Controlled Synthesis of 3D Nanostructures using Proximity-Field Nanopatterning Lithography and Graded Temperature ALD

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Outline

What is Proximity-field nanoPatterning (PnP)?

- Creating 3D structures in SU8® photopolymer
- Phase mask geometry and resulting 3D structure
- ALD coating of nanostructures and different SU8®

The Temperature Effect on 3D Polymer Nanostructures

- Optical methods for observing temperature stability
- ALD using *graded* and *constant* temperature

Quartz Crystal Microbalance Results

- Nucleation and growth of Al_2O_3 on SU8® photopolymer
- QCM results from ALD on 3D nanostructures

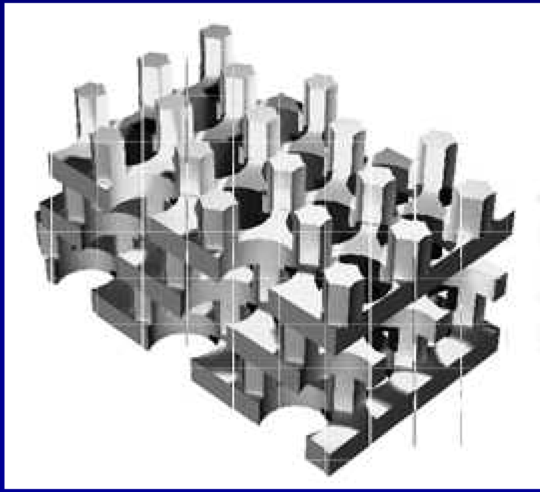
Example Depositions and Conclusions

Periodic Three Dimensional Nanostructures

Present Methods

- e-beam lithography
- interference lithography
- Opal self-assembly

➢ Resulting in: costly, slow poor yield, & limited geometries



photonic lattice[1]

Applications

- photonic lattices
- catalyst supports
- micro electrodes
- filtration membranes
- metamaterials

Needed

- Fast, cheap, simple equipment
- Large areas (long range order)
- Predictive / control
- High yield

[1] *Yablonovitch, Gmitter, Leung, Phys. Rev. Lett. 67 2295 (1991)*

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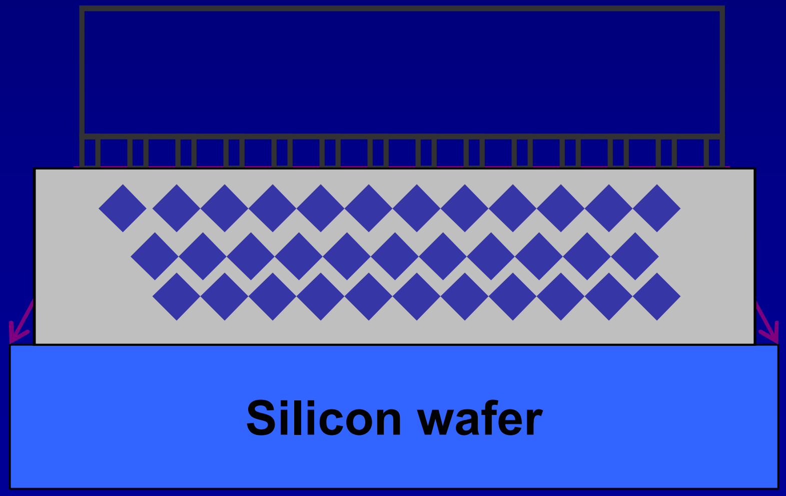
Proximity-field Nanopatterning (PnP)[2]

The PnP Process:

1. Spincoat SU8® photopolymer
2. Apply phase mask
3. Expose sample with λ = 365 nm
4. Develop out monomer

® MicroChem Corp

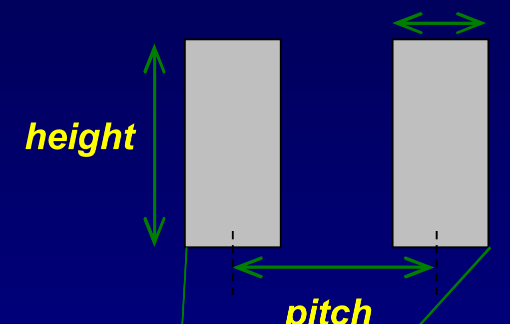


- SU8® has particular pre/ post bake and spin conditions
- Role of phase mask is important
- Exposure time is critical
- SU8® is a negative photo resist

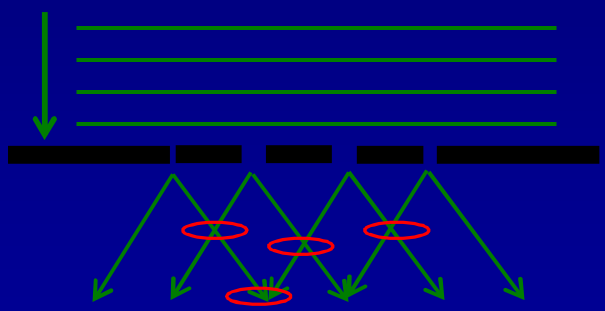
[2]*Invented by John A. Rogers, UIUC PNAS* ***101*** *12428 (2004)*

Phase Mask Geometry Controls Resultant Nanostructure Shape

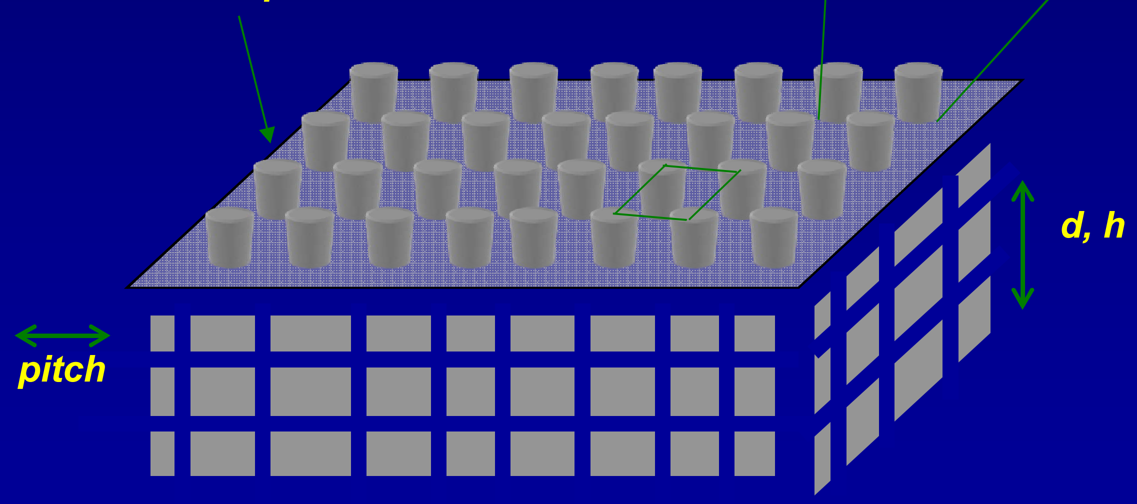
- The geometry of the phase mask is transferred to the photo polymer[3]
- Post *height*, *diameter* and *pitch* are key parameters
- Control the periodicity and “wall” thickness of resulting structure



Two slit diffraction



constructive interference create localized volumes of cross linking



PDMS = polydimethylsiloxane

[3]*Su, El-Kady, Reda Taha, Christodoulou, PFNA,* ***121*** *1 (2007)*

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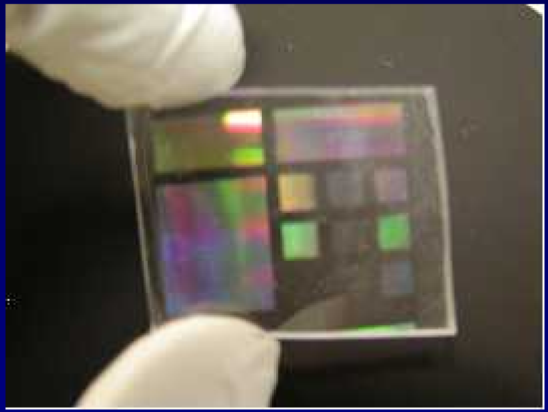
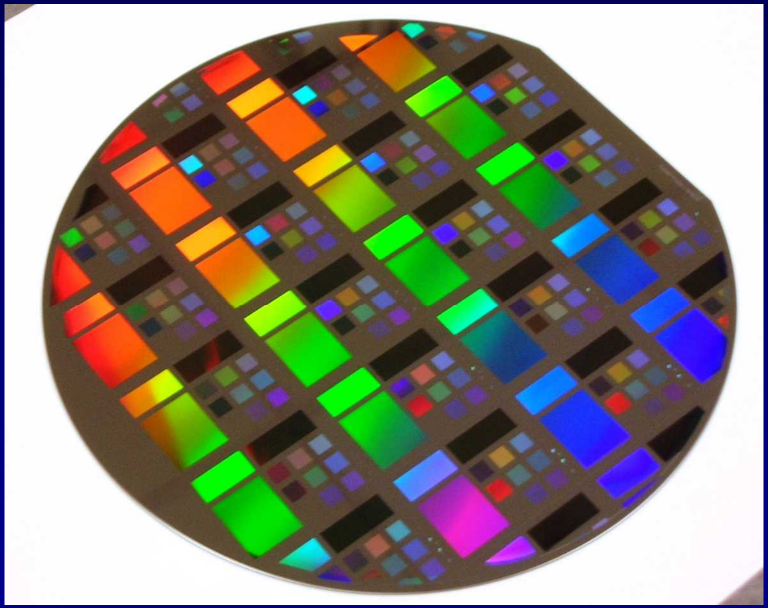
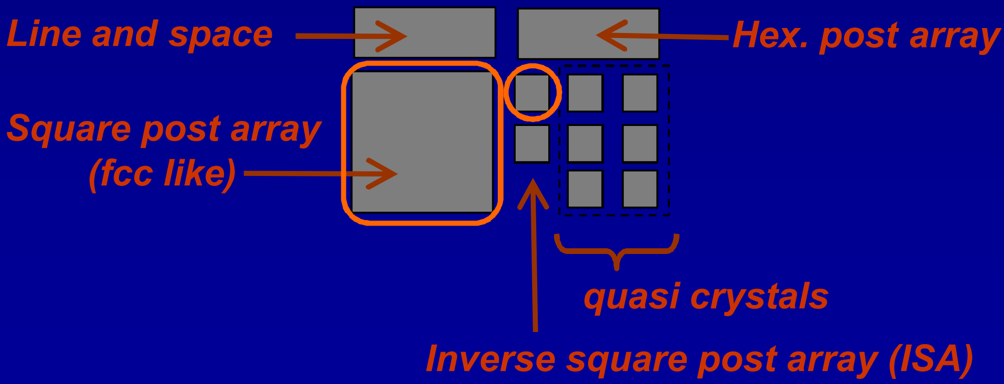
Phase Mask Produces a Variety of Structures Across Six Inch Wafers

