Imprint Lithographic Techniques for Micro- and Nano- Patterning

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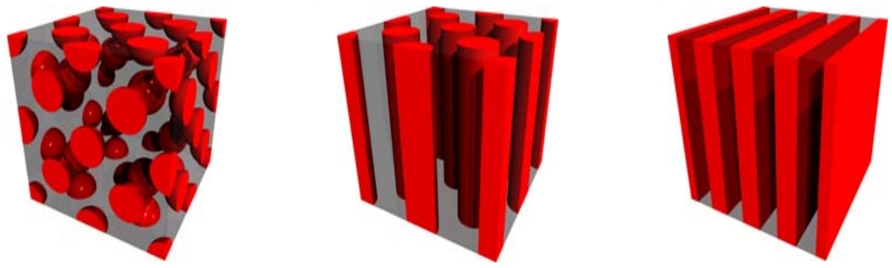
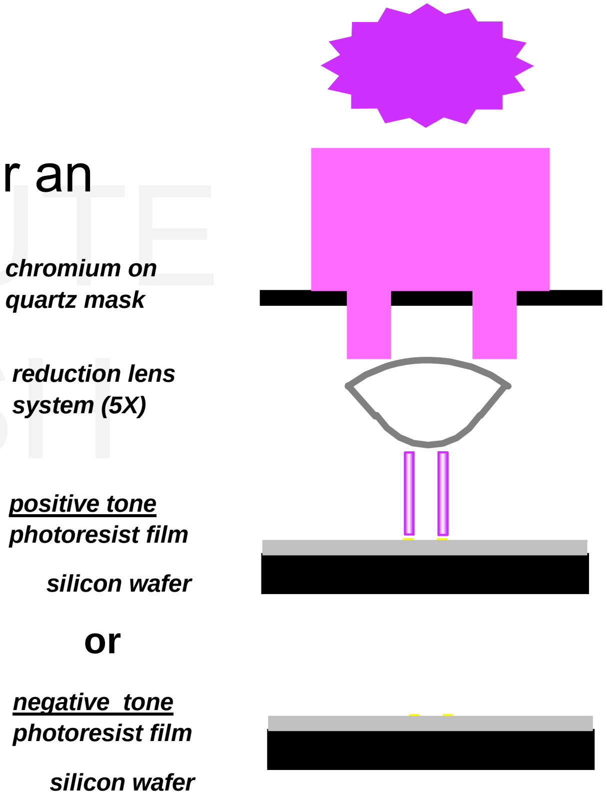
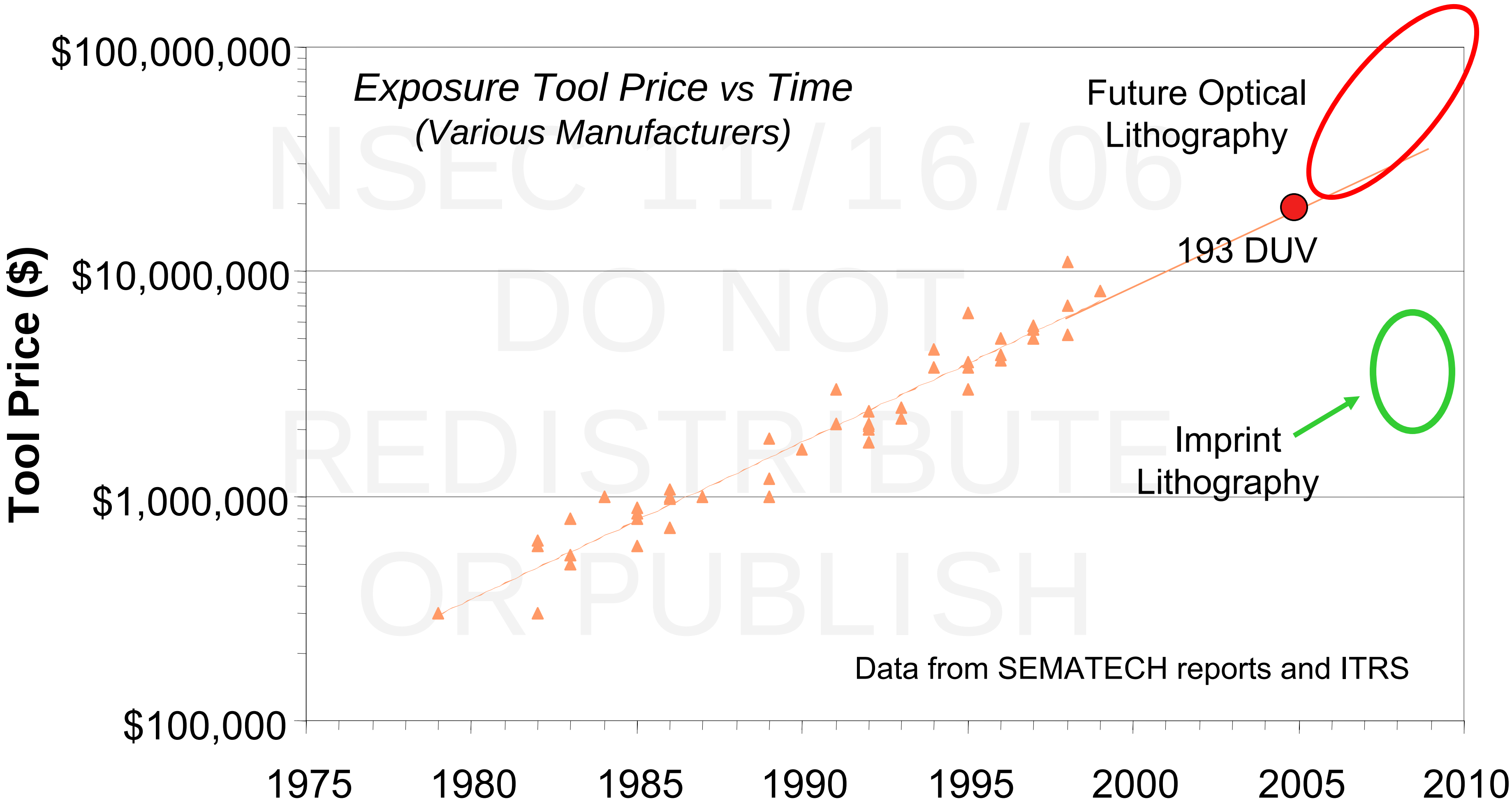
Making Useful Small Things

- Challenge of 21st Century will be to “mass produce” small functional devices – ***ENABLE NANOTECHNOLOGY***
- Quickly approaching devices and structures on the molecular or even atomic scale (< 10 nm)
- Current photolithography (top down) getting complex and expensive
- Self-organizing systems (bottom-up)
  - Challenges regarding manufacturability
- Imprint and Contact patterning techniques offer an interesting alternative
  - Combine best of top down and bottom up methodologies





Financial Implication of Moore's Law



Data from SEMATECH reports and ITRS

Environmental Process Considerations

Photolithography

- Multiple process steps
  - Spin coat liquid resist
  - Pre-bake / solvent evaporation
  - Expose
  - Post exposure bake
  - May use PFOS PAGs
  - Development in aqueous base
  - Rinse
  - Etch

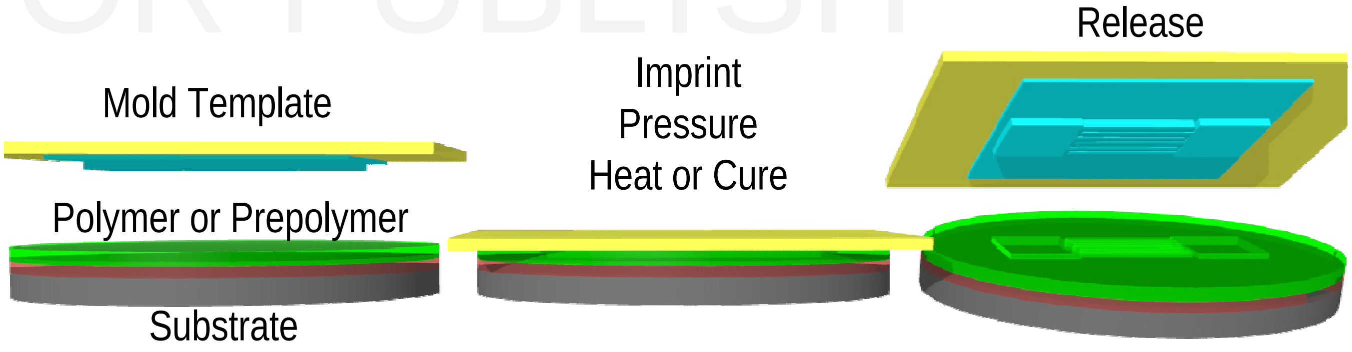
Imprint Lithography

- Fewer process steps
  - Spin coat or apply resist
  - Emboss/contact
  - Expose
  - Etch

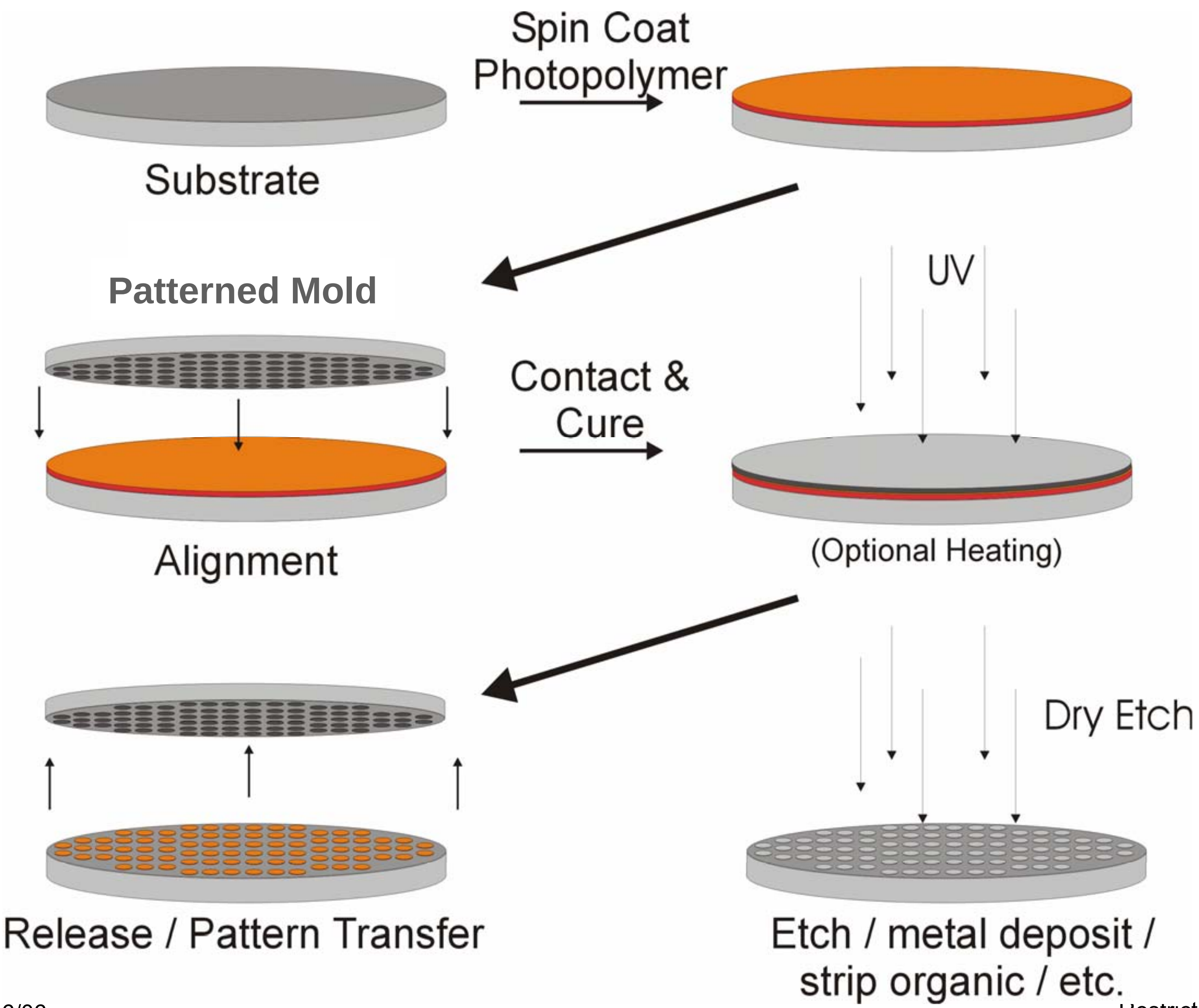
Imprint Lithography

Imprint lithography is generally practiced in several forms

- Thermal Imprint Lithography
  - Emboss pattern into thermoplastic or thermoset with heating
- Micromolding In Capillaries (MIMIC) soft lithography
  - Curing material confined in of channels in PDMS
- UV-Assisted Imprint Lithography
  - Curing polymer while in contact with hard, transparent mold



Nano-Contact Molding (NCM) Process



Substrate

Spin Coat Photopolymer

Patterned Mold

Alignment

Contact & Cure

UV

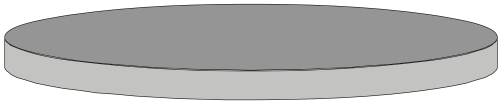
(Optional Heating)

Release / Pattern Transfer

Dry Etch

Etch / metal deposit / strip organic / etc.

