# Fabrication and Modeling of Large-Area 3D Nanostructures by Proximity-field nanoPatterning Lithography

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LABORATORY DIRECTED RESEARCH & DEVELOPMENT

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# Lithography and Assembly Methods for 3D Nanostructures

- 3D Nanostructures are technologically important
  - Photonic crystals, controlled-lightpath filters, sensors
  - Large-area surfaces for catalysis, filtration
  - Microfluidics, fuel cell electrodes
  - Scaffolds for tissue growth

- Difficult to generate in a cost-effective, straight-forward process
  - Conventional: cycles e-beam lithography + selective removal
    - Costly, slow, limited 3D
  - Unconventional: colloidal self-assembly, phase separation, template-controlled growth, holographic/interferometric lithography, direct-write, molds/imprinting
    - Complex optical setups, poor yield, limited predictability

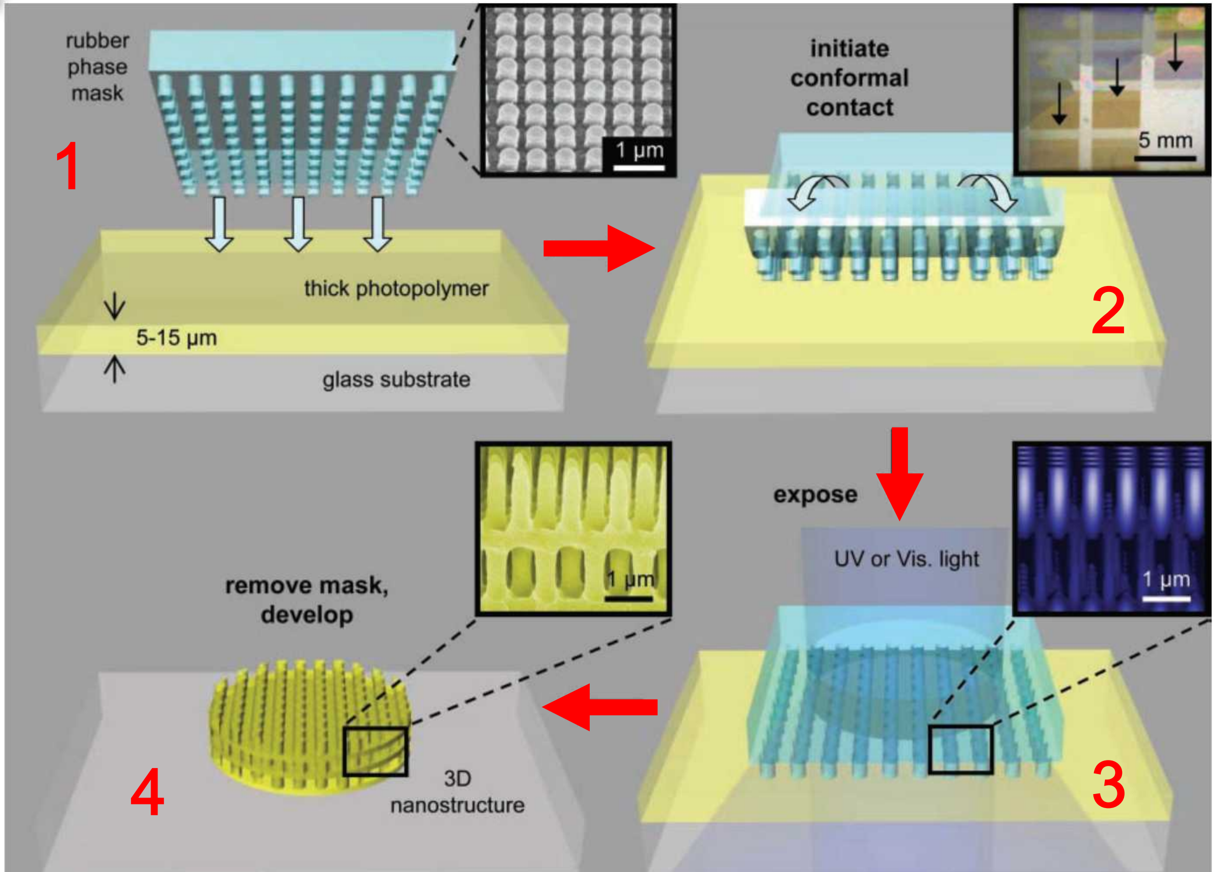
# Phase nano-Patterning (PnP)

1. PDMS phase mask

2. Conformal contact

3. Expose photopolymer
$\lambda$ = 355 nm
~4mm spot

4. Develop photopolymer



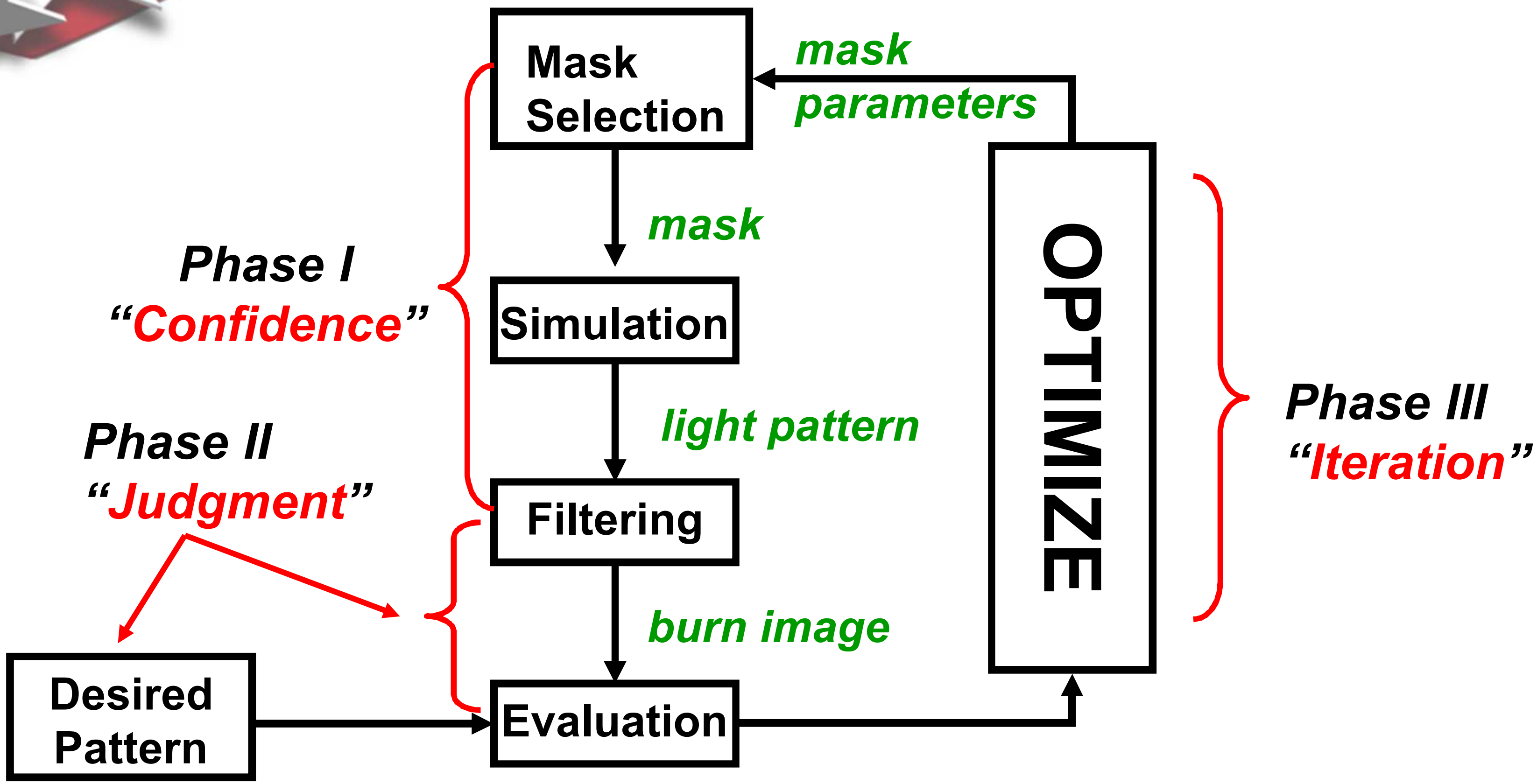

J. A. Rogers at UIUC (PNAS **101**, 12428 (2004))

- Relief dimensions (x, y, and z) on phase mask ~ $\lambda_{exposure}$
- Passing light through phase mask generates 3D distribution of intensity
- Exposes photopolymer in certain locations throughout its thickness

# Goal: Full Modeling and Scale Up

- Scale up fabrication from 12 $mm^2$ to 17671 $mm^2$
  - Modeling and Simulation
    - Inverse approach
    - Processing support
  - Processing
    - Mask masters and phase masks
    - Photoresist
      - Substrates, adhesion, spin uniformity, bakes, develop, drying
    - Exposure
      - Dispersion, collimation
      - 1-photon, 2-photon
    - Chemical modifications
      - Sensitization to 532 nm
      - Shrinkage
      - ALD
    - Applications
      - Photonic lattices
      - Scaffolds for cell growth and controlled-release drug delivery