PDMS phase mask



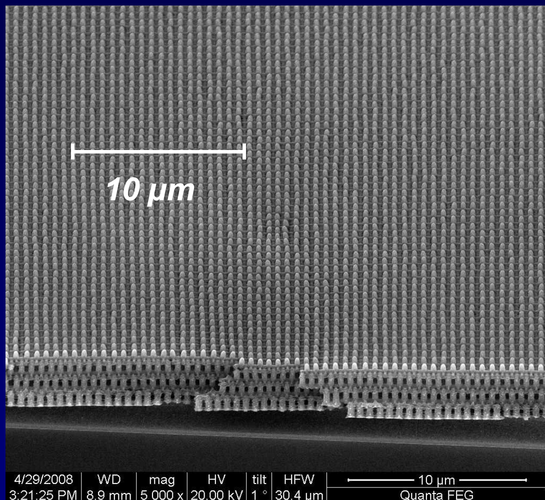
6 inch wafer of PnP nanostructures





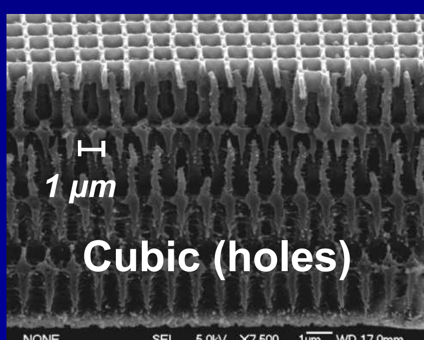
- **Focus on two PnP structures: *"fcc like"* and *ISA.***

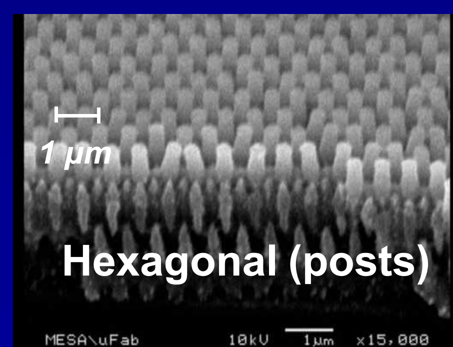
SEM Images of Various PnP Structures

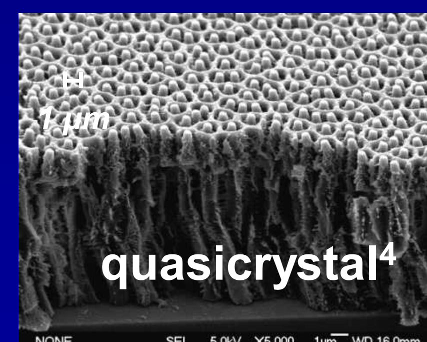


- **Thicknesses up to ~ 30-50 µm obtained**
- **Construction is problematic:**
  surface roughness, light exposure, collimation, solvent bake process, etc.
- **Versatile technique for nanostructure synthesis!**

Nanostructure examples:







[4]*Shir et al. J. Phys. Chem. B* ***111*** *12945 (2007)*

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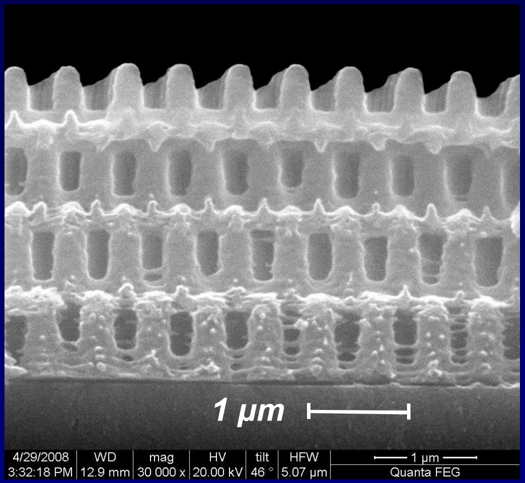
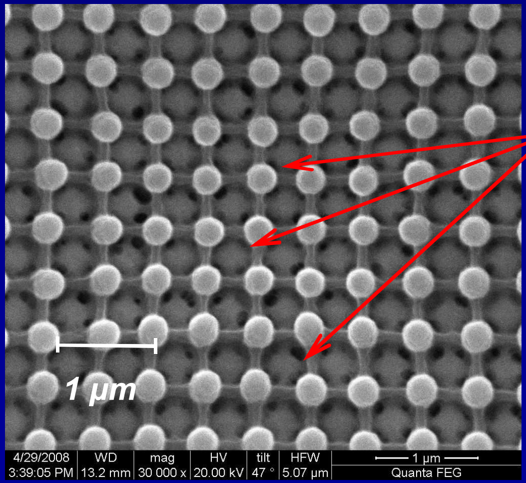
PnP "fcc like" Nanostructure Geometry

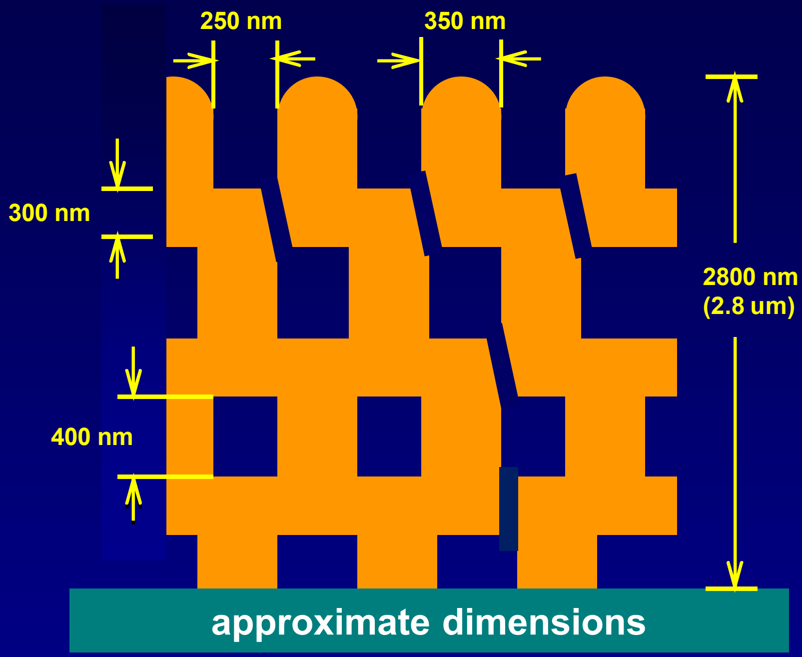
Side view



Top down



~ 150 nm diameter holes

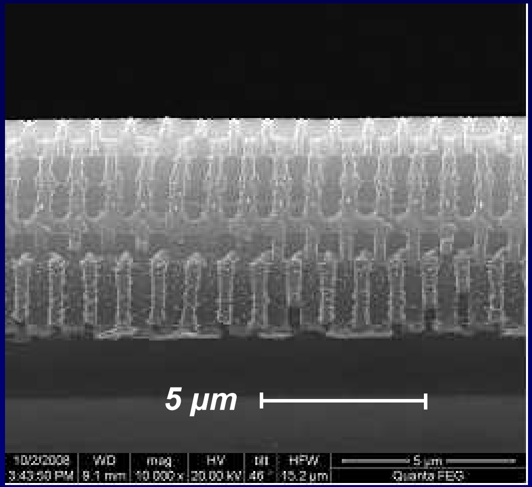


"fcc like"

