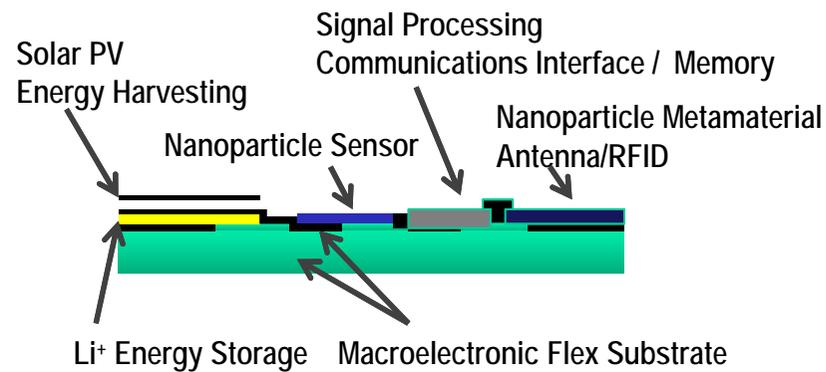
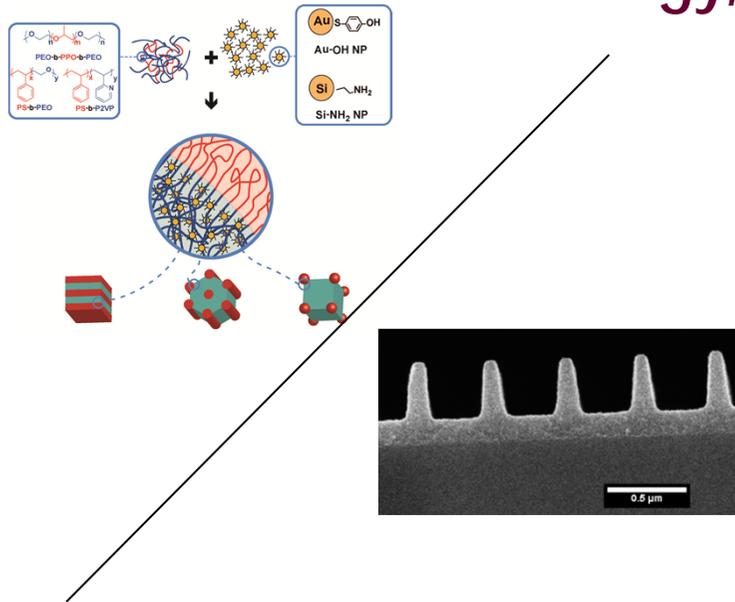


Solution-Based R2R Nanomanufacturing: Technology, Scale-up and Transition



Jim Watkins

Polymer Science and Engineering Department
and Center for Hierarchical Manufacturing
University of Massachusetts Amherst

Center for Hierarchical Manufacturing (CHM)



Nanoscale Science and
Engineering Center

Snapshot:

- An NSF Nanoscale Science and Engineering Center
 - Funded through NSF's Division of Civil, Mechanical and Manufacturing Innovation
- \$4 million/year in NSF Support
 - The CHM is funded by NSF through 2016
- 39 Faculty in 8 disciplines at 6 Institutions (27 Faculty at UMass)

A Strong Coupling With Leading Polymer Research



Polymer Science and Engineering Dept. at UMass Amherst

18 Faculty

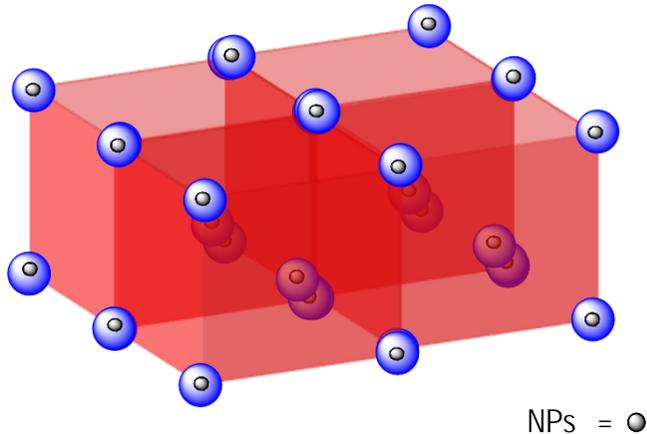
120 Ph.D. Students

40 Post-Docs

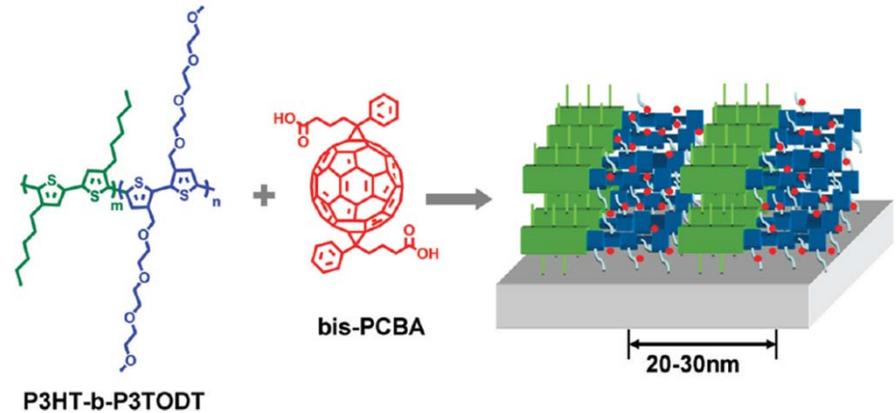
← Conte National Center for Polymer Research

Controlling Morphology at the Nanoscale Can Be Critical to Device Performance: CHM Examples

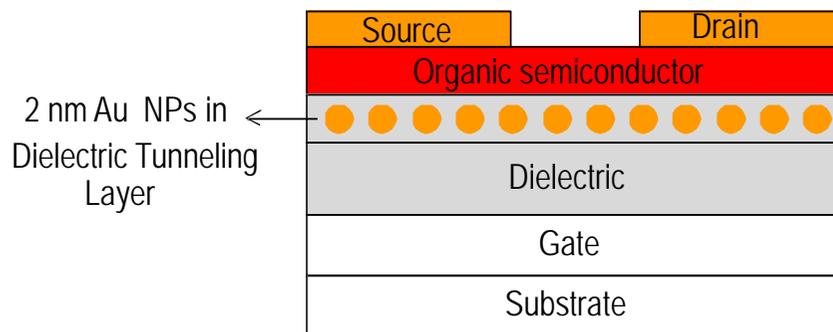
Ordered Metamaterials



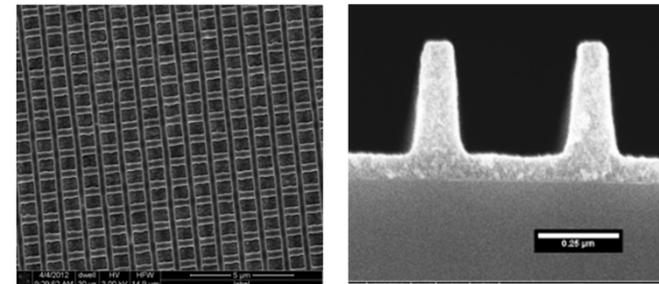
PV Heterojunctions



Device Architectures on Flex



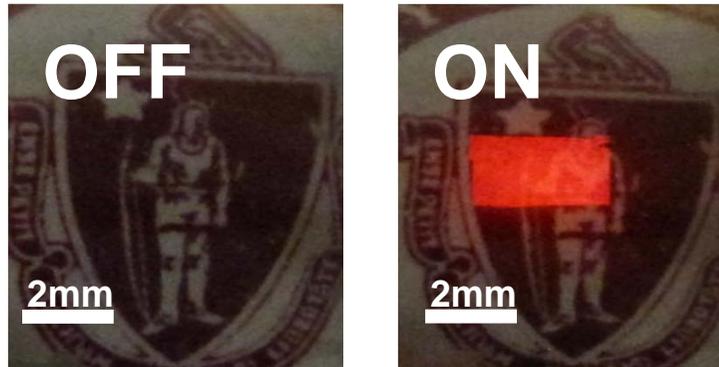
Printed Hybrid and Inorganic Nanostructures



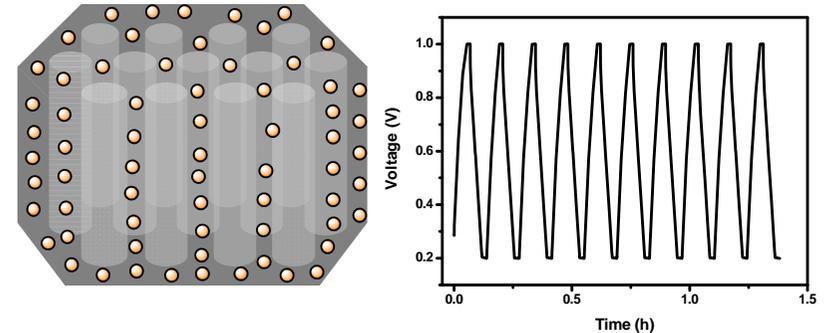
- Many applications require large active areas
- Both morphology control and morphological stability are needed

Controlling Morphology at the Nanoscale Can Be Critical to Device Performance: CHM Examples