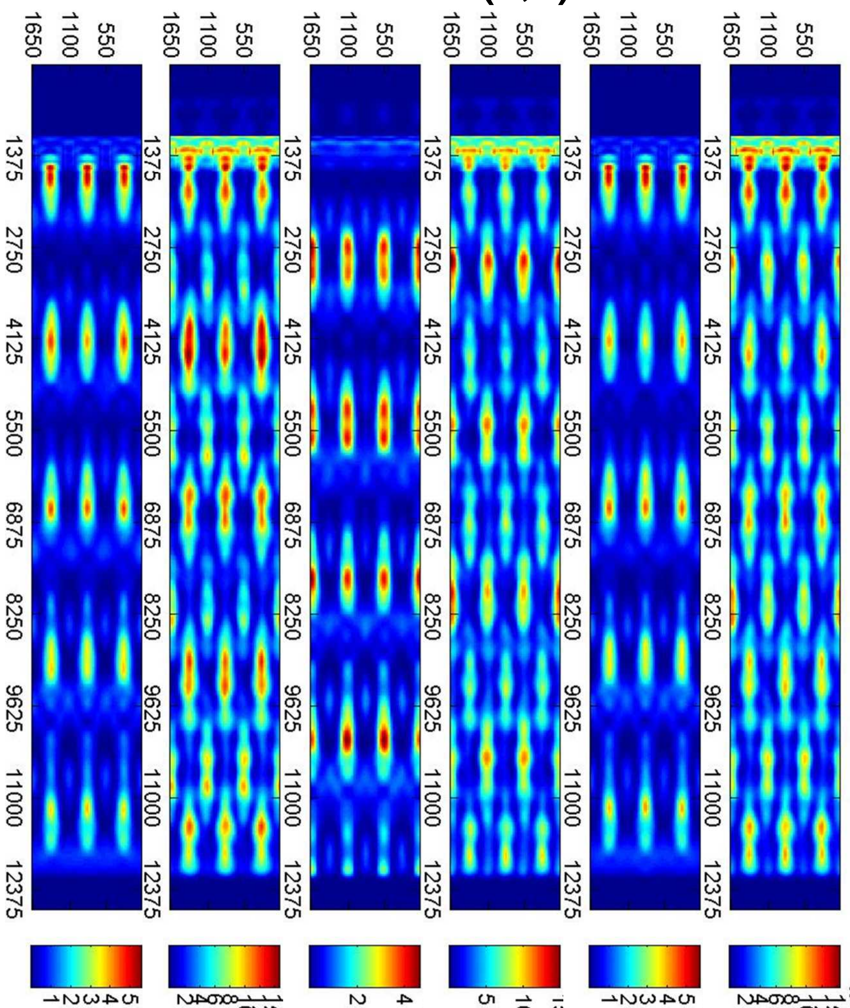
# PnP Modeling Pathway

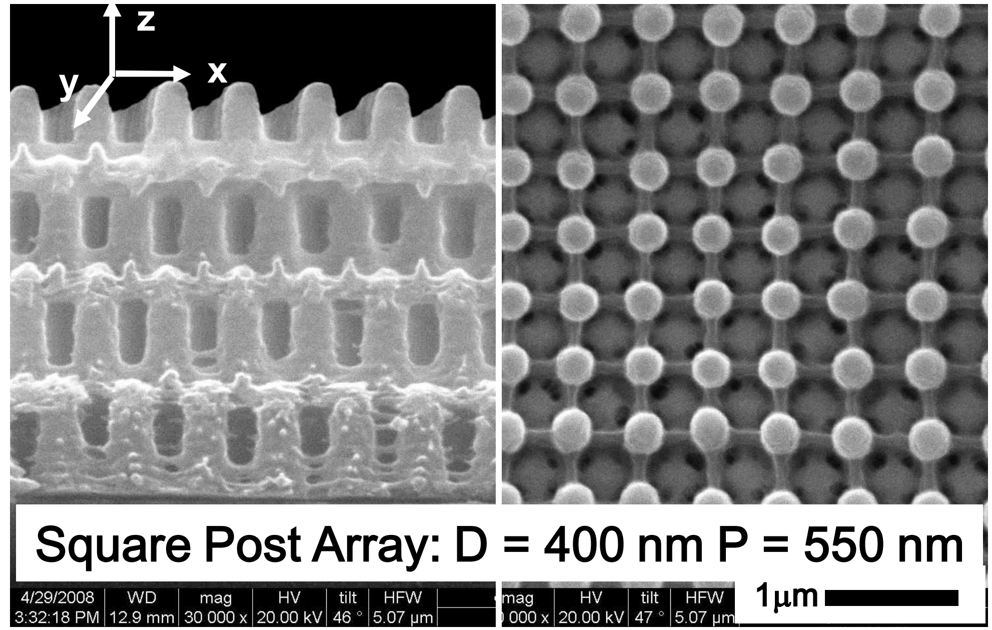



- Simulation engine is a high-performance, Open MP parallelized Finite Difference Time Domain (FDTD) simulator
- Optimized to run on shared memory symmetric multiprocessors (SMP)
- Periodic structures run in 14 minutes
- Aperiodic (quasicrystal) structures run in 27 hours
  - 24 parallel processors, 72 Gbytes memory, 600 Gflop/sec

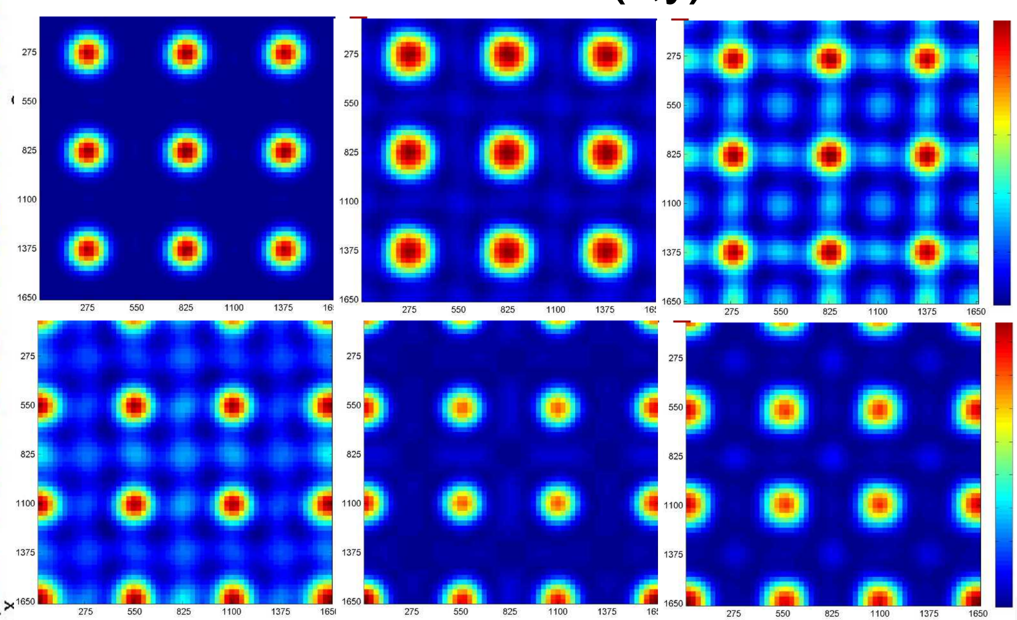
# Comparison of Model and Structure: Hexagonal