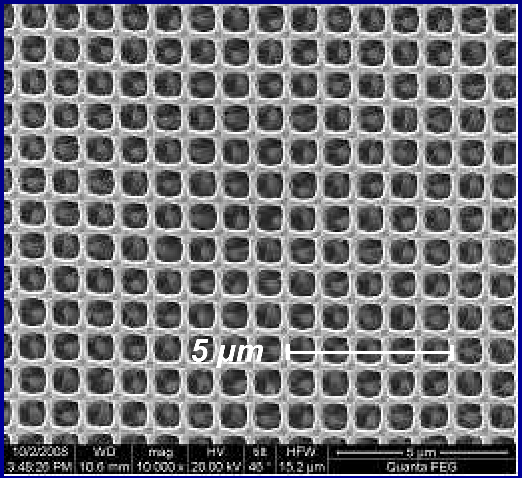
- Phase mask: D = 400nm, P = 550nm (square post array)
- Aspect ratio L/d ~ 200
- Torturous reactant path

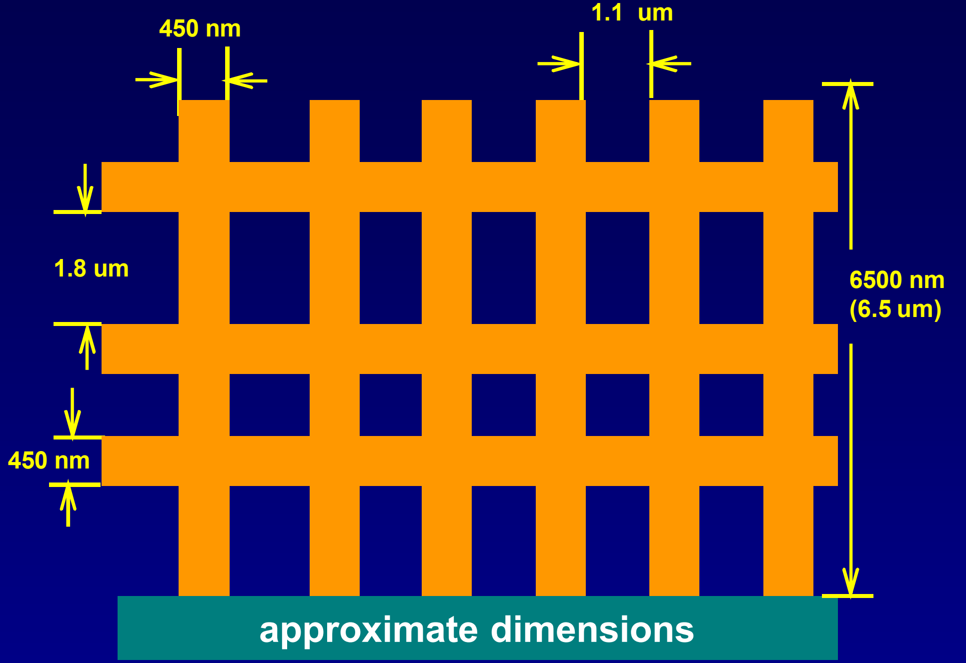
PnP Inverse Square Array (ISA) Nanostructure Geometry

Side view



Top down





"cubic like"

- **Phase mask: D = 800nm, P = 1000nm (inverse square array)**
- **Aspect ratio L/d ~ 10**
- **"Via" type reactant path**

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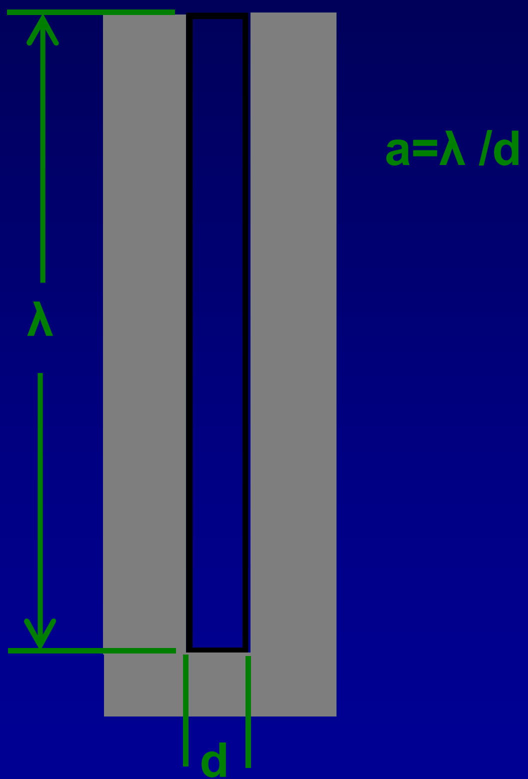
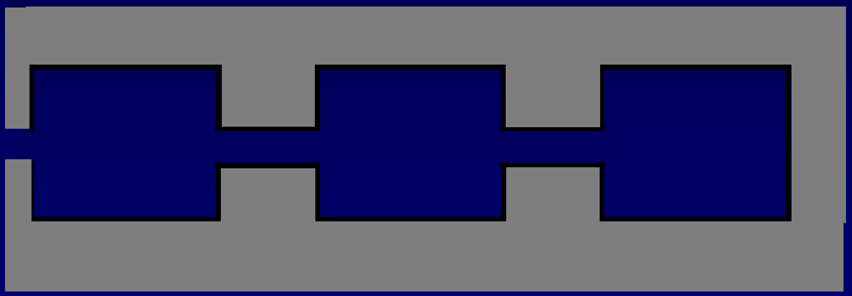
Calculating Exposure Needed to Coat Nanostructures

"via" type structure





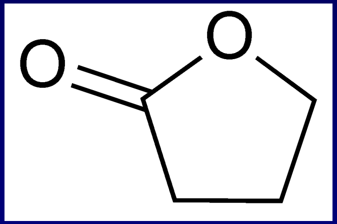
Put equation here….

$$(Pt)_{total} = S\sqrt{2\pi mkT}\left[1 + (19/4)a + (3/2)a^2\right]$$

[5]*Gordon, Hausermann, Kim, Shepard, CVD, **9** 73 (2003)*

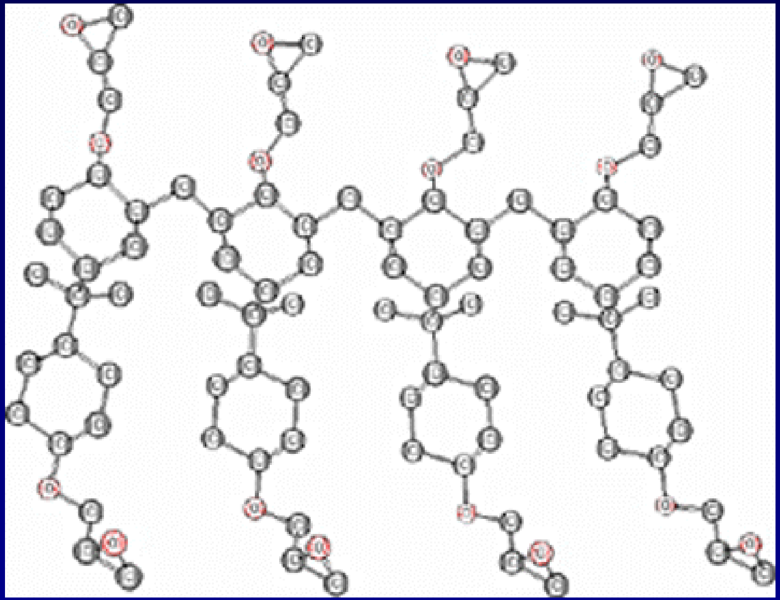
SU8® Photopolymer Has Different Solvents

