Convergence of Polymer Self-Assembly and Roll-to-Roll Process Technology for High Volume Manufacturing of Nanotechnology-Enabled Devices

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Center for Hierarchical Manufacturing (CHM)

An NSF Nanoscale Science and Engineering Center funded through CMMI

Multidisciplinary Expertise of 39 Faculty in 8 Disciplines

- Chemistry
- Chemical Engineering
- Electrical & Computer Engineering
- Food Science
- Mechanical & Industrial Engineering
- Physics
- Plant, Soil and Insect Science
- Polymer Science & Engineering

Academic and National Lab Partners (financial support or MOU)

- University of Puerto Rico – Rio Piedras
- Mount Holyoke College
- Indiana University
- Binghamton University
- MIT
- NIST
- Rice University
- University of Michigan
- STCC

International Collaborations

Tohoku University (World Premier Institute – Advanced Institute of Materials Research), Institut de Chimie de la Matière Condensée de Bordeaux , National Centre for Scientific Research (ICMCB/CNRS) – University of Bordeaux, University of Nottingham

Industry Research Collaborators and Advisors

Aerodyne, Alenas Imaging, AMD, Applied Materials, Cabot, Endicott InterConnect, E-Ink, FLEXcon, FlexTech Alliance, Hitachi, Holographix, IBM, Inframat, Kodak, Konarka, MicroContinuum, Nano-C, Novellus, Panasonic Boston Labs, Porifera, Saint-Gobain, Seagate, Semiconductor Research Corporation, StorBurst Technologies, 3M

Sponsored Research

Aerodyne, AMD, Benchmark/Holographix, Boston Scientific, Inframat, Kodak, Kuraray, Marubeni, Nexgen, Novellus, Panasonic Boston Labs, Porifera, Saint-Gobain, SciDose, Seagate Technologies, Semiconductor Research Corporation

Selected CHM Perspectives on Nanomanufacturing

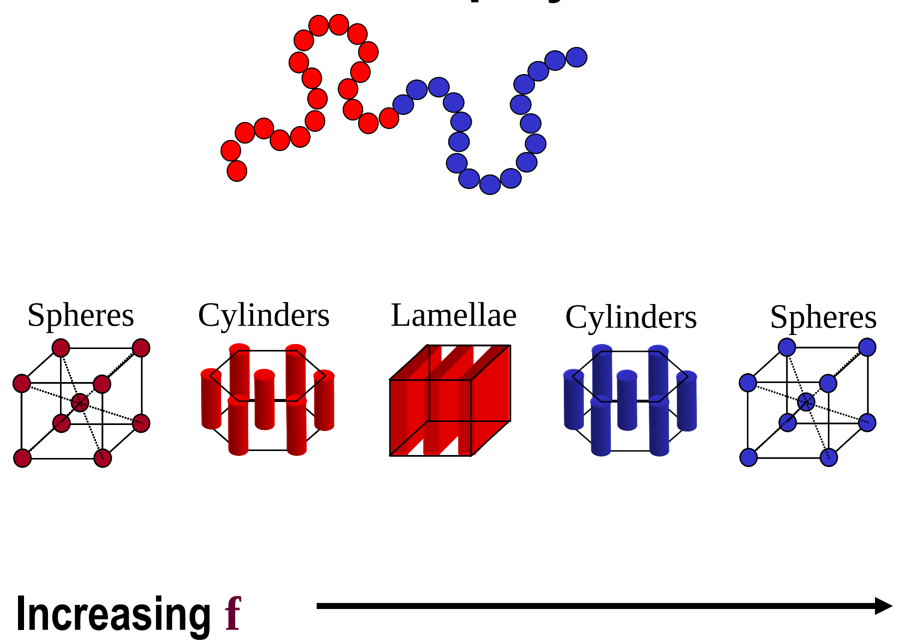
Challenges:
- two and three-dimensional integration across disparate length scales
- cost-effective nanomanufacturing
- metrology

Solutions:
- self and additive-driven assembly
- nanoimprint lithography
- continuous manufacturing technologies
  - roll-to-roll process tools
  - integration with flexible and printed electronics
- strategic partnerships

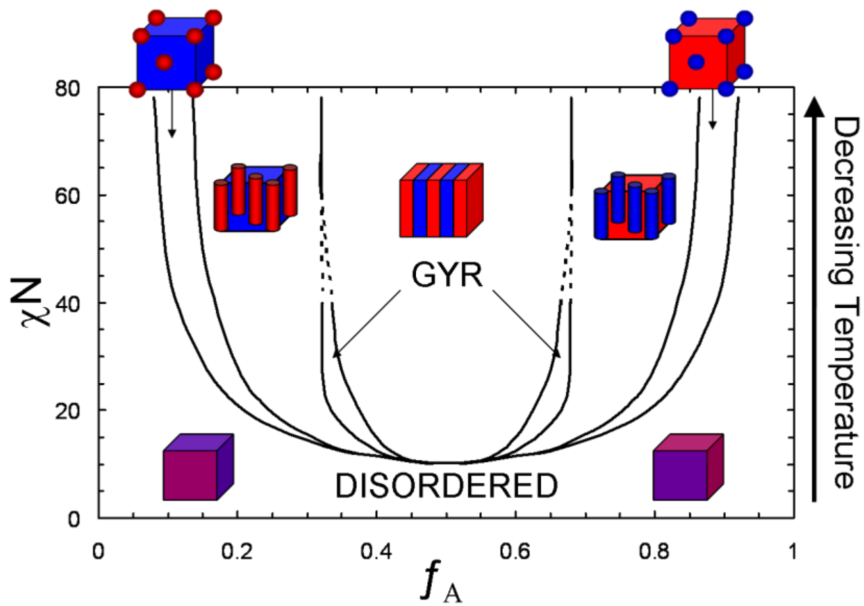
Impact:
- industry friendly adaptation
- platform tools
- regional development clusters

Block Copolymer Templates:
Spontaneous Assembly upon Spin Coating, Complete Control of Morphology

Di-block Copolymer



BCP Phase Diagram

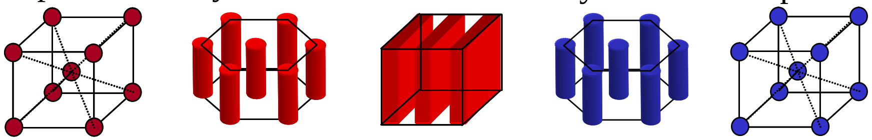


(Adapted from Bates, 1994; Matsen, 1996)

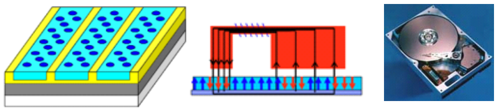
Key Parameters: block volume fraction, f → controls morphology
Flory Parameter, χ → χN controls segregation
degree of polymerization, N → controls domain size

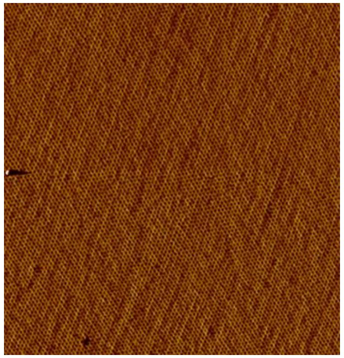
small N requires large χ for strong segregation

Block Copolymer Lithography for Integrated, Precision Electronics



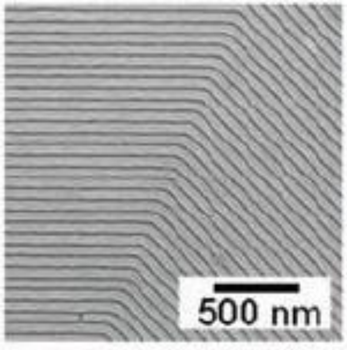
Bit Patterned Media





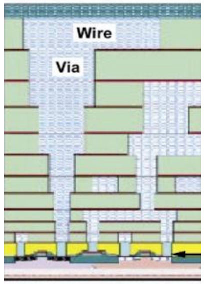
(Russell, Science 2009)

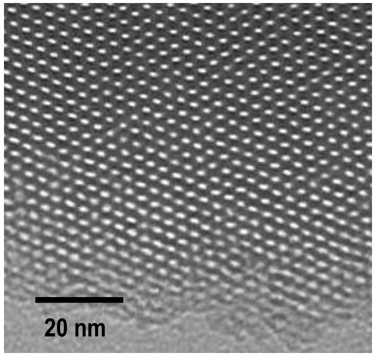
Small, Low LER Device Features (UW)



(Nealey, Science 2005)