## Model Vertical (x,z) Slices




## Model Horizontal (x,y) slices

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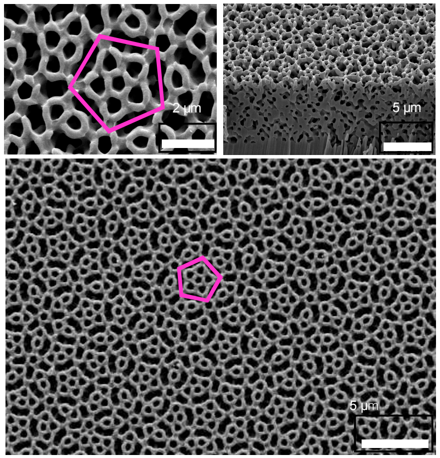
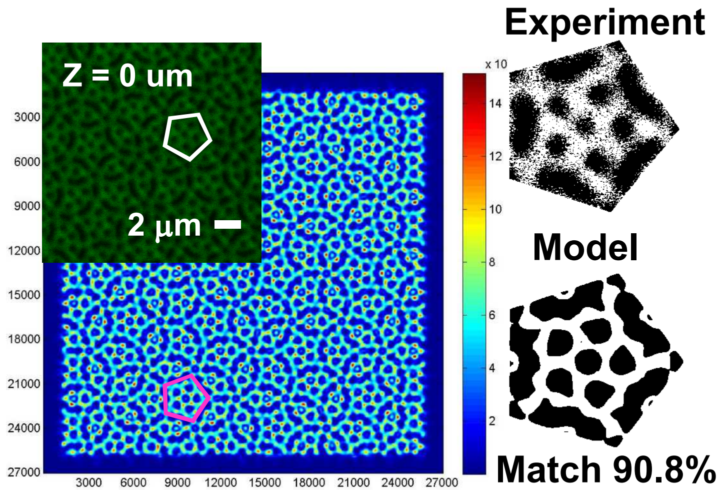
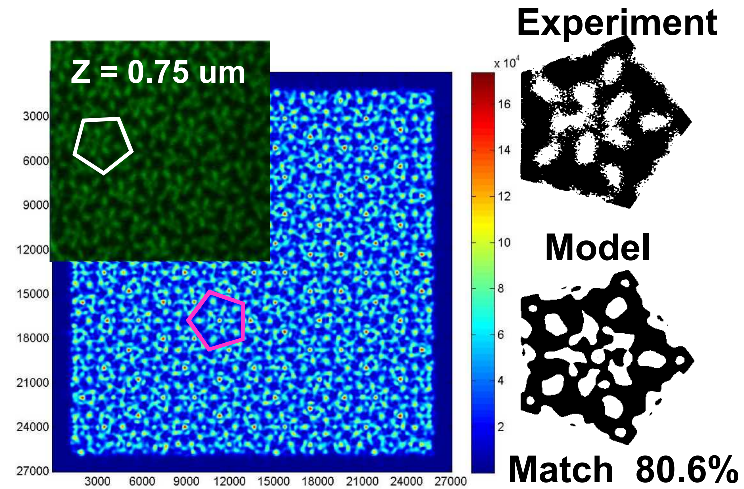
# Comparison of Model & Structure: Quasicrystal

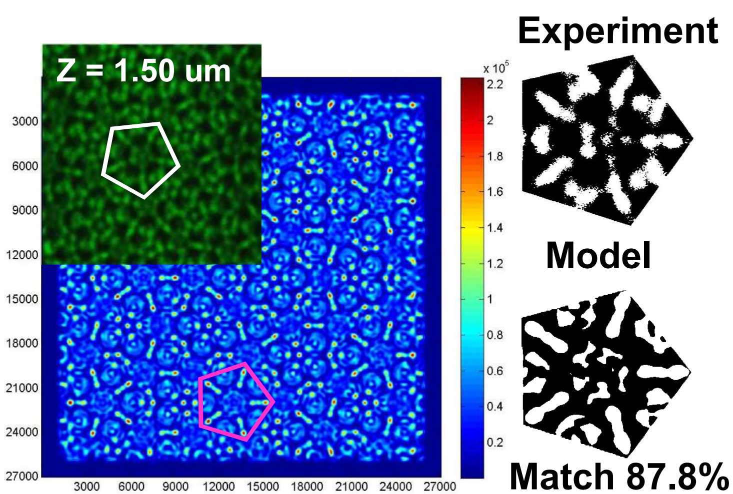
**FDTD model of Penrose Quasicrystal 3D nanostructures and confocal images of exposed resist (inset) at different depths and pattern recognition between model and exposed resist images**

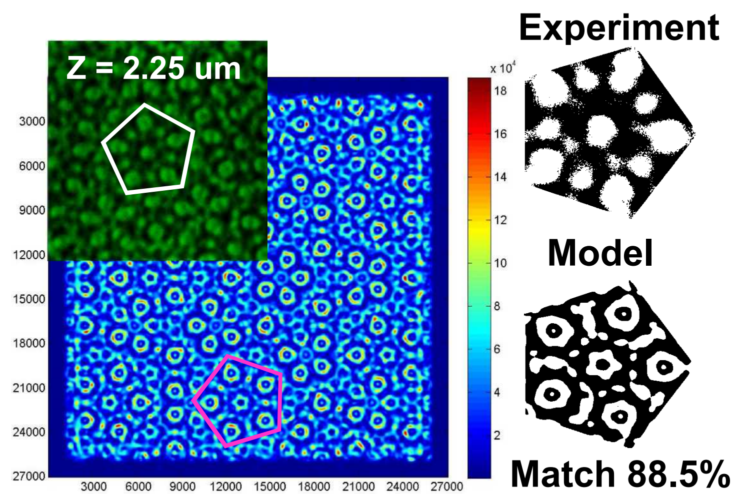
**Penrose Quasicrystal 3D resist structure**



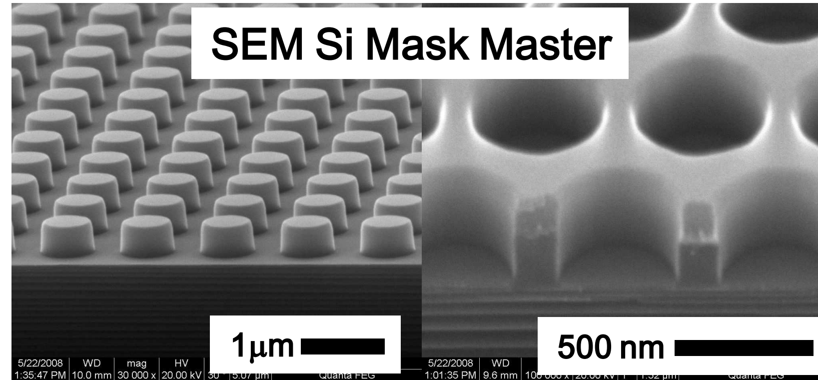



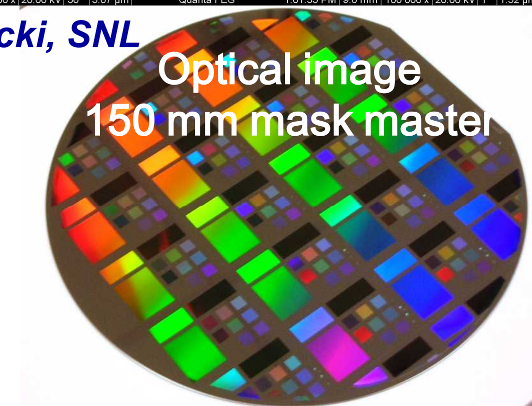

***Accurate, predictive modeling of periodic and aperiodic 3D nanostructures***

# Phase Mask Fabrication at 150 mm

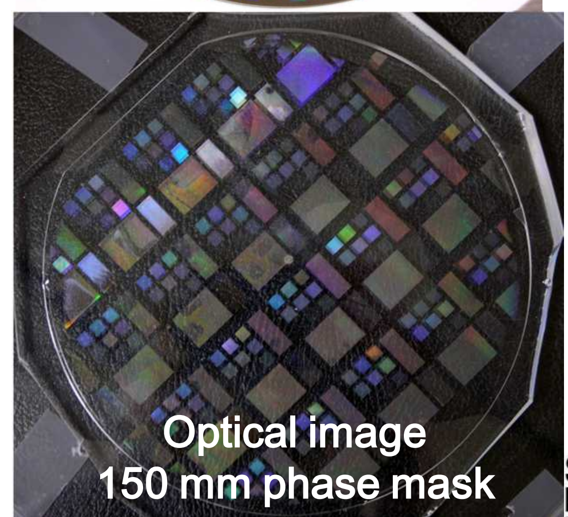
- Mask master: photoresist on Si wafers
  - 248nm projection scanning lithography
  - Feature sizes 400-800 nm
  - Transfer pattern directly into Si
    - More durable than resist




*Rob Jarecki, SNL*

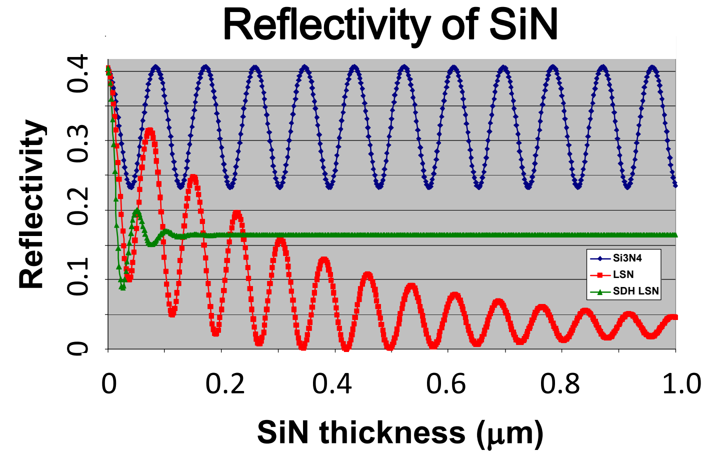



- Bi-layer of poly(dimethylsiloxane) (PDMS)
  - Spin-coat initial thin PDMS (10 MPa)
    - Stiff to reproduce master pattern with high fidelity
  - Spin-coat secondary thick PDMS (2 MPa)
    - Soft rubber to facilitate handling
  - Fully cure and peel away from master yields conformable phase mask
- Distortions <4 μm over 36 square-inch area