Traditional SU8®

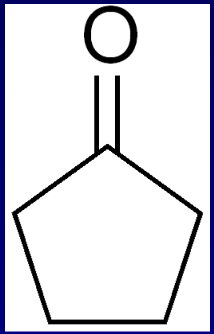


γ-butyrolactone
boiling point = 204 °C

SU8® SUPER MOLECULE



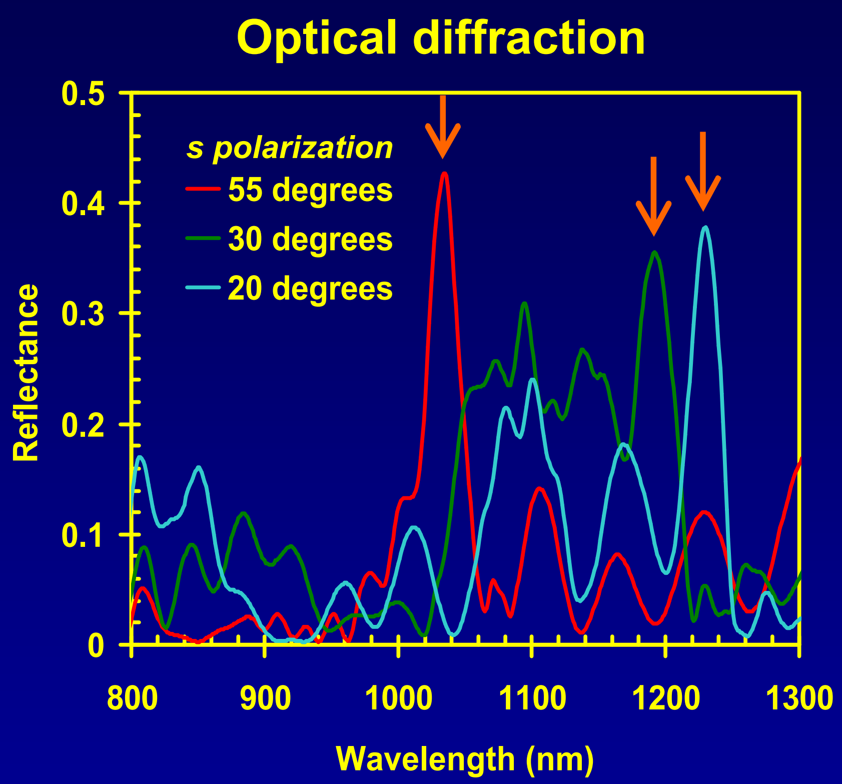
2000 Series SU8®

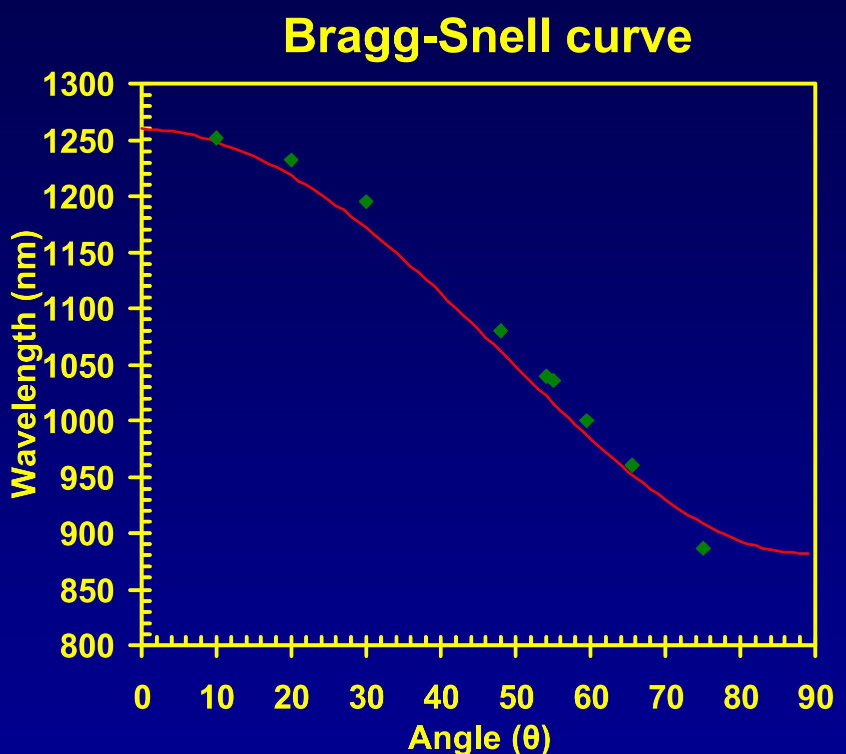


cyclohexanone
boiling point = 130 °C

- SU8® super molecule has eight epoxide groups
- Uses photo-acid to initiate polymerization (365 nm)
- Solvent has profound effect on thermal stability

Optical Diffraction Observed on "fcc like" PnP Nanostructure





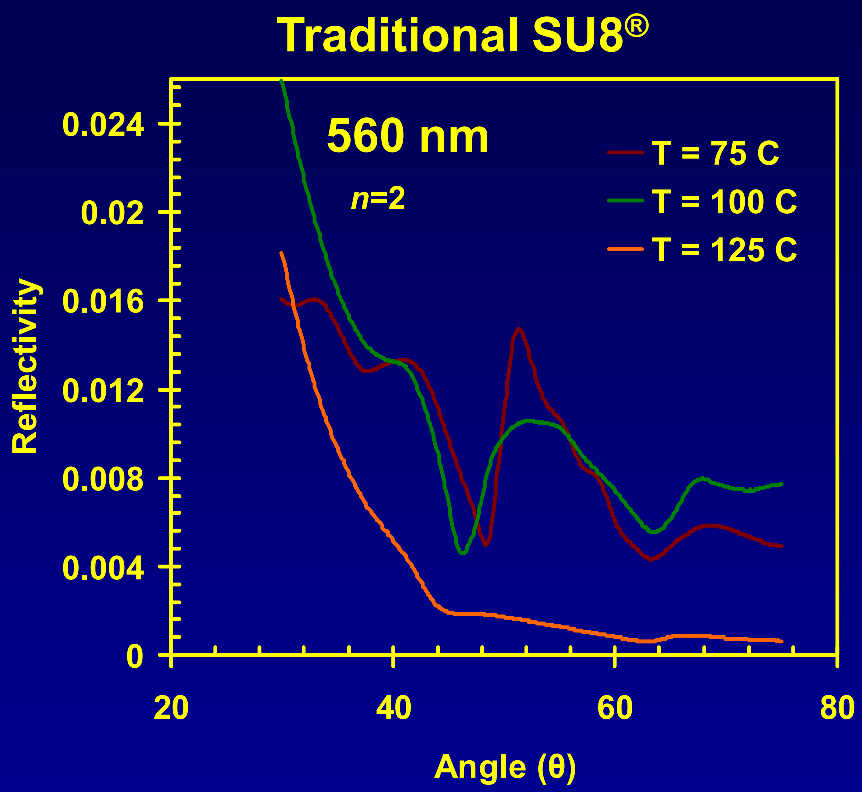
- **Diffraction fits the Bragg-Snell law[6]**
- **d = 470 nm, n_{eff} = 1.37**

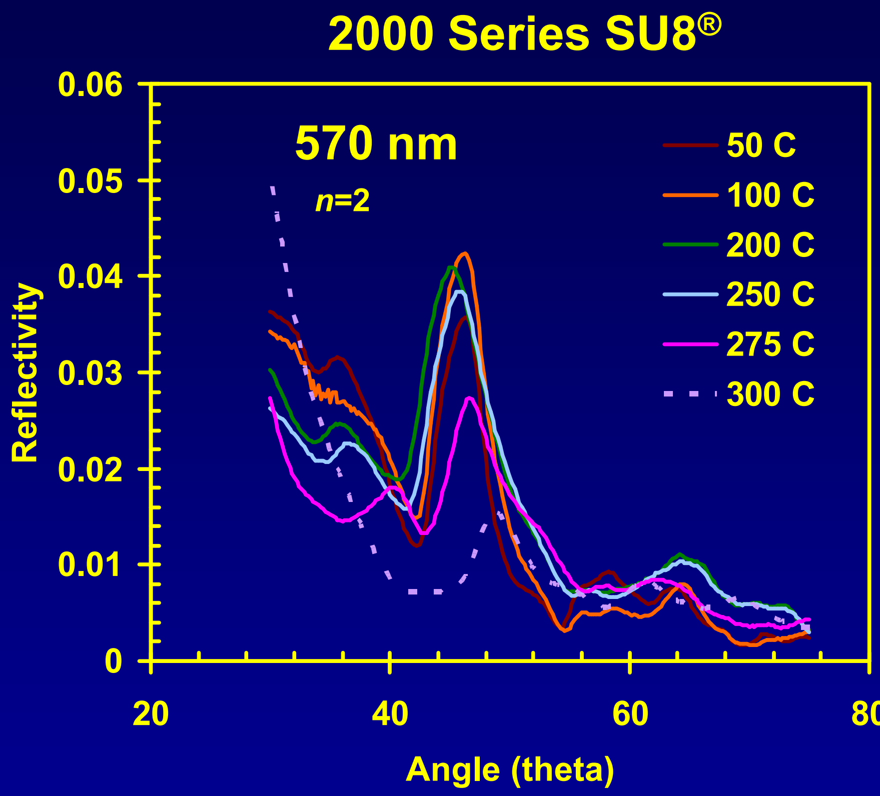
Bragg-Snell equation

$$n\lambda = 2d\sqrt{n_{eff}^2 - \sin^2\theta}$$

[6]*Lopez, Vazquez, etal., Superlattices Microstruct.* **22** *399 (1997)*

Optical Diffraction Monitors Thermal Stability

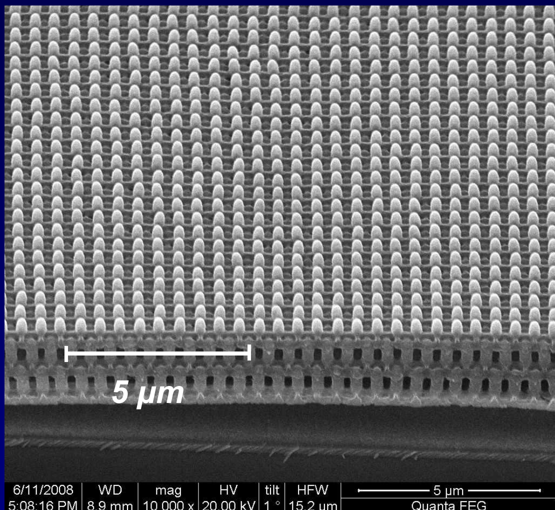




- Used variable angle spectroscopic ellipsometer (VASE) with hot stage.
- Dramatic differences in thermal stability!