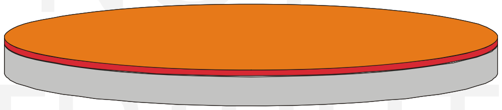
Nano-Contact Molding Process

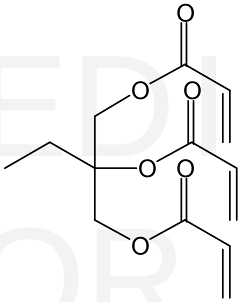


Substrate:
- Silicon
- Metals
- Polymer

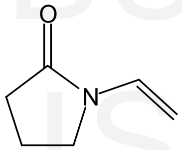
Spin-Coat

Photopolymer Solution

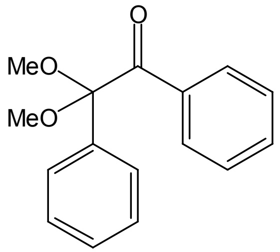




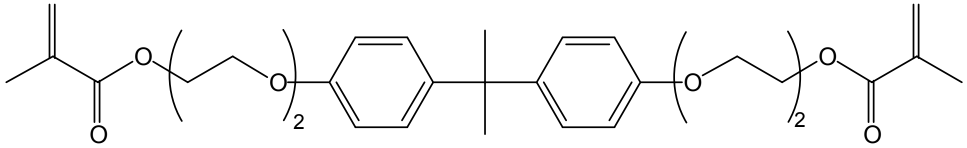
Trimethylolpropane triacrylate



N-Vinypyrolidone



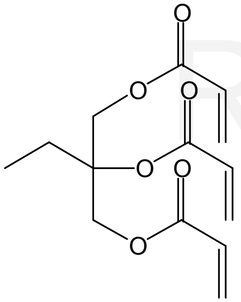
2,2-Dimethoxy-2-phenylacetophenone



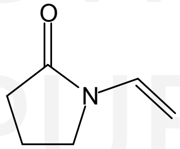
Ethoxylated (3) bisphenol A dimethacrylate

Nano-Contact Molding Resists

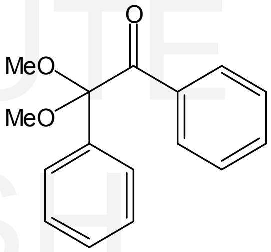
- Based on methacrylate chemistry
- High aromatic ring content
- Issues regarding
    - Plasma resistance (O_2 Plasma rate 70-90 Å/s)
    - Viscosity
    - Oxygen sensitivity



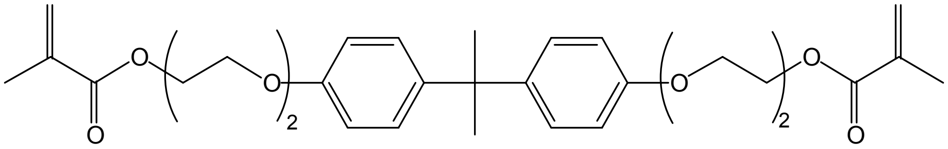
Trimethylolpropane triacrylate (15-33%)



N-Vinypyrolidone (0-15%)

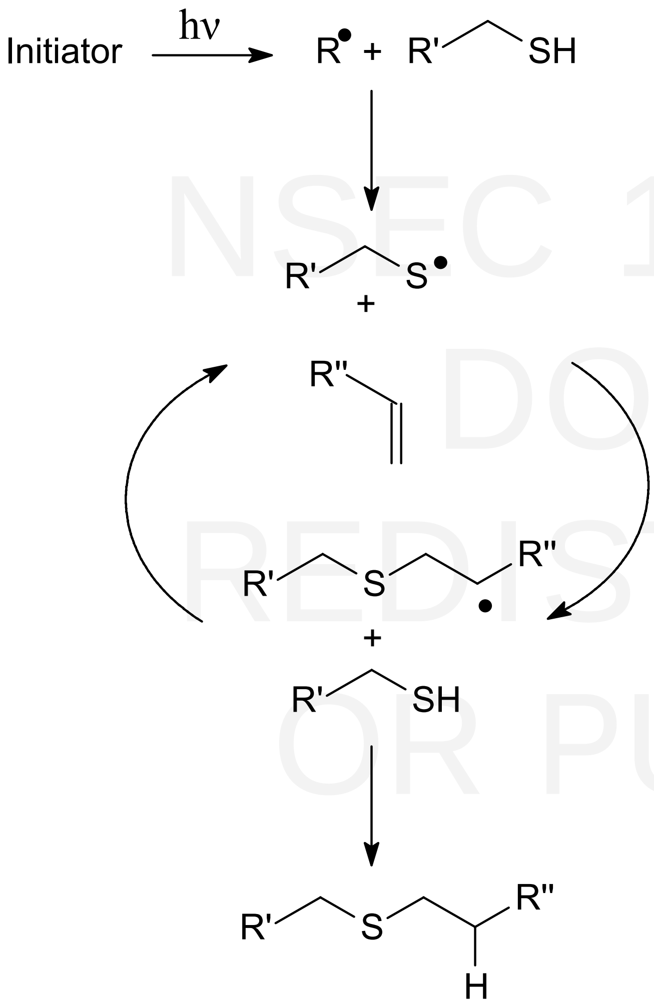


2,2-Dimethoxy-2-phenylacetophenone (2%)

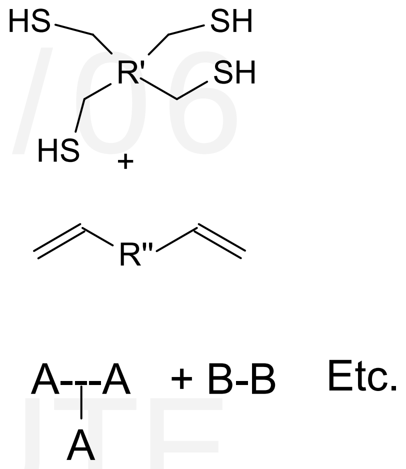


Ethoxylated (3) bisphenol A dimethacrylate (65%)

Thiol-Ene Step Polymerization



Crosslinked Polymers



Thiol-Ene Step Polymerization

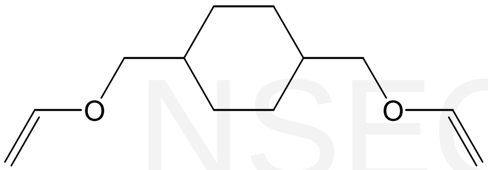
Advantages:

Photopolymerizable
Monomer viscosity selectable
Low oxygen sensitivity
Tunability of crosslink density and mechanical properties
Range of functionality available (for example etch resistance)

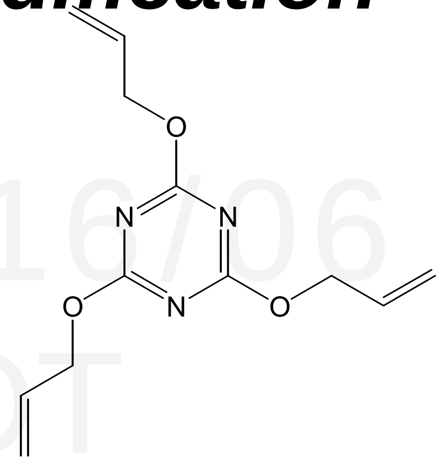
Challenges:

Adhesion to substrate
Release from mold
Ultimate resolution???
Etch resistance???

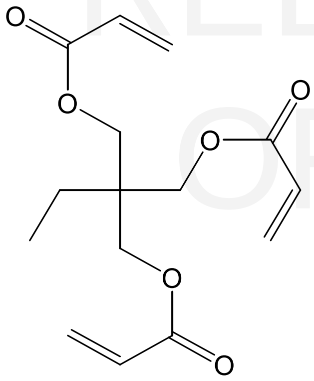
Variation of Mechanical Properties Via Structure Modification



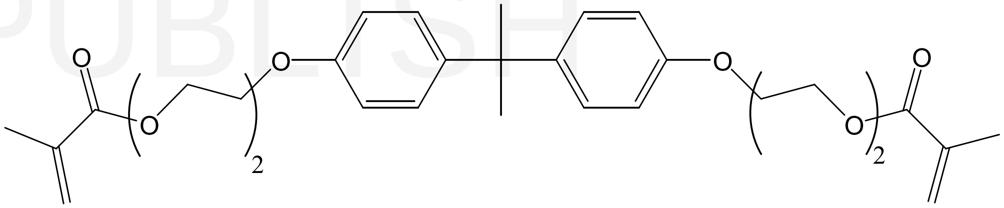
1,4-Cyclohexanedimethanol Divinyl Ether



2,4,6-Triallyloxy-1,3,5-Triazine



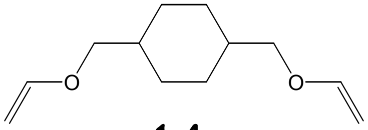
Trimethylolpropane Triacrylate



Ethoxylated (2) Bisphenol A Dimethacrylate

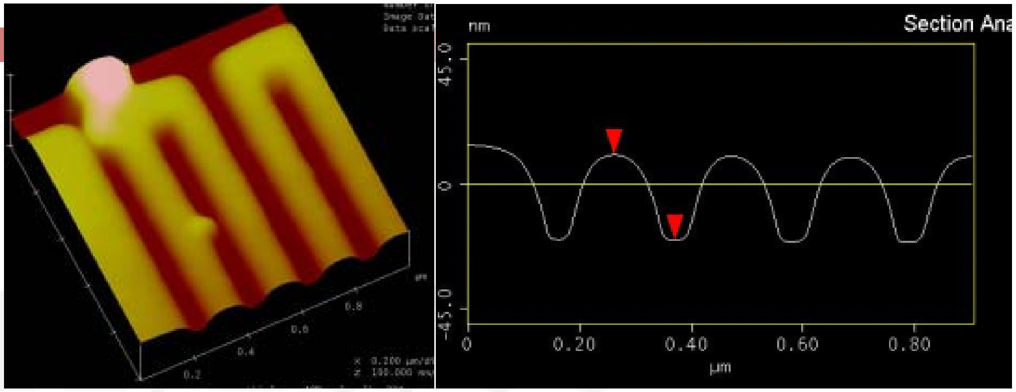
Hagberg, et. al., **2006**, submitted for publication.

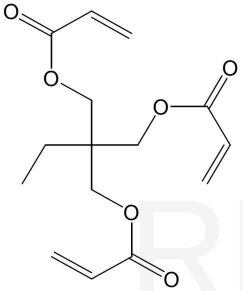
Hagberg, et. al., **2006**, submitted for publication.