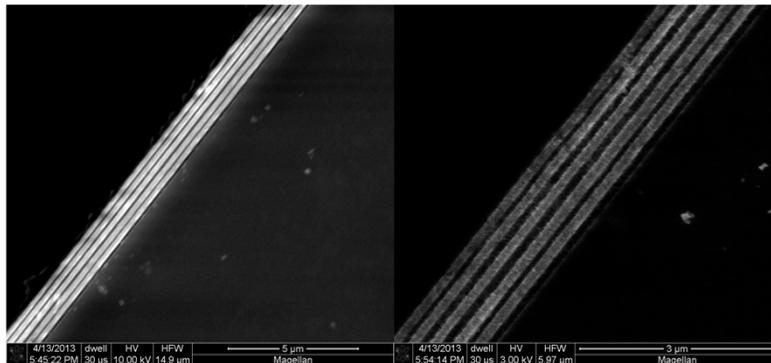
Transparent QD-Based LECs



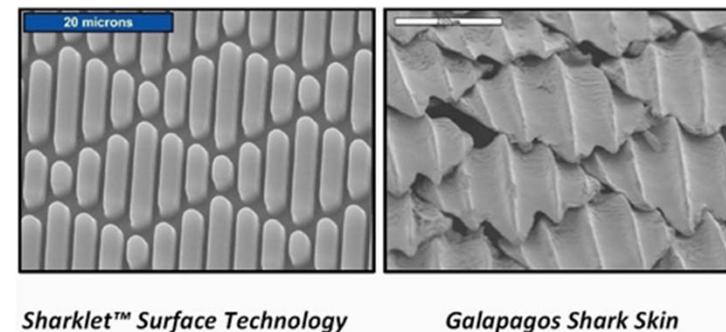
Nanostructured SuperCaps



Planar and Patterned Films for Light Management

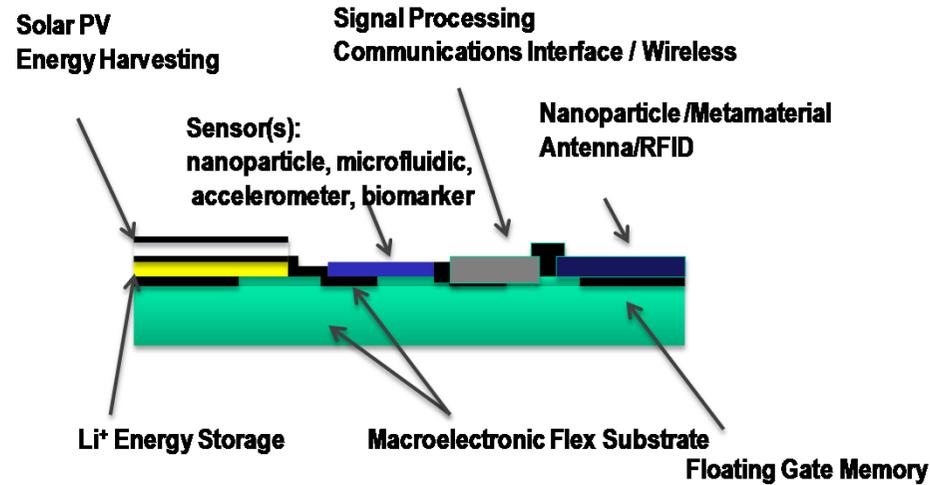


Bio-Mimetic Anti-Microbial Surfaces



- Many applications require large active areas
- Both morphology control and morphological stability are needed

One Goal: Integrated Low-Cost, Flexible Device or Patch



The NSF Center for Hierarchical Manufacturing is developing nanotechnology-enabled and high-performance, hybrid device layers for advanced device fabrication using novel R2R platforms and tools. These advances can be combined with silicon-chip pick-and-place assembly for expanded sensor platform capability

Personalized Health Monitoring

Personal Health Monitoring

Vital signs and medical information Are measured and reported to local wireless hub

Respiration, ECG

Lab-on-a-Chip Measures drug levels, biomarkers

PPG, blood pressure, vascular performance

3-axis accelerometer Measures activity, falls



Real Time Medical Tracking

Medical Information is continuously monitored

Health Care Providers

Medical professionals can monitor in-home patients in real time



First Responders

Automatic notification In event of emergency

Distributed Sensing Networks & Security

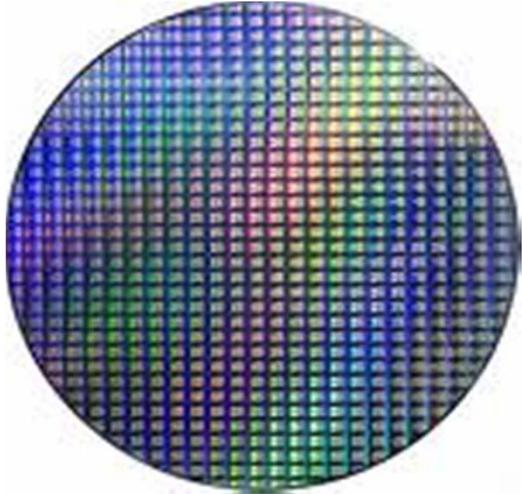


Building and Infrastructure Integrated Systems



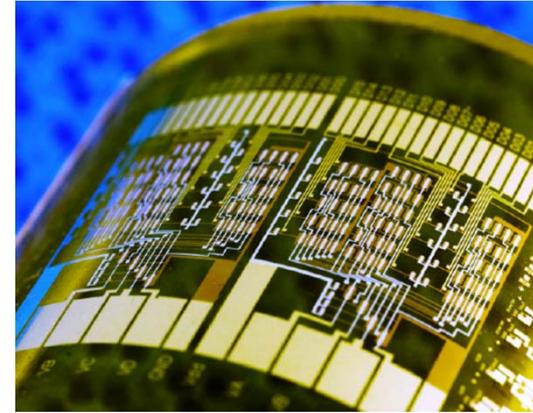
New \$46 million capital investment at UMass including \$23 million for R2R facility

Challenge 1: Manufacturing Platform Drives Cost



\$25,000/m²

Si wafer-based, precision devices
Now: 32 nm features in production
New Fab = \$4-6 Billion

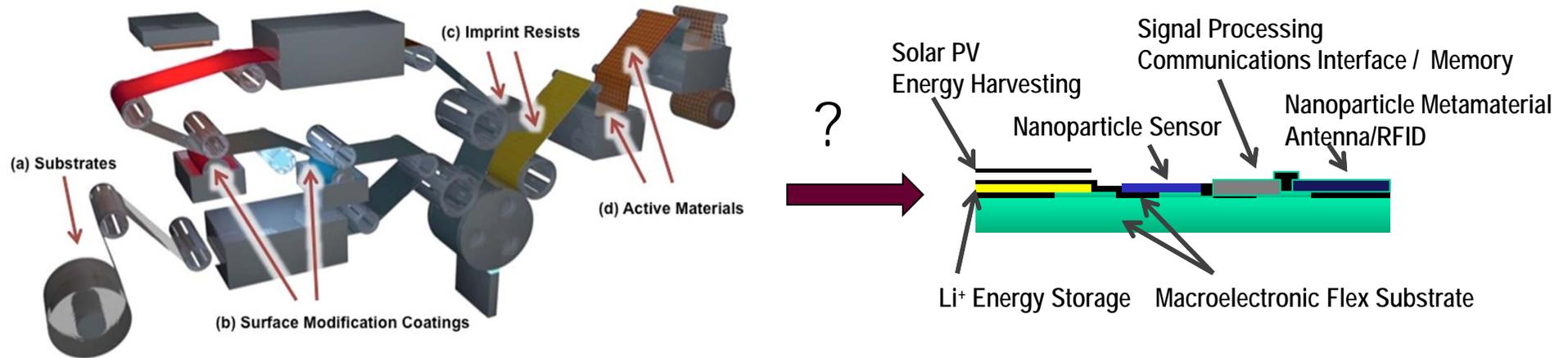


\$25/m²

Flexible Devices via Roll-to-Roll
vs. Now: Macroelectronics, limited functionality
Low cost, high volume

- Nanotechnology-enabled, high performance devices on a low-cost R2R manufacturing platform
- R2R not intended to compete with traditional Si based technology for high end computing
 - hybrid approaches where needed
- Addressing opportunities that require new functionality, large areas, unique form factor etc.

Challenge 2: Low-Cost Capable Devices by Combining Printed Electronics and Nanostructured Device Layers



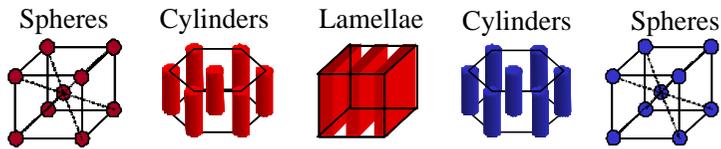
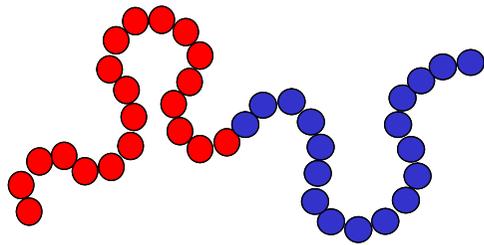
Defining Needs:

1. New materials and process to improve performance
2. Organize (order) nanostructured active layer (3 - 50 nm)
 - nanoparticles, fullerenes, nanorods, etc.
3. High speed pattern on web at device scale (50 nm – 5 micron)
 - interconnect, micro/nanofluidic, optical, active surface
4. Solution-based processing, eliminate vacuum and high T
5. Additive approach where possible
6. Compatible with Si pick and place for some applications
7. Integrated device and systems development
8. Build tools for partner access, technology demonstration

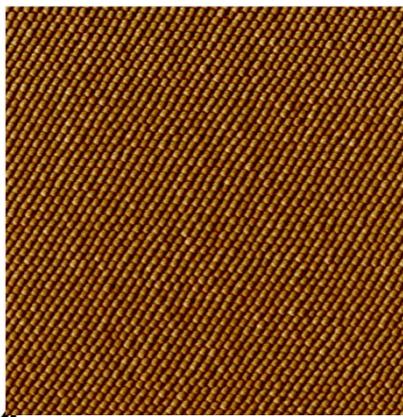
Ordered Structure at Length Scales Less Than 50 nm

Spontaneous Assembly from Solution, Complete Control of Morphology

Block Copolymer Assembly

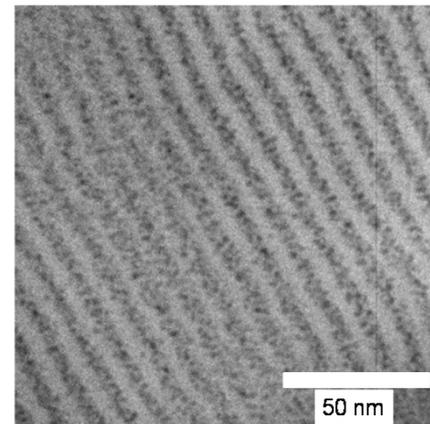
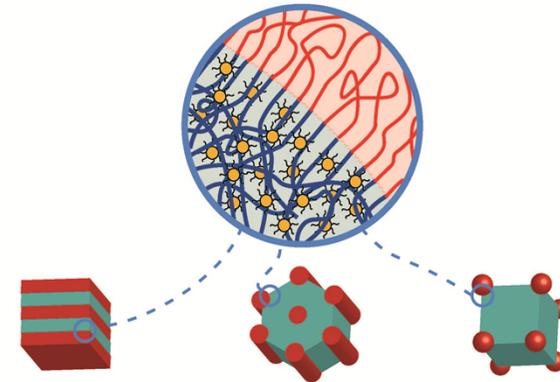
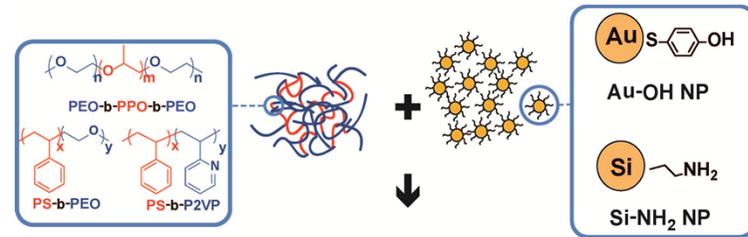