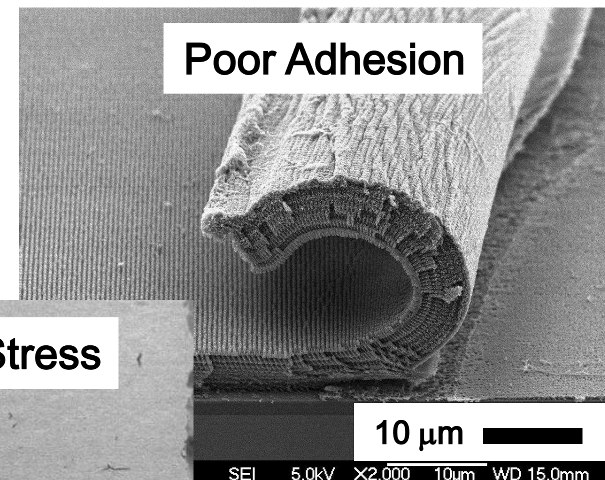


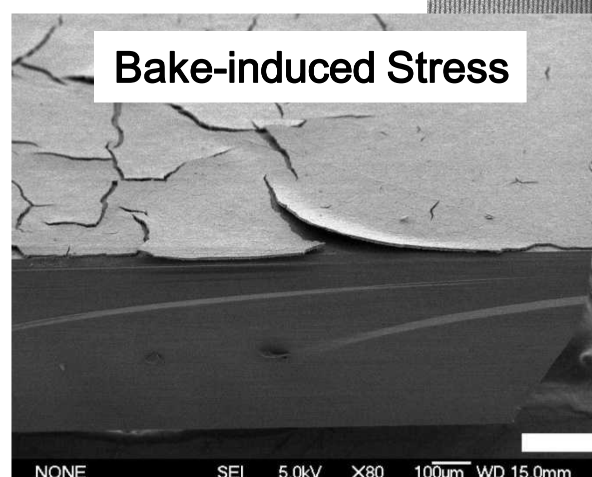
# Scale-Up Processing to 150 mm

- Si substrates with low-stress/high refractive index silicon nitride
- SU-8 Epoxy resist (Microchem)
  - Spin uniformity ~2% across 150 mm
- Hardbaked SU-8-2 for better adhesion
- Prebake 15 min 65°C, 20 min 95°C hotplate, leave overnight, tented (thickness dependent)
- Expose Karl Suss MA-6 I-line contact-proximity printer
  - Dispersion, collimation
- Post-exposure bake 20 min 65°C oven, tented
- Develop 30 min, puddle, 1 exchange, 30 min soak IPA, $N_2$ dry




*David Peters, SNL*

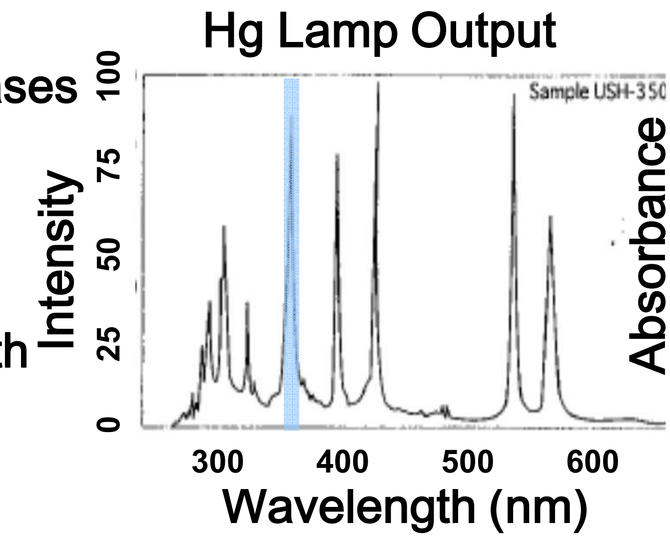


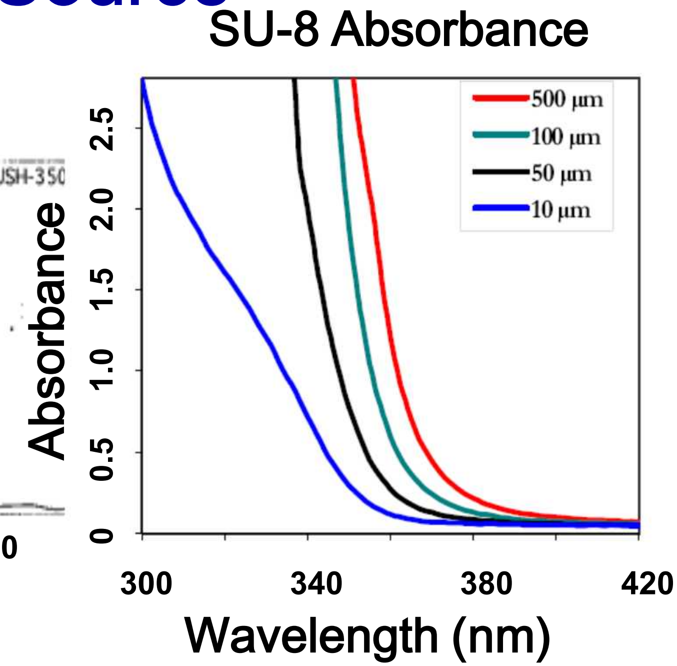



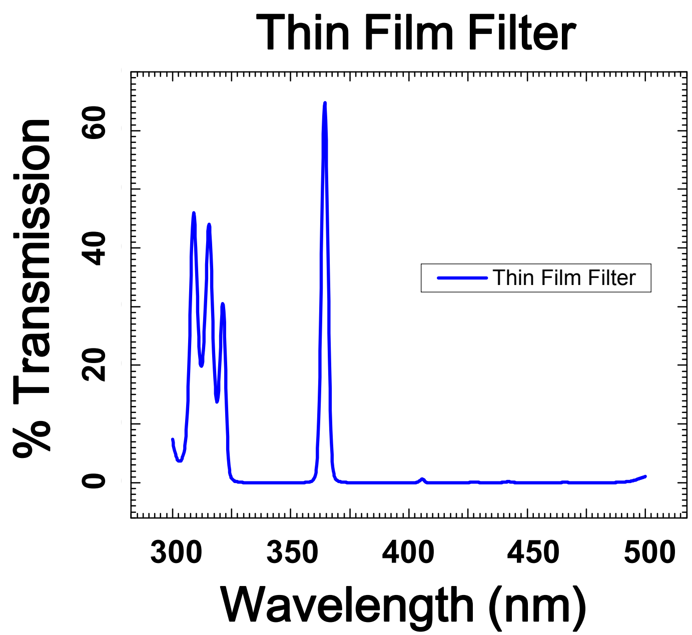

00 µm

# Broadband Exposure Source

- SU-8 absorbance increases rapidly >360 nm
- Karl Suss MA-6
  - Exposure wavelength broadband
  - No bandpass filter
  - UV400 optics, passing >313nm
  - Significant intensity below 360 nm
  - Added 75 mm, 364.5±1.6 nm thin-film narrow bandpass filter with 360 nm longpass filter to block 309-321 nm peaks

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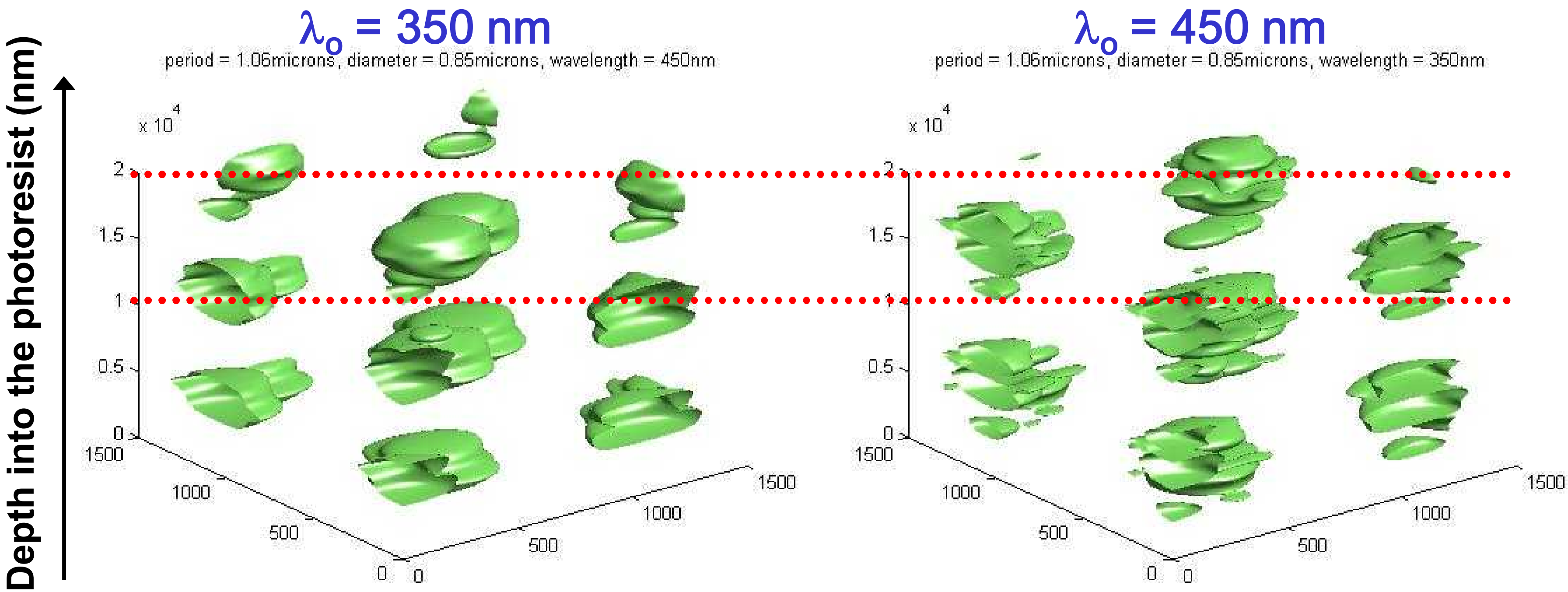
# Effect of Dispersion on Interference Pattern