1,4-Cyclohexanedimethanol Divinyl Ether

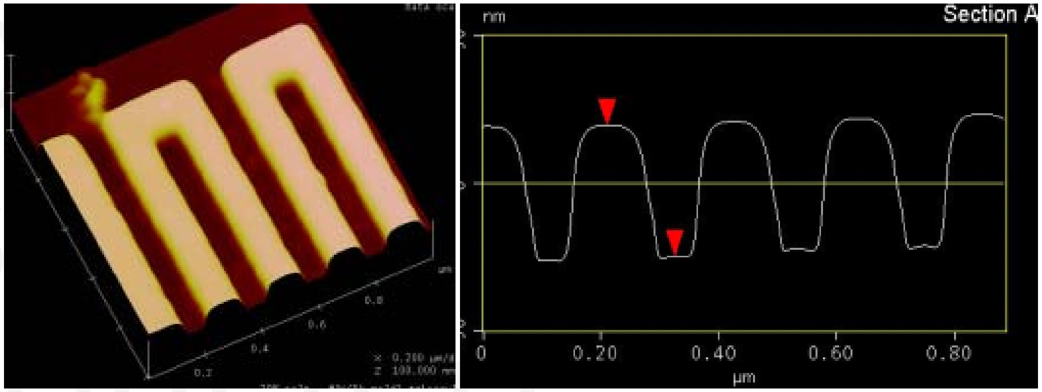
3 MPa

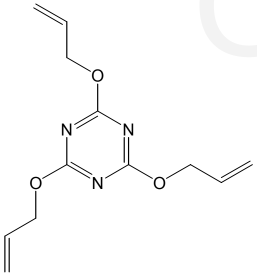




Trimethylolpropane Triacrylate

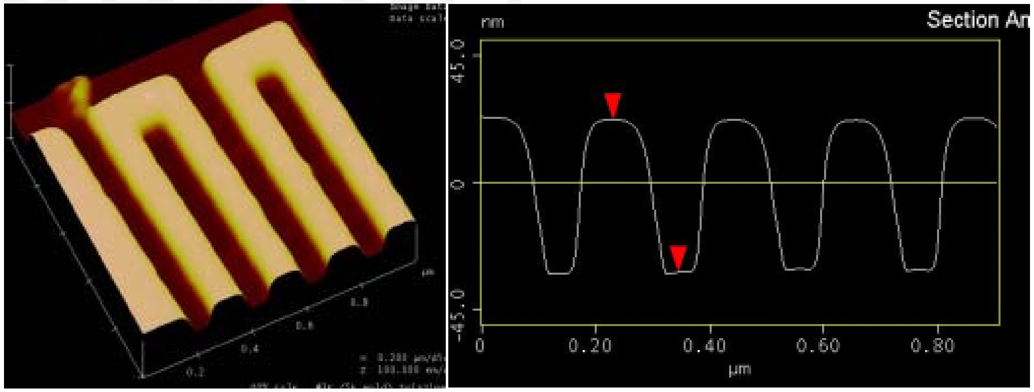
75 MPa





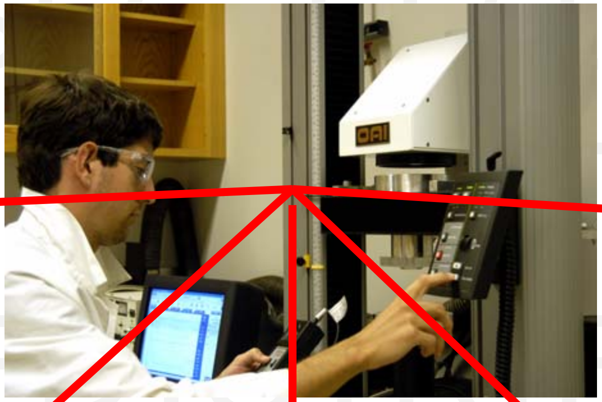
2,4,6-Triallyloxy-1,3,5-Triazine

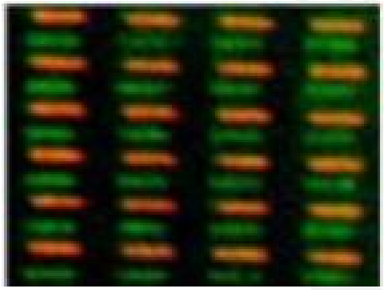
1375 MPa



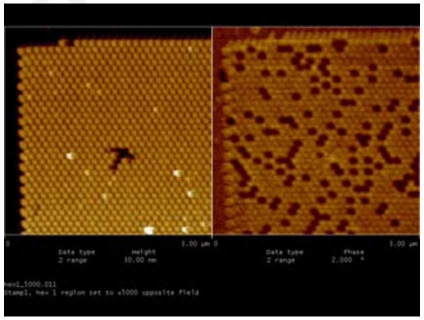
Imprint Lithography

Power & Utility

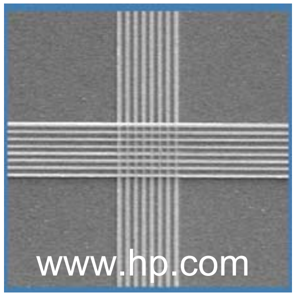




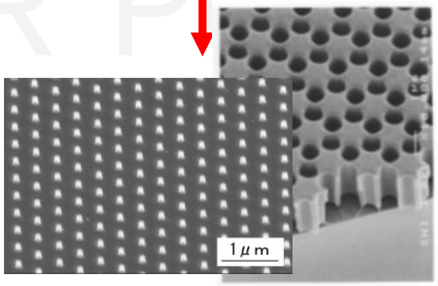
Biochips, Diagnostics
Sensors



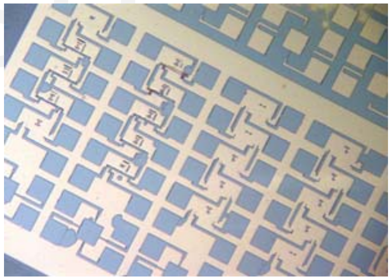
Patterned
Magnetic Media



High Density Storage
Crosspoint Memory



Waveguides
Photonic Crystals

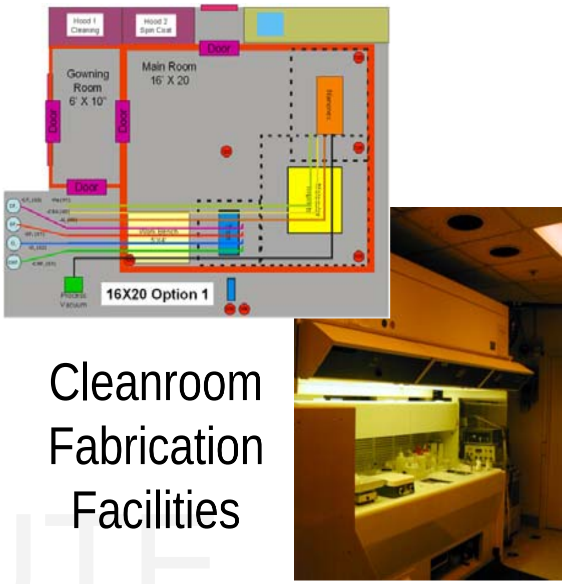


Conventional Circuits
CMOS / BEOL
Packaging

UMass Nanofabrication Facilities & Resources

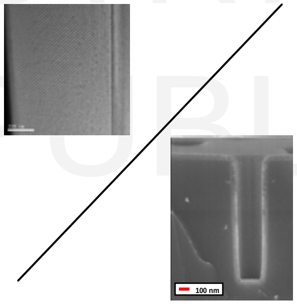
Molecular Imprints
MI-55 SF-IL Tool

Nanonex NX-2000
Nanoimprinter



Cleanroom
Fabrication
Facilities

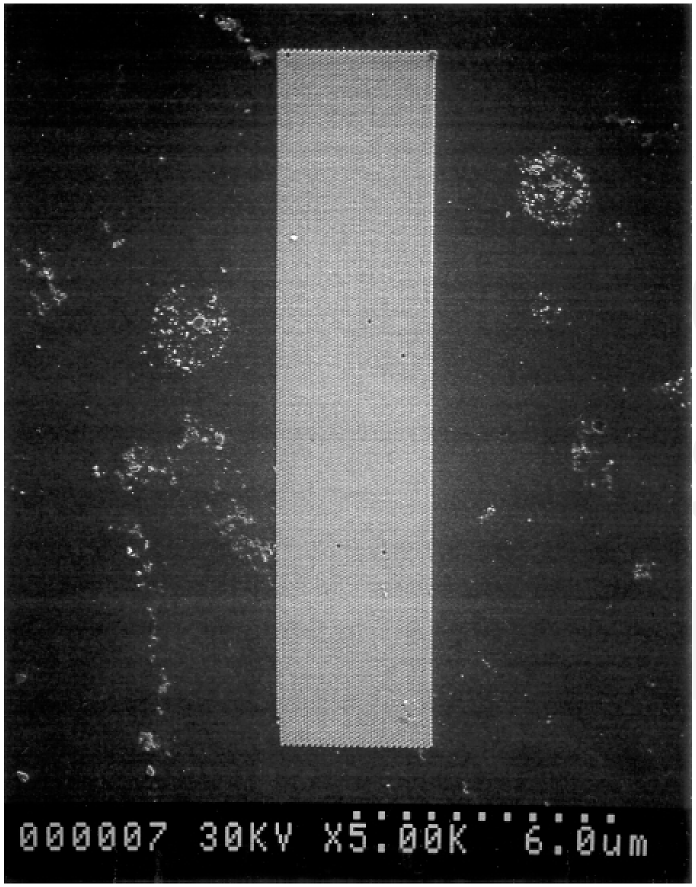
Trion Systems
ICP Etch Tool



SCF Full Wafer Tool
Low k/metals/metal oxides

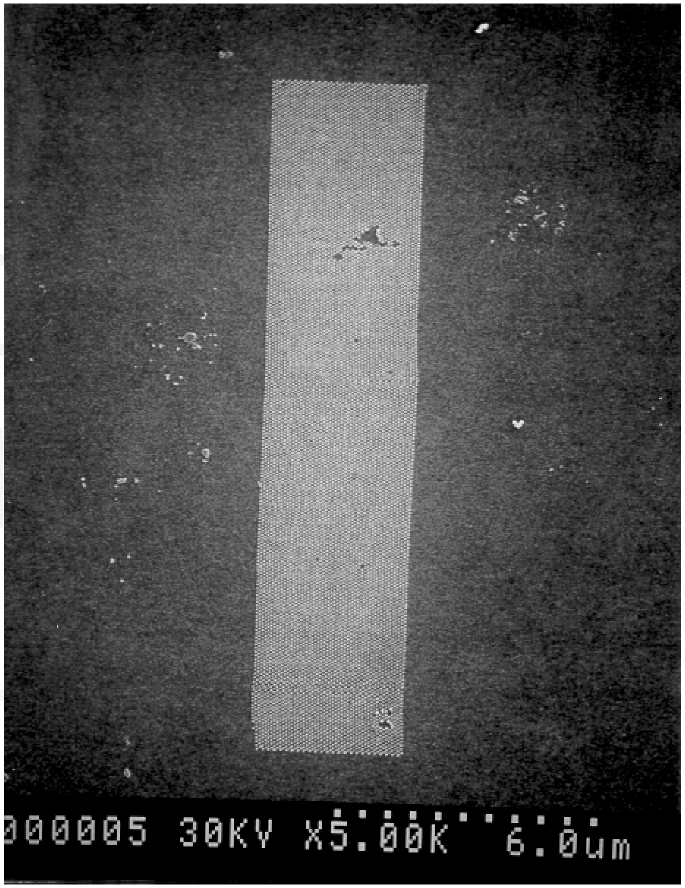
One-of-a-kind
Nanoimprint
Lithography
Facility

High Resolution Pattern Transfer



Master (e-beam)

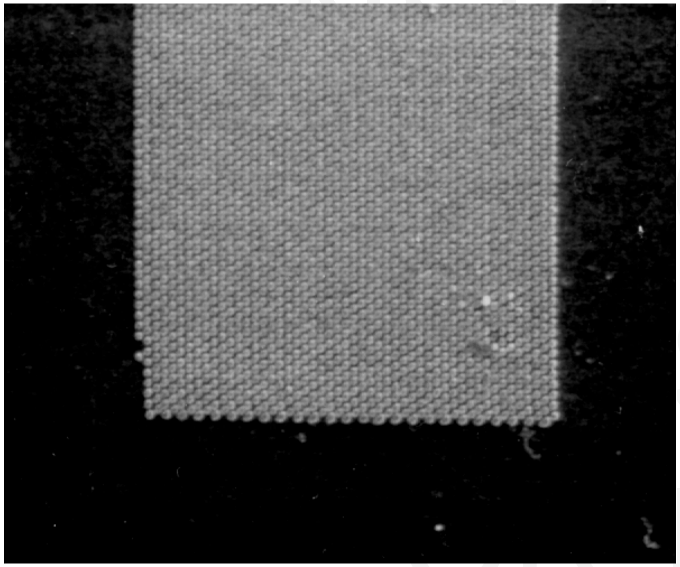
Contact
Molding
Process



Replica (etched SiO_2)

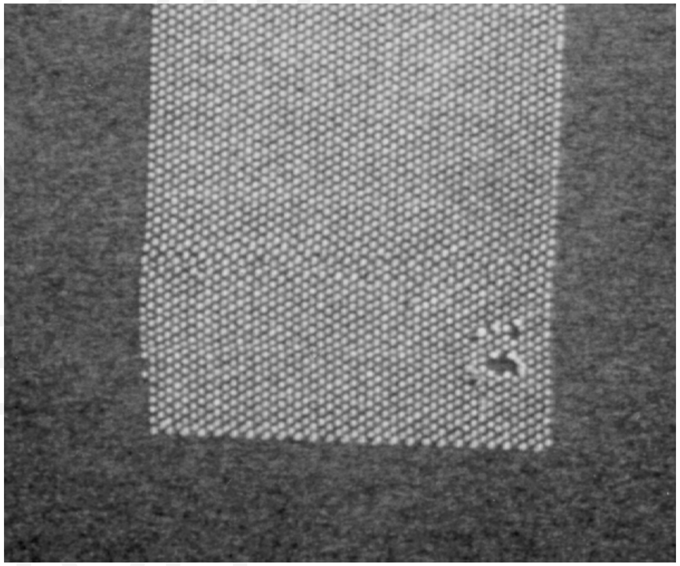
10,000 pillars / 4 X 16 um

High Resolution Pattern Transfer



Master (e-beam)

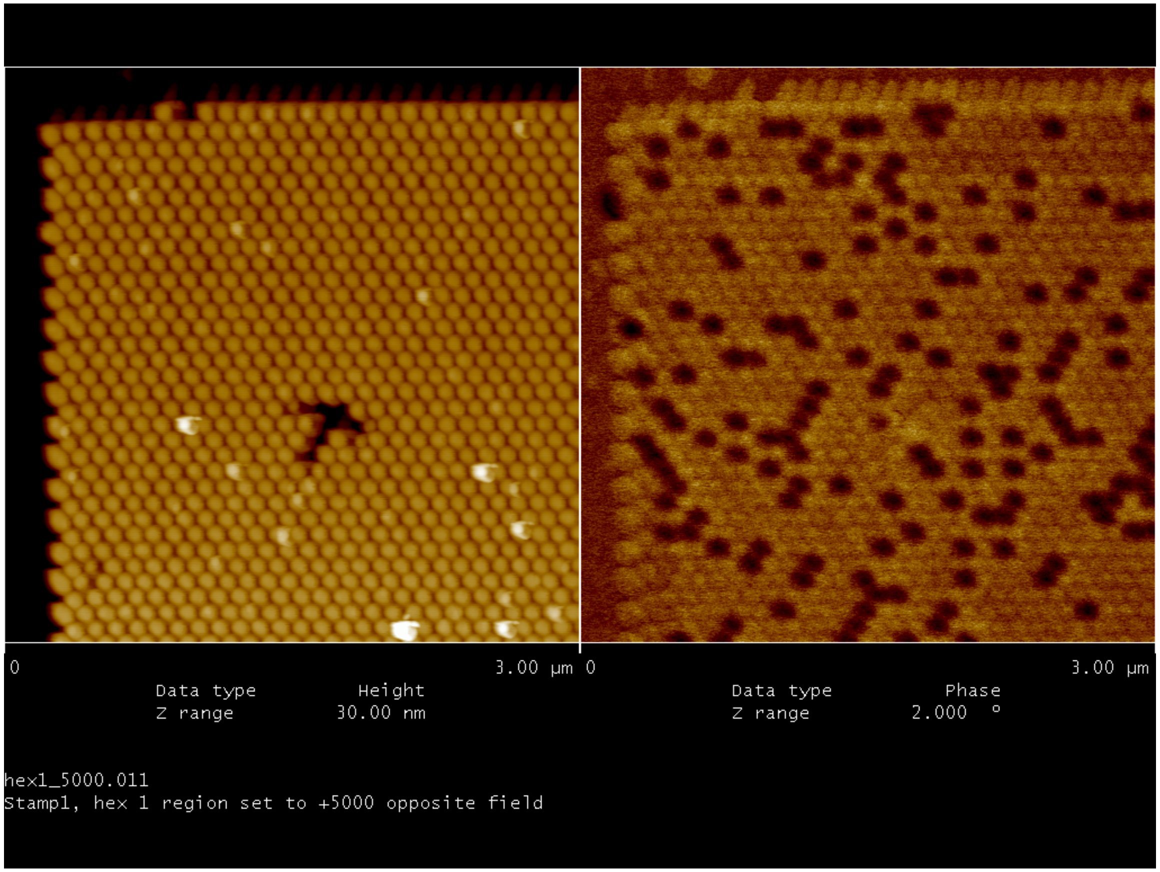
Contact
Molding
Process



Replica (etched SiO_2)

Example – Patterned Magnetic Media

McClelland, Hart, Rettner, Best, Carter, and Terris, *Appl. Phys. Lett.*, **2002**, *81(8)*, 1483.