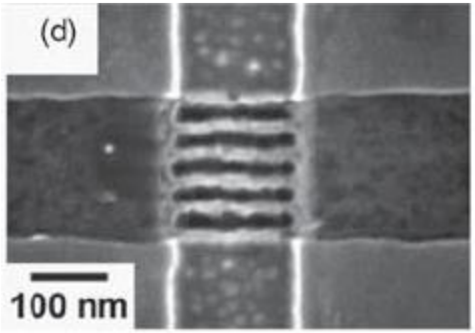
Porous ULK





(Watkins, Science 2004)

Nanowire FETs (IBM)



(Black, APL 2005)

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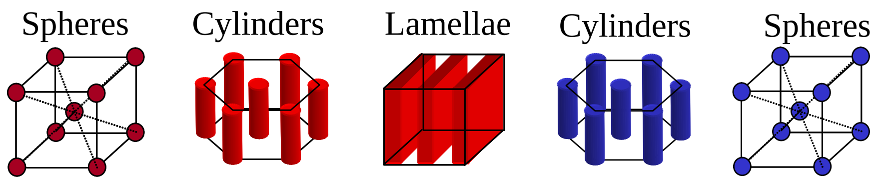
Block Copolymer Lithography for Precision Electronics



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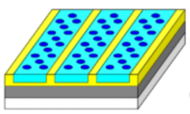
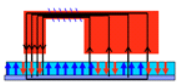
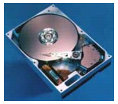
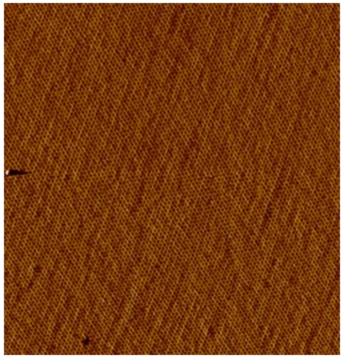


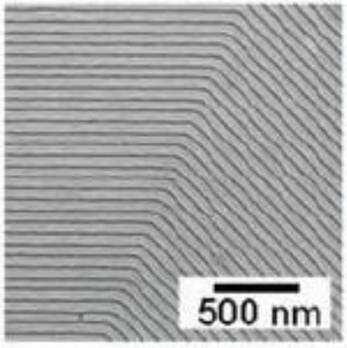






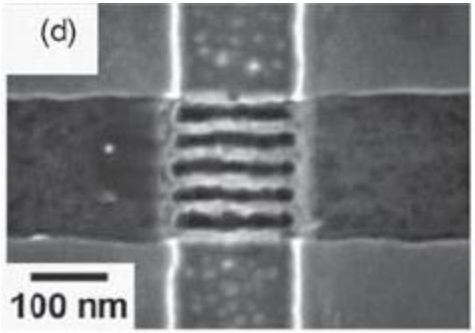
(Russell, Science 2009)

Small, Low LER Device Features (UW)



(Nealey, Science 2005)

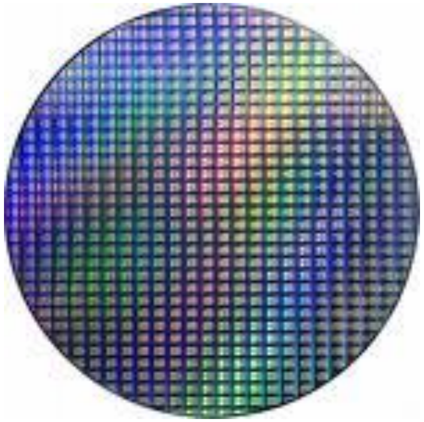
Nanowire FETs (IBM)



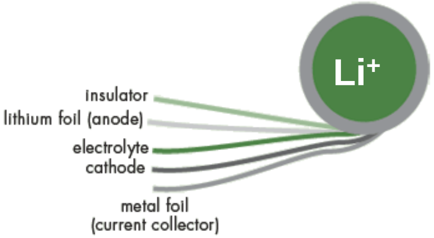
(Black, APL 2005)

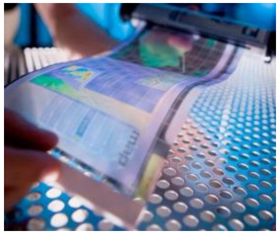
- BCP is a mask or template
- BCP is an insignificant contribution to cost
- Batch processing

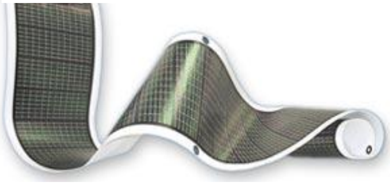
Nanotechnology Is Enabling but Many Important Applications are Cost Sensitive
Energy, Water, and Flexible Electronics
Nanomanufacturing Must Adapt to Serve Low Cost Per Area Devices



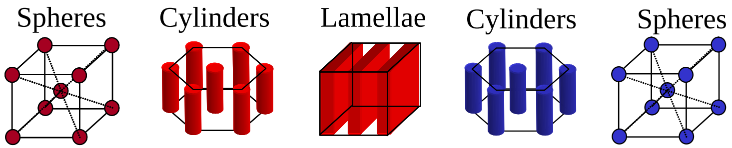
$25,000/m²







Target ~ $25/m²



- Morphology remains important
- BCP template is a significant cost
- Hybrid materials for functionality
    - co-assembly required
- Roll-to-Roll manufacturing
- Integration with Top down processes

Nanotechnology Is Enabling but Many Important Applications are Cost Sensitive: Nanomanufacturing Must Adapt to Serve Low Cost Per Area Devices

New Global Foundries Fab in NY
cost = $4.6 Billion
Wafer Cycle Time = 30 – 60 Days
Significant Barriers to Entry, Change
Few Players

Commercial Slot-Die Coater
cost = $350,000
Web Speed = 10 meters/minute
Inherent Flexibility, Low Barriers to Entry, Change
1000's of Players

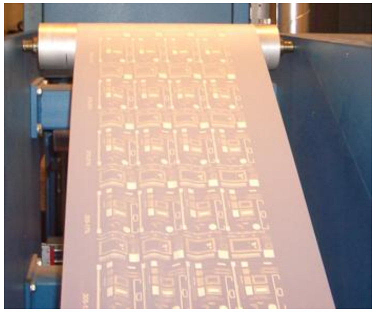
A necessary condition for this transformation is the translation of bottom-up processes such as self-assembly from Si-based methodologies to high volume, low cost platforms

Requires new materials sets and solutions to fundamental issues in the assembly of hybrid materials

Goal: Produce nano-enabled materials and devices using the tools of the flexible electronics and advanced coatings industries

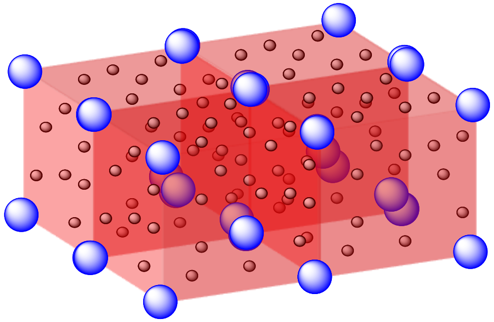
Low Cost Nanodevices by Combining Printed Electronics and Nanostructured Device Layers

- **Start with Printed Macroelectronic Substrate**
  - low cost, low performance
  - simple devices
  - micron ++ length scales

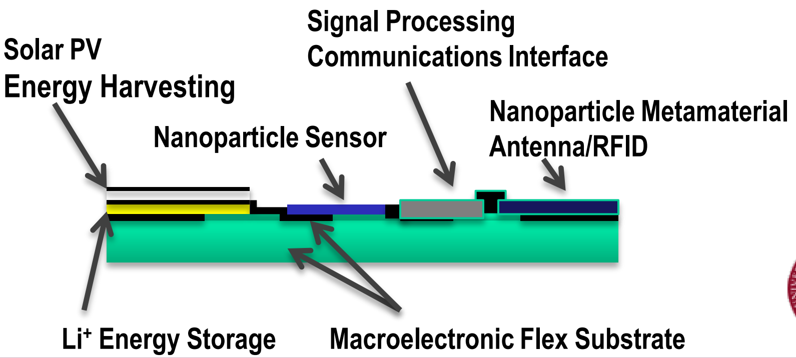


printedelectronicsnews.com

- **Add Nanostructured Device Layers via Low Cost Processing**
  - low cost, large area
  - enabled or enhanced functionality due to nanostructure
  - length scales less than 50 nm
  - may sit on top of printed macroelectronic substrate
  - PVs, energy storage, magnetic metamaterials, sensors