Increasing f \longrightarrow



2 μm

Additive-Driven Assembly of Hybrids

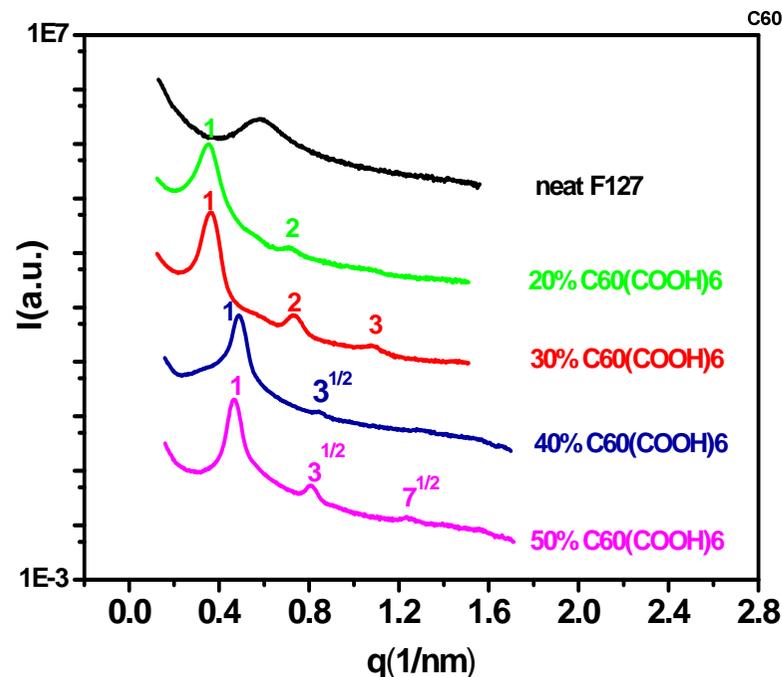
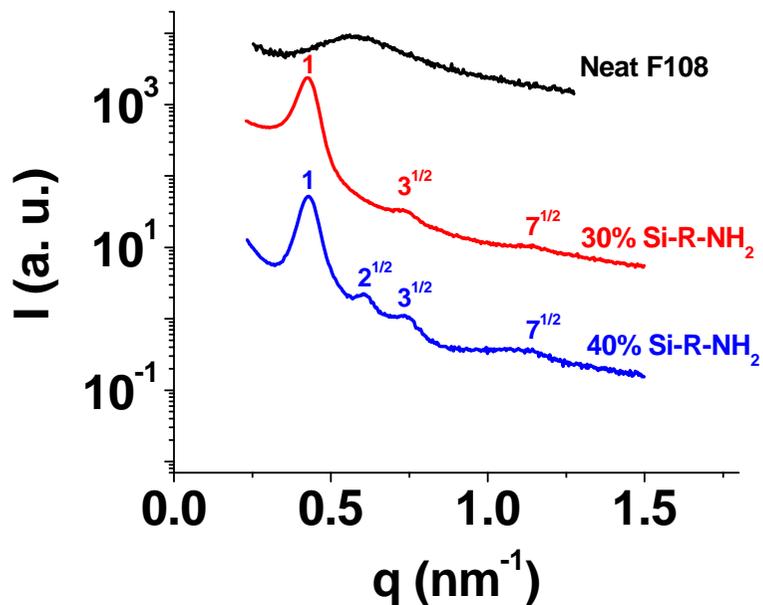
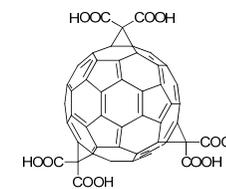


50 nm

Nanoparticle-Driven Assembly of Well-Ordered Hybrid Materials

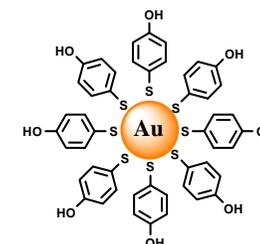
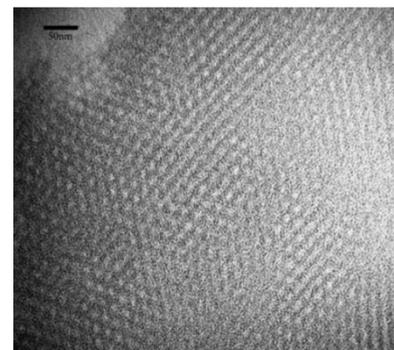


Disorder-to-Order Transitions in PEO-PPO-PEO Copolymers Induced by Functionalized Si, Au Nanoparticles or Fullerenes



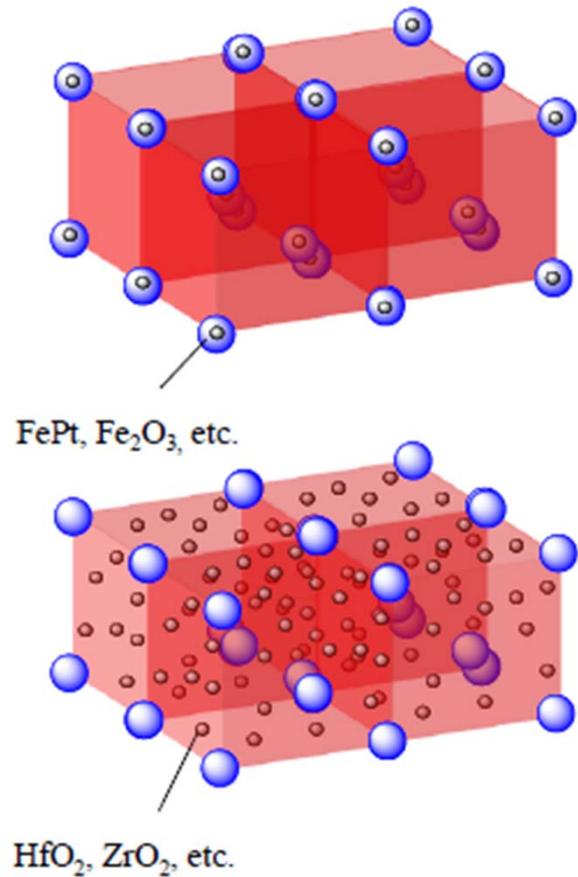
Disorder \rightarrow Cylinders \rightarrow Spheres

- First demonstration of nanoparticle-induced order!
 - Addition of NPs drives system order
- Robust, rapid, precision assembly of hybrid materials
- Low molar mass ligands, high NP content



Can We Control the Placement Discreet Populations of NPs?

Phase-Targeted Loading of Dual NP Systems Using Orthogonal NP-Segment Interactions

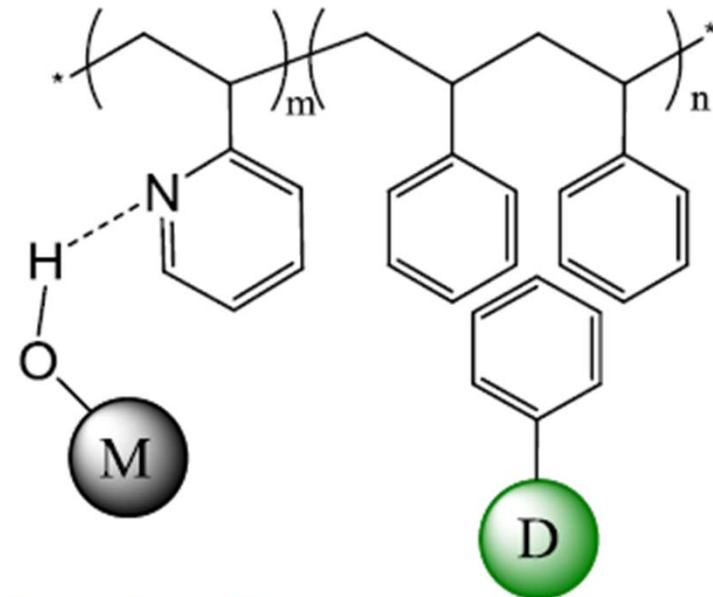


miniaturize

$$L \sim \frac{1}{\sqrt{\mu}}$$

impedance match

$$Z = Z_0 \sqrt{\frac{\mu_r}{\epsilon_r}}$$

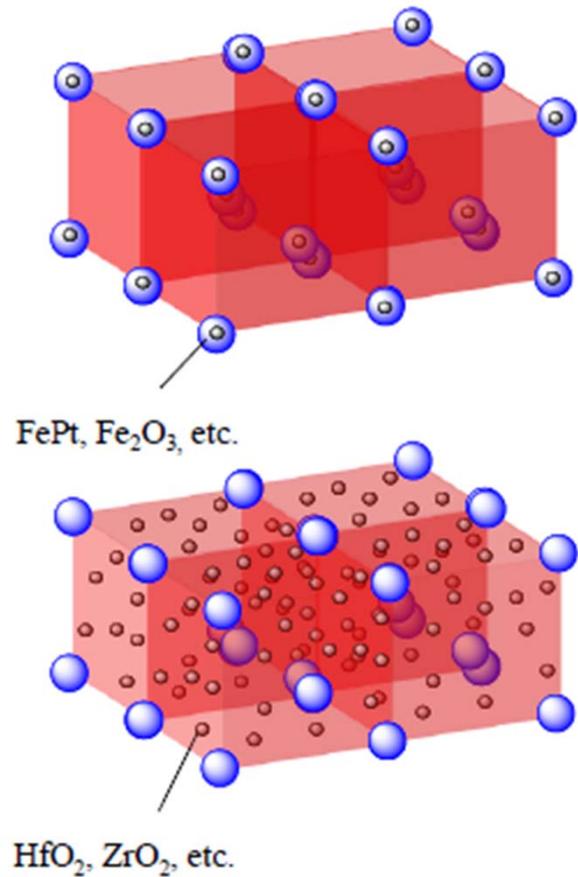


H-bonding with magnetic NPs

π - π stacking with dielectric NPs

Can We Control the Placement Discreet Populations of NPs?