- •Molded 55 nm photopolymer pillars
- •Etched pattern into substrate
- •Sputtered 11 nm CoPt film
- •Observed isolated magnetic domains

Cloning Device Structures by NCM

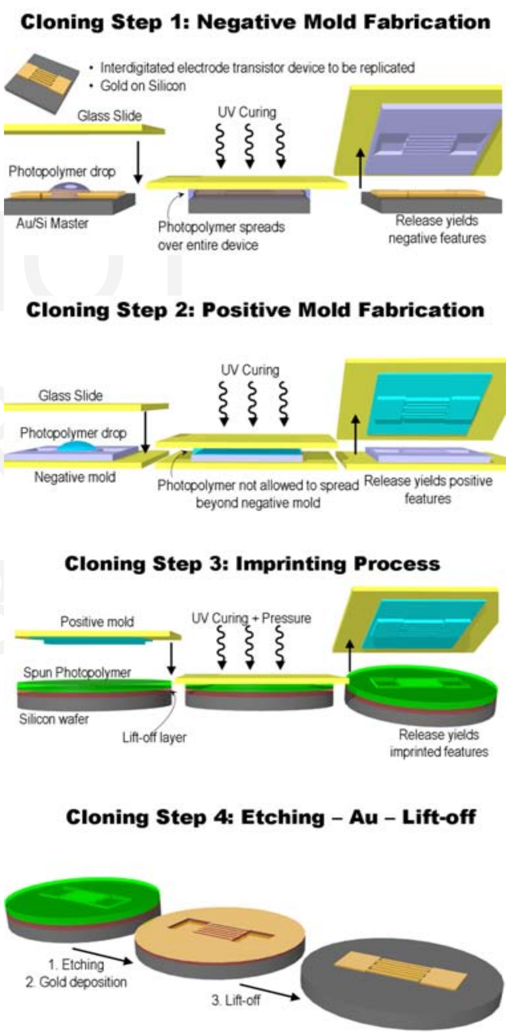
Participants: I. W. Moran, Sarav B. Jhavari, Yuval Ofir, Vincent M. Rotello, K. R. Carter

Goal:

New method of fabrication of electronic device structures

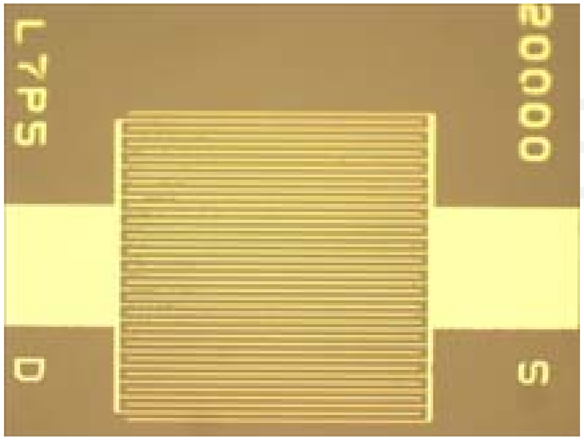
Method:

- New contact molding procedure has been developed for cloning existing device structures
- Using this method, any prefabricated structure on a solid substrate can be quickly replicated
- This non-destructive approach was successfully employed in duplicating multiple forms of devices in an inexpensive and reproducible manner

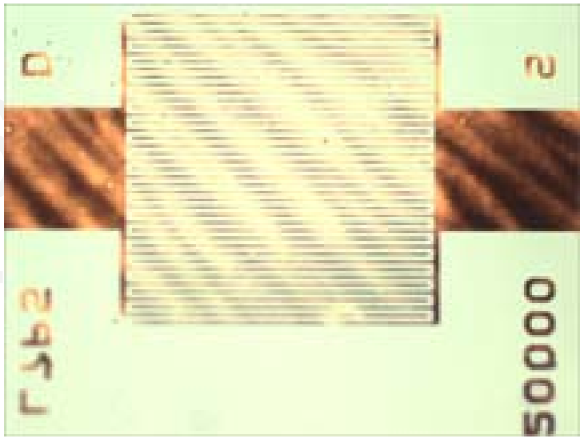


Cloning Device Structures by NCM

Replicated Interdigitated Electrode with W/L = 20000/7.5

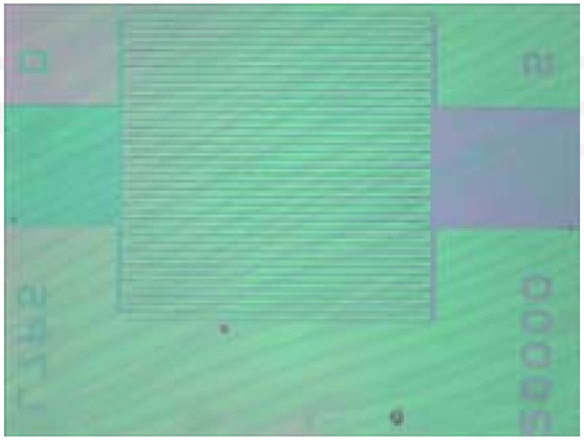


Original Circuit Pattern



Cloned Circuit Pattern

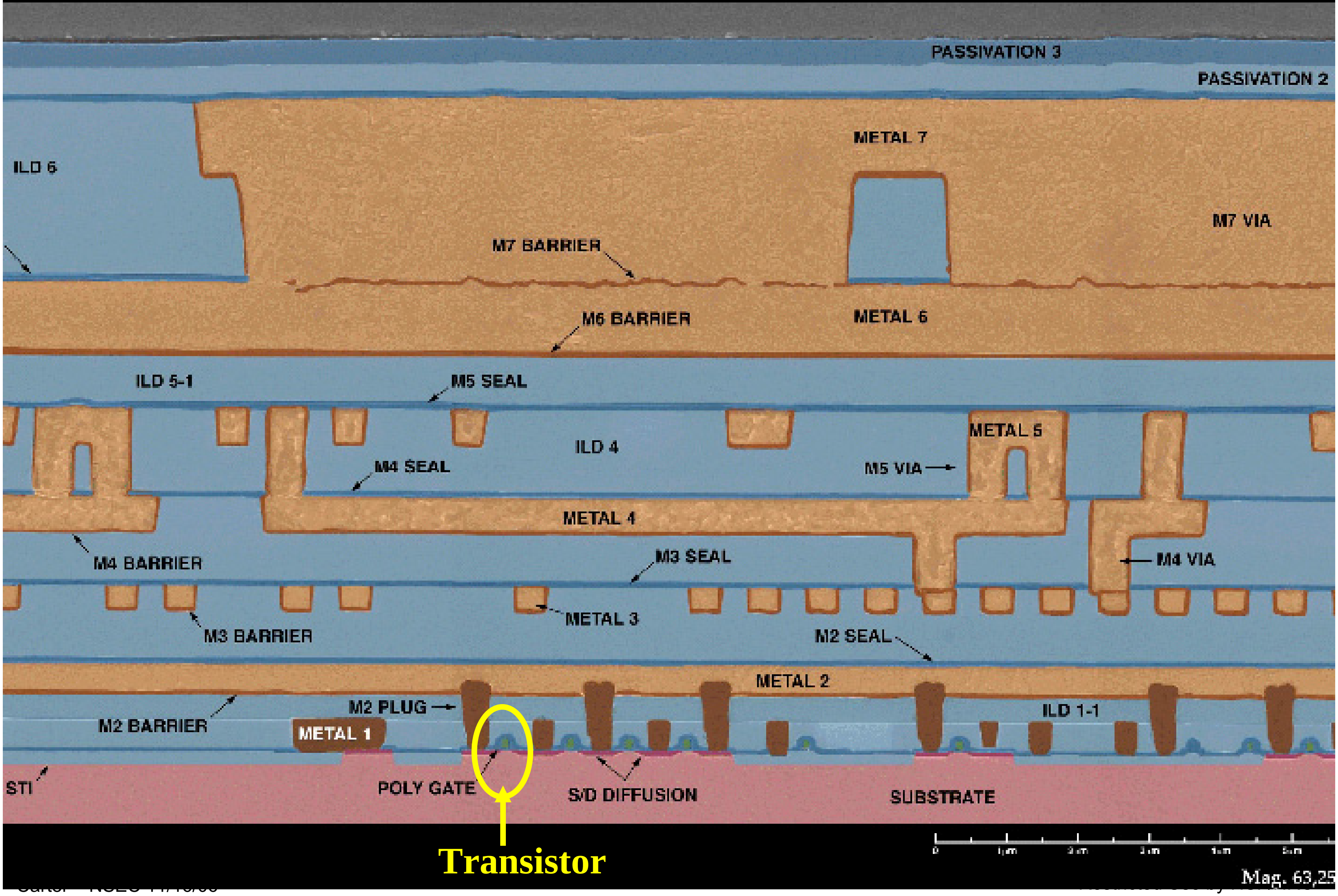
1. Obtain and clean
2. Cast mold
3. Imprint resist



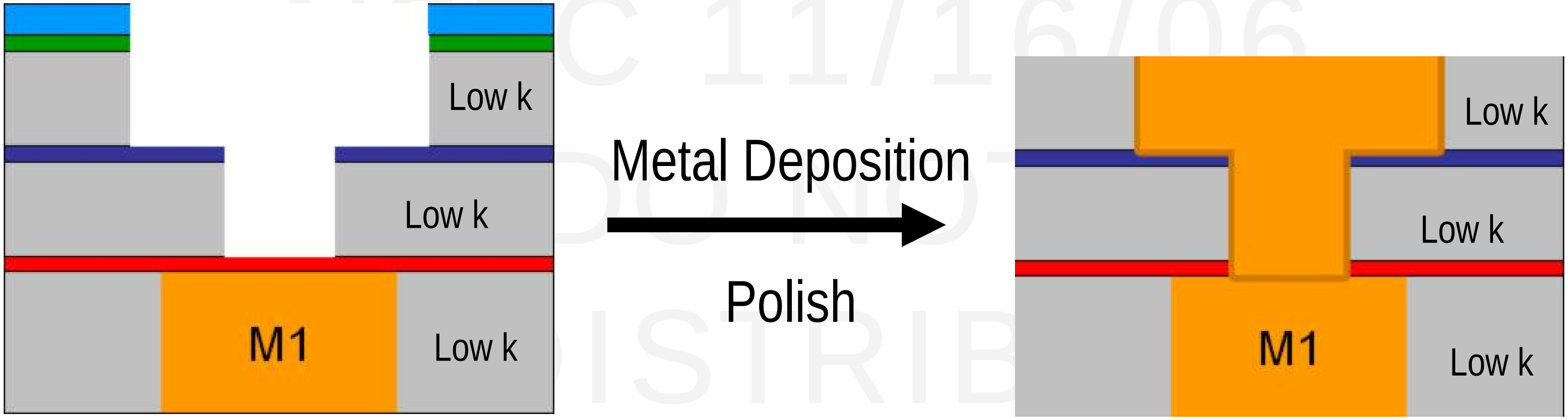
Cast Imprint Mold

4. Etch
5. Cr/Au Evaporation
6. Lift-off

IBM's Power PC750 Microprocessor

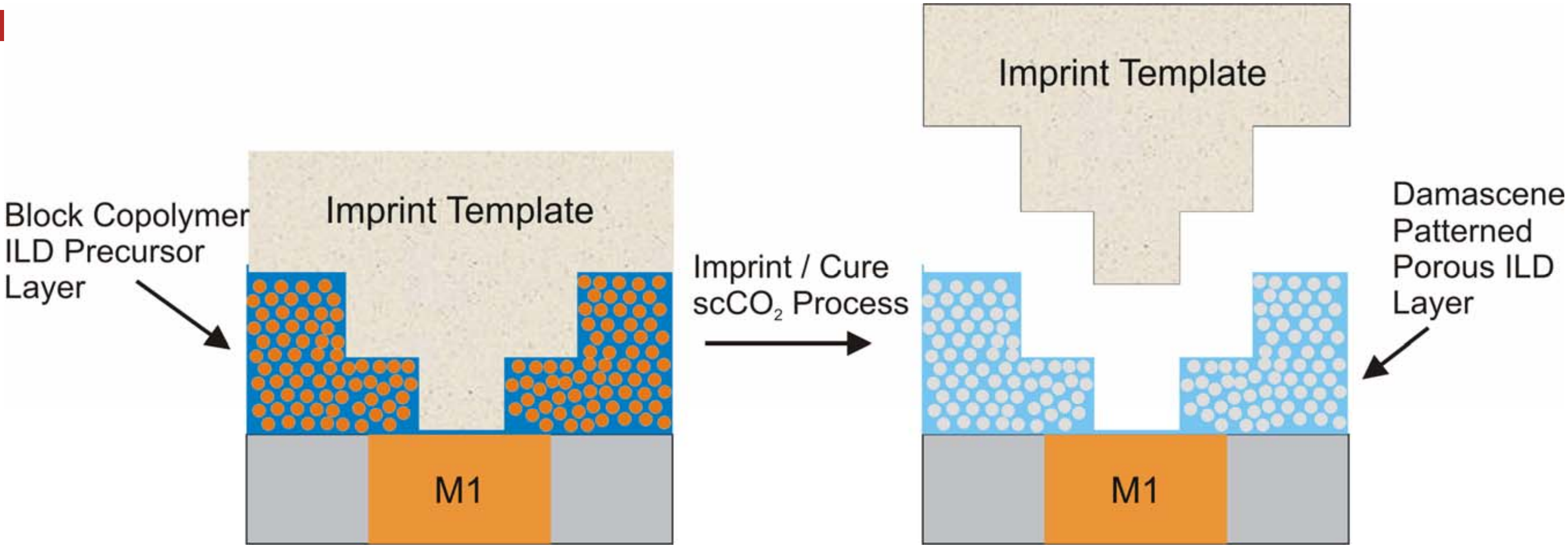


The Dual Damascene Challenge

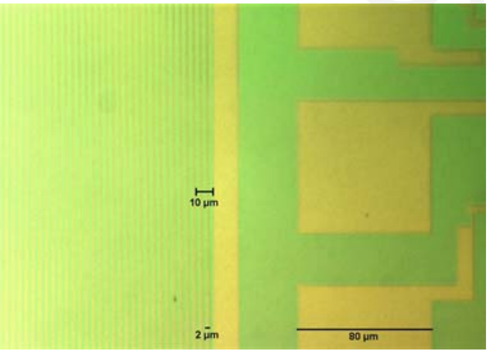


- > 20 Process Steps to create this structure
- Costly, complex and materials limited