- **Produce Low Cost, High Performance Nanotech-enabled Device**
  - single purpose first
  - PV, battery, sensor, antenna
  - integrated devices



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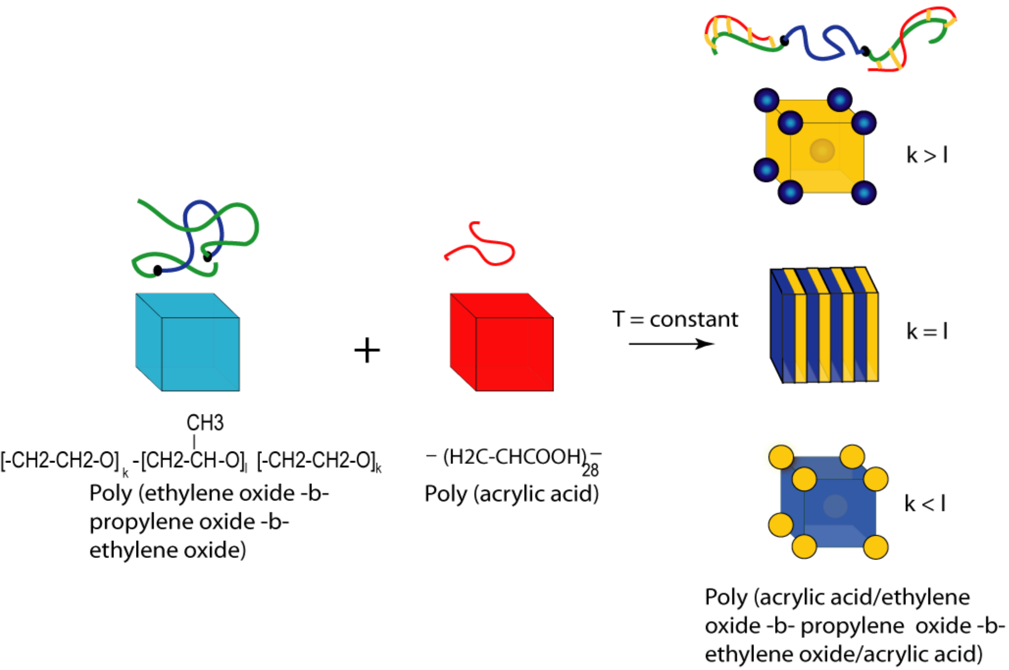
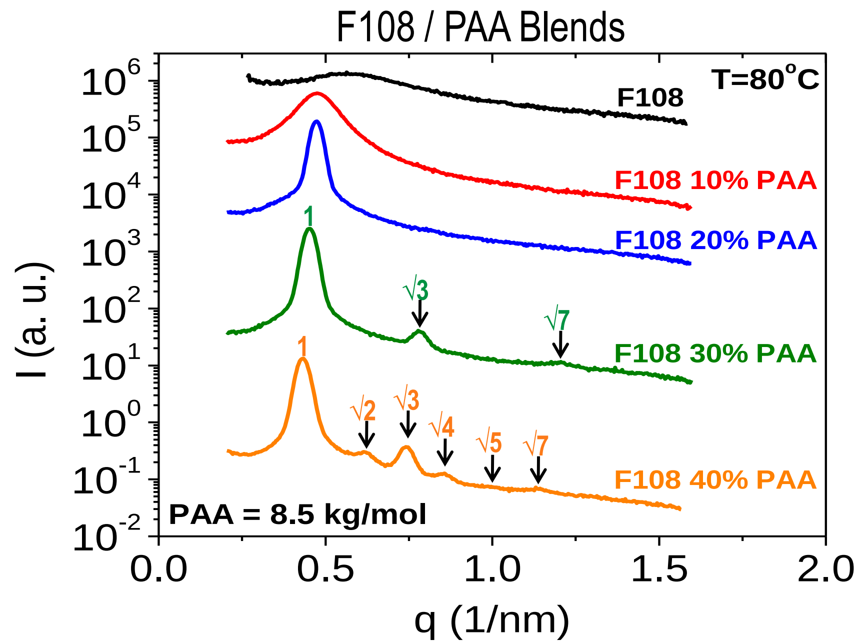
Extension of Self-Assembly for High Volume Fabrication of Nanostructured Materials and Devices

Key Issues and Strategies:

- **Commodity scale availability for low cost/high volume systems**
- **Creation of technologically useful materials: functionalize to realize electronic, mechanical, optical properties**
- **Create well-ordered nanoparticle/BCP systems with prescriptive placement of NPs and high NP loadings**
- **Develop robust R2R manufacturing platform**
  - **scalability, process models, manufacturability, metrology, QA, process control**

Strengthening Phase Segregation via Segment Specific Interactions: Well-Ordered Materials by The Barrel

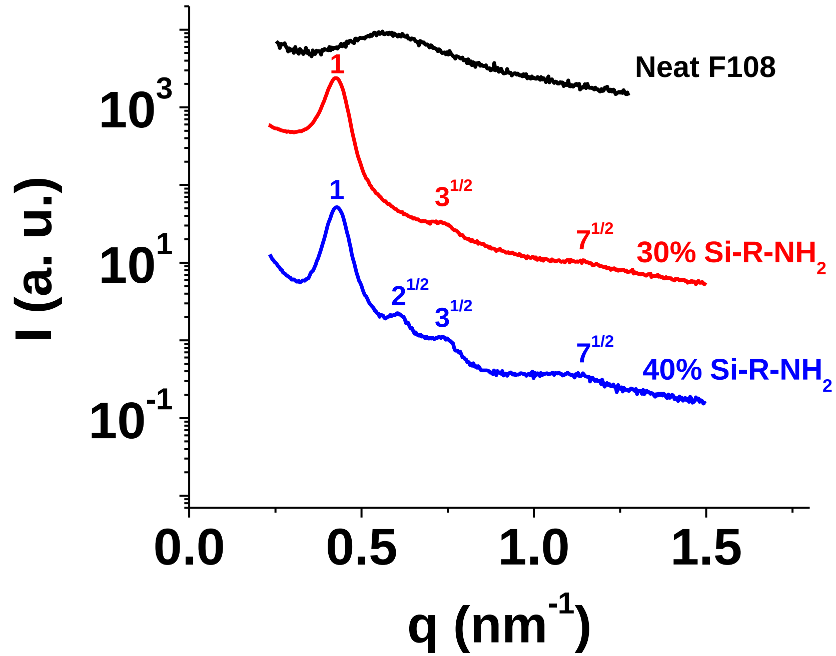




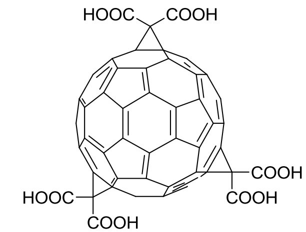
We find blending with homopolymers that H+ bond to the majority PEO block yields exceptionally well-ordered materials by increasing segregation

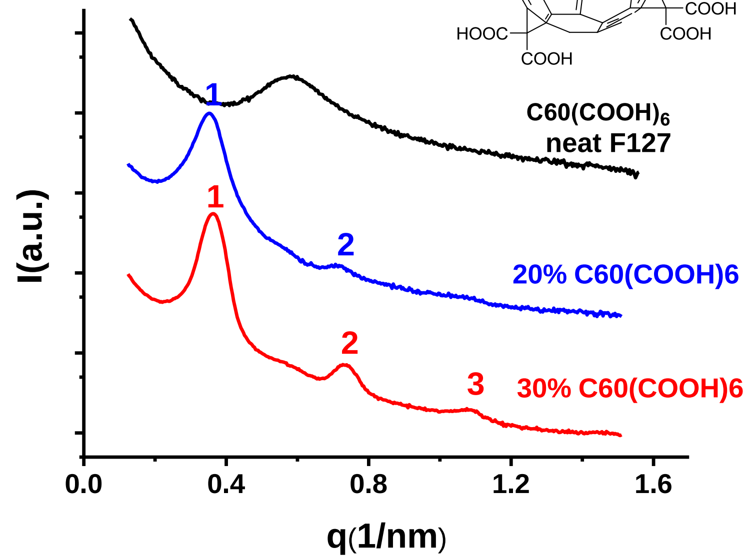
- Demonstrates the role of strong selective interactions in polymer assembly and block copolymer thermodynamics
- Will enable use of BCP templating in low cost applications (roll to roll, extrusion)
- Increases in χN will reduce feature size