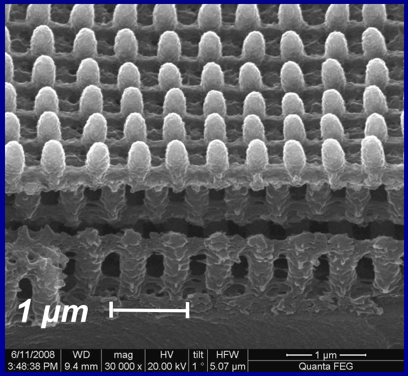
Temp Stability of PnP Using Traditional SU8®

"fcc like" array test structure

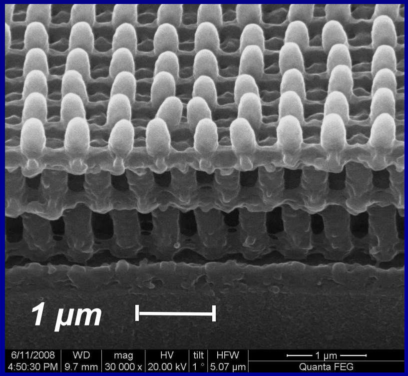


- **Compared cleaved edges from same structure**
- **Heated under ALD reactor conditions**
- **By 125 °C structure shows signs of collapse**
- **ALD has to be performed at reduced temperature**

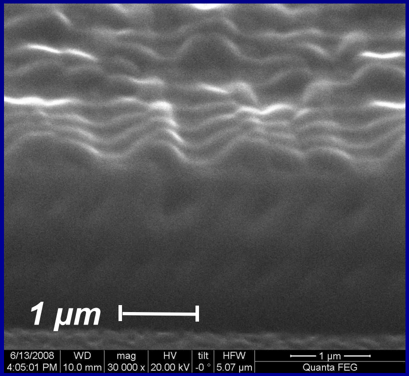
No thermal treatment



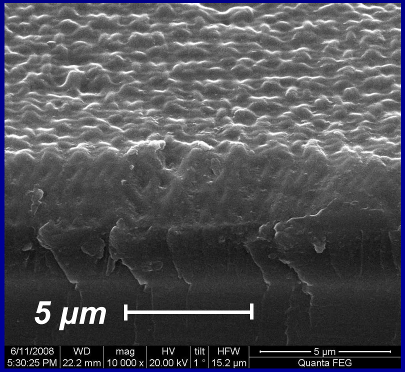
85 °C for 24 hours



125 °C for 25 hours



200 °C for 64 hours



~ 200 Å Au/Pt Plasma sputtered on to non-conducting substrates

NNSA National Nuclear Security Administration

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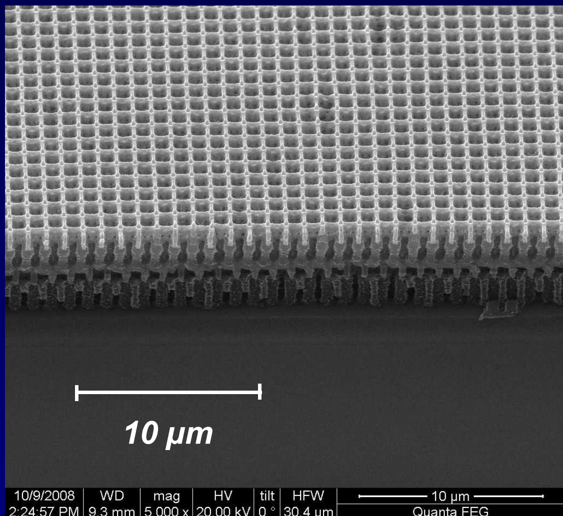
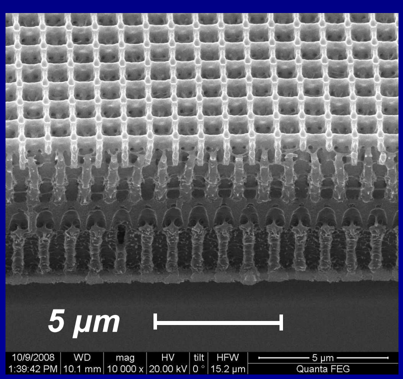
Temp. Stability of PnP Using 2000 Series SU8®

ISA array test structure

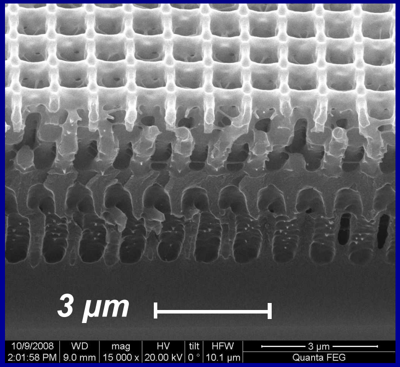


- Compared cleaved edges from same structure
- Heated under ALD reactor conditions
- At 300 °C structure shows no signs of collapse
- ALD can be performed at high temperatures!

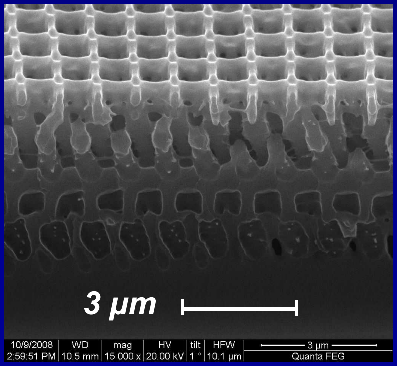
150 °C for 20 hours



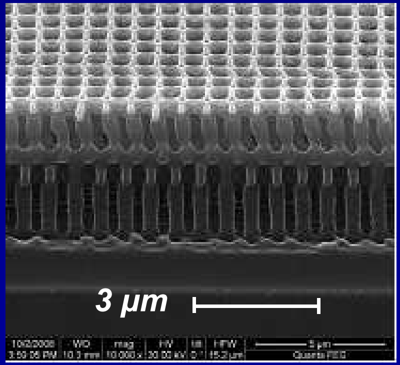
200 °C for 18 hours



250 °C for 12 hours



300 °C for 17 hours



250 C

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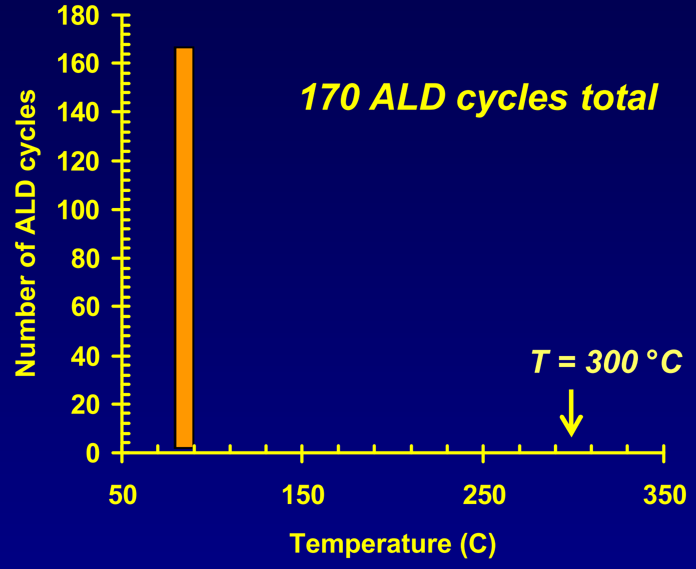
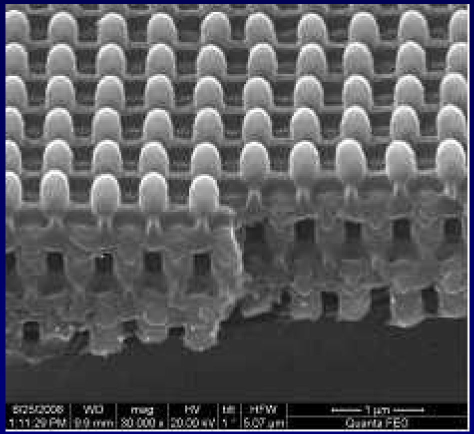
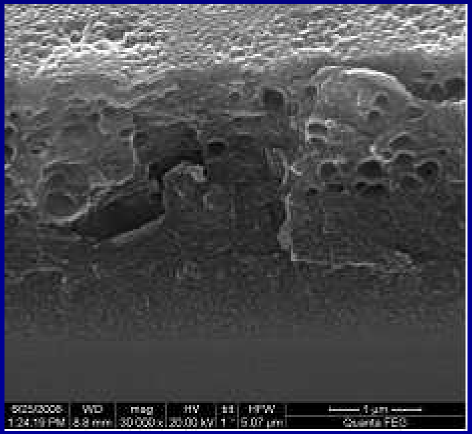
Temp. Stability on Structures Using Traditional SU8®, T = 85 °C



Before ALD



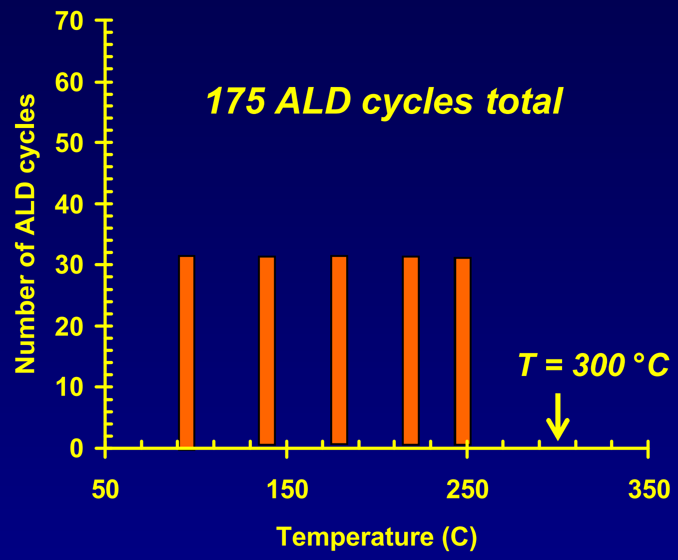
After ALD & anneal



- Run 170 ALD cycles of Al_2O_3 at 85 °C[7]
- All cycles 2.5s pulse, 35s purge, TMA, H_2O
- Heated nanostructure to 300 °C (6 °C/min)
- Observed some partial collapse