- Square array of cylinders:  D = 850 nm  P = 1060 nm
- Energy in each of the diffracted orders changes considerably
- Looked 20 μm in depth at the interference pattern
- First high-intensity region shifts, gets worse with depth



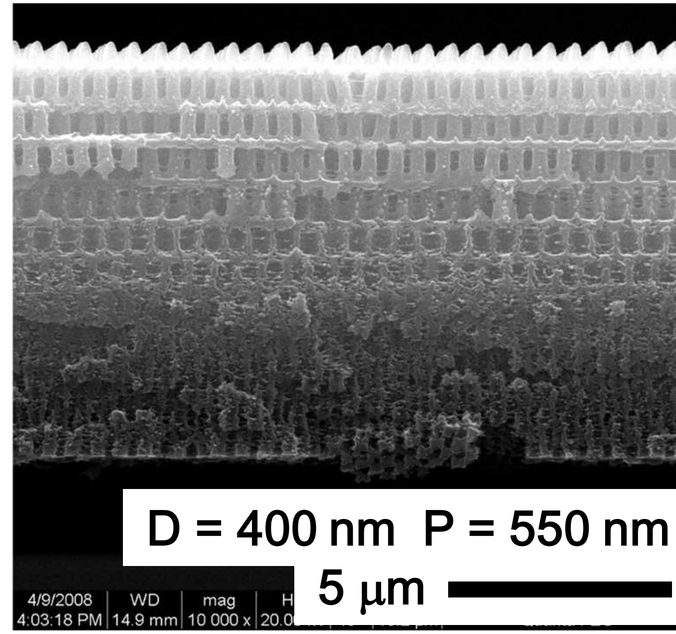

- *Conclusion:  wide bandwidth will completely wash out features within a few microns*

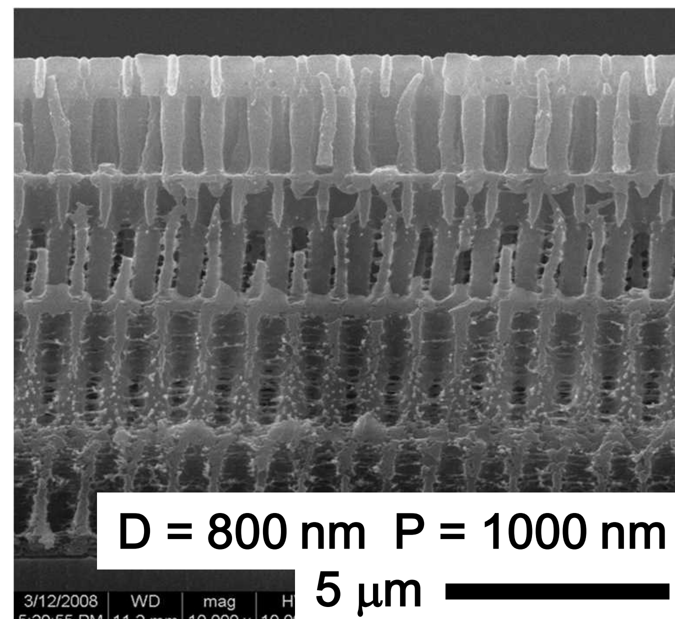
David Peters, SNL

# Exposure Source Collimation

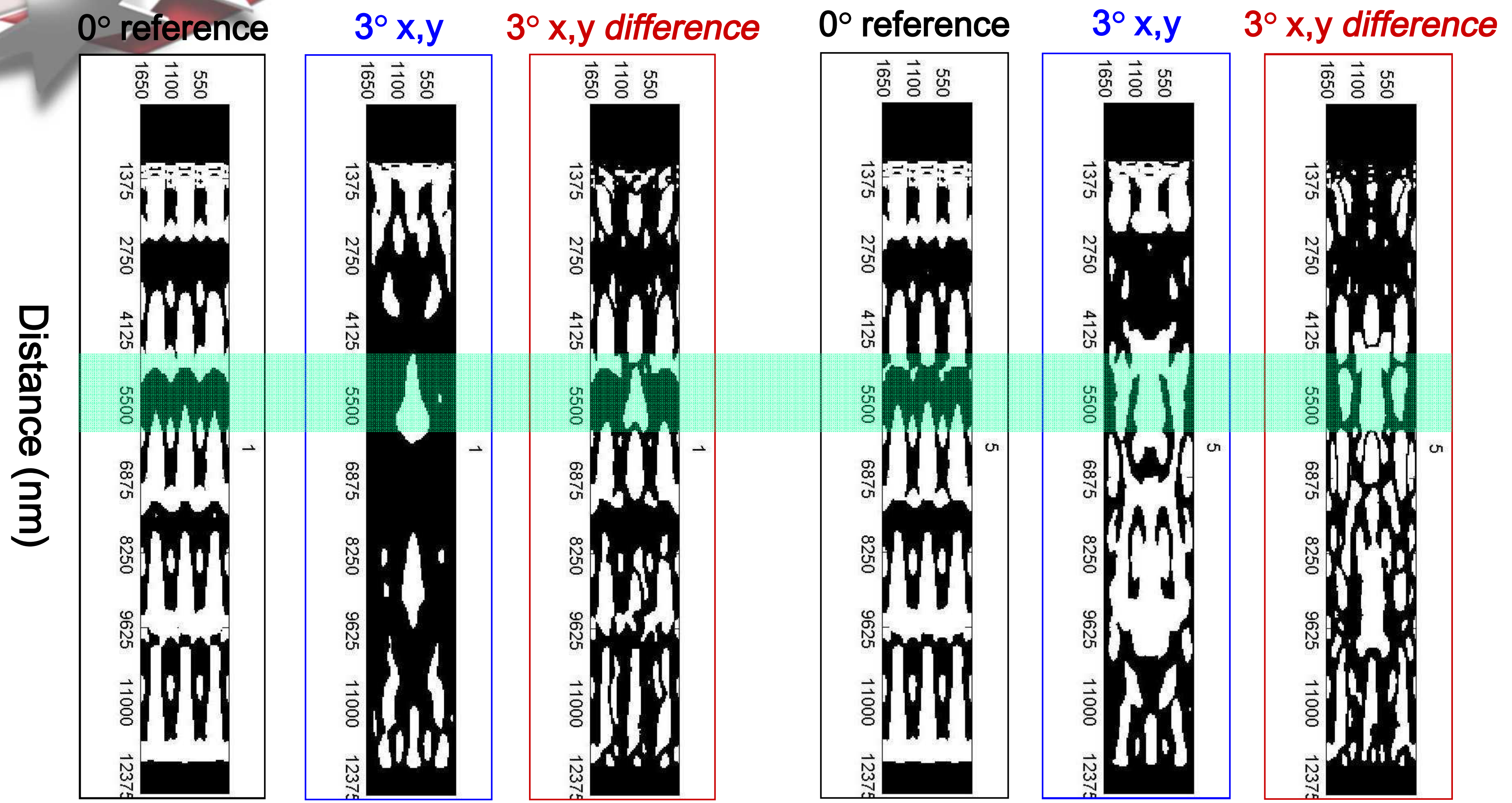
- For D,P <500 nm, see pattern resolution failure at ~4-5 μm deep into resist
- Pattern resolution good for D,P >700 nm, but observe resolution loss near substrate

- Karl Suss MA-6 has 3° ½-angle collimation
  - UIUC observed graded pattern at 3° off-angle laser exposure (APL 89 253101 (2006))
- Two approaches:
  - Modeling comparison of 0° and 3° angle
  - Expose on ASML I-line (365 nm) stepper (<3° angle)
    - 2 μm focus depth, 5:1 reduction
    - DOE matrix for exposure dose and focus depth/plane