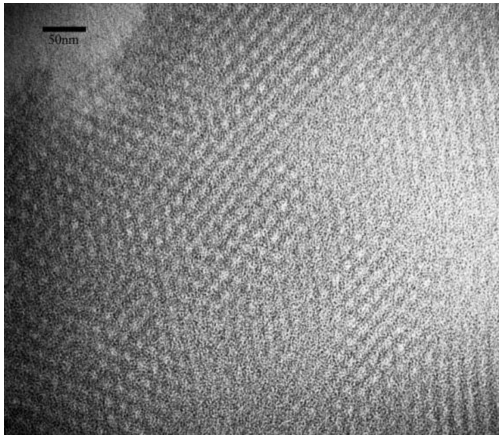
Nanoparticle Driven Assembly of Well Ordered Hybrid Materials: Disorder to Order Transitions in PEO-PPO-PEO Triblock Copolymers Induced by Functionalized Si, Au Nanoparticles or Fullerenes

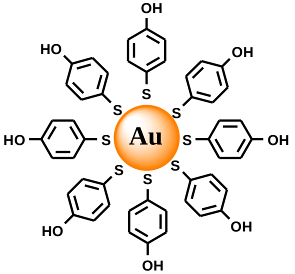


• Disorder → Cylinders→ Spheres









- 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

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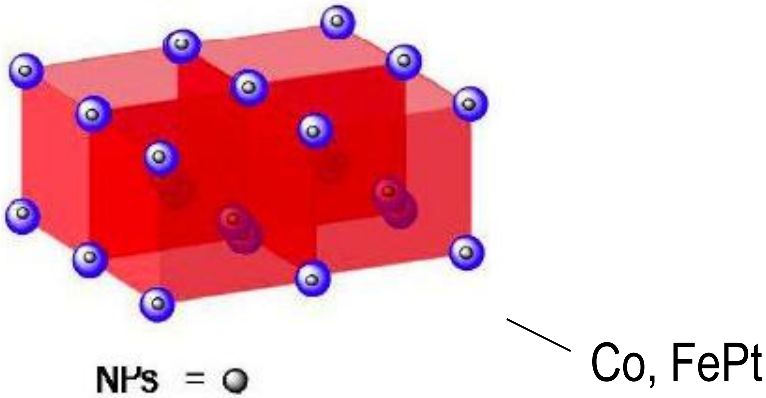
Next: Selective Placement of Different Populations of NPs Example - High Permeability Magnetic Metamaterials for Miniature, High Band Width, Low-Loss Antennas

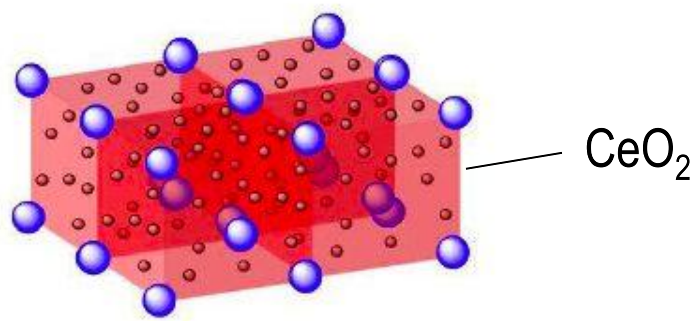
miniaturization

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

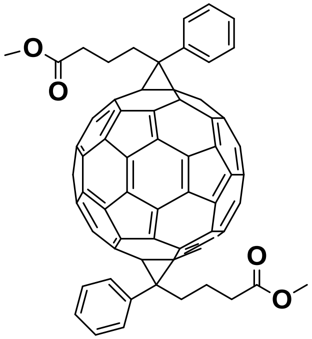


impedance matching

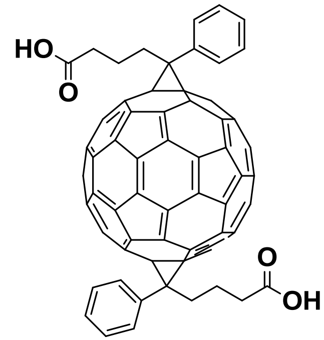
$$Z = Z_0\sqrt{\frac{\mu_r}{\varepsilon_r}}$$



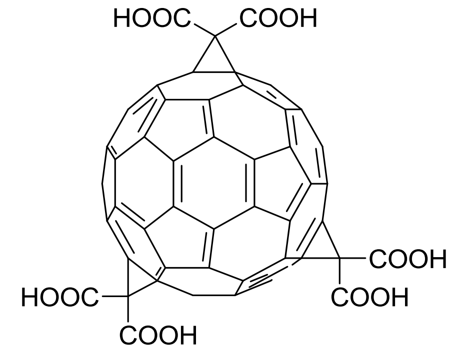
Assembly Using Fullerene Derivatives



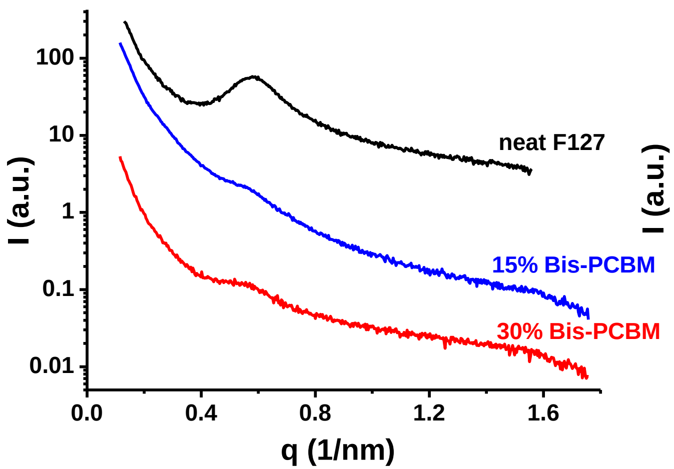
Bis-PCBM

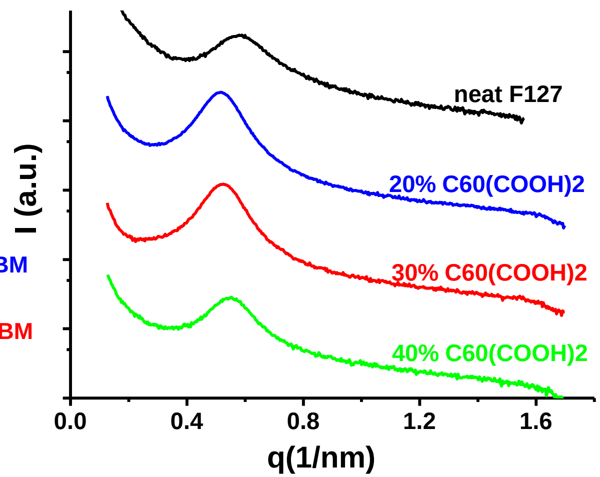


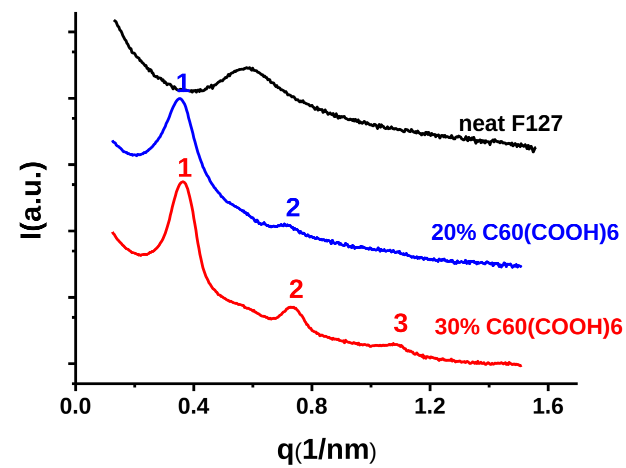
C60(COOH)$_2$



C60(COOH)$_6$

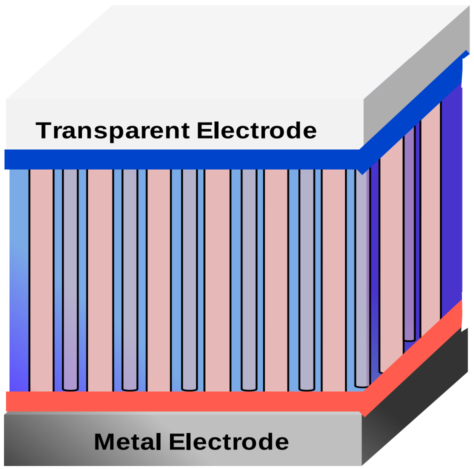


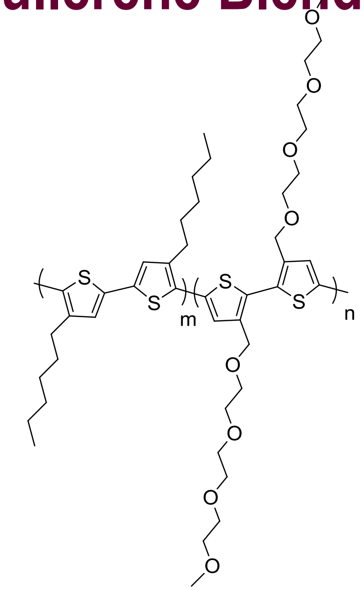


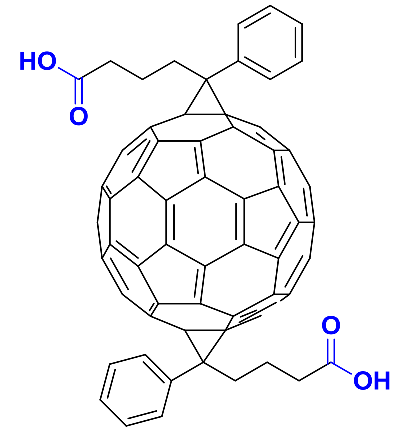


H-bonding exists between PEO and C60-COOH
Higher functionality, more favorable interaction, more order

