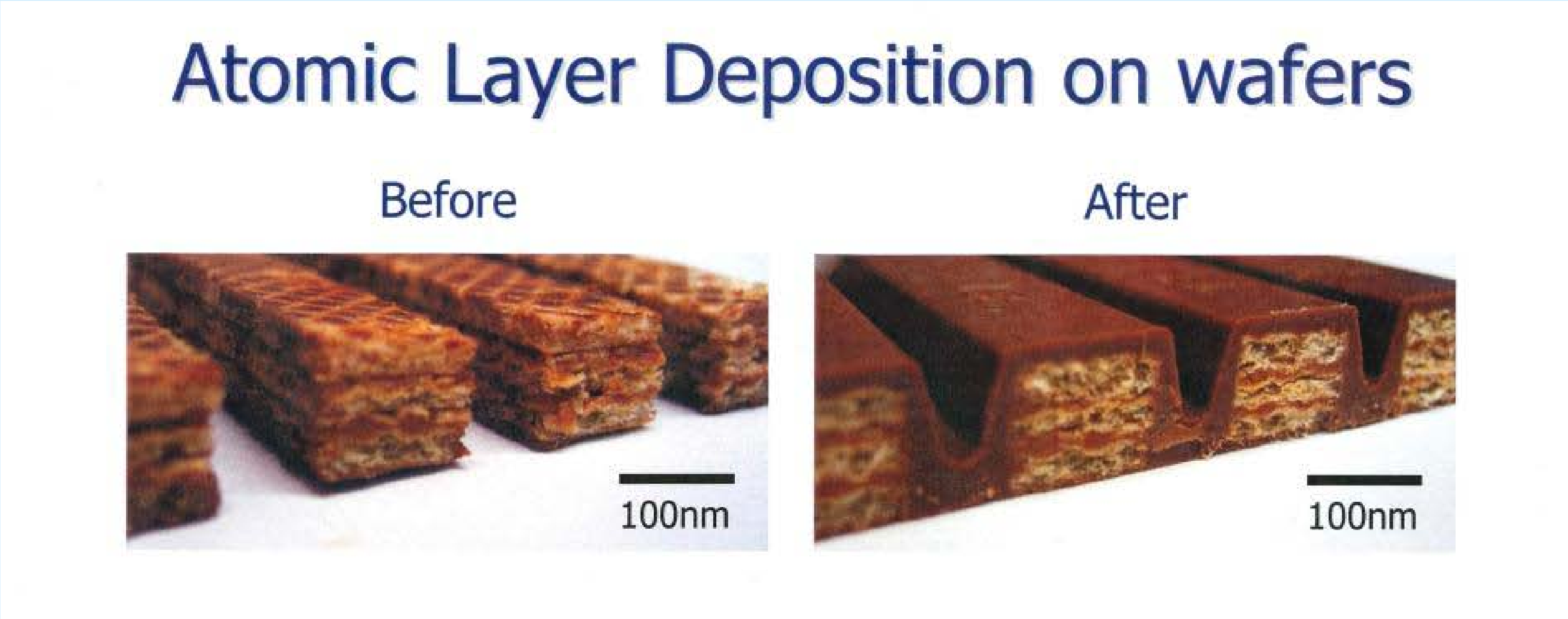
XRR analytical software courtesy of Hongtao Wang – Gordon Group – Harvard University