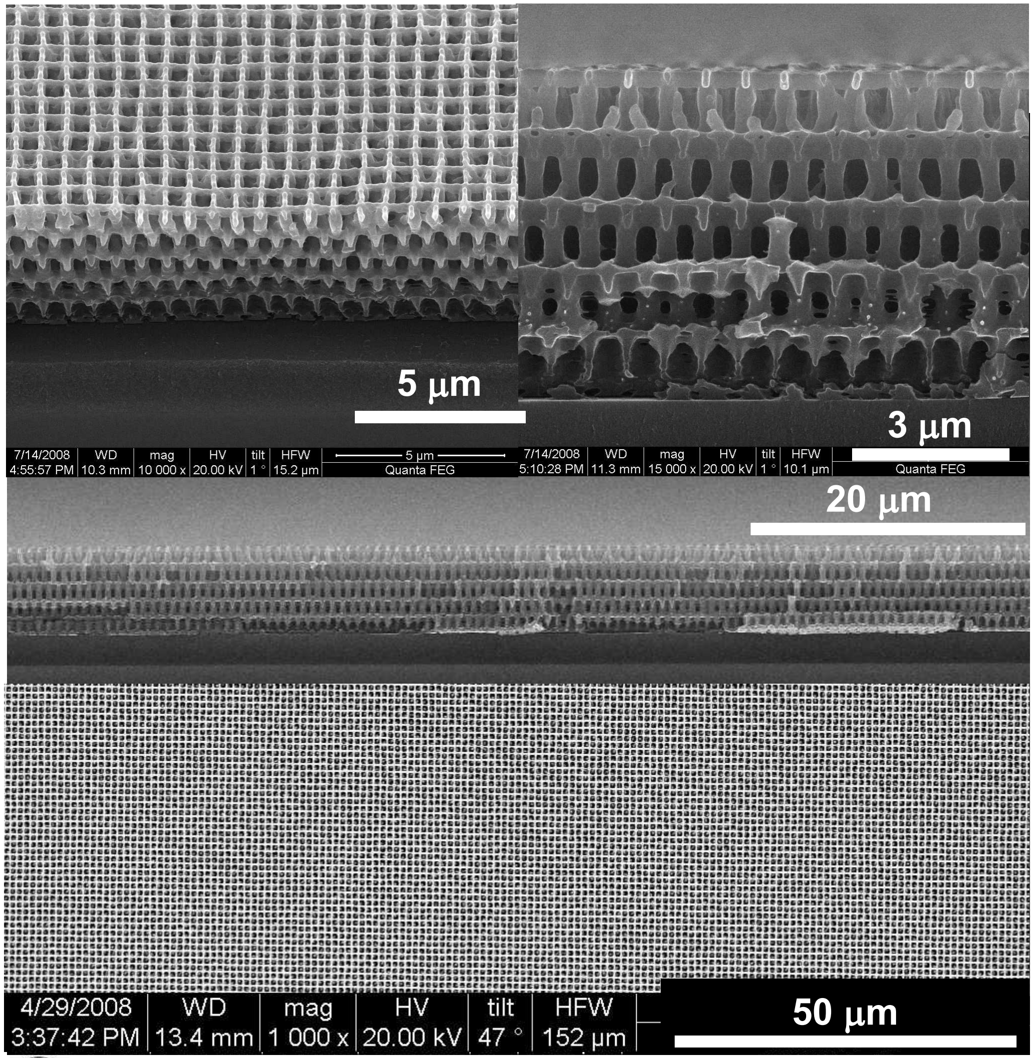
# Simulation of 3° Off-angle Exposures



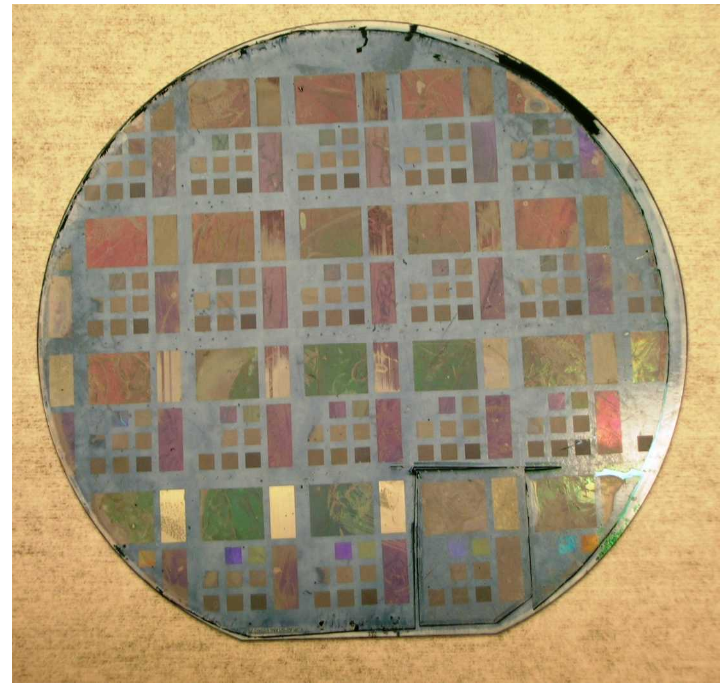

- *Difference* images show extra resist at 3° as compared to 0°
- Extra resist significant at ~4-5 μm down from surface
- Well-resolved pattern re-emerges at ~10-12 μm from surface

# Large Area PnP Structures

**SEM images of square array of holes pattern**




**Optical photograph of 150 mm PnP wafer**



*Achieved scale-up to 150 mm with limitations on thickness due to limited collimation of large-area exposure source*

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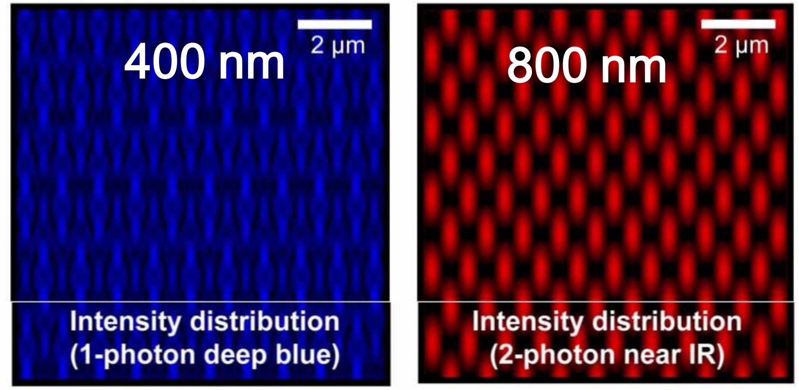
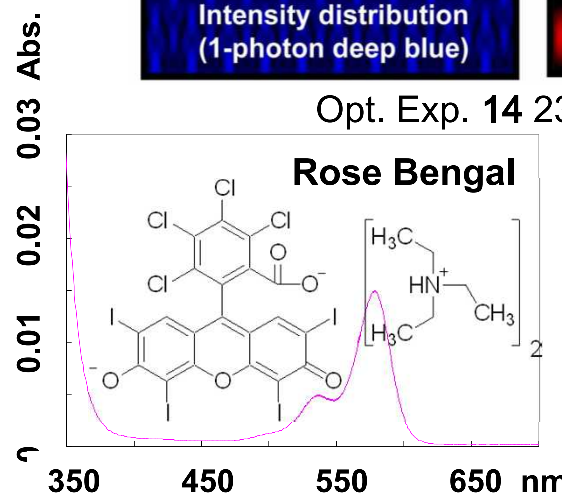
# Chemical Modifications of Resist Sensitization to 532 nm

- Two-photon exposure reduces # diffraction orders by ~75%
- Produces structures without fine substructure
- 2-photon requires ~1 TW/cm$^2$
- Large-area exposure needs big laser system: SNL Z-Beamlet (1054 nm)
  - ~1TW/cm$^2$ over 140 mm
  - 1-photon = 527 nm
  - Need resist to respond to ~530 nm energy

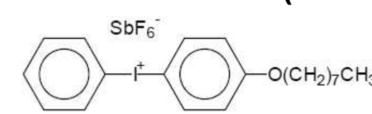
- Successfully sensitized SU-8 resist to 530 nm and formed PnP 3D nanostructures



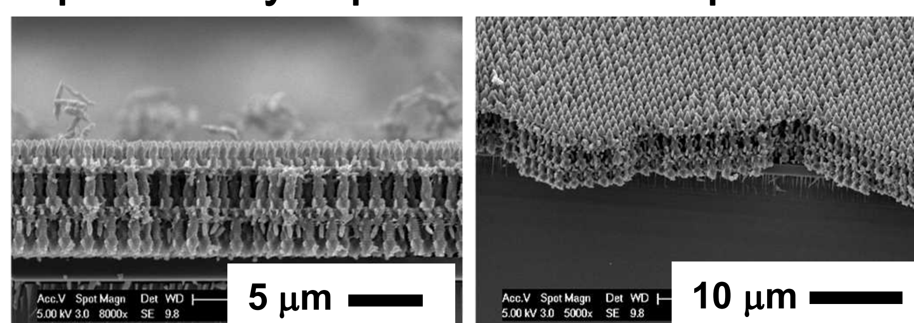

Opt. Exp. **14** 2300 (2006)