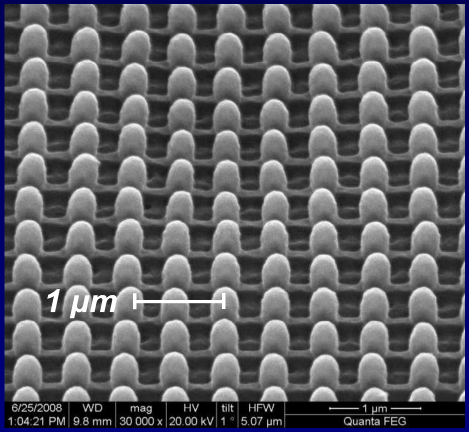
[7]*Groner, Fabreguette, Elam, George, Chem. Mater.* ***16*** *639 (2004)*

Graded Temperature Constant ALD Cycles Using Traditional SU8® Photopolymer

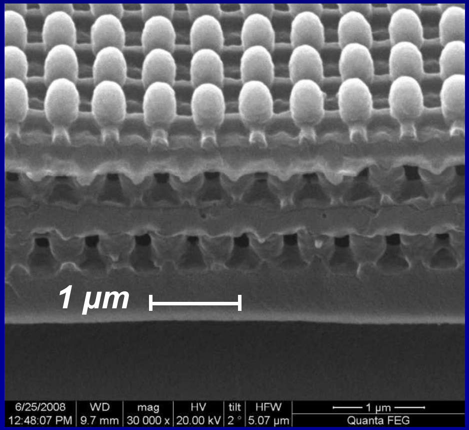


- Spread 175 cycles <u>*evenly*</u> over five temperatures
- All cycles 2.5 s pulse, 35 s purge
- SEM shows structure is intact
- Details of surface show “clumping”

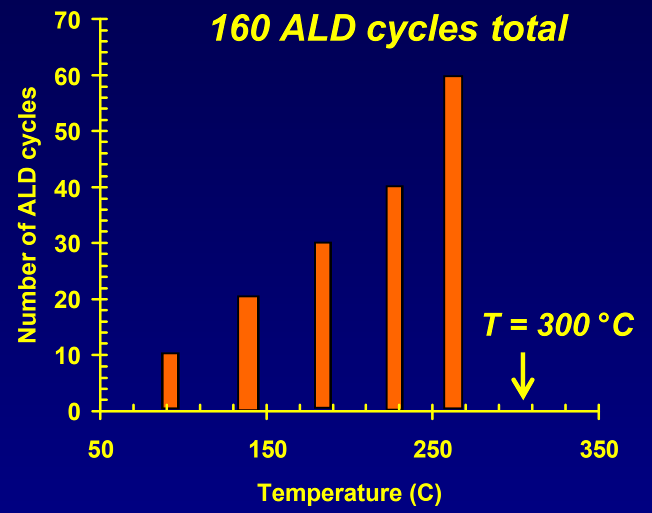
Before ALD



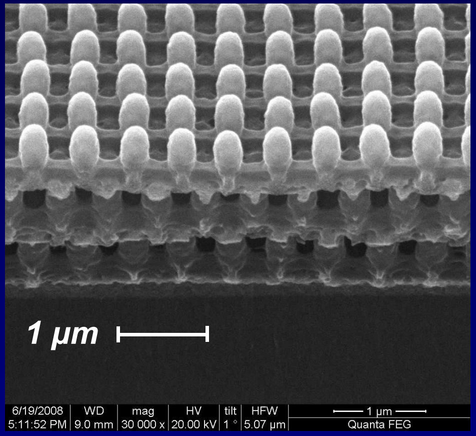
After ALD



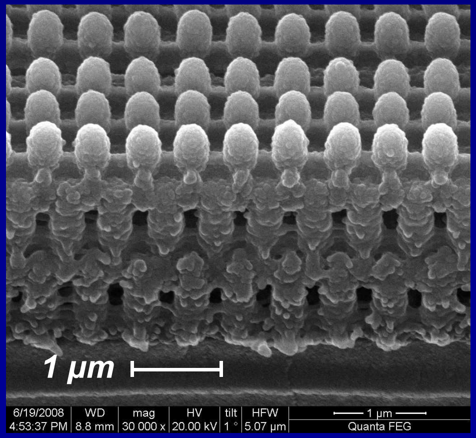
Graded Temperature Increasing ALD Cycles Using Traditional SU8® Photopolymer



Before ALD

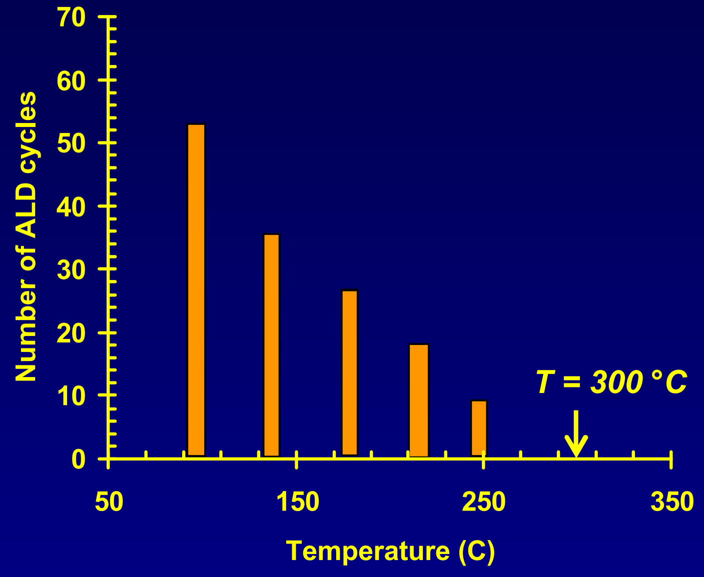


After ALD

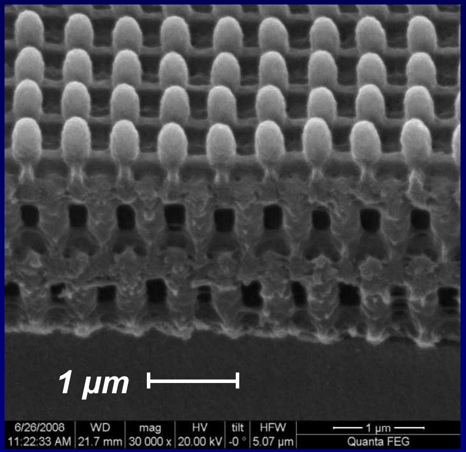


- Spread 160 cycles ***increasingly*** over five temperatures
- All cycles 2.5 s pulse, 35 s purge
- SEM shows very fuzzy coated structure

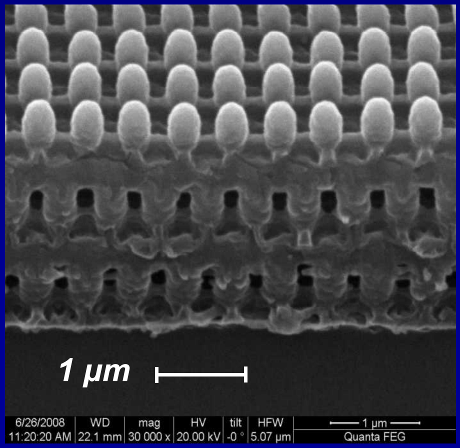
Graded Temperature Decreasing ALD Cycles Using Traditional SU8® Photopolymer



Before ALD

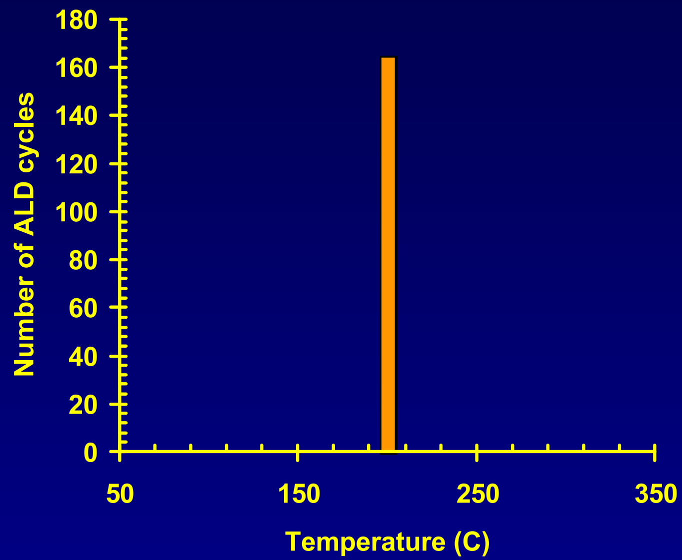


After ALD

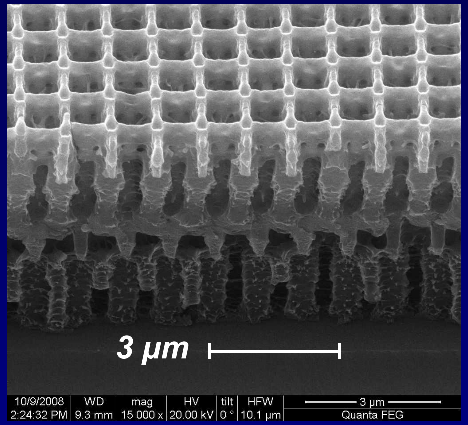


- Spread 175 cycles ***decreasingly*** over five temperatures
- All cycles 2.5s pulse, 35s purge
- Smooth deposition on surface of polymer
- The structure can be templated

