Materials and Process Integration Challenges for the Fabrication of Nanotechnology Enabled Devices

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Nanofabrication and Integration Across Multiple Length Scales

Example: Next Generation ICs

A challenge that can only be solved by employing self-assembly

Top-down meets bottom-up
Bridging Manufacturing Lengths Scales Through Directed Self-Assembly and Nanopatterning

Computing
- Nano: Self Assembled Templates & Pores
- Micro: Interconnects
- Systems: Chips

Energy
- Nano: Patterned Media
- Micro: Sectors
- Systems: Memory

Health
- Nano: Self-assembled Heterojunction
- Micro: Patterned Electrode
- Systems: Solar Cell

- Molecular Recognition
- Separation/Detection Array
- Biosensor

Bottom-up
Top-down
Integration
Manufacturing of Nanodevices: High Level View of Overarching Challenges

Massively Parallel Generation of Well-Defined Nanostructures
- Directed Self-Assembly
- Nanoimprint and Capillary Force Lithography
- Bio-assisted Assembly
- Other

Functionalization of Device Structures
- 3-D Replication of Self-Assembled Templates
- Deposition within Nanoscale Features
- Incorporation of Nanoparticles and QDs
- Other

Integration into Viable or Existing Process Platforms
- Si-Wafer Technology
- Roll-to-Roll Processing
- Insertion of one or more new nano processes

Rapid, Cost-Effective, Defined Need
- Unique Performance Advantage = Adaptation
- Application Verification

Nanofabrication Technologies

Process Technologies

Considerations for Commercialization
CHM Nanofabrication Research Platform

Nanoscale Process Platform Technologies
- Nanoimprint Lithography
- Block Copolymer Patterning
- Bio-Assisted Assembly
- Nanoscale Deposition
- 3-D Replication
- Functional Additives

Integrated Multiscale Process Platform Technologies
- Top-down Si Wafer Technology
- Continuous Feed Roll-to-Roll Technology

Nano-Enabled Applications
- Energy
- Computing
- Human Health

Structure Generation, Functionalization, Integration, Device Design, Market

Nano Scale, Micro Scale, Device/System Scale, Product

Partners: Univ. of Puerto Rico - Rio Piedras ● Mt. Holyoke College ● Springfield Technical Community College ● Binghamton University ● UC Riverside ● TIAX LLC ● Alcatel-Lucent
Block Copolymer Templates: Spontaneous Assembly upon Spin Coating, Complete Control of Morphology

Key Parameters:  
- block volume fraction, \( f \) controls morphology  
- degree of polymerization, \( N \) controls domain size  
- Flory Parameter, \( \chi \) controls segregation

Di-block Copolymer

Increasing \( f \)

BCC Spheres  
HEX Cylinders  
Gyroid (\( \text{Ia}_3d \))  
Bicontinuous Lamellae

BCP Phase Diagram

SCFT Theory vs. Experiment (PEP-b-PEE)

(Bates, 1994; Matsen, 1996)
Hierarchical Processing

- Multi-length scale assemblies
- Structural control on local and device level

Lithography

- PMS-PHOST BCP 248 nm Resist

Domain Alignment

- Aligned PS-PEO cylinders

Nanoimprint

- PS-PMMA using NIL

Epitaxial Assembly

- Aligned PS-PMMA
Self-Assembled Templates for Device Applications

Strongly Segregated BCP/Surfactant Blends on Flexible Substrates

- Increase segregation strength $\chi^N$
- Sub-micron coating
- Phase selective functionalization or etch
- 5 nm resolution resists and etch masks
- H+ additives
- H+ homopolymers

Directed Assembly of BCPs with Long Range Order on Si Wafer

- Ion complexation
- Metal deposition
- Data storage
- PVs, flexible electronics, displays
Integration of Self-Assembly within Process Flows?

Implementation Challenges:
- Simple, rapid, cost-effective, non-disruptive process
- Long-range ordering is necessary for many applications
- Increase strength of segregation to decrease feature size
- Low/no defect tolerance
- Commodity scale availability for ordered systems
- Patterned media
- Metrology
Exploiting Cooperativity Across Length Scales: Hierarchical Processing Using Block Copolymers

Evaluation of self assembly for ordered magnetic media

Current requirement for magnetic data dots for BPM:
Size and position distributions <5% per data sector

Block Copolymers: Jitter of 4.5% !!

With Oleg Myrasov Seagate Technologies
Recent Progress: Vertical Orientation Via “Zone Refinement” and Near Perfect Lateral Ordering Through Solvent Annealing

As-spun (PS-b-P4VP: 47.6k-20.9k)

Solvent annealing

(PS-b-P4VP: 47.6k-20.9k)
Hierarchical Self-Assembly: Clusters in Wells

MULTISTATE DATA STORAGE

Interacting Nanomagnet Cluster — Overcomes R/W lateral resolution

[Diagram showing LLG Simulation and 8 stable magnetic states]

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4-State Data Storage Element

MFM images of a 3-nanomagnet cobalt cluster

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Self-Assembled Templates for Device Applications

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Bulk-Scale Well-Ordered Block Copolymer Materials?