An Example of a Device Based on Additive Driven Assembly: Block Copolythiophenes/Fullerene Blends for Photovoltaics

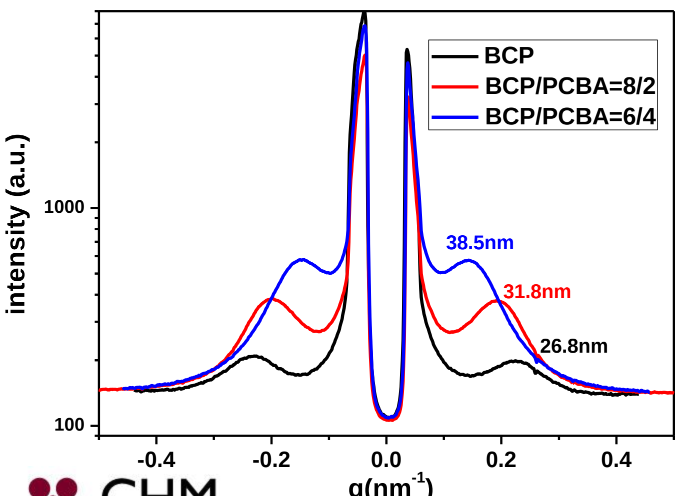






Bis-PCBA

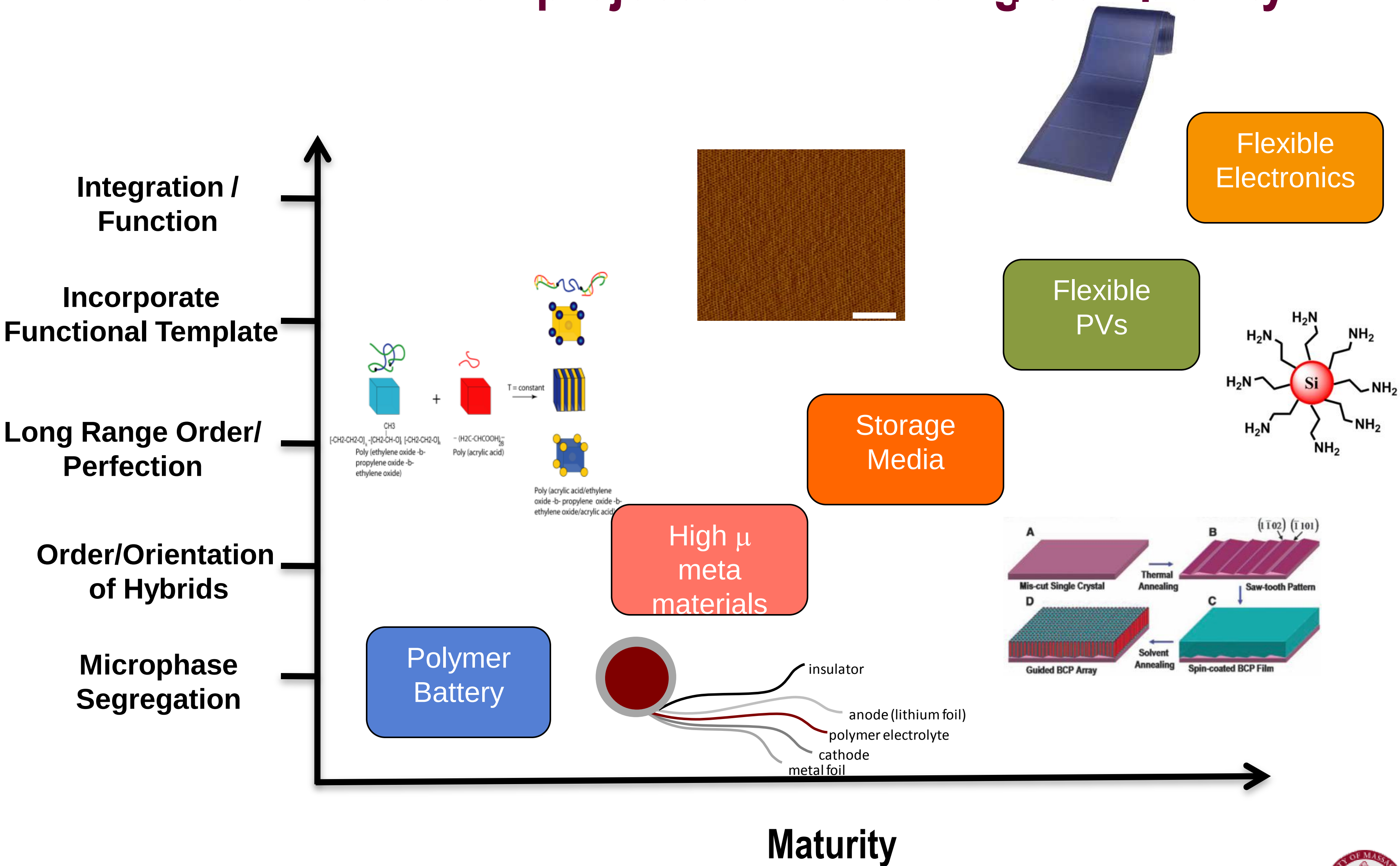
GISAXS – Ordered Structure



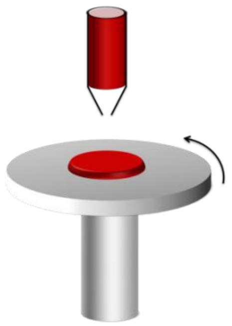
PCE VS. Processing Conditions

	V_{OC} (V)	FF(%)	J_{SC} (mA/cm^2)	PCE (%)
as spun	0.57	53.58	6.23	1.90
pre-annealing 150C 10min	0.60	54.27	6.29	2.04
post-annealing 150C 10min	0.59	52.46	6.37	1.97

Roll-to-Roll Self Assembly in the CHM: Demonstration projects of Increasing Complexity