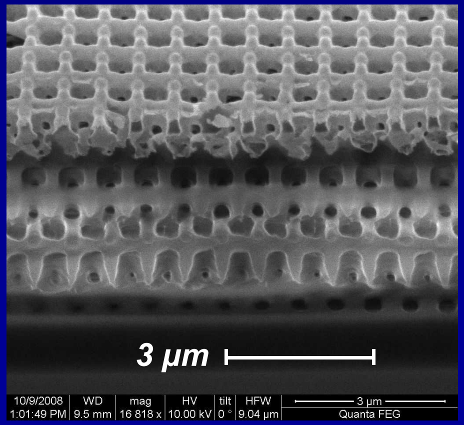
Constant Temperature ALD Cycles Using 2000 Series SU8® Photopolymer, T = 200 °C



Before ALD



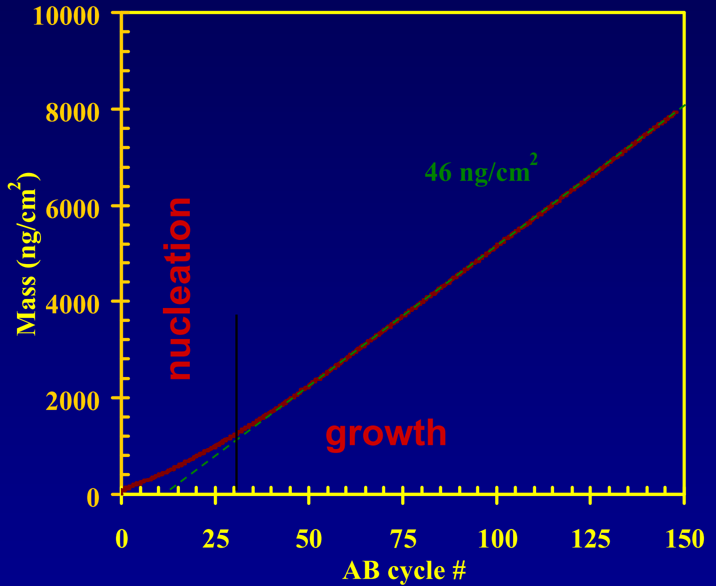
After ALD



- Ran 175 cycles *at constant* temperature
- All cycles 2.5s pulse, 35s purge
- Smooth deposition on surface of polymer
- The structure can be templated

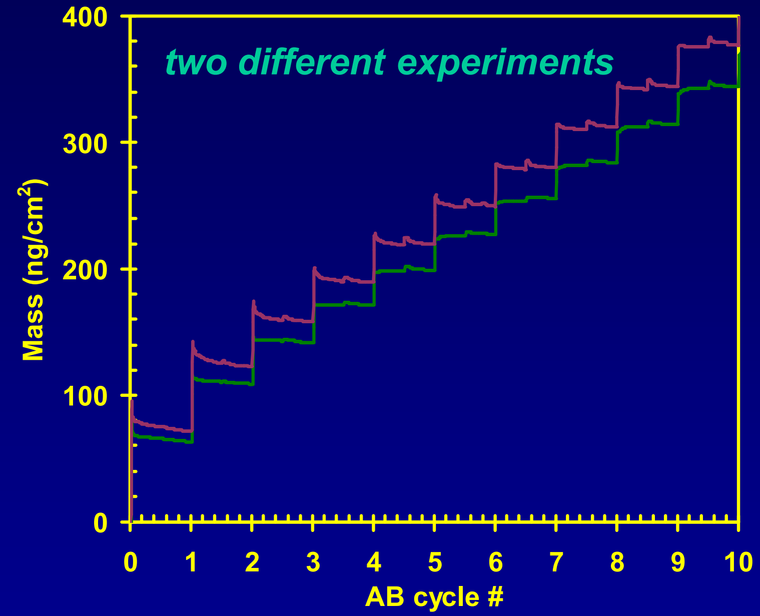
QCM Results of ALD Al_2O_3 on Traditional SU8® Photopolymer

QCM of Al_2O_3 ALD on SU-8



ALD Al_2O_3 growth rate 1.1 A/cycle ~ 36 ng/cm²

QCM of nucleation region



- T_{react} = 85 °C, P = 1 Torr
- 2s pulse, 35s purge TMA and H_2O
- Back-purged QCM[8]

- Short nucleation observed
- Small TMA solubility in polymer
- Linear after ~ 30 AB cycles

[8]*Elam, Groner, George, Rev. Sci. Instr.* ***73*** *2981 (2002)*

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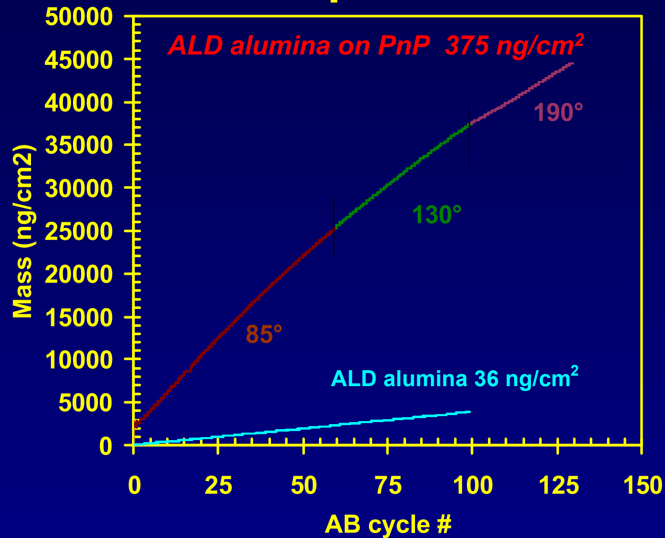
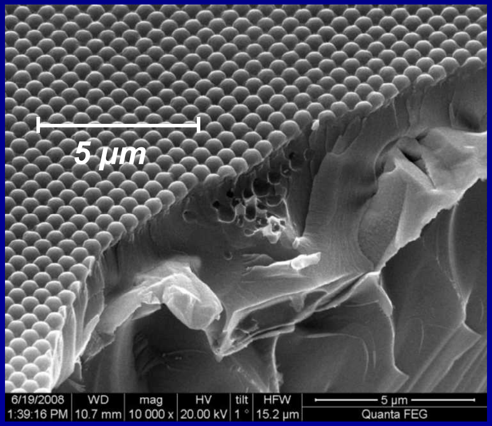
QCM Results of ALD Al_2O_3 on Nanostructure Using Traditional SU8®, T = 85 °C

- Spun and developed PnP polymer structure on QCM crystal[9]
- ~ x10 mass enhancement
- SEM observed <u>no</u> 3D structure
- Odd H_2O pulses at low temperature