- High degrees of order generally require high purity, low polydispersity
- Commodity block copolymers are polydisperse, contain impurities
  - e.g. Pluronic surfactants \([-\text{CH}_2-\text{CH}_2-\text{O}]_m -[\text{CH}_2-\text{CH(CH}_3)-\text{O}]_n -[\text{CH}_2-\text{CH}_2-\text{O}]_m\)
    - Commercially available and inexpensive
    - Weakly segregated domains, PDI = 1.2, diblock impurities

- Pluronics do not exhibit phase segregation in the melt

Low \(\chi_{\text{PEO-PPO}}\): \(\chi(T) = -0.122 + 66.8/T\);
\(\chi_{\text{PEO-PPO}}@80^\circ\text{C} = 0.066-0.068\);

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Total MW (g/mol)</th>
<th>(f_{\text{PEO}})</th>
<th>(\chi N) (calc.)</th>
<th>(\chi N^*) (critical)</th>
<th>Est. ODT (K)*</th>
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<td>L92</td>
<td>3,450</td>
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<td>P105</td>
<td>6500</td>
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<tr>
<td>F108</td>
<td>14,600</td>
<td>0.8</td>
<td>20.29</td>
<td>32</td>
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<tr>
<td>(E_{70}(dP)<em>{31}E</em>{70})</td>
<td>8400</td>
<td>0.8</td>
<td>12.5</td>
<td>32</td>
<td>227</td>
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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.

Impact: Will enable use of BCP templating in low cost applications (roll to roll, extrusion). Increases in \( \chi N \) will reduce feature size.
Strengthening Phase Segregation via Segment Specific Interactions: Stable Functional Templates

SANS dF68/ 40% homopolymer

Evidence of Enhanced Segregation

dF68

dF68/PAA

Broad Class of Behavior

Introduction of Functional Groups Facilitates Modification

Impact: functional self-assembled templates that can be coated at high rate
Functionalized CdSe Nanorods: Induce Compatibility and Corralling in Polymer Templates

Emrick and Russell
3-D Template Replication Using Phase-Selective Chemistries

- Phase-selective chemistries
- Catalyst localization

Impact: Transfer hierarchical structures easily obtained in BCPs into other materials

Precursor in Humidified CO$_2$

Porous silica

Porous carbon

High fidelity preservation of morphology
Easily integrated with existing technologies
Rapid, robust, scalable
Mesoporous Silicate (ULK) Films Prepared in CO₂

First generation films exhibit excellent performance for ULK

- k< 2.2 demonstrated
- Rapid process times, 1st generation survives CMP
- Low stress, high crack threshold
- First principles molecular dynamics simulations providing structure-property guidance

Two Important Observations:

- Small pores are accessible via template blends
  - increase in $\chi_n$ reduces feature size
  - 3 nm is inaccessible via typical BCPs
- Ability to decouple alkoxide condensation from template assembly will enable complete definition of desired hierarchical architecture in a suitable template

Leveraged with SRC Support
Micro-Patterned Mesoporous Silica Films

Simultaneous Domain (nanoscale) and Device (microscale) Control: Chemical amplification and Silica Condensation in PS-b-PtBocSt Films

- UV exposure
- Post-exposure bake & Silica infusion
- Template removal

Chemical reactions:
- Photo acid generator
- Generated Acid

Materials:
- PtBocSt
- PS
- TEOS in SC CO₂

Outcome:
- Patterned silica film

Center for Hierarchical Manufacturing (CHM)
Patterned Mesoporous Silica Films from PBOCStyrene Films

1. UV exposure
2. Post exposure Bake (PEB)

- PAG
- Hydrophobic
- Hydrophilic

Regeneration of acid

- Good pattern replication with sharp boundaries.
- Device level features down to few microns in size
Direct Patterning of Silica Films via Hybrid Processing: AFM Images

**Simple Contact Mask Lithography**
- PtbocSt and PtbMA Templates
- AFM Images
  - Good pattern replication
  - Device level features below 100 nm!
  - No etching: significant process advantage
  - Template optimization with partners underway

**Off-the-Line 193 Resist from Partner**
- (Acrylate-based, first attempt: No optimization)
- AFM Images
  - Impact: Potential for streamlined integration of ULKs and cost savings via process simplification
Biocompatible monolayer provides >95% efficiency in assembly of Brome Mosaic Virus (BMV)

Encapsidated particles self-assemble into ordered structures.
Ordered 2-D and 3-D DNA-BCP Nanostructures

Repeating DNA patterns used to create simple objects (e.g., tetrahedra)

Electrostatic interactions allow for site-specific registration of DNA objects with BCP films

Subsequent metallization using low temperature SCF approaches planned
Opportunities

• Self assembly can be integrated with top down processing
  - precision assembly on Si wafer platforms
  - high rate, low cost assembly for roll-roll processing

• Elements accessible from self assembly offer both new possibilities and constraints for device design

• Hybrid processes can offer performance and economic advantages

• Biological elements combined with synthetic self assembly platforms offer new versatility
  - deterministic assembly on surfaces may be required

• Functionalization and metrology remain challenges