CHM Efforts: Fundamental Science through Demonstration Requires a Team



Fundamentals

Test Bed

Adaptation

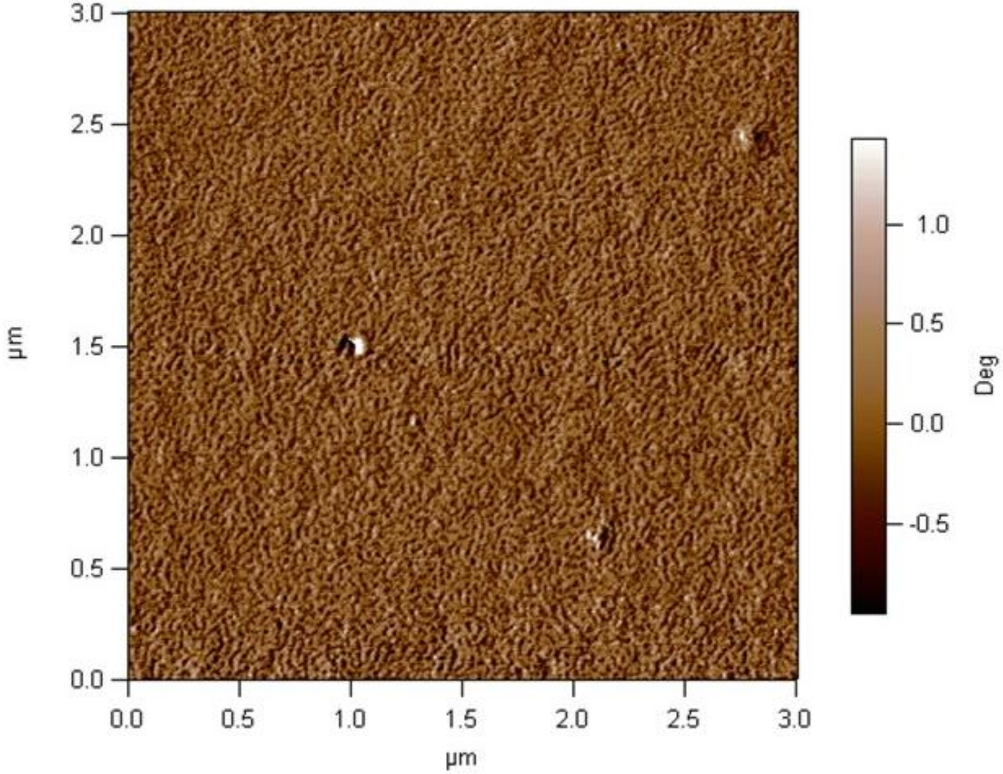
Image: www.frontierindustrial.com

Fundamentals of Assembly	Briseno, Crosby, Emrick, Gido, Grason, Rotello, Russell, Watkins Adschiri (Tohoku), Aymonier (ICMCB Bordeaux), Soles (NIST)
Dynamics/Rheology/Flow/Mechanics	Aliev (UPR), Bhatia, Crosby, Pasquali (Rice), Rothstein, Watkins
R2R Coating / R2R Imprint Lithography	Carter, Guo (UMich), Rothstein, Tang
Process Models/Metrology/Manuf. Sci.	Anthony (MIT), Boning (MIT), Gallatin (NIST), Hardt (MIT), Liddle (NIST),
Test Bed Facility/Project Manager	Tang (Ph.D. Materials Sci. (MIT), 13 years exp. precision coating)
IAB	15 members

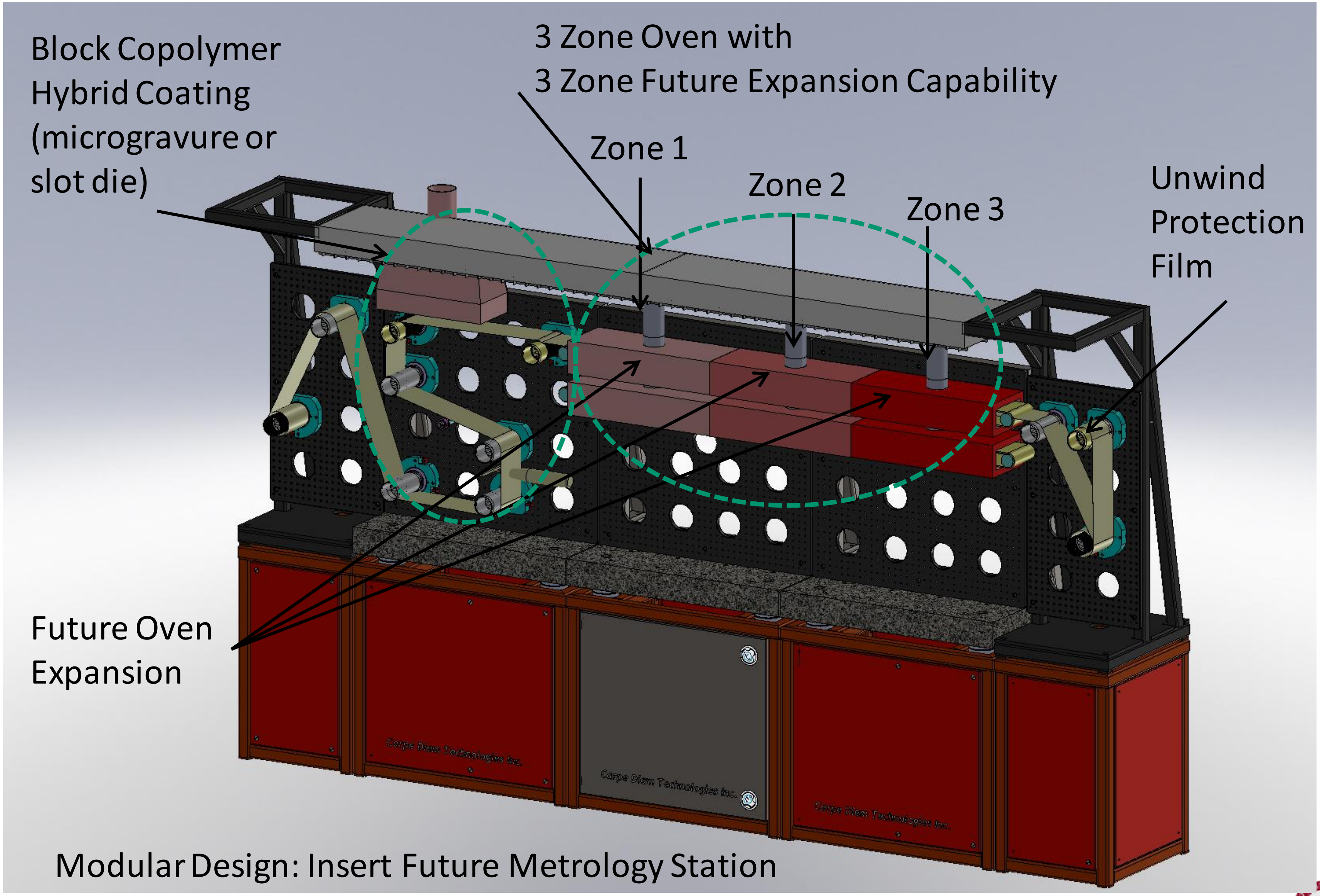
R2R Processing of Single Domain Block Copolymer Thin Film

MiniLabo Microgravure Coater

PS-*b*-P2VP (55k-b-25k) on Teonex PEN 125 um
Planerized Film : Phase Image



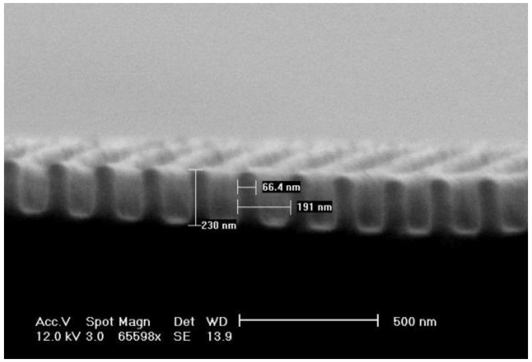
Roll-to-Roll Tool For Nanostructured Hybrids