Phase-Targeted Loading of Dual NP Systems Using Orthogonal NP-Segment Interactions



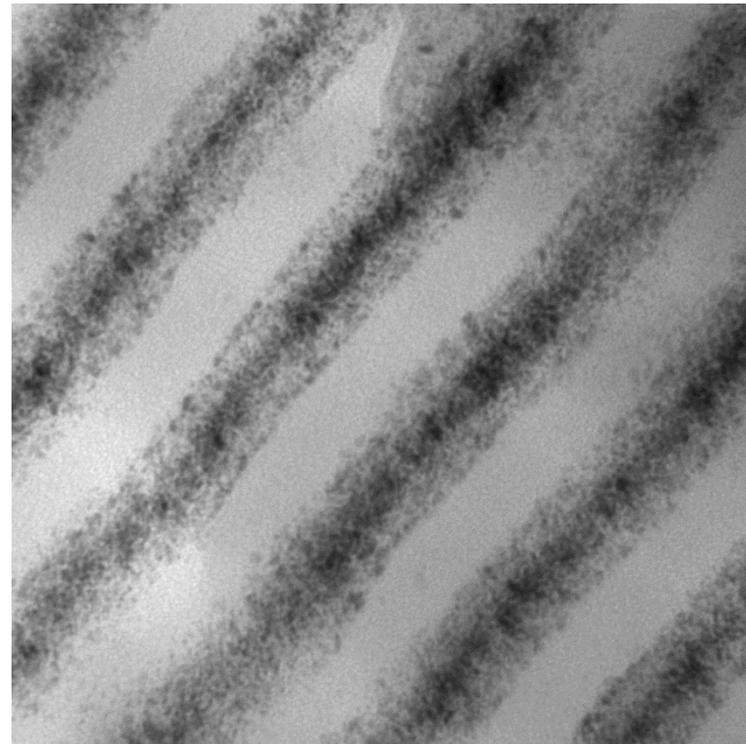
miniaturize

$$L \sim \frac{1}{\sqrt{\mu}}$$

impedance match

$$Z = Z_0 \sqrt{\frac{\mu_r}{\epsilon_r}}$$

FePt, ZrO₂ in PS-b-P2VP

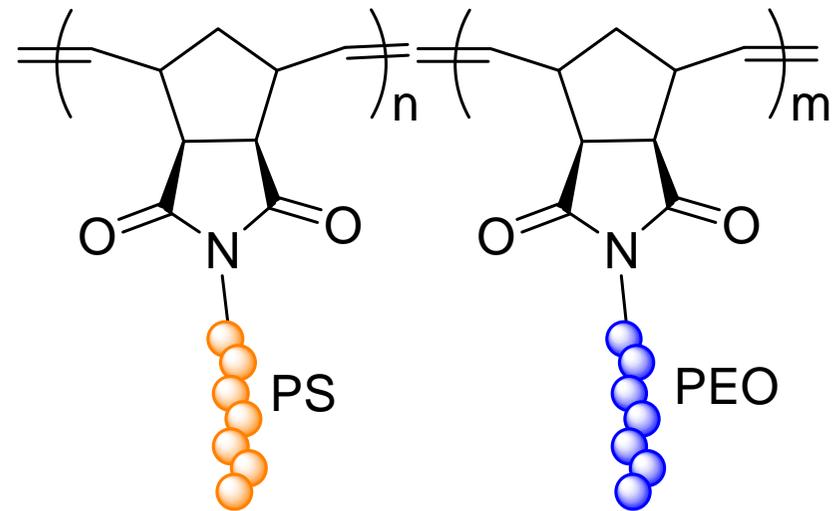
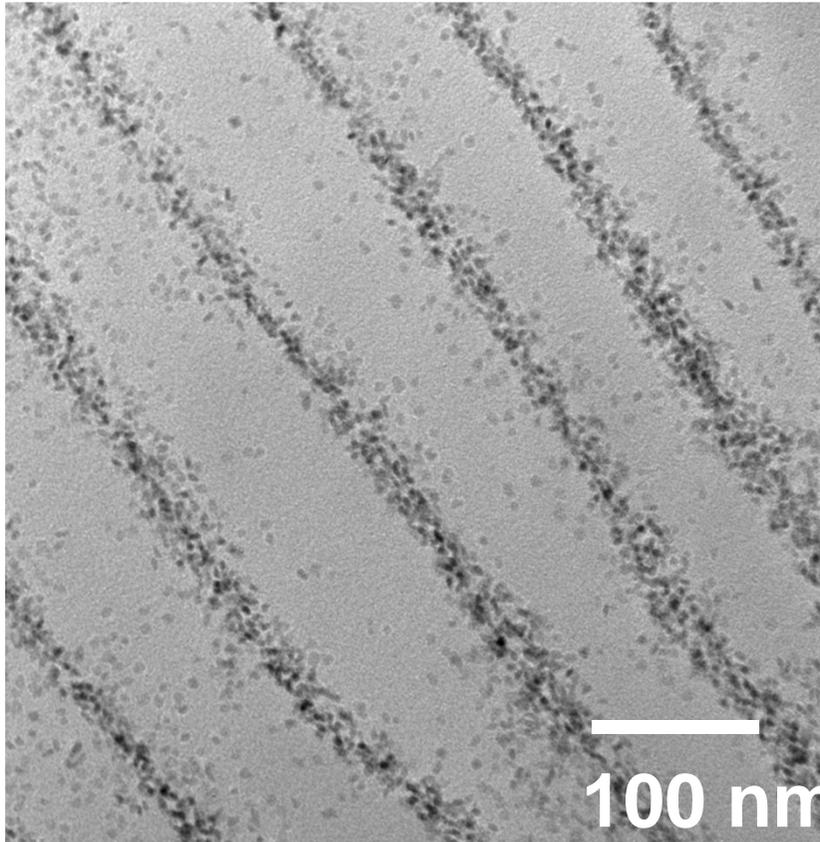


XWANG stained 03-25-13018
 PS-P2VP(199k)+10%FePt-OH+5%ZrO2T/10mg4PPy
 Cal: 0.14828 nm/pix
 6:12:43 p 03/25/13

20 nm
 HV=200.0kV
 Direct Mag: 80000x
 X:na Y:na T:

Can We Apply Self Assembly to Large or Optically Active NPs? Control Interactions, Use Templates with Large Periodicities that Assemble Rapidly

ZrO₂ in PS-PEO Bottle Brush

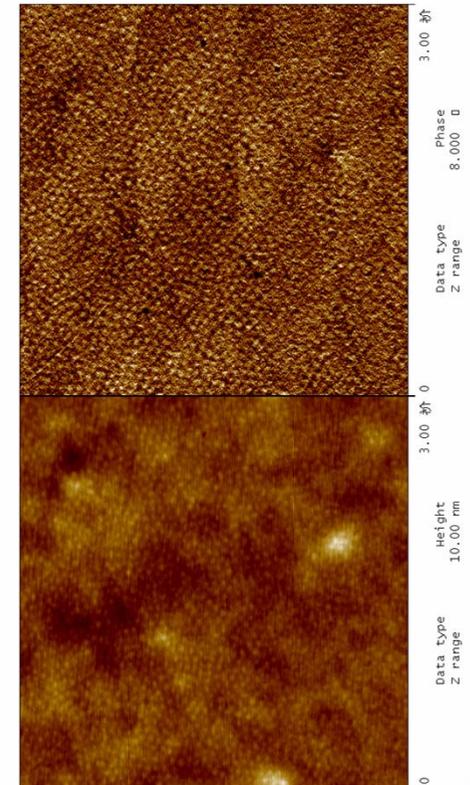


Scale-Up --- Roll-to-Roll Coating of Ordered Hybrids

- Two interchangeable microgravure coaters placed in series (swappable with slot-die)
- First coater used to apply a planarization layer
- Second coater used to apply thin block copolymer or hybrid layer on planarized film.
- Three independently controlled ovens



PS-PtBA on
Planarized PEN



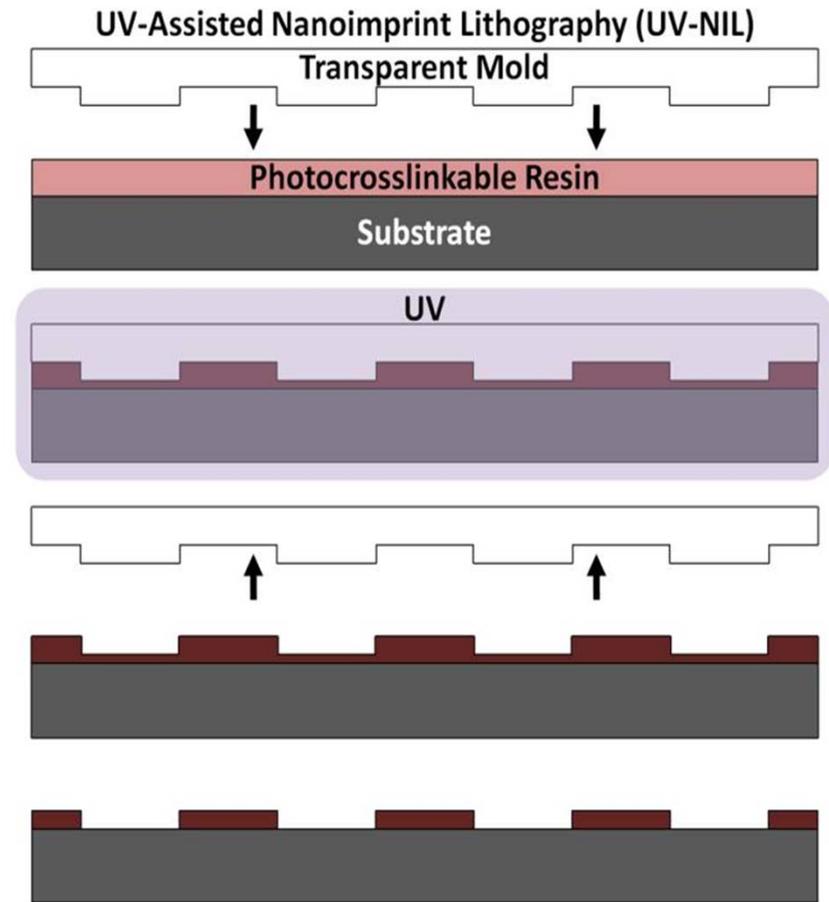
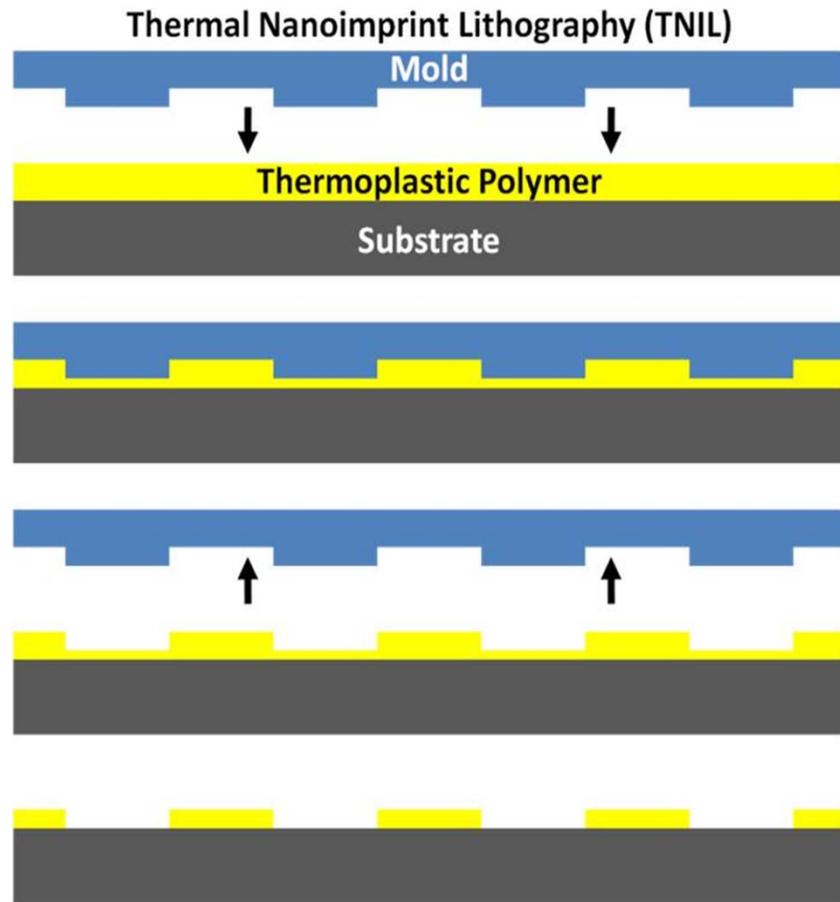
- Use “known” tools but new materials and process
- Validate structures, capabilities and scaling
- CHM research includes experiments and simulation