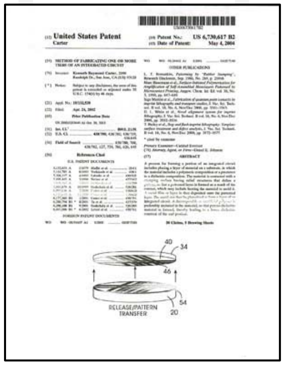
The Imprint Dual Damascene Solution



- Feasibly can be done in less than 7 Process Steps to create this structure
- Decreased cost, less complex and new low k materials set
- Can yield structures not possible by photolithographic processes



Demonstration of Imprinted low k dielectric film



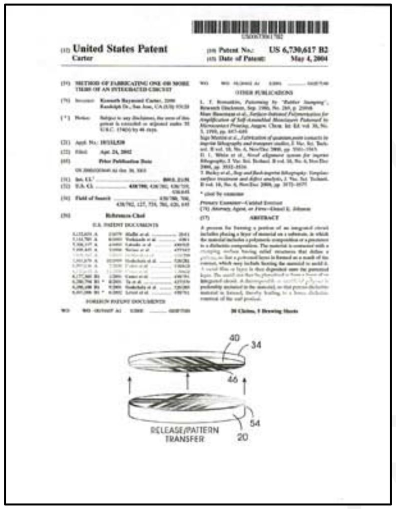
(12) United States Patent
Carter

(10) Patent No.: US 6,730,617 B2
(45) Date of Patent: May 4, 2004

Only US Patent allowed on imprinted Dielectrics, inventor Carter

Direct Patterning of Porous Dielectrics

Carter, K. R. *US Patent* **6,730,617** – *May 4, 2004*



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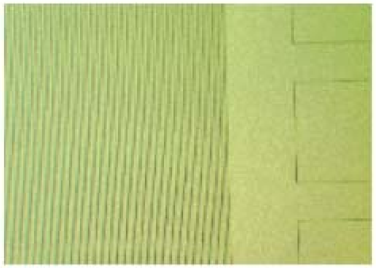
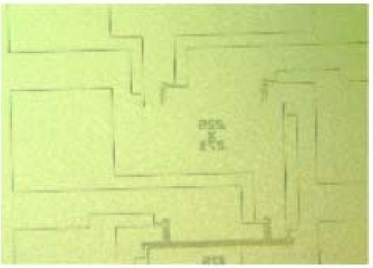
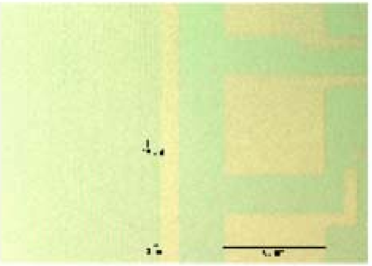
IBM Almaden Research Center



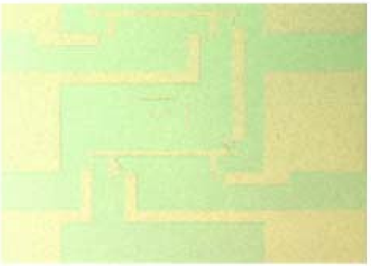
Acrylate Stamp
2 um lines / spaces



Acrylate Stamp
test structures



Stamped Dendriglass
on silicon wafer
2 um lines / spaces

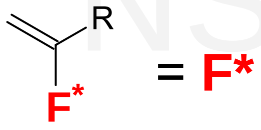


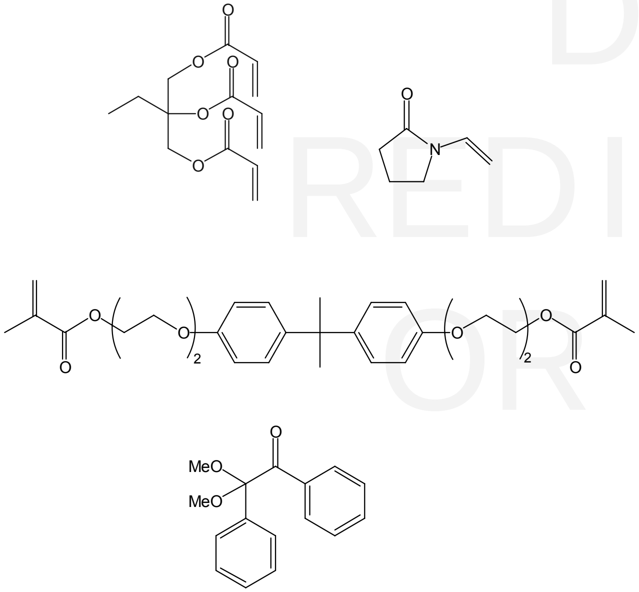
Stamped Dendriglass
on silicon wafer
test structures

- IP Describes direct patterning of porous dielectric layers by imprint lithography

Concept of Embedded Functionality

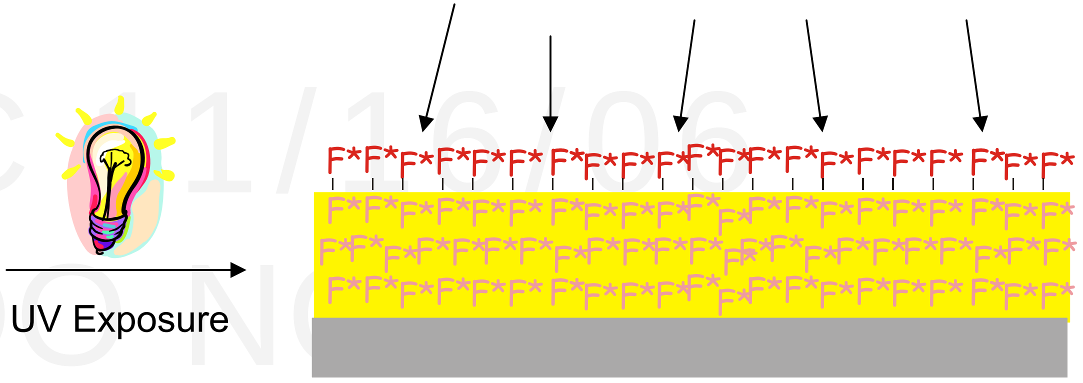
Functional Co-Monomer
5-30 wt %





Photopolymerizable Solution
70-95 wt %

Certain fraction of functionality advantageously located at or near surface of network available for subsequent reactions



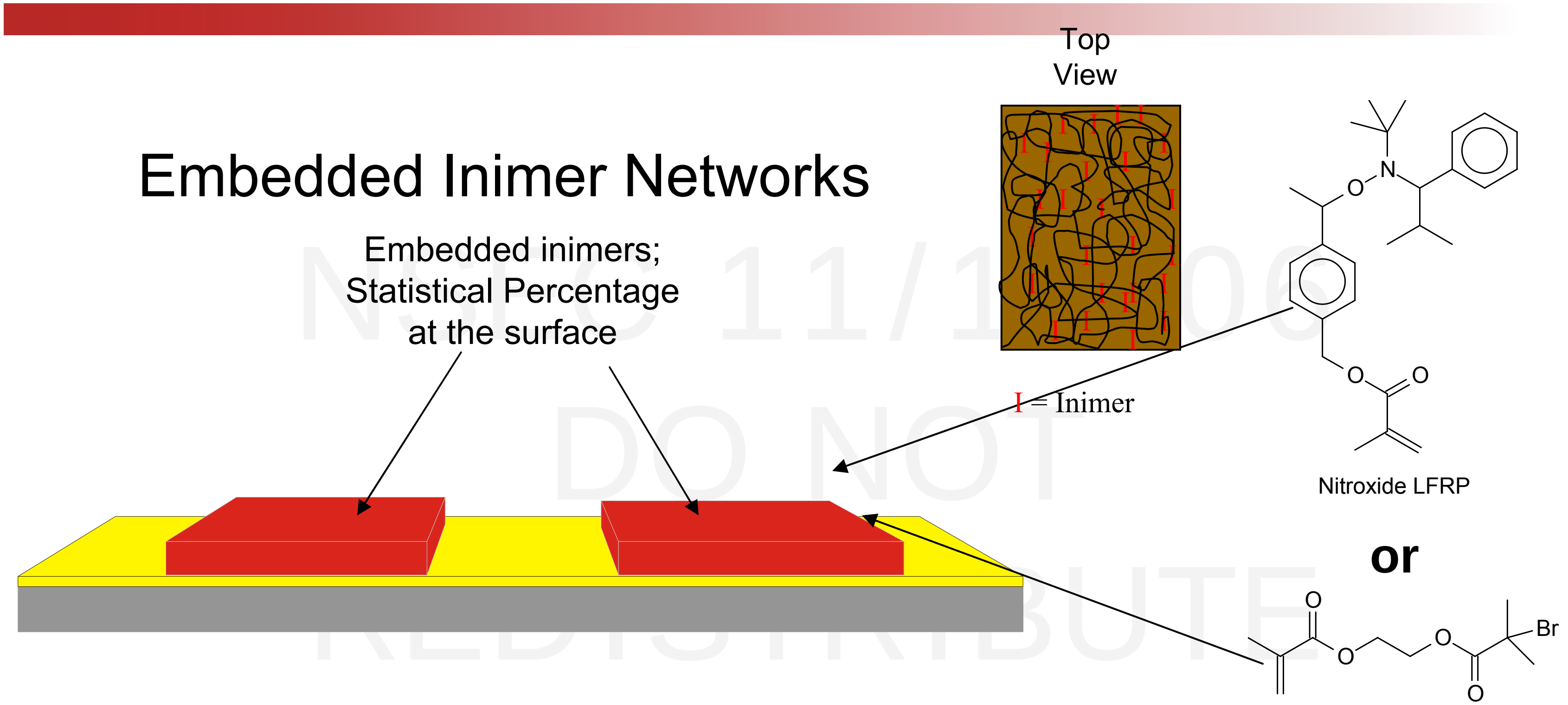
Functionalized Crosslinked Network

Advantages

- No need for complex surface functionalization
- More robust anchoring than SAMs
- Limited substrate effects
- High surface area available for reaction
- Opens synthetically accessible chemistry