XRR trace – peaks selected



XRR Data – Thickness calculation

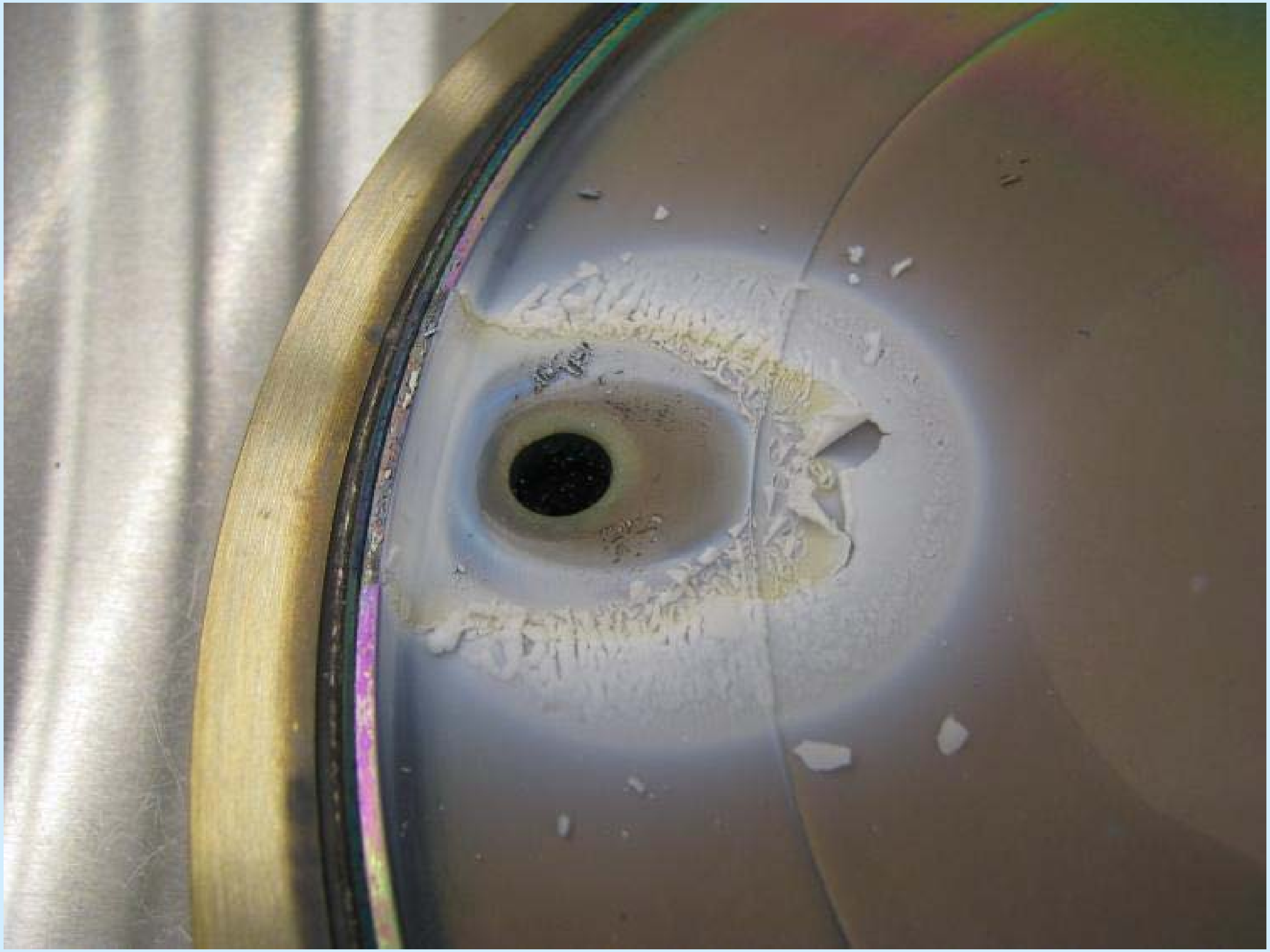




- Major issue:

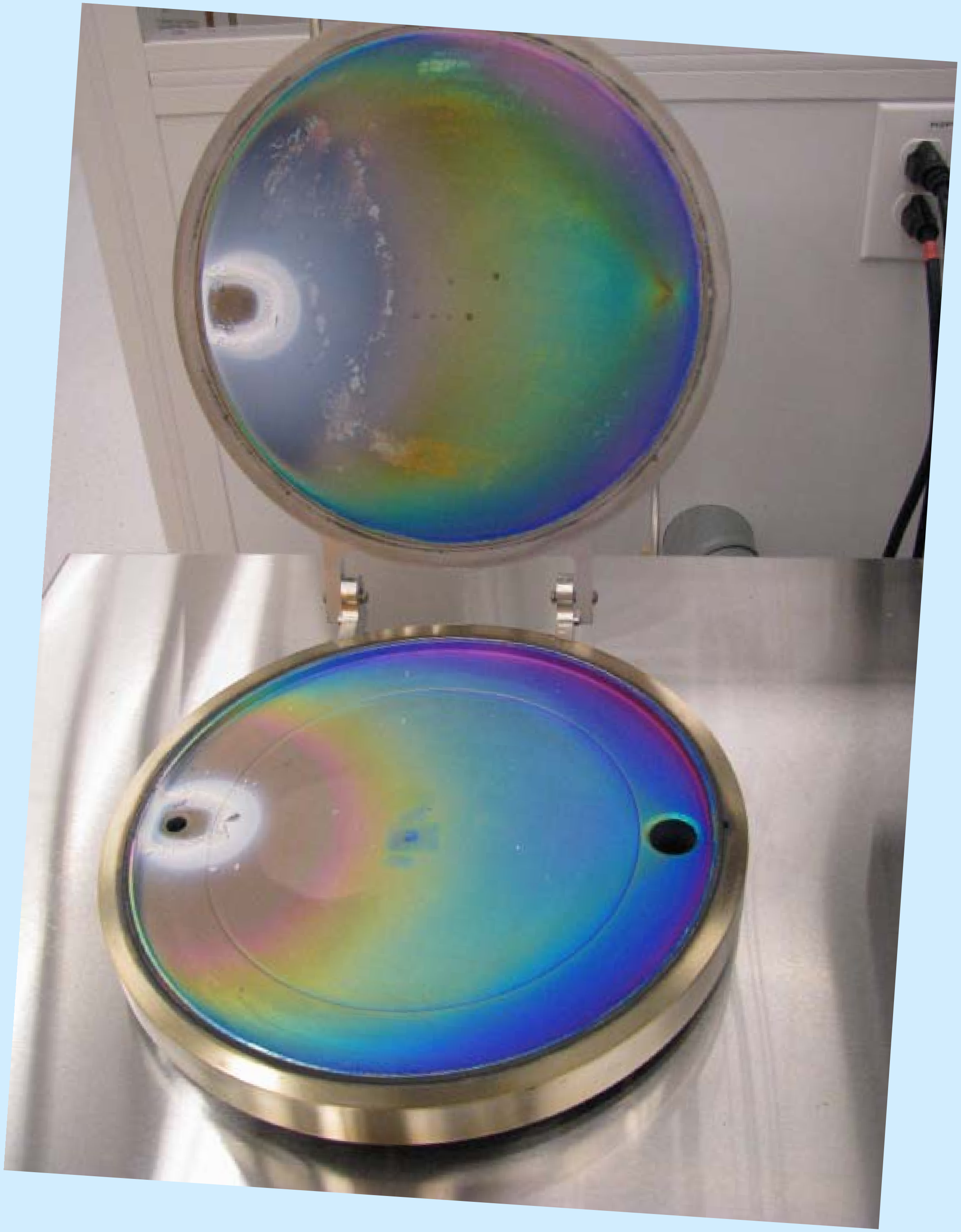
  Consumption of precursors and substrate before, during and after processing

Problems can occur.