Patterning at Length Scales > 50 nm

Nanoimprint Lithography: Two Modes

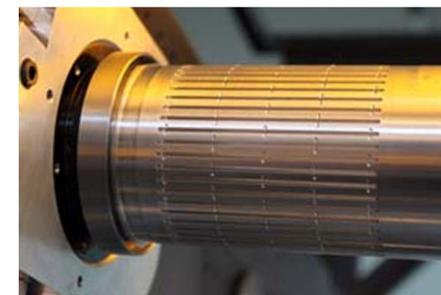
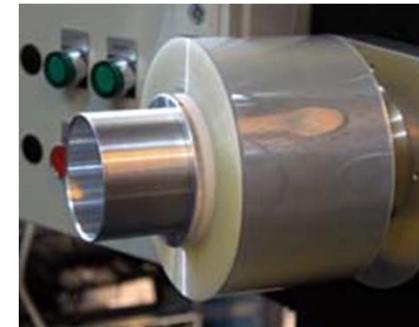
Thermal: Emboss thermoplastic or thermoset using heat, pressure

UV-Assisted: Contact UV-curable resin with master, photocure



Scale-Up: UMass / CHM R2R NIL Tool

UMass NANOemBOSS R2RNIL constructed with Carpe Diem Technologies (Franklin, MA)
Profs. Ken Carter and Jonathan Rothstein Test Bed Coordinators

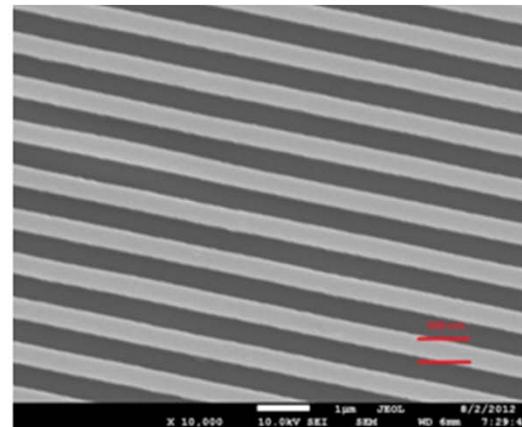
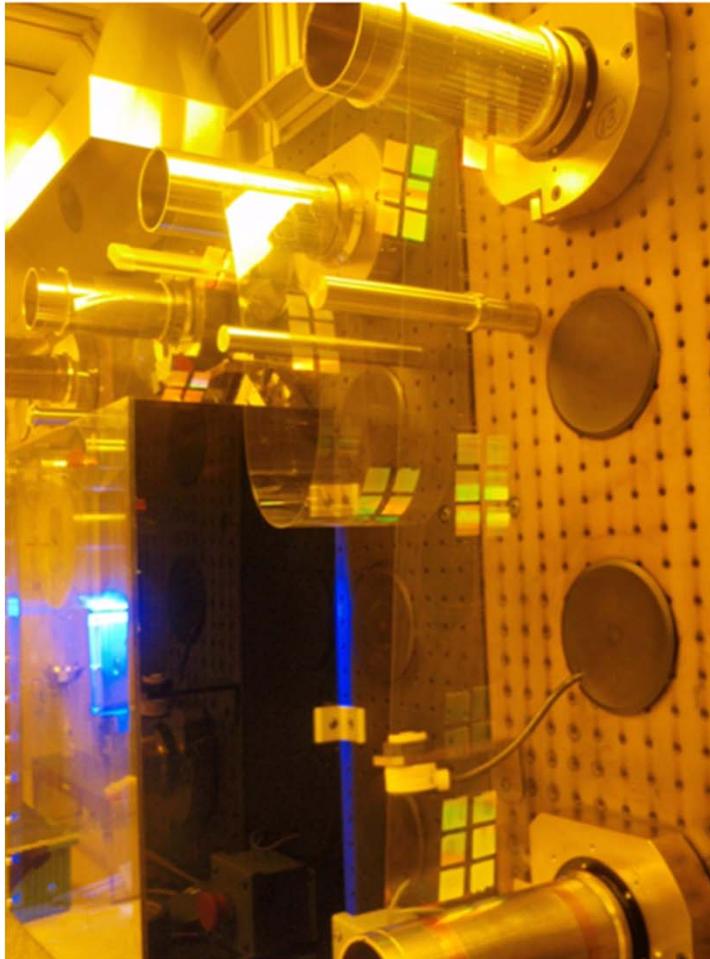


CHM
Center for Hierarchical Manufacturing
University of Massachusetts Amherst

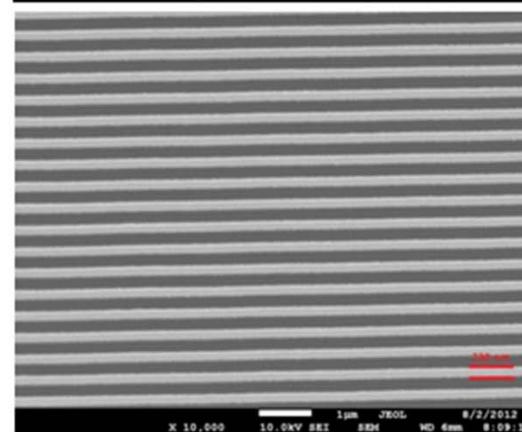
Transitions/Implementation Require Robust Demo Tools



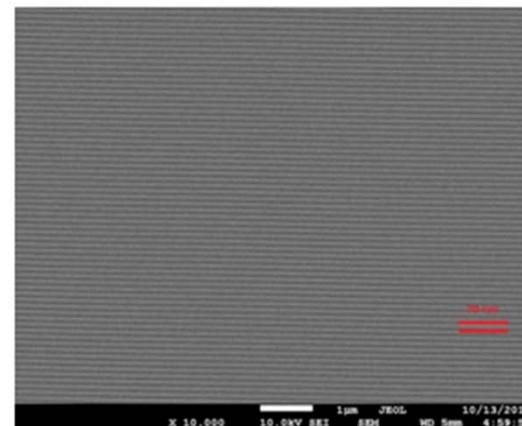
R2RNIL – 500 nm to Sub-100 nm Gratings



500 nm

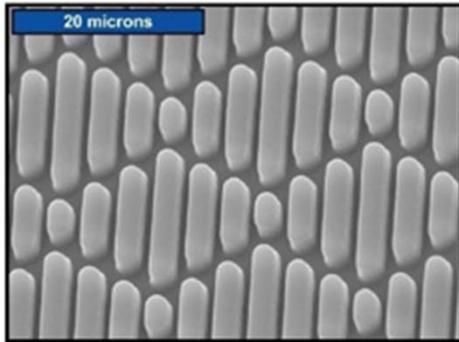


230 nm

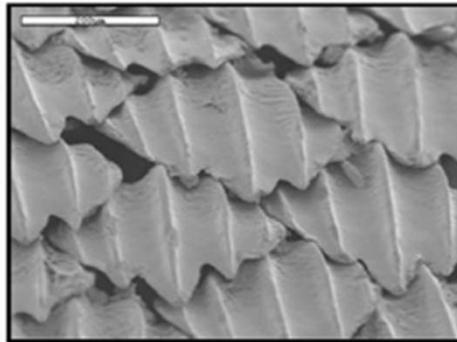


70 nm

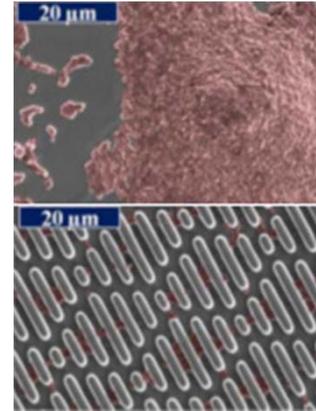
Large Area Antimicrobial Textured Layers



Sharklet™ Surface Technology

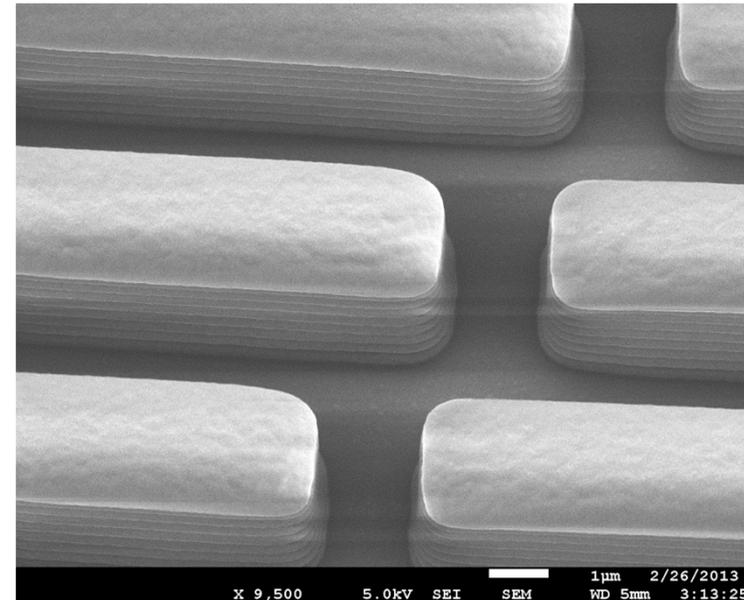
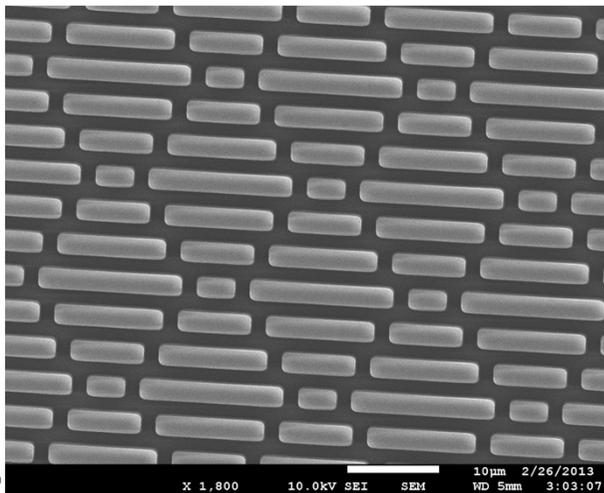