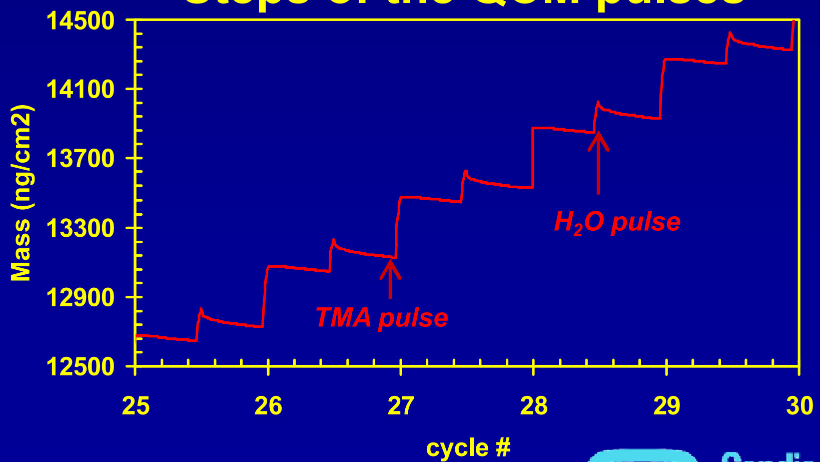
Graded temperature QCM



SEM of "fcc like" PnP on QCM crystal



Steps of the QCM pulses



[9]*Wilson, Grubbs, George, Chem. Mater.* ***17*** *5625 (2005)*

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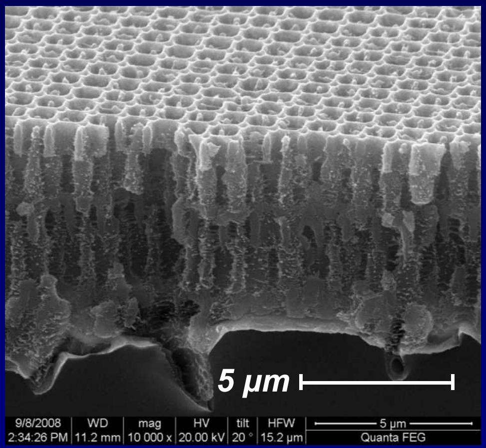
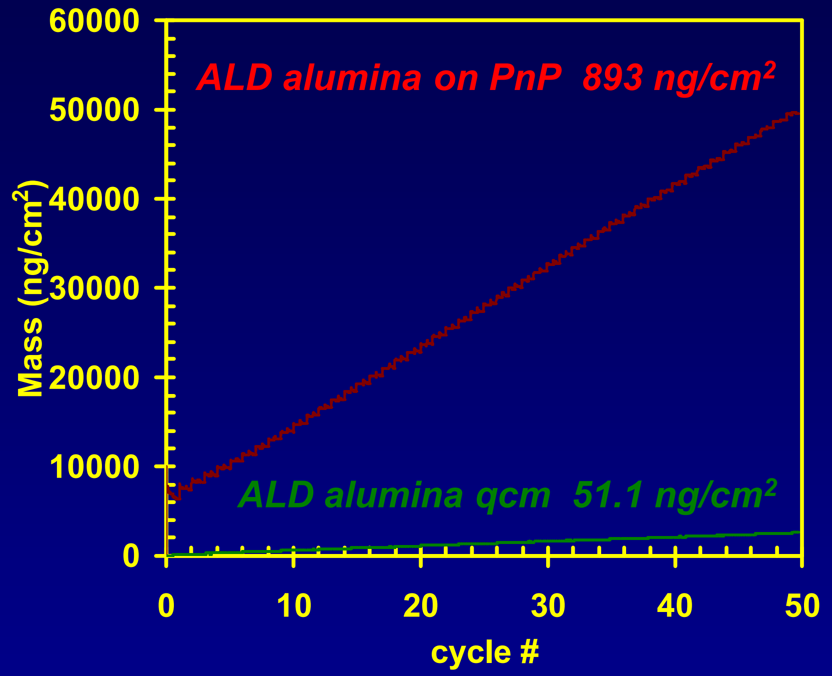
QCM Results of ALD Al_2O_3 on Nanostructure Using 2000 Series SU8®, T = 85 °C

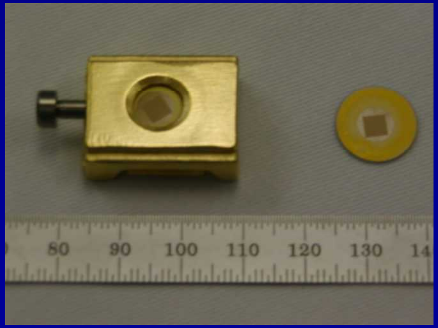
SEM of ISA PnP on QCM crystal





- Used ISA PnP structure on QCM
- SEM observed 3D structure
- ~ x17 mass enhancement
- "cob-webs" in structure could increase surface area

QCM with ISA PnP



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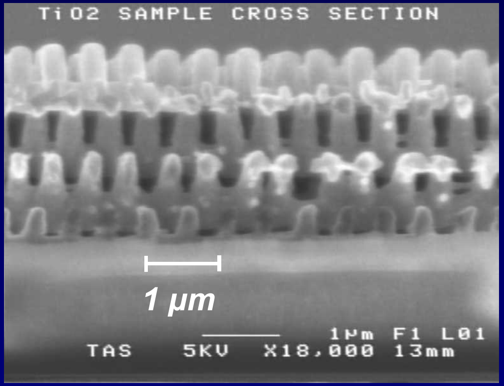
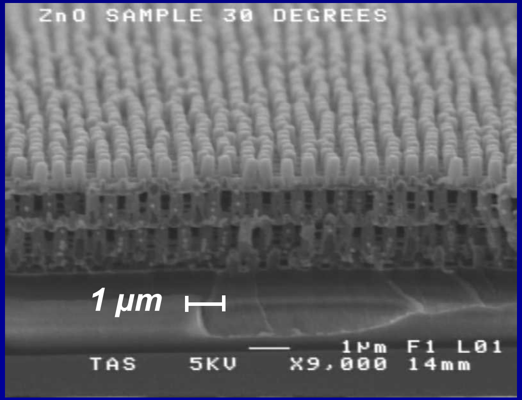
SEM Examples of Coated PnP Structures

TiO_2 ALD template decreasing ALD cycles

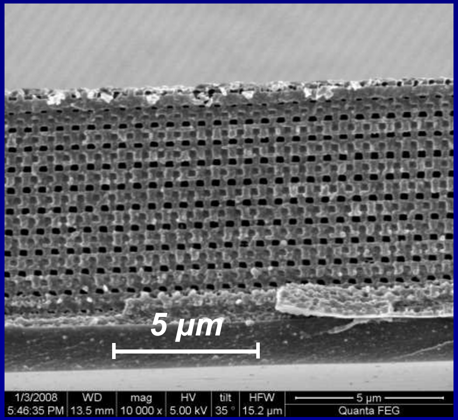


- **Have deposited ALD TiO_2, ZnO, ZrO_2 and Pt metal**
- **Graded temperature approach worked with TiO_2**
- **Detecting ALD conformality on nanostructures using TEM analysis was inconclusive**

~ 150 Å ZnO on Al_2O_3 ALD templated nanostructure (decreasing cycles)



"fcc like' lattice with ~ 200 Å Pt ALD[10]



[10]*Aaltonen et al. J. Mater. Res.* ***19*** *3353 (2004)*

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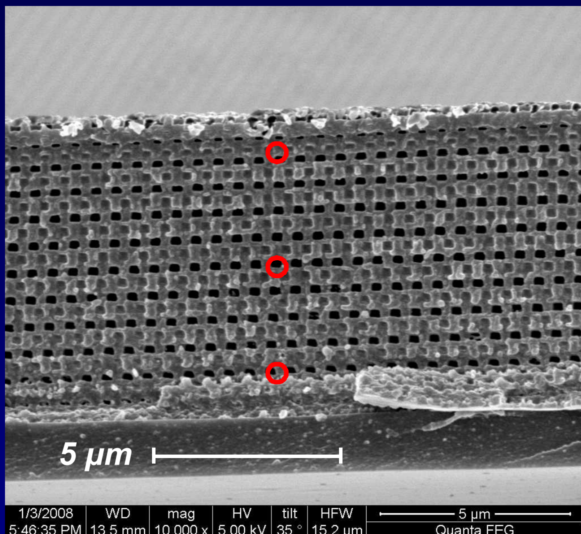
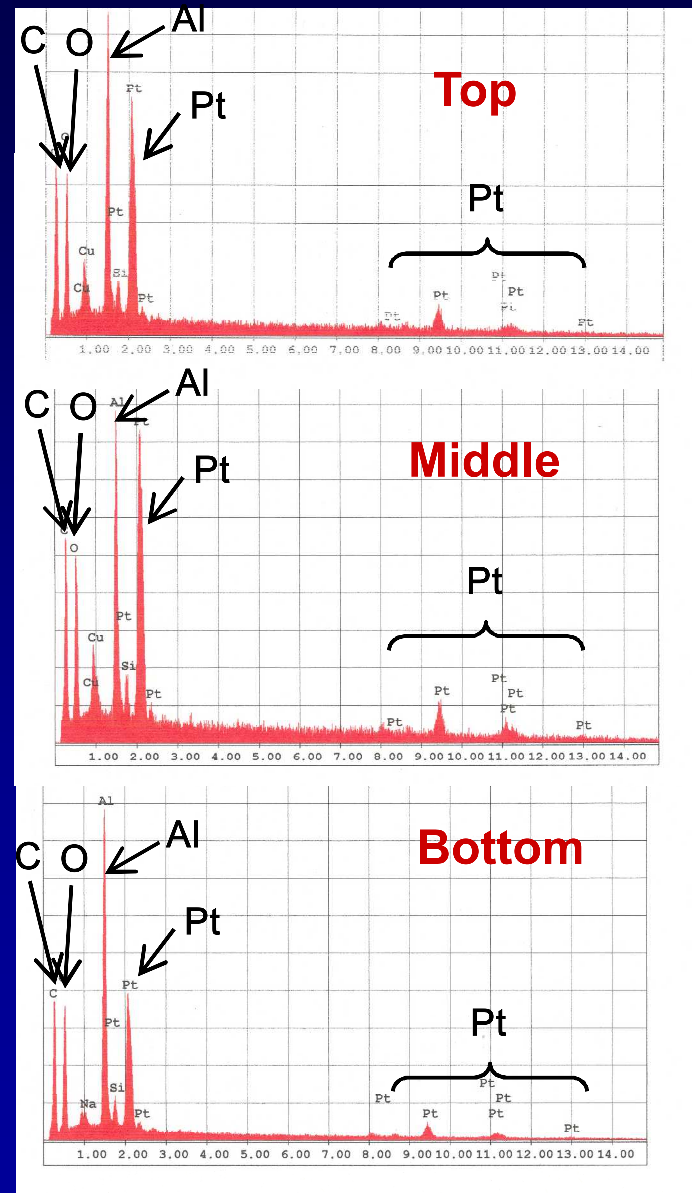
Micro-EDX Shows Presence of Pt Metal

Pt coated Al_2O_3 templated PnP



- **Spot size of EDX was ~ 500nm**
- **C, O, Al and Pt observed in spectrum**
- **Bottom shows different ratios of Al/Pt**

EDX = energy dispersive x-ray



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Conclusions:

- The predictive and general PnP formed nanostructures can be used as templates for ALD coatings
- PnP nanostructures made from Traditional SU8® collapse at < 125 °C
- PnP nanostructures made from 2000 series SU8® are stable to temperatures > 200 °C
- Graded temperature ALD is necessary for Traditional SU8®
- TiO_2, ZnO, and Pt metal ALD have been deposited on templated nanostructures
- QCM indicates short nucleation of Al_2O_3 ALD on SU8®
- PnP structures on QCM crystals showed dramatic surface area enhancement