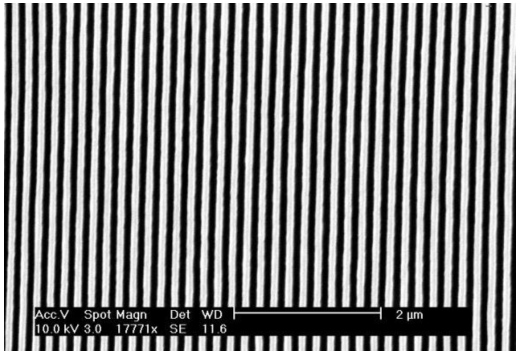


- **Roll-to-Roll system was designed in collaboration with industry partner**

Device-Level Patterning by R2R

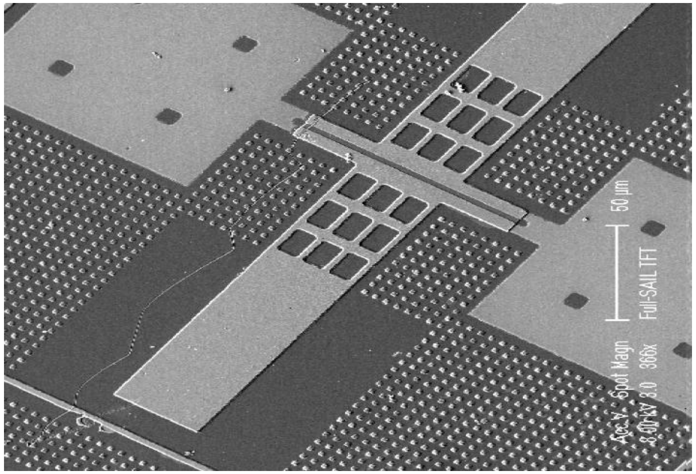
L. Jay Guo, Michigan
UV R2RNIL



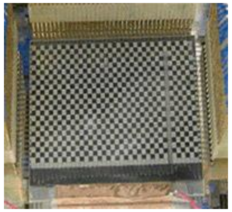


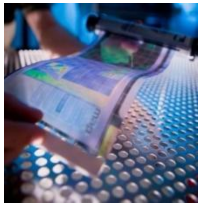
Guo, Adv Mat. 2008

HP SAIL TFT Backplane

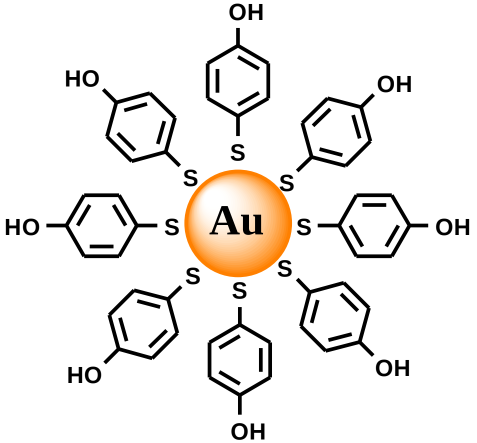


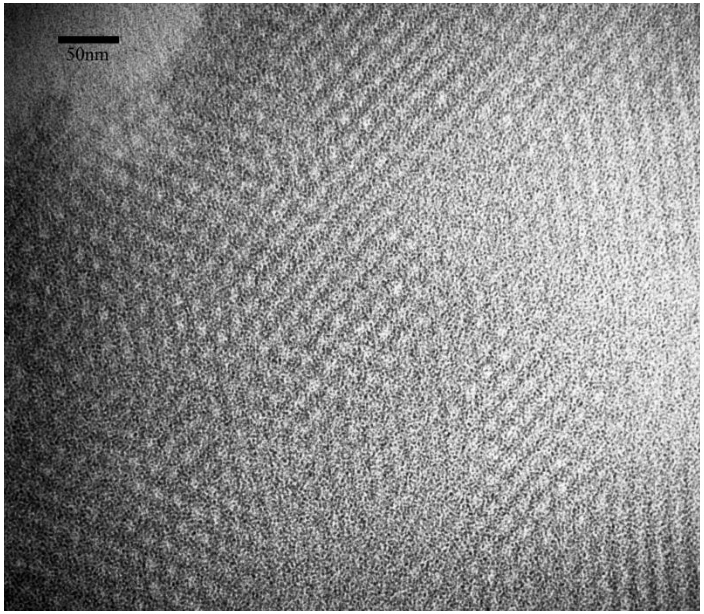
Taussig, HP Labs

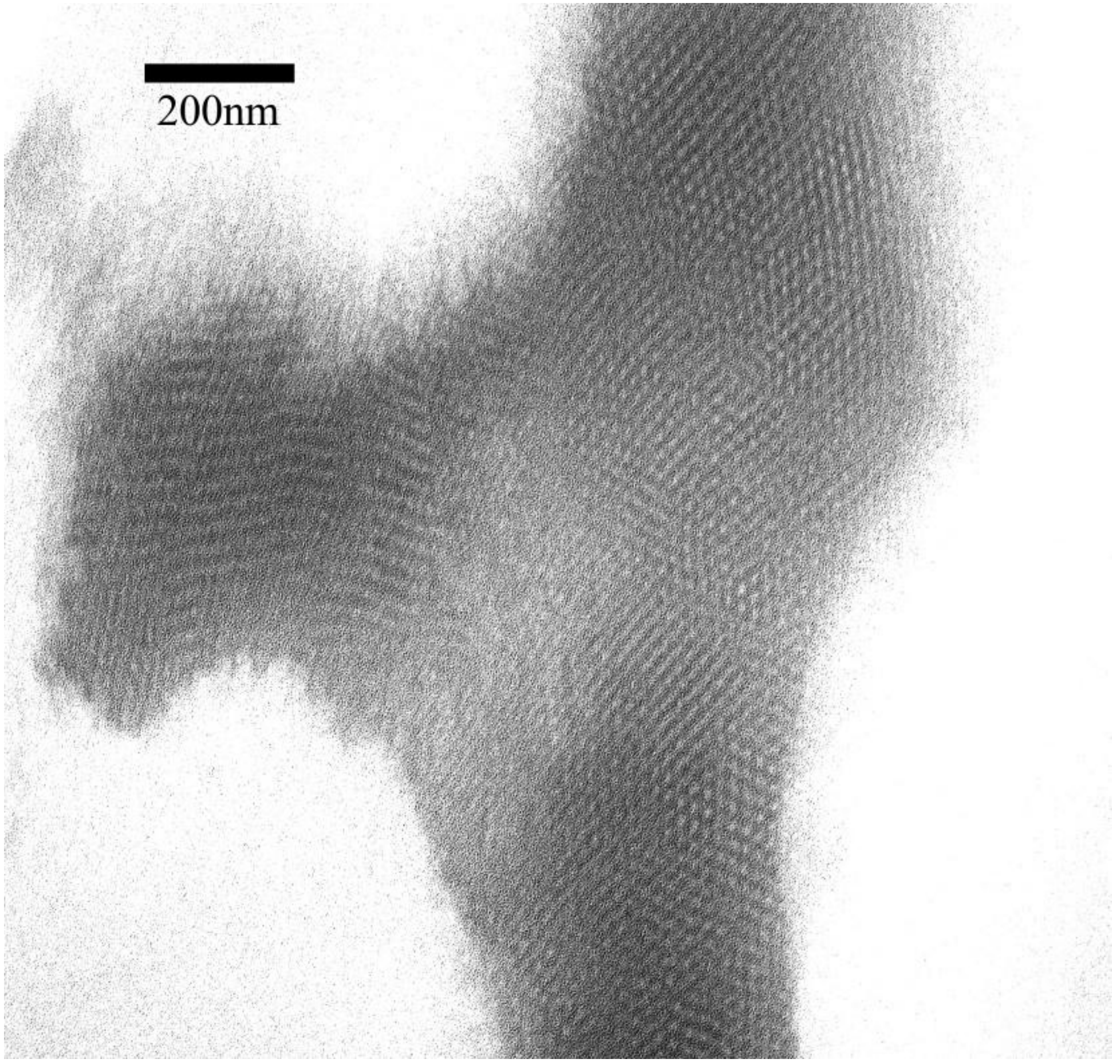




20% Gold Nanoparticles in F108: Excellent Local Order

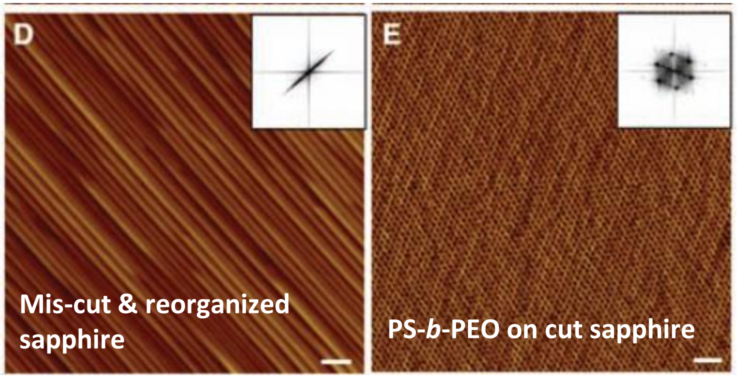




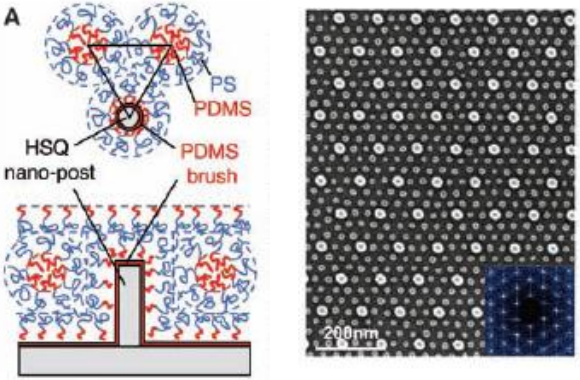


but, some applications will require long range order

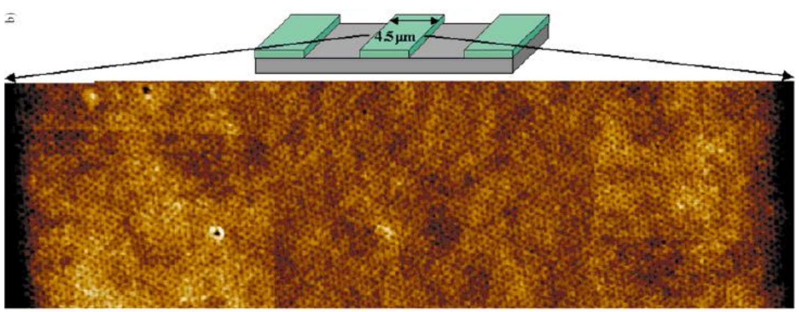
Topographic Constraints Can Guide Long Range Order