Galapagos Shark Skin

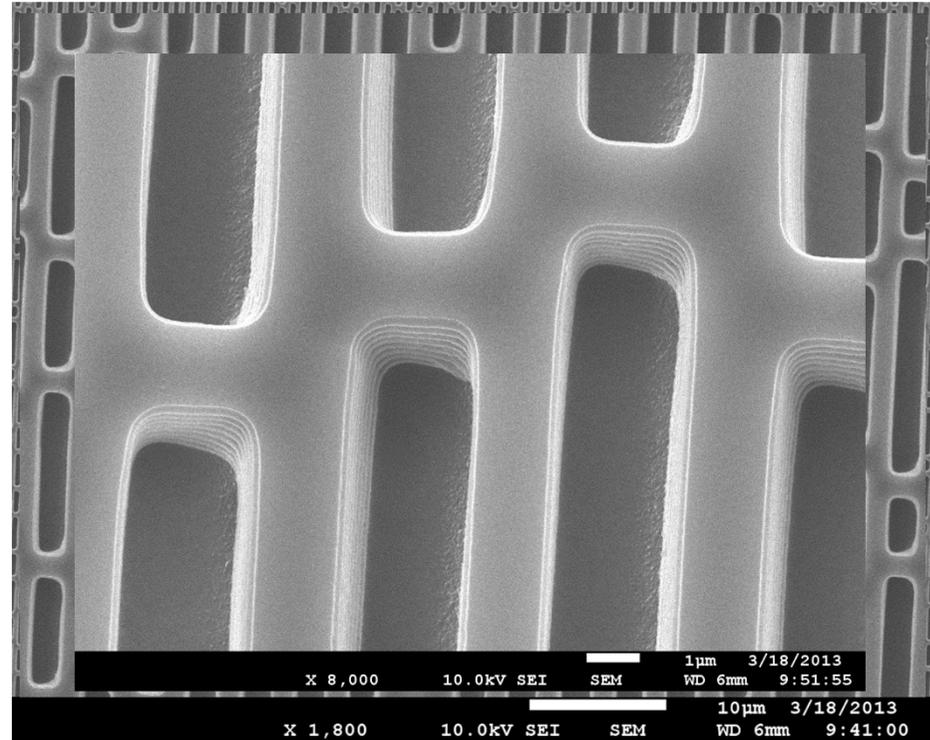
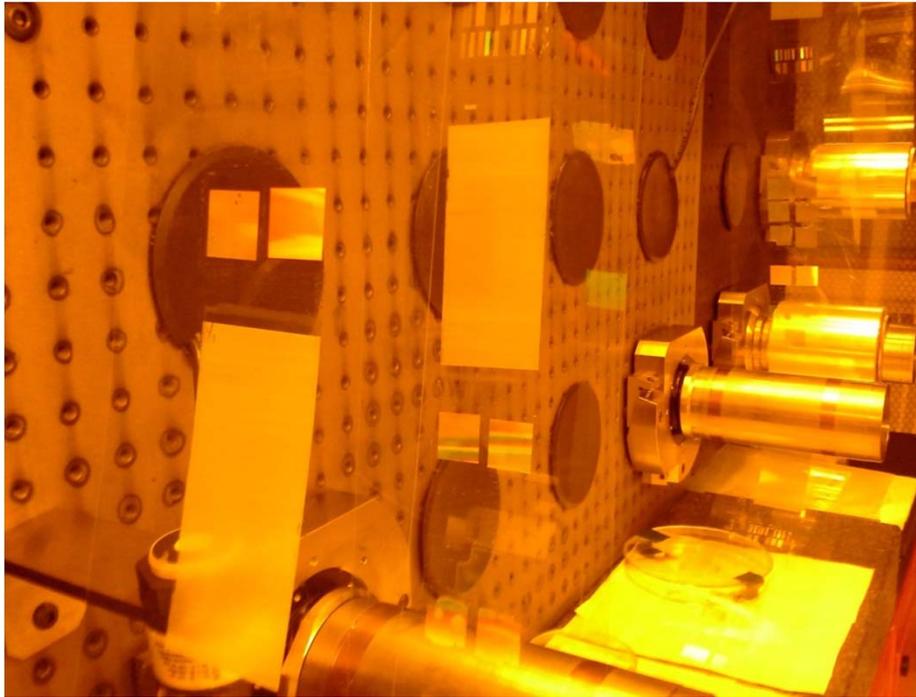


NIIL and R2RNIL Challenge: Can we replicate Sharklet pattern?

PFPE daughter mold from 6 inch master



R2RNIL on CHM Nanoemboss



Mold Preparation:

- Negative of Sharklet features on 6 inch wafer was replicated on to PFPE on PET hybrid mold

Substrate Treatment:

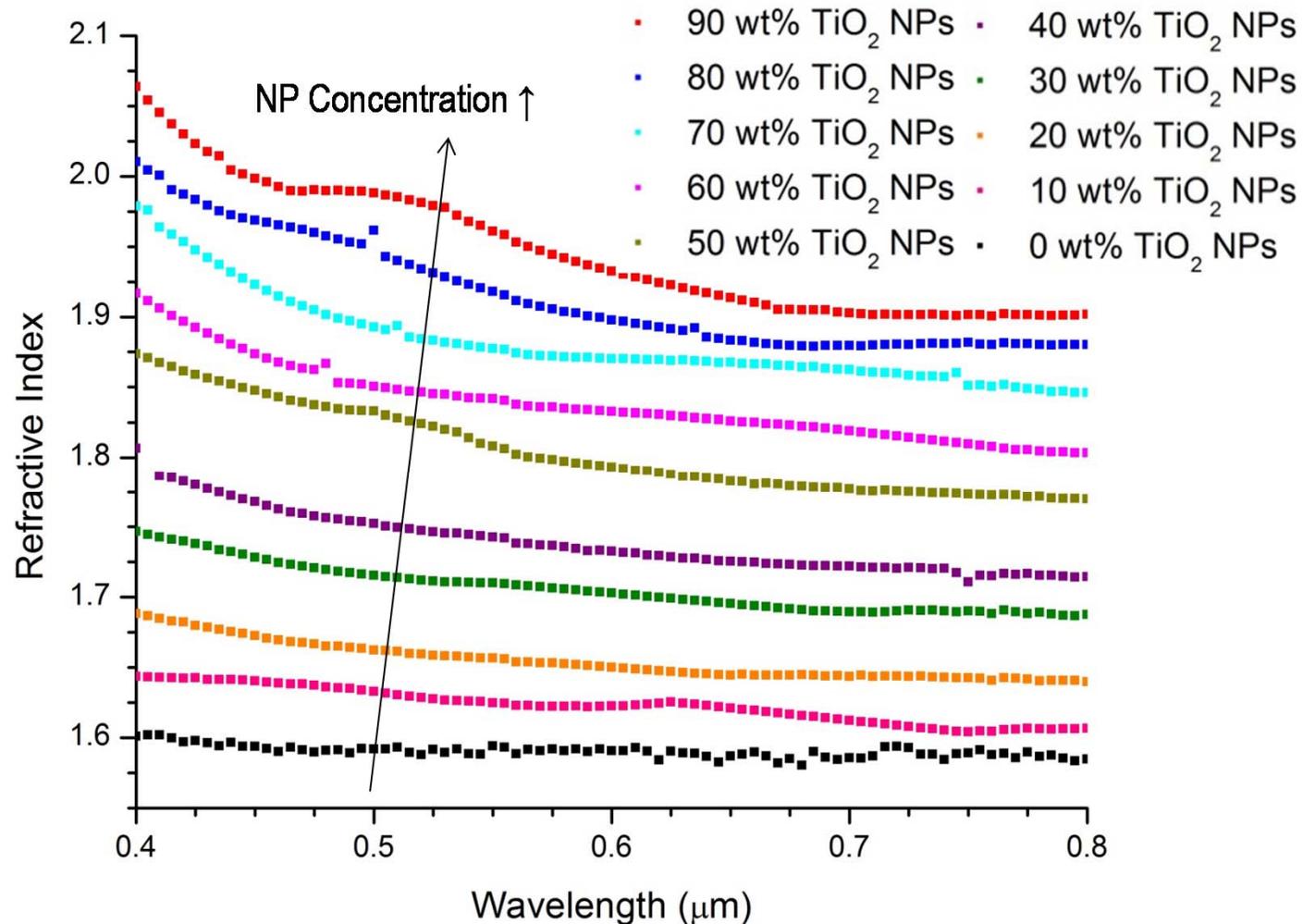
- PET web was coated with an adhesion agent then a photoresist layer was applied
- This PET pre-treatment improves the quality of imprinted features in long runs

R2RNIL Conditions:

- Resist: NOA adhesive - 40 v/v % in PGMEA
- Speed: Imprinter was run at 10 -12 inches / minute
- Exposure at 365 nm

Solution Coatable Patterned and Planar Hybrid Device Layers: Polymer / NP Composites with Tuned Material Properties

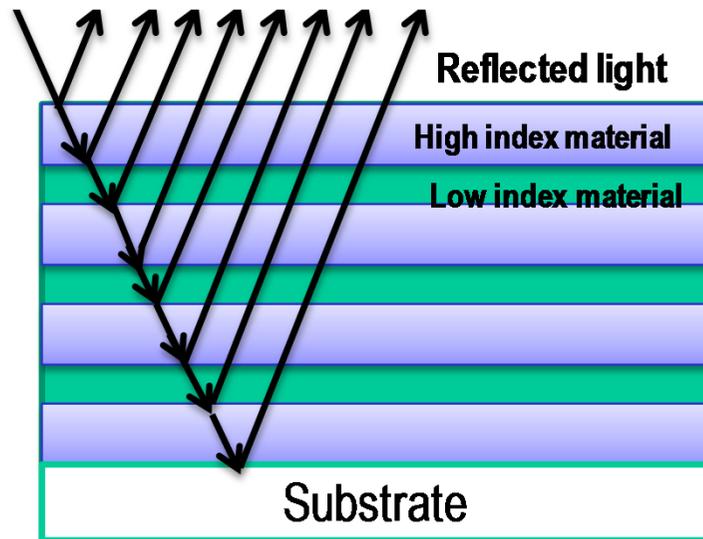
Refractive Index of Transparent Polymer / TiO₂ NP Hybrids