**Uvacure 1600 (PAG)**




Square array exposed 532 nm 1 photon mode

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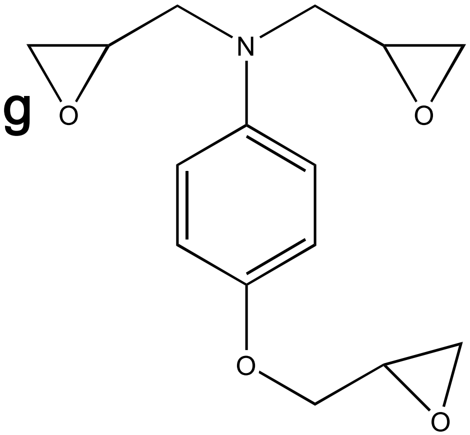
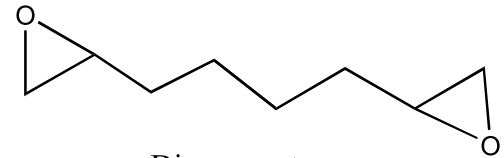
# Chemical Modifications of Resist Study Shrinkage

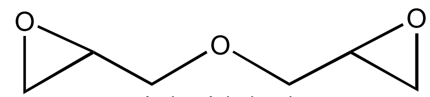
- Estimated that SU-8 “shrinks” during processing by 5-15%
- Most shrinkage due to solvent evaporation
- Replace solvent with solid reactive (epoxide) diluents
- Form viable structures with ~20-30 wt.% additives
  - Measurements in progress
  - Low-volatility additives give “sticky” films during processing



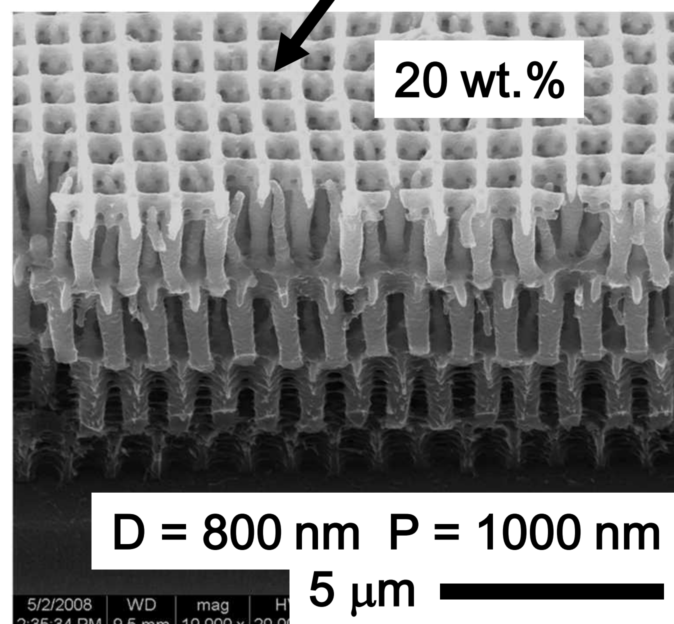

Diglycidylglyciidylooxyanaline




Diepoxyoctane

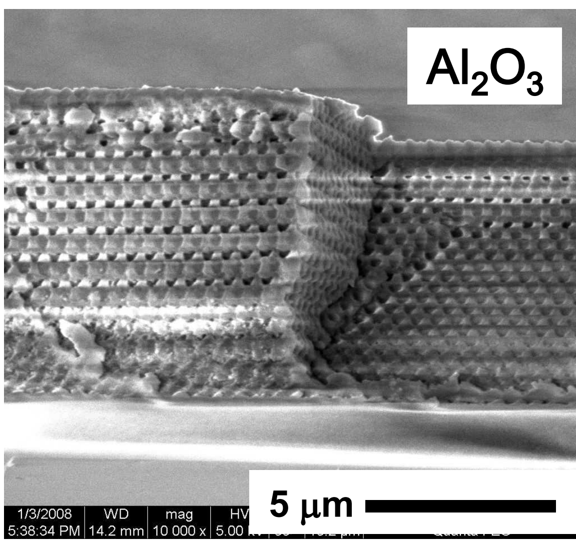


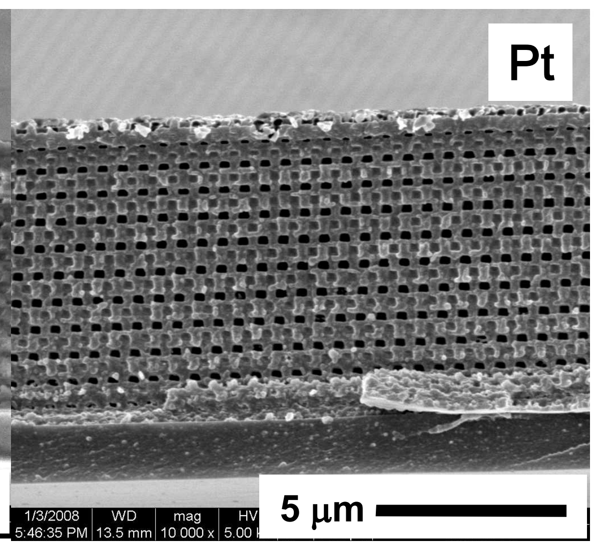

Diglycidyl ether

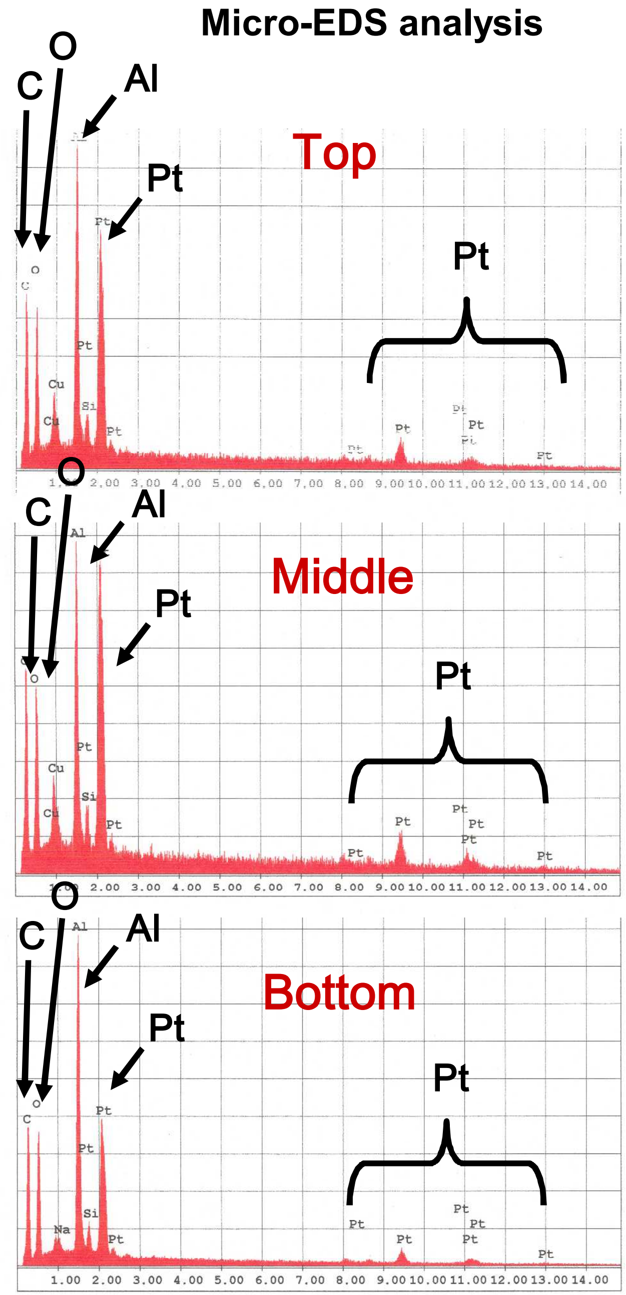


# Chemical Modifications of Resist Atomic Layer Deposition (ALD)

- Challenge to coat resist structures without degradation
- Developed graded temperature approach
- Can deposit $Al_2O_3$, $TiO_2$, $ZnO$, $ZrO_2$, Pt
- Micro-EDS (SEM) analysis shows deposition at both surface and through structure to substrate