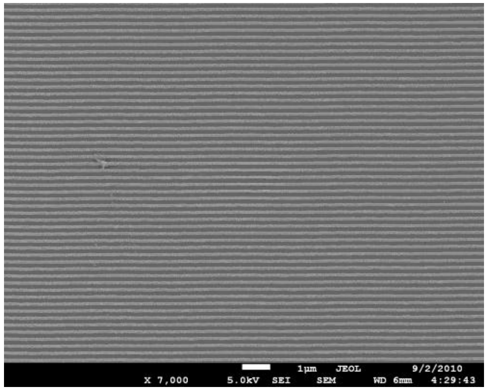
Park & Russell, Science, 2009



Ross, Thomas, Berggren, Science, 2008



Segalman and Kramer, Advanced Materials 2001

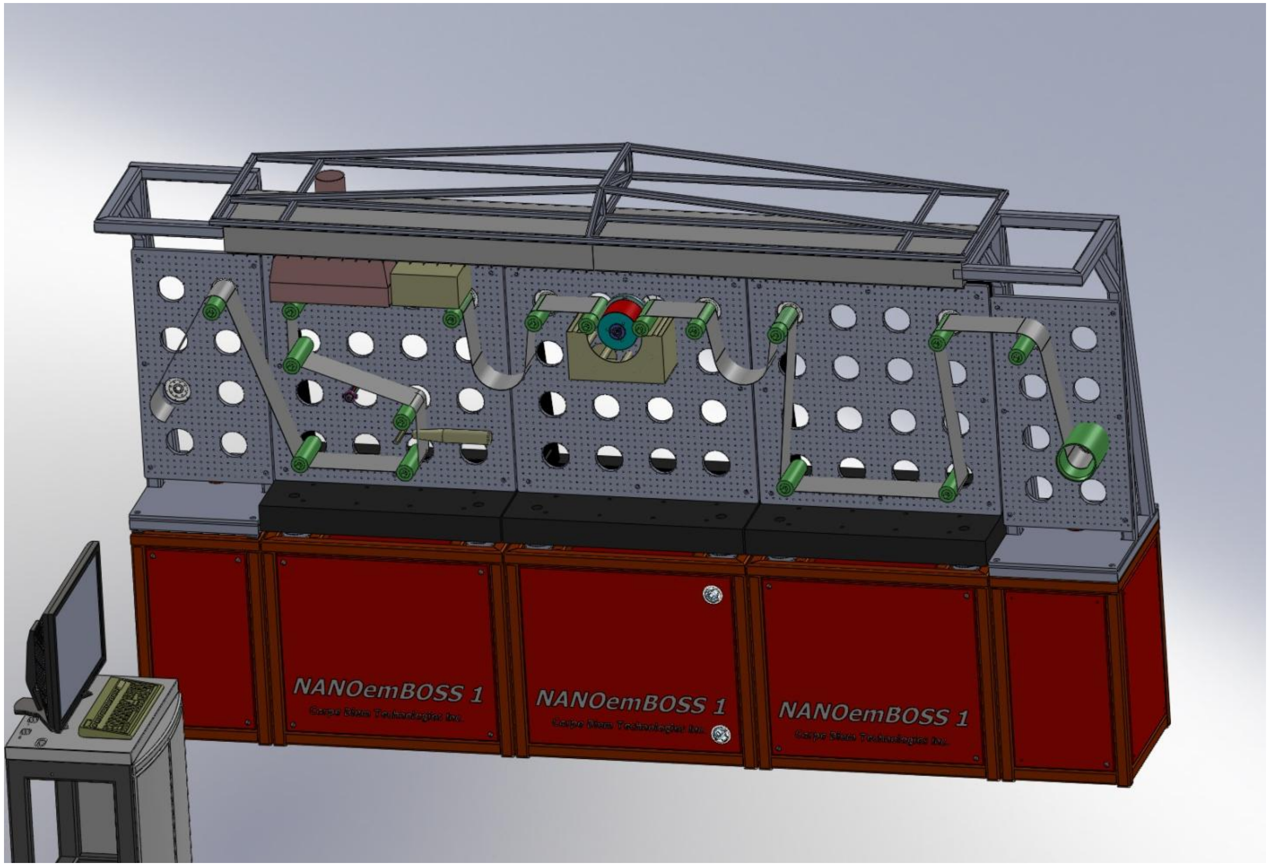


Create NIL Masters for Guided Alignment

Texture Surfaces using R2R NIL

Roll-to-Roll Nanoimprint Lithography Tool

- Roll-to-Roll system was designed in collaboration with commercial partner.
- Device currently being fabricated with commercial partner and progressing nicely.
- Delivery: March 2011

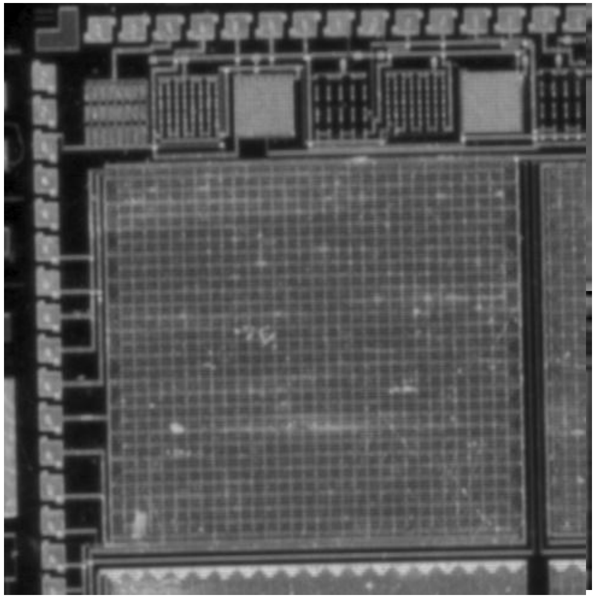


Roll-to-Roll Nanoimprint Lithography Tool

Metrology for Roll-to-Roll NIL

- Hardt and Anthony (MIT) will acquire optically averaged (aliased) observations of nanoscale features in order to measure variations over the large area.
- Control and vary conditions of the image acquisition state to capture set of raw videos
- Raw video is then used to estimate a three-dimensional map of the observed film with 10x increase resolution.
- Currently have super resolution system working for wafer-based measurement – film-based system currently under development

Super Resolution Image with
10x Greater Resolution



CHM Perspective on Nanomanufacturing Challenges: Key Issues and Strategies

- Continue to develop fundamental capabilities for self-assembly, additive driven assembly and other bottom up or massively parallel techniques

- Align nanomanufacturing process cost with product market tolerance
  - batch processing ok for some markets
  - increasing shift towards continuous production, including R2R
  - there are fundamental issues to be explored

- Engage in device and process design that exploit emerging capabilities

- Develop real-time metrology tools for process/product monitoring

- Develop robust tool platforms that can be adopted readily
  e.g. R2R manufacturing platform

- Engage regional manufacturing ecosystems / clusters to maximize tech transfer and probability of success
  - regional technology hubs that partner NSECs with legacy and emerging industries
  - R2R platform consistent with mill, printing, and advanced coating industries and their high tech offspring in MA

some more difficult than others, but no obvious show stoppers

Center for Hierarchical Manufacturing

UMASS AMHERST

Fundamental Research

Technical Research Groups

TRG 1: Nanoscale Materials & Processes
TRG 2: Nanoscale, Devices, Systems and Metrology
TRG 3: Sensors and Environmental Monitoring

Synergy & Collaboration

National Nanomanufacturing Network

Catalyst for Collaboration and Information Sharing
Web and Workshops
InterNano Digital Library & Clearinghouse

Translational Research

System-Level Process Test Beds

Identify Barriers to Implementation
Address Fundamental Research Challenges
Demonstrate Process Platform
Pursue Applications with Partners

Education & Outreach

Lesson Modules and Multimedia Content

Visual Learning Content for Education
K-12, Undergrad, Graduate, Workforce
Comprehensive Diversity Strategy

Technology Transfer

Industry Partnering

MassNanoTech Partners, sponsored research, licensing, and company consortia

Societal Implications

Technology and Economic Analyses

Implementation, Supply Chain, Workforce

Partners: Univ. of Puerto Rico - Rio Piedras ● Mt. Holyoke College ● Springfield Technical Community College ● Binghamton University ● MIT● Rice ● NIST

CHM
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University of Massachusetts Amherst