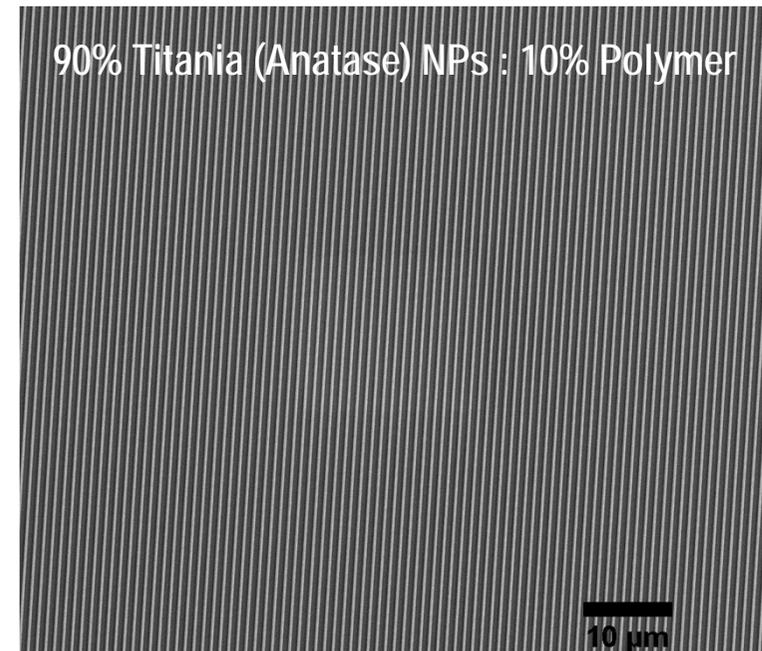
Solution Coatable Patterned and Planar Hybrid Device Layers

Example: Tuned Material Properties, Patterns by Nanoimprint Lithography

Wavelength Selective Bragg Mirrors



NIL Patterning of Composites

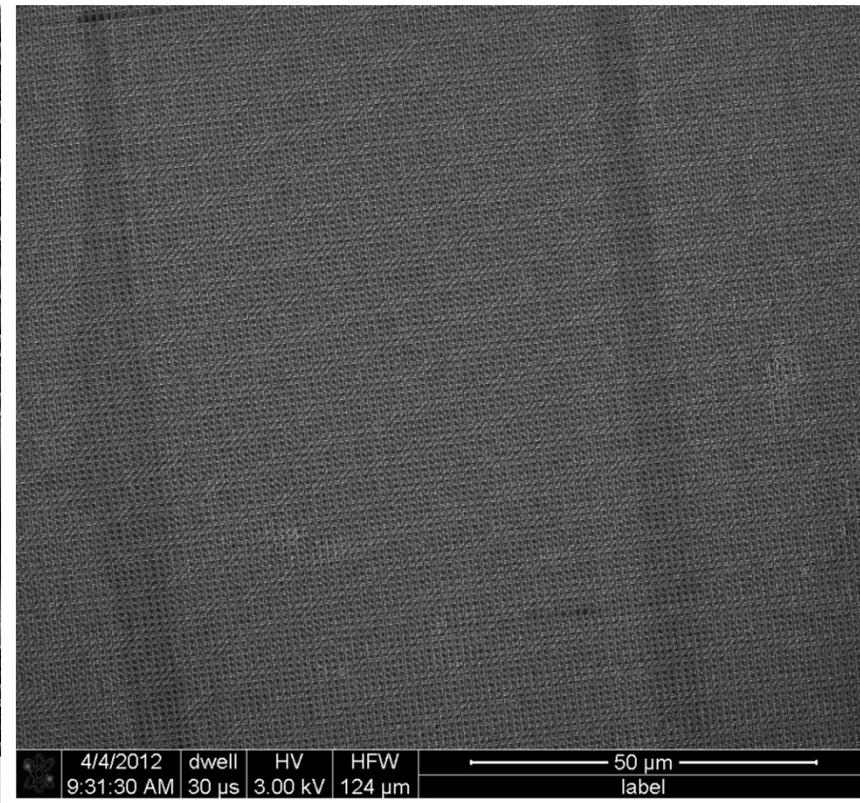
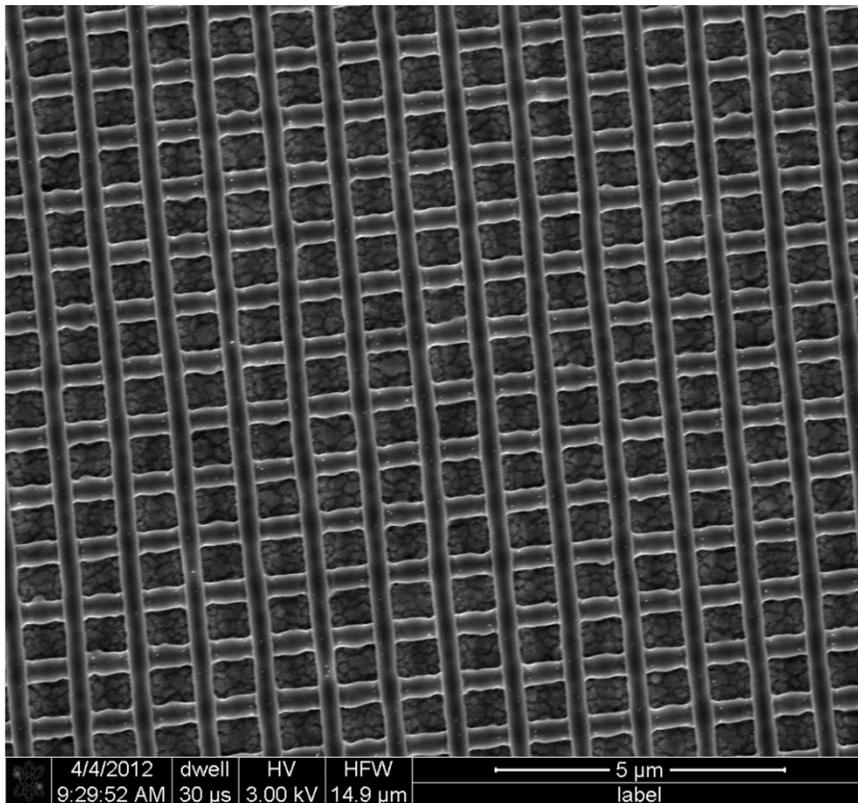


. U.S. Appl. 13/900,248

We can create, coat and pattern smooth polymer/NP and NP films
Ranging from 100% polymer to 90% stabilized NPs
metal oxides/high k /high RI / low RI
Crystalline NPs / structures –Low Temperature Processing

Fabrication of True Three-Dimensional Patterns

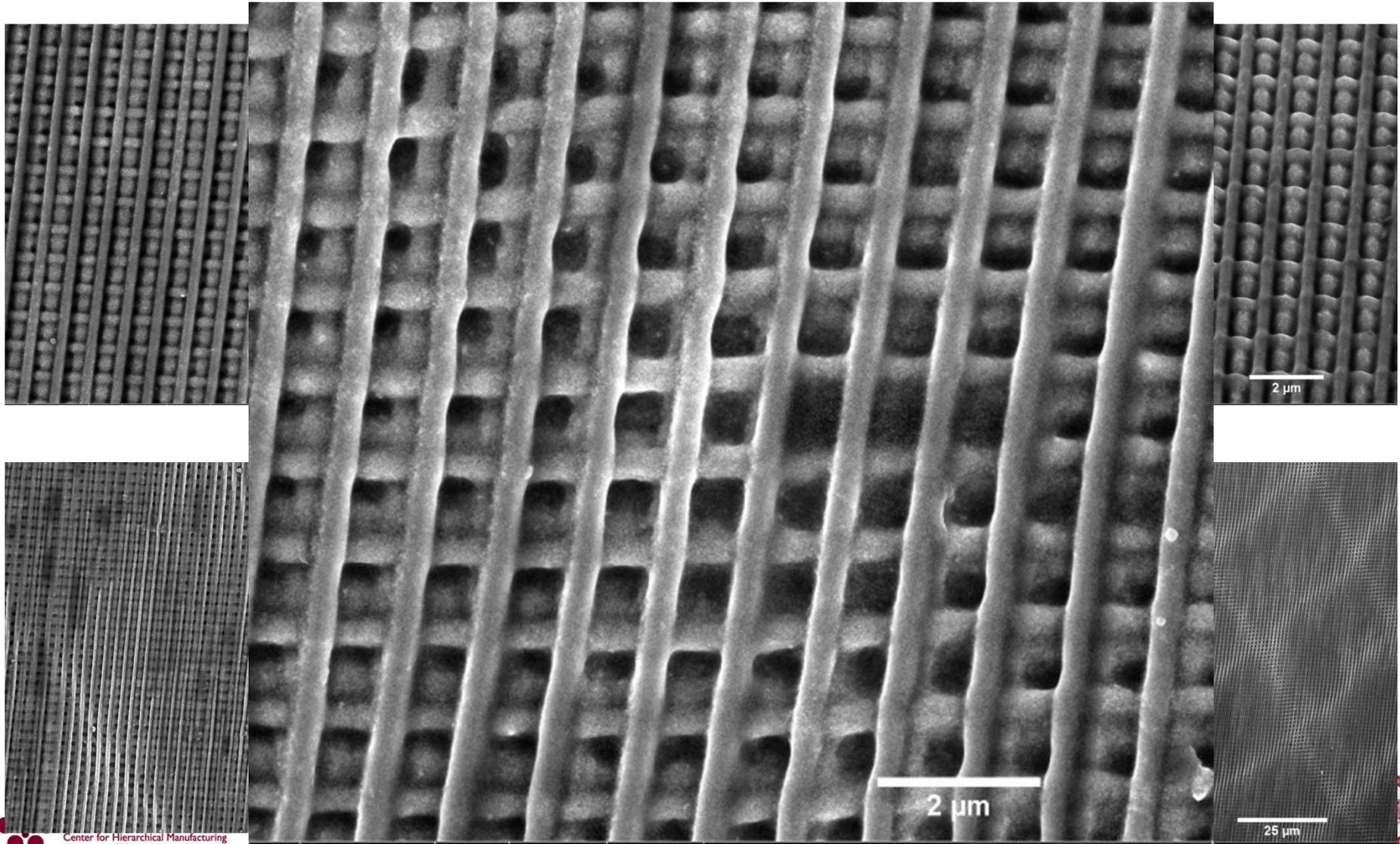
Lift-Turn-Stack



Many, many geometries possible, not limited to grid patterns
Features below 100 nm readily accessible
Extend to R2R