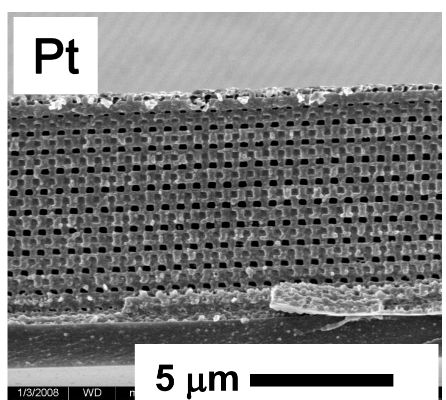



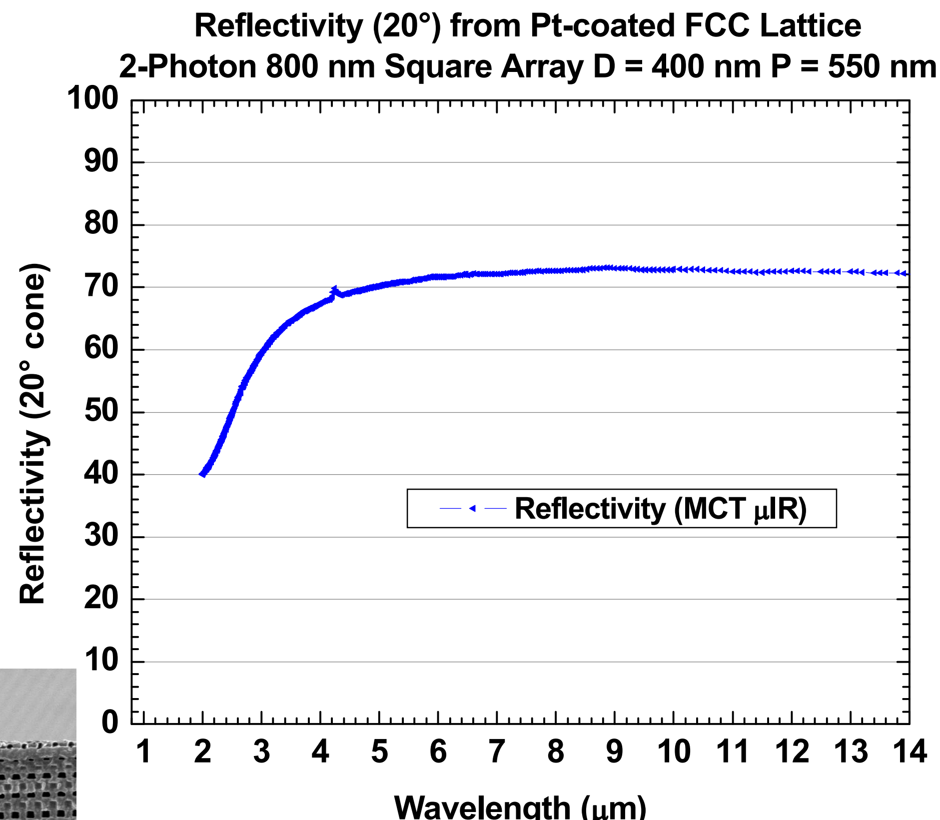



# Applications: Photonic Lattice

- Photonic lattice
  - Square array of posts (D = 400nm, P = 550 nm) generates FCC lattice with 2-photon exposure at 800 nm (UIUC)

- Preliminary Reflectivity measurements for Pt-coated structure
  - Possible band-edge at 1.9 µm

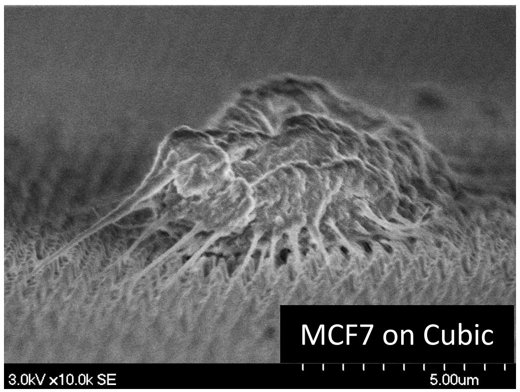


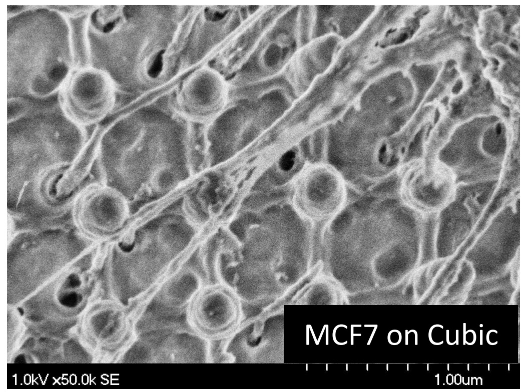



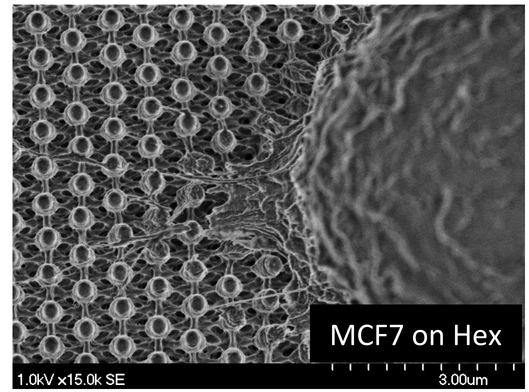
# Applications: Scaffolds for Cell Growth

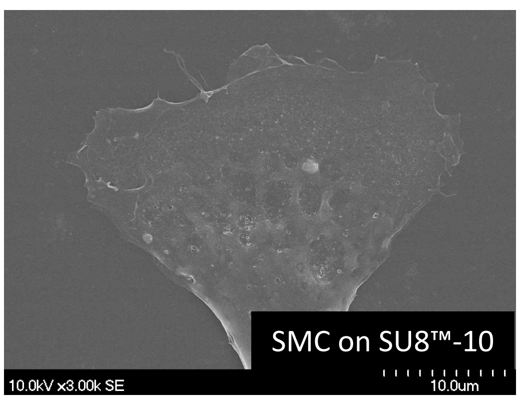
- Cells grow on patterned surfaces
- Philapodia sense different topographies
- Affects cell function/gene expression

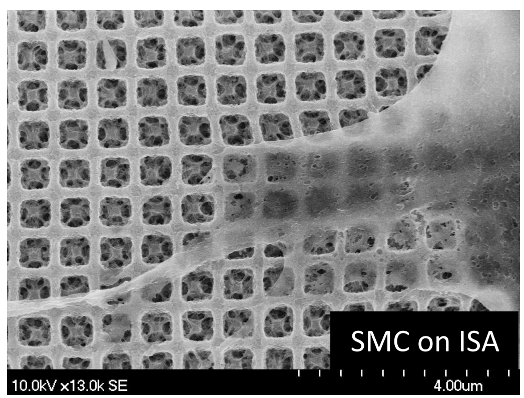

Prof. Elizabeth Dirk UNM
Akinbayowa Falase (IGERT/NSF, ACS)
Chemical & Nuclear Engineering
University of New Mexico

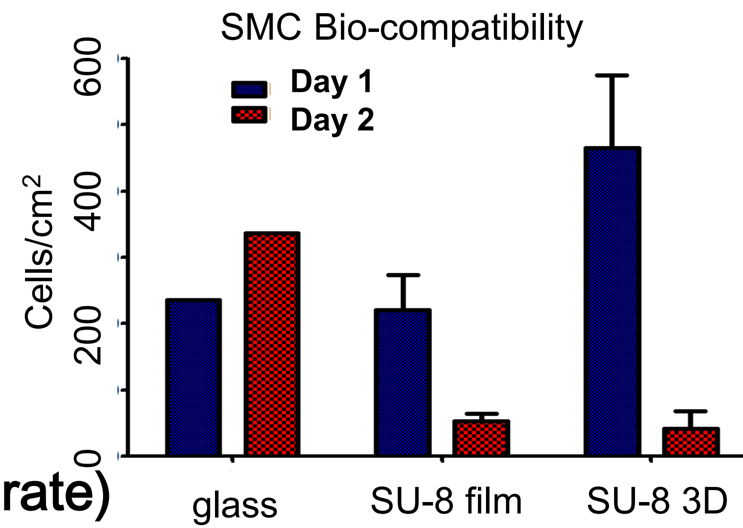



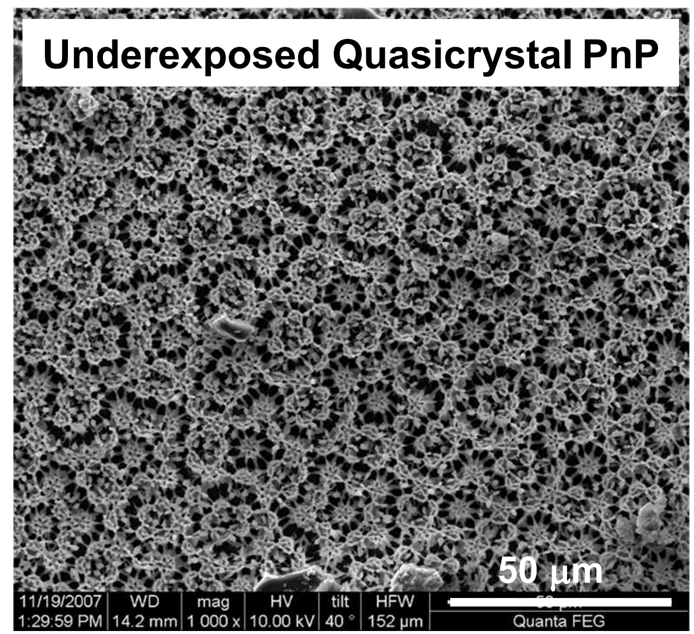




- Investigate poly-(propylene fumarate)
  - FDA approved for *in-vivo* use, photosensitive

# Summary

- PnP viable method for large-area fabrication of 3D nanostructures
  - Fast, cheap, simple optics, cleanroom compatible
  - Accurate, predictive FDTD simulations for both light-intensity patterns and resist burn stuctures
  - Chemically modify resist to function in atypical wavelength regimes
  - Chemically modify material and surface chemistry of structures for enhanced stability, robustness, reactivity
  - Can scale to 150 mm
    - Exposure collimation
    - Across-wafer uniformity
  - Wide variety of applications

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