Controlled Grafts from Polymeric Surfaces

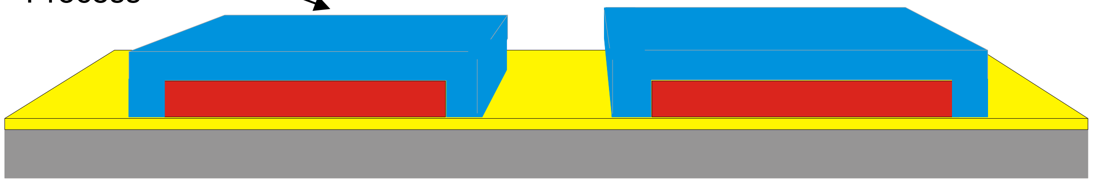
Embedded Inimer Networks



Embedded inimers;
Statistical Percentage
at the surface

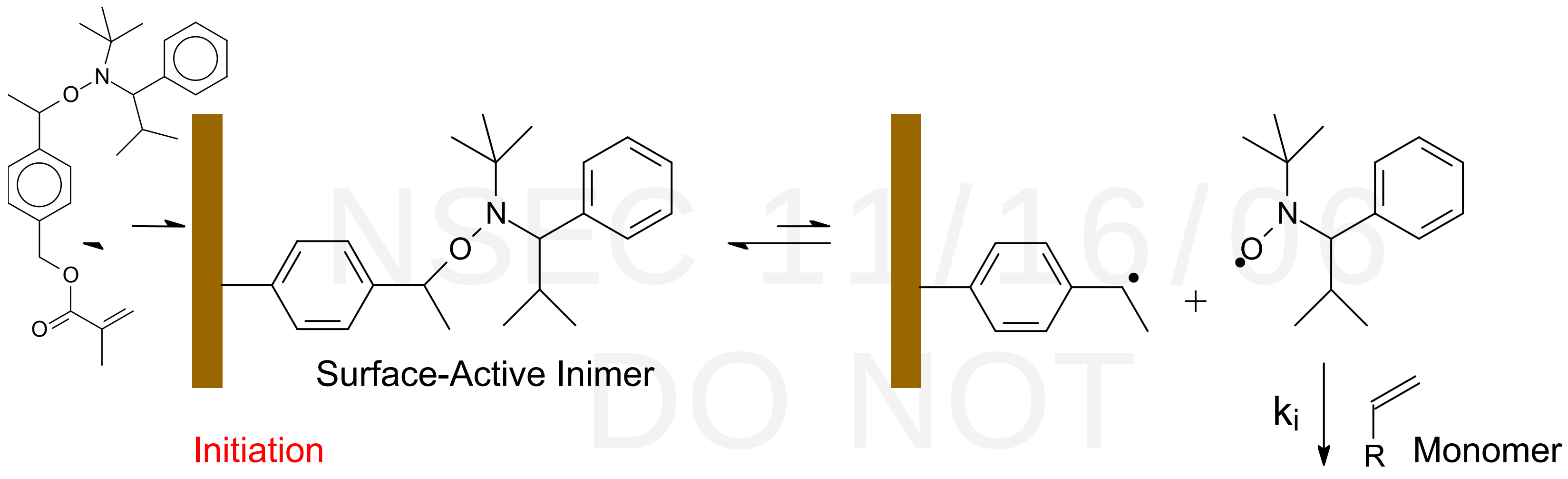
ATRP

“Living” RP Growth
Process

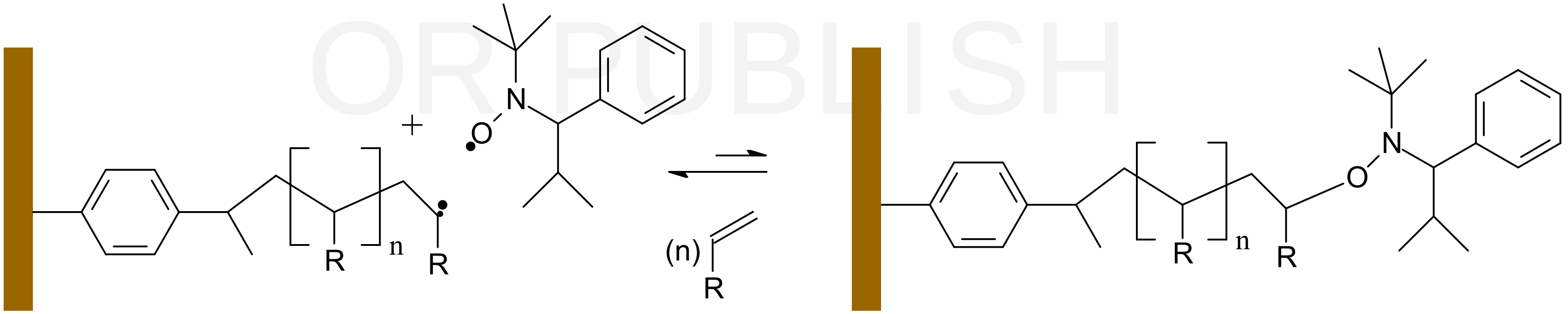


Embedded Inimers

Nitroxide-Mediated Surface Polymerization

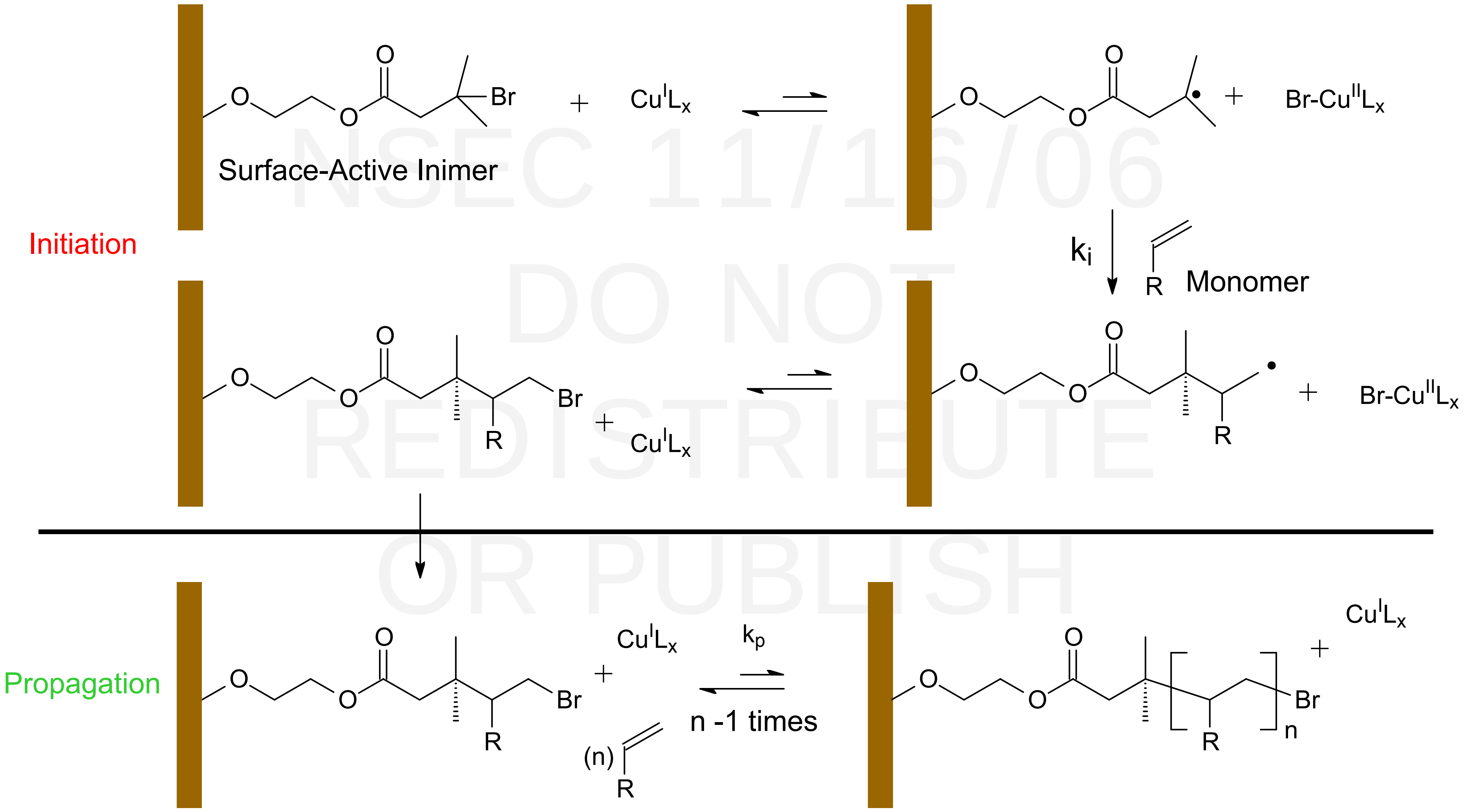


Initiation

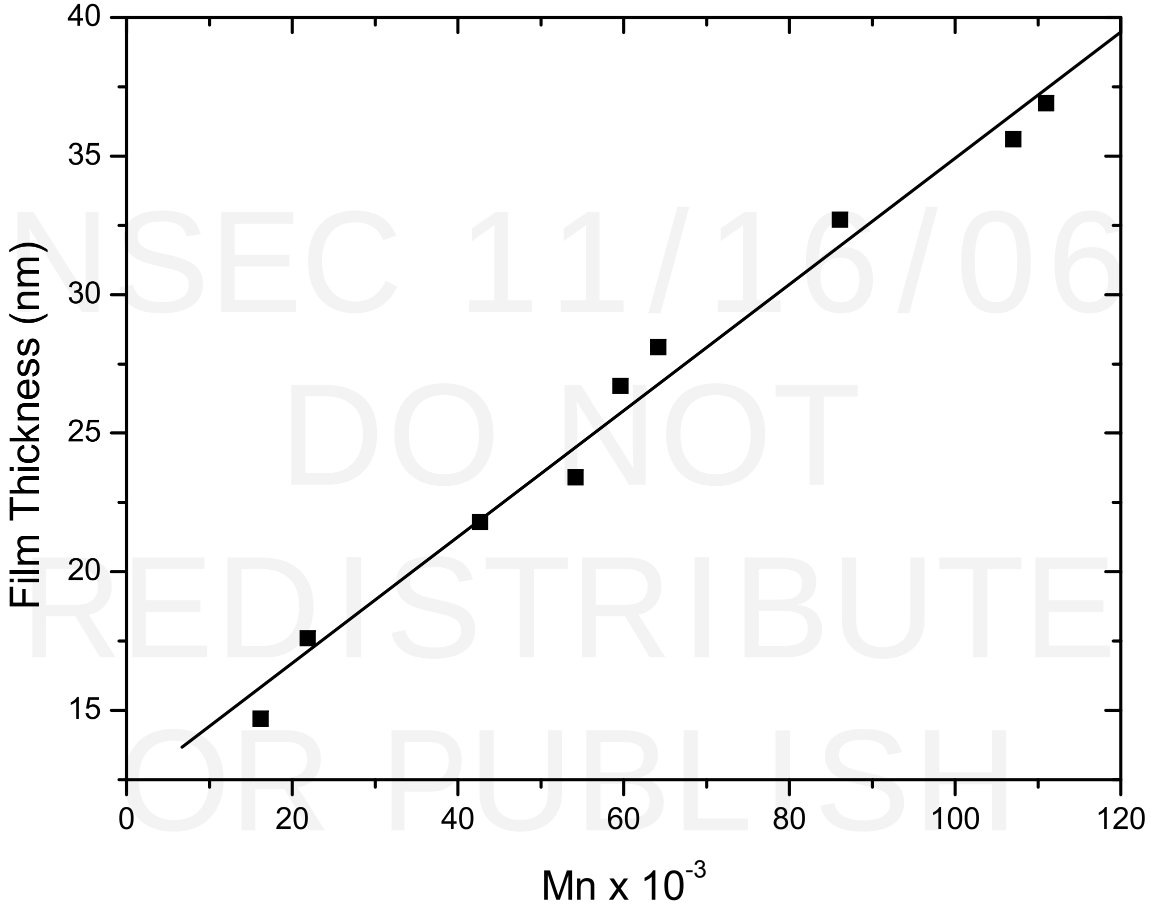


Propagation

Atom Transfer Radical Polymerization - ATRP



Thickness Change vs Brush Mw

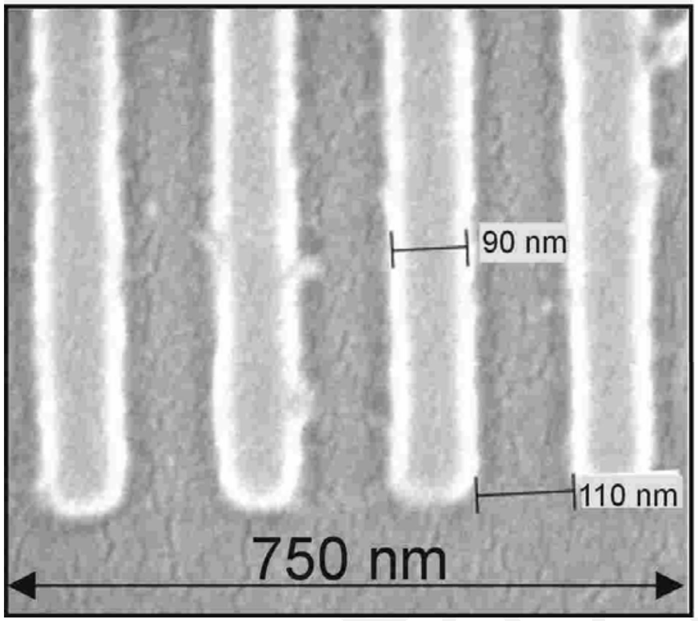


- Brushes were grown from the surface in the presence of “free” initiator
- Solution polymer Mw was examined as a measure of brush Mw
- Excellent agreement between thickness and brush Mw

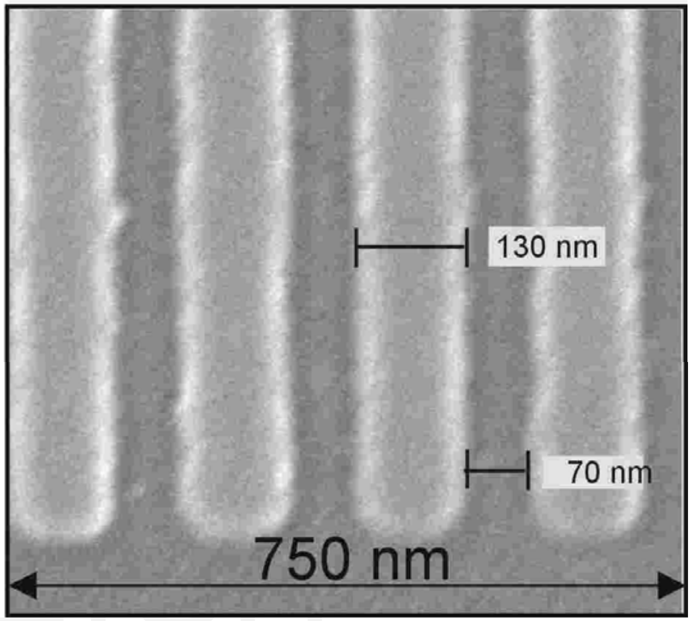
Surface Size Control

J. Am. Chem. Soc., **2003**, *125(13)*, 3831.
Science, **2003**, *299*, 1816.

After Molding



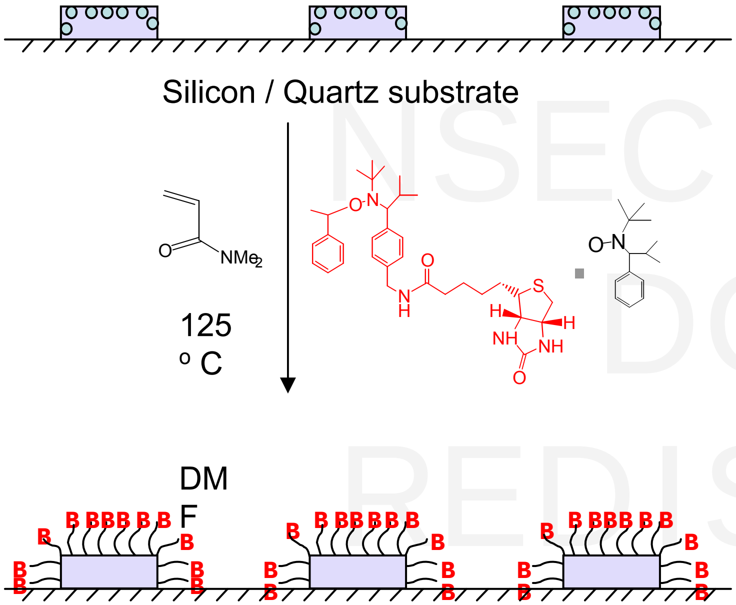
After Brush Growth



Controlled Brush Growth From Imprinted Surfaces:

- Demonstrated the ability to mold (imprint) nanostructures and chemically modify surface by unique photopolymer design
- Accomplished by polymer brush growth from patterned resist
- Ability to control and modify size and chemistry of nano-features

Bioresponsive Surfaces


Silicon / Quartz substrate

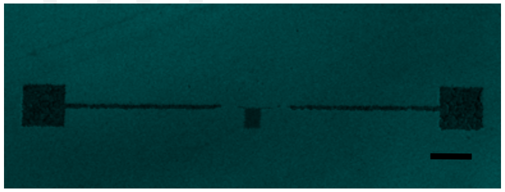
125 °C

DMF

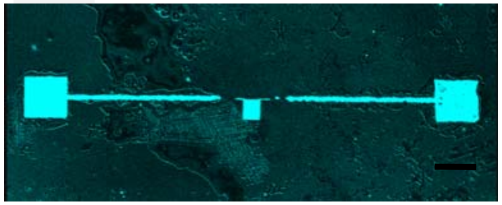
Alexa Flor labelled streptavidin

10 mM HEPES buffer

PDMA no Biotin



Biotinylated PDMA

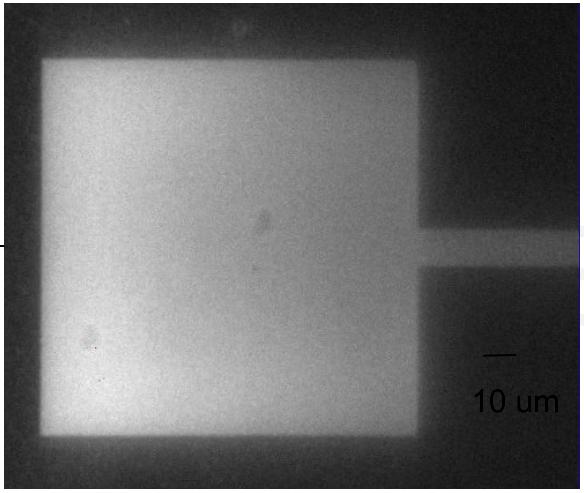


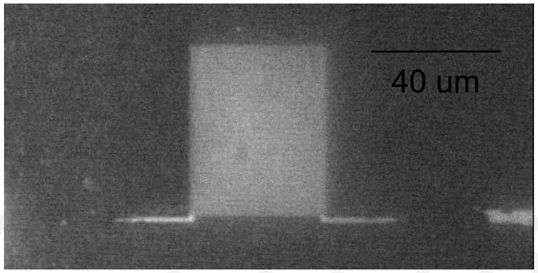
Run#	Sub.	M_n	PDI
1	Silicon	8.75 K	1.16

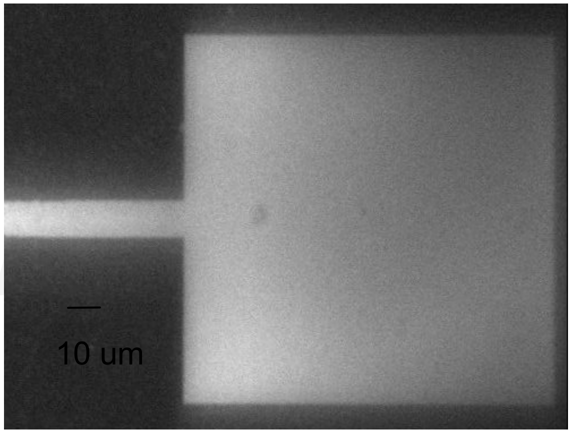
Scale bar = 100um

Sarav Jhaveri & Kai Qi

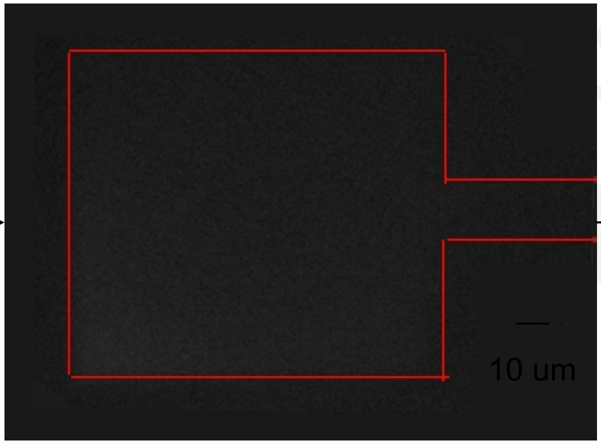
IgE / Dinitrophenol Interactions



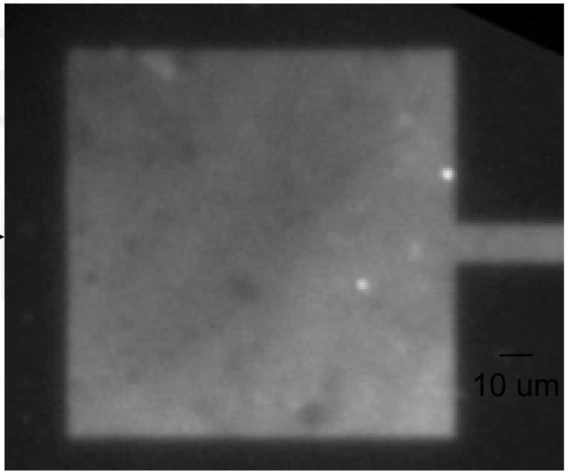




(1) First IgE
Treatment



(2) DNP-BSA Hapten
Detachment Treatments

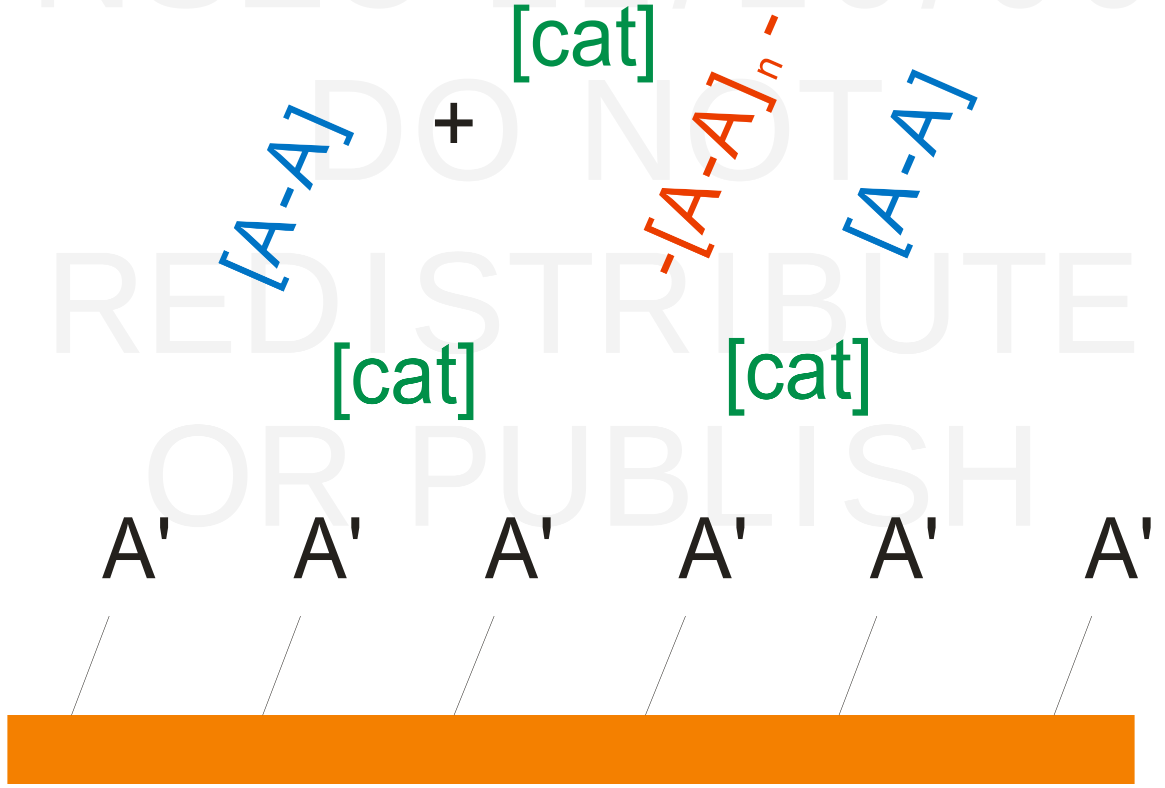


(3) Second IgE
Treatment

Sarav Jhaveri & Kai Qi

Polymer Brushes via Polycondensation

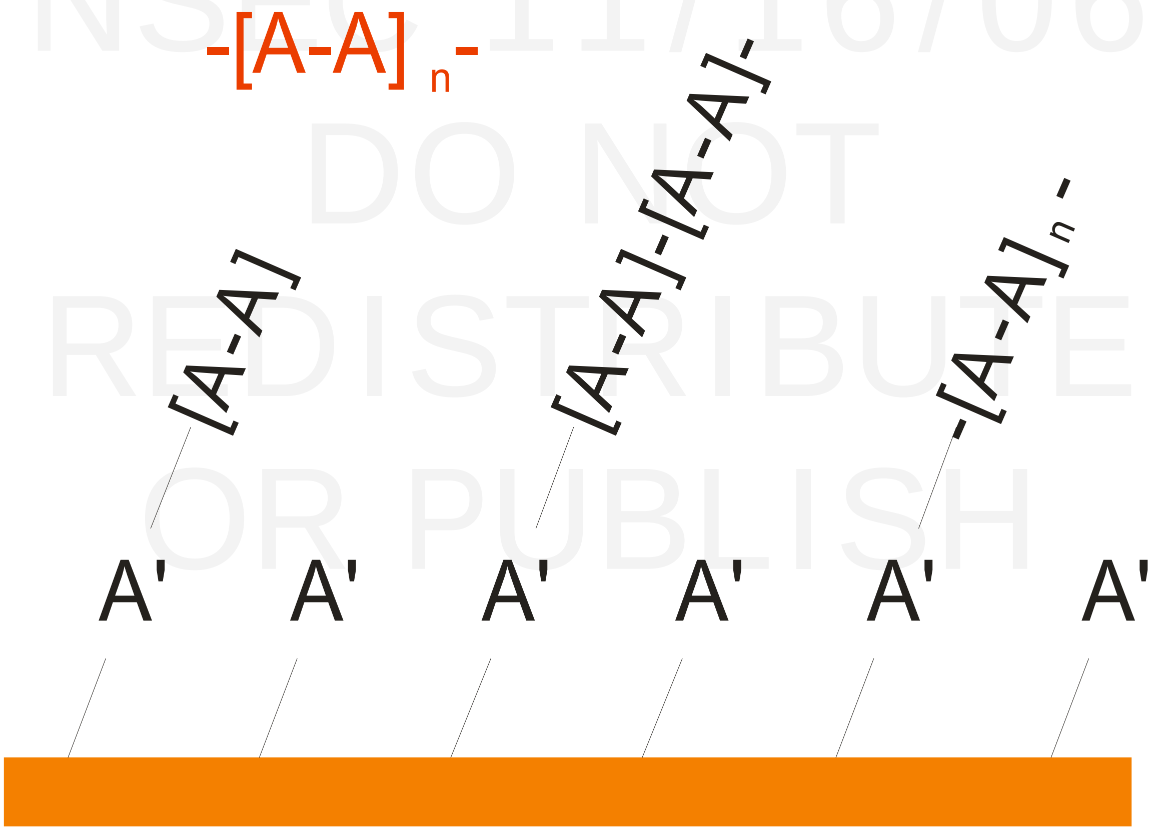
A_2 Polymerization: $|\text{-A'} + n\ \text{A-A} \xrightarrow{[\text{Cat}]} |\text{-A'-[A-A]}_x\text{-} + \text{-[A-A]}_{n-x}\text{-}$



Combination of Grafting “from” & “to”

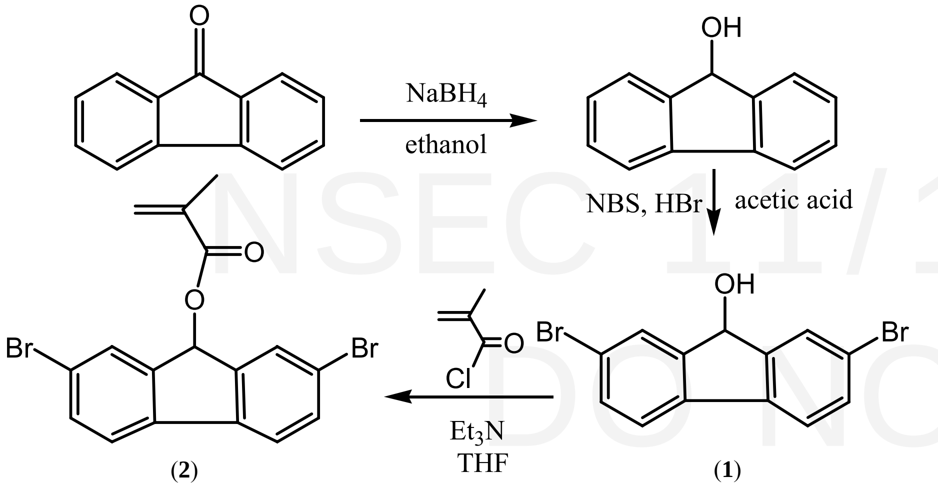
Polymer Brushes via Polycondensation

A_2 Polymerization: $|\text{-}A' + n\ A\text{-}A \xrightarrow{[Cat]} |\text{-}A'\text{-}[A\text{-}A]_x\text{-} + \text{-}[A\text{-}A]_{n\text{-}x}\text{-}$