3D Patterning: Tetralayer

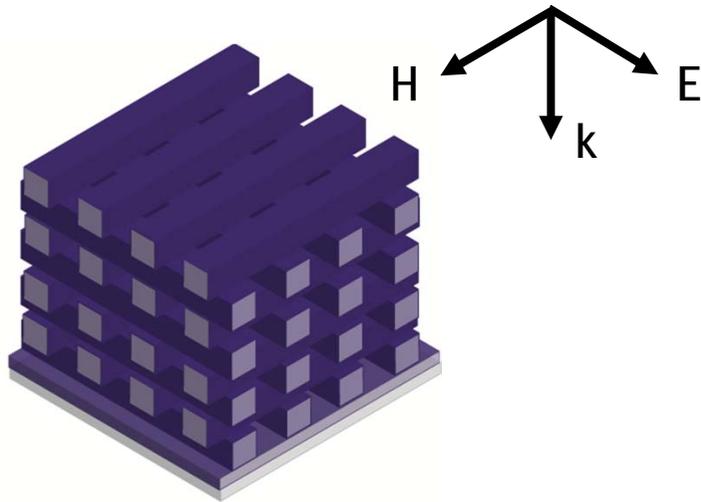
- SEM Images: 50% TiO₂, 50% NOA60



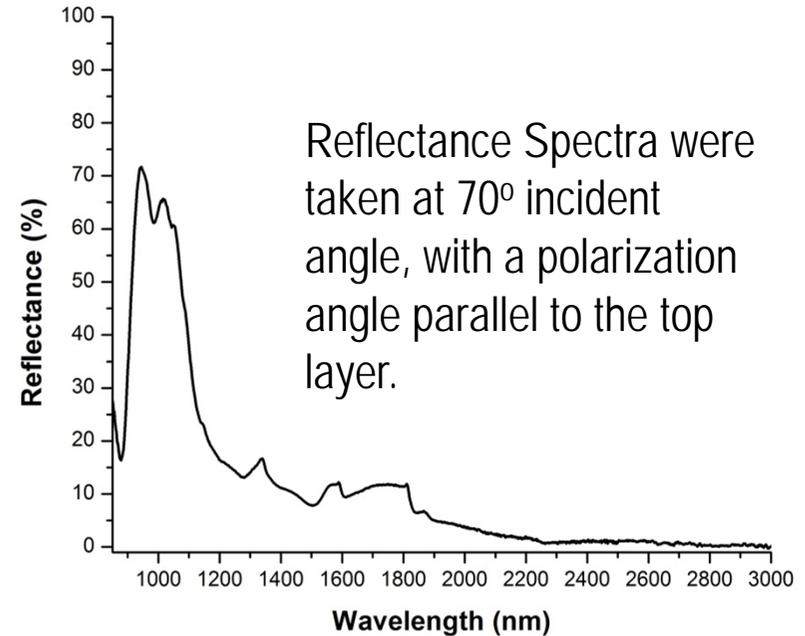
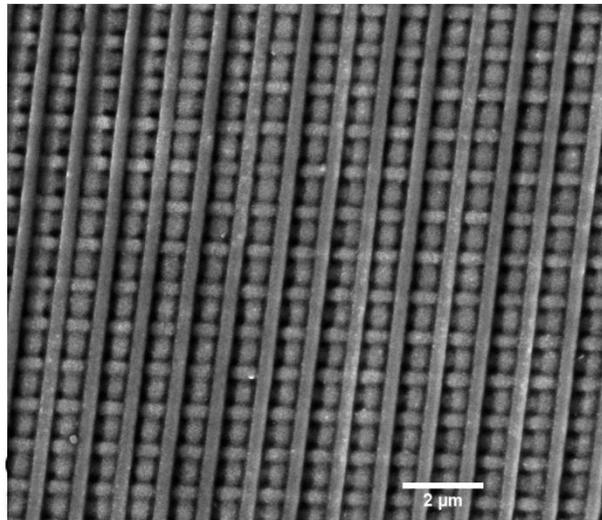
Printing of True 3-D Nanostructures

Print, Lift, Turn and Stack for Photonic Log Pile Structures

6-layer Photonic crystal made from 50 wt.% anatase TiO_2 nanoparticles and 50 wt.% photoresist



Top Down SEM View



Many geometries possible, not limited to grid patterns
Features below 100 nm readily accessible
Extend to R2R



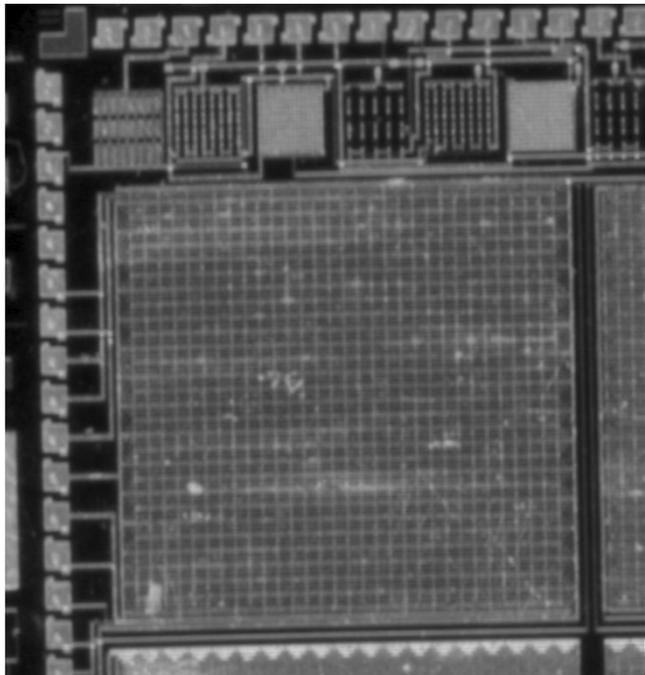
Challenge 3: Run Fast → Make Mistakes Fast

On-line Metrology of Nanostructures for R2R

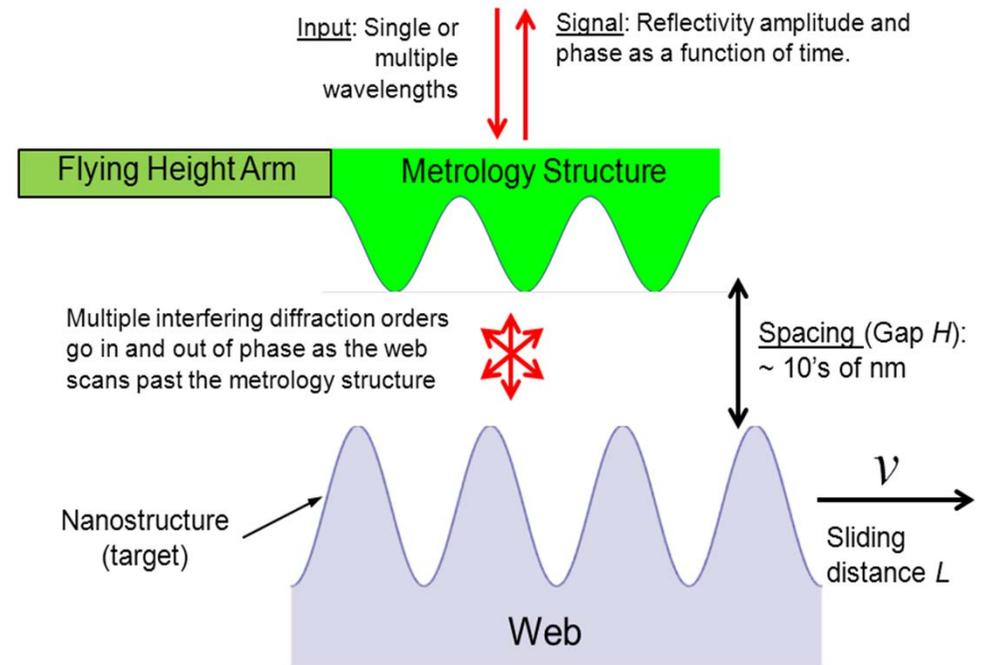
MIT (Hardt/Anthony)
Super-resolution Imaging



Super Resolution Image with
10x Greater Resolution



NIST (Liddle/Gallatin)
“matched optical filter” approach
(near field grating interferometry)



Challenge 4: Reduce Risk of Exploration/Adaptation/Commercialization by Industry Partners

- Emerging Fields Characterized by Fragmented Developments with Variable Readiness Levels – Reality Does Not Follow Roadmaps
- New Materials and Processes Will Require Validated Tools and Scaling
- “New” Tools Typically Must Be Compatible with Existing Lines
- Maturing of New Technology May Require Demonstration Facilities with Multi-University/Industry Partnerships and Professional Staffing
 - Potential for Follow-On/Parallel Funding for Academic Research Centers
- Incremental Successes Build Foundations for Game Changers
- Pre-competitive Partnerships Can Add Value

New Example at UMass Amherst

R2R Facility for Life and Nanosciences at the Heart of CPHM*

- Novel R2R Process Tools based on UMass/CHM Technology
- Novel R2R Process Tools based on Emerging Technology w/ Partners
 - ALD, Graphene, R2R Test Frames for Processes
- State of the Art Commercial Technology
- Common 6" Wide Web Platform
- Professional Staff (Goal)
- Early Engagement of CHM R2R Advisory Board and Stakeholders
- Cluster R Precompetitive Consortium – Emerged from CHM
- Partnership Space
- Emerging Technology Workshops

*\$46 million capital investment in Center for Personal Health Monitoring by Commonwealth of Massachusetts
\$30 million equipment (\$15 in New R2R Manufacturing Tools)
\$16 million facilities including industry partnership space



Challenge 5: Build Communities of Practice

- Trade Associations / Roadmaps
- Supply Chains
- Information Exchange



Serving the nanomanufacturing R&D community with technical information, workshops, and technology roadmaps



Summary of Needs

- **New Materials Sets Required for Increased Performance**
 - fabricate devices that meet market and consumer (civilian or DOD) demands
- **Demonstrate Manufacturability of Lab-Scale Materials and Devices**
 - will stretch capabilities of many academic labs / groups
- **Develop Viable Tool Platforms**
- **Stage Priorities:**
 - large area light and energy management as “low hanging fruit”
 - obtain “inorganic “ device performance via R2R processing (transistors first)
 - integrated electronics and system development (e.g. autonomous sensor)
- **Metrology is Largely Missing**
- **Reduce Risk of Partner Exploration and Adaptation**
 - demo facilities staffed with professionals and training (who pays?)
- **Funding Agencies Have Needs Across TRLs or MRLs but Tend Not to Provide Funding Across TRLs**
 - opportunities for Multi-Agency Activity Coordinated Investment
- **Build Communities of Practice and Supply Chains**