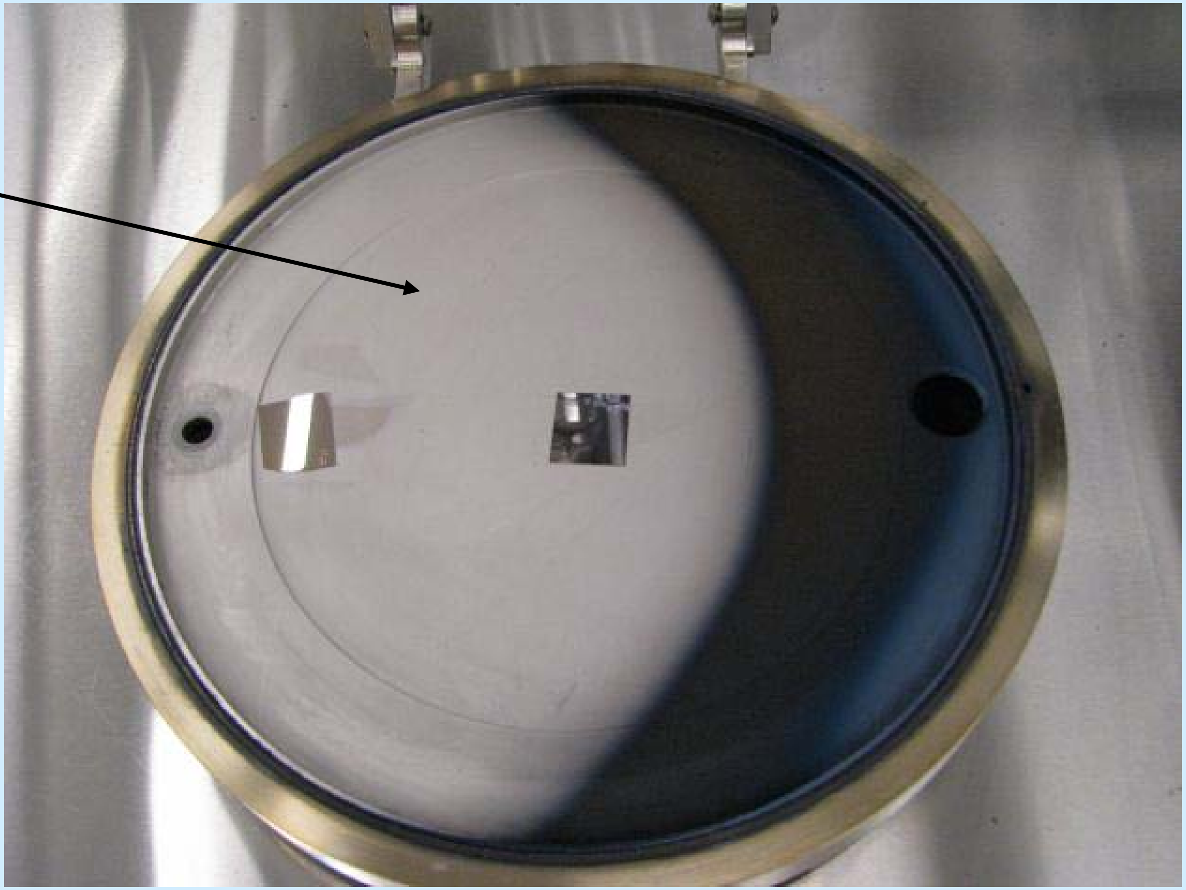
Condensation of precursor causes distinctly non-monolayer deposition

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



- "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

Potential New System?...

- Arradiance GEMStar
  - Tabletop unit
  - 8 precursor ports
  - Excellent temperature control
  - Greater flexibility
  - Specifically optimized for Pt

The GEMStar™ Benchtop ALD System

Future Directions for ALD at CNS

- Currently, our system allows for 6 precursors, limiting us to 5 materials, assuming all use H_2O.
- TiO_2 is released, and ZnO is under test.
- A second machine will allow us to provide **greater access** to our standard oxide offerings, more metal and nitride options, and allow us to explore metal deposition in greater depth, including better process characterization of Pt, Cu, CoN, and others.
- **Structures of interest** - Pt-coated nano-structured materials for higher efficiency electrode materials, nano-structured materials for use as nanowire templates.
- **Films of Interest** – Pt, Cu, “pure” ALD-SiO_2,TiO_2, ZnO, CoN, $SrTiO_3$, diamond-like films, *selective Pt, selective Cu?...*

Acknowledgements

- J.D.Deng - Raman, Hou Yu Lin - XPS, Jason Tresback - AFM
- Prof. Roy Gordon, Harvard University ALD-meister, for his ground-breaking work in ALD precursor synthesis and process development, and the kindly use of some of his slides.
- Cambridge Nanotech (Jill Becker, Ganesh Sundarum, Eric Deguns, et al.), makers of the Savannah 200, for their copious technical help, and handsome molecular graphics.
- Dr. Bill Croft – keeper of the Cintag XRD system, for his assistance with XRR technology.
- Hongtao Wang, recently graduated from Harvard University (Gordon group), for his help with Pt film characterization.
- Boaz Pokroy, recently of Harvard University (Aizenberg group), for samples.
- Omair Saadat, MIT, for film characterization data.