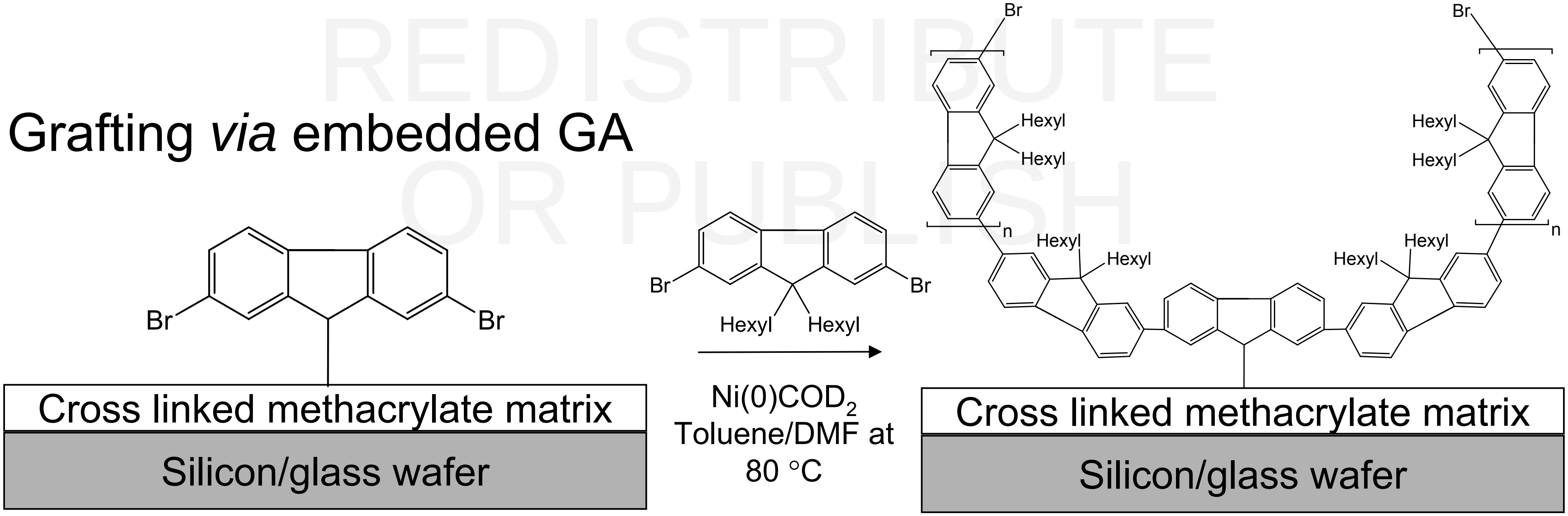
Combination of Grafting "from" & "to"

Inimer Selection Increases Graft Efficiency



Synthesis of FI-MA

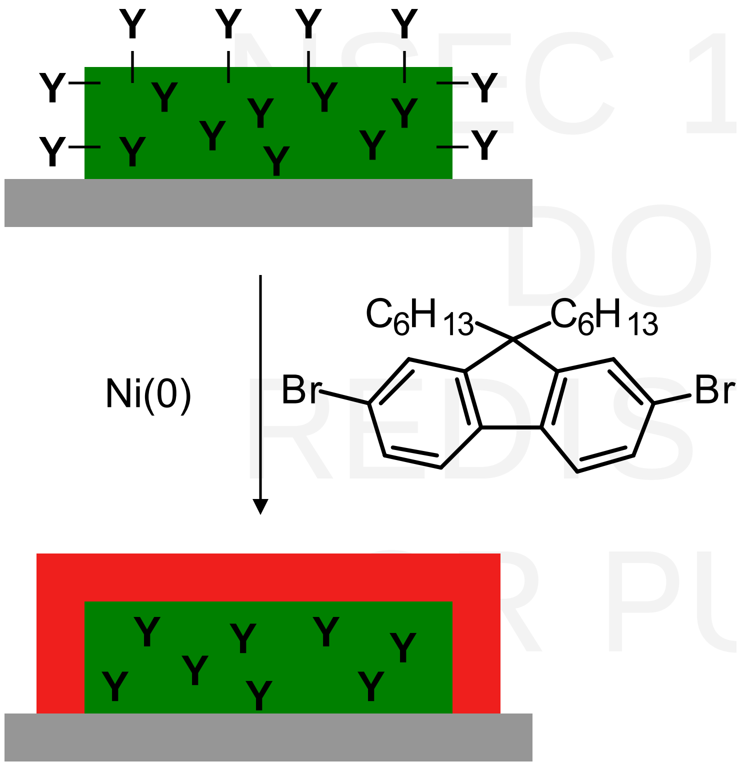
Grafting *via* embedded GA

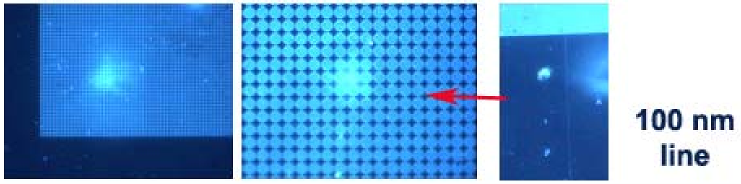


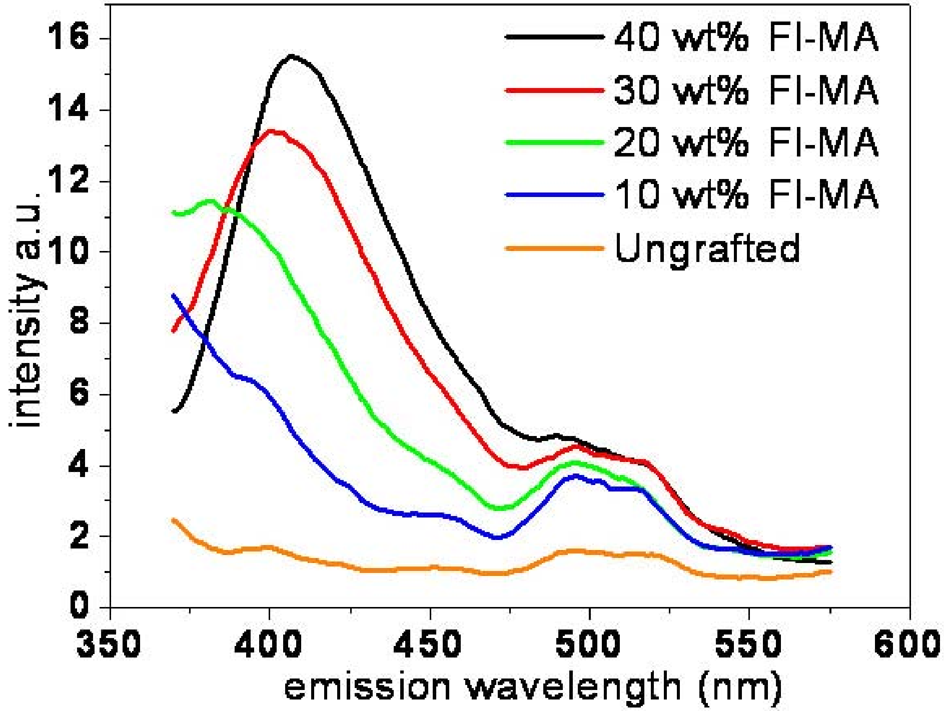
Ni(0)COD$_2$
Toluene/DMF at
80 °C

Imprint & Grow - Polyfluorene Grafts

Dr. Isaac Moran & Dr. Matthias Beinhoff

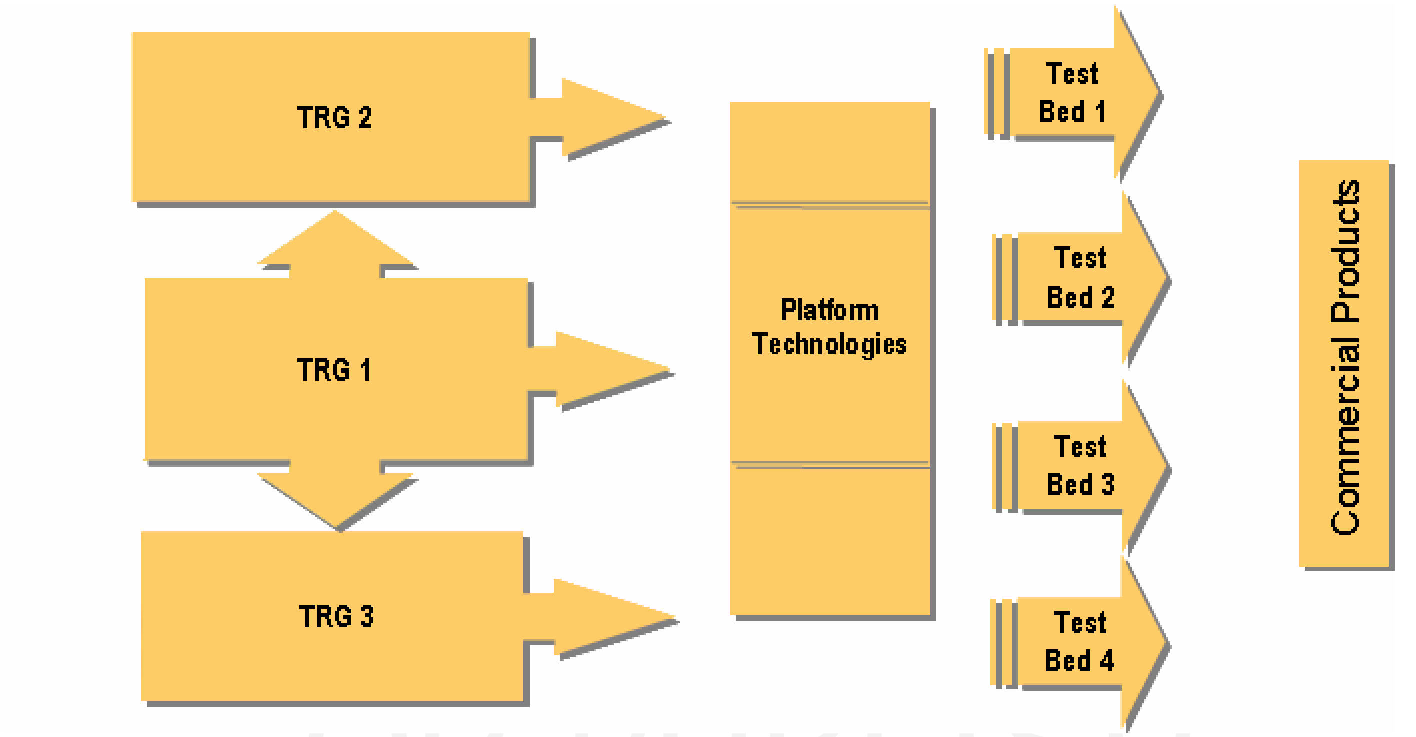






Beinhoff, M.; et. al., *Langmuir,* ***2006***, 22(6), 2411-14.
Mora, I. W.; et. al., *Chem. Mater.,* ***2006***, submitted for publication.

UMass NSEC: Center for Hierarchical Manufacturing


TRG 2

TRG 1

TRG 3

Platform Technologies

Test Bed 1

Test Bed 2

Test Bed 3

Test Bed 4

Commercial Products

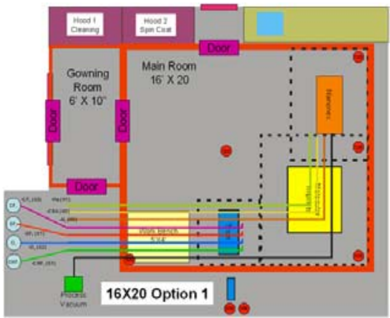
Multidisciplinary -- 29 Faculty

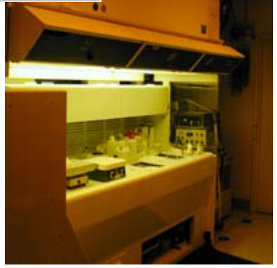
- Chemistry
- Chemical Engineering
- Electrical & Computer Engineering
- Mechanical & Industrial Engineering
- Physics
- Polymer Science & Engineering

On Campus Nanofabrication Facilities & Resources

Molecular Imprints
MI-55 SF-IL Tool

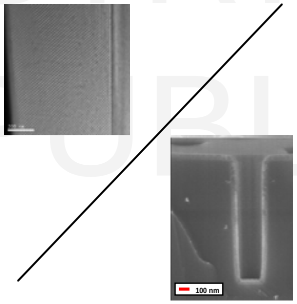
Nanonex NX-2000
Nanoimprinter





Cleanroom
Fabrication
Facilities

Trion Systems
ICP Etch Tool



SCF Full Wafer Tool
Low k/metals/metal oxides

One-of-a-kind
Nanoimprint
Lithography
Facility

Summary

- Imprint lithography is a powerful tool for the rapid fabrication of nanostructures
- Imprint lithography can pattern large areas in few steps
- Process can take virtually any original nanostructured surface and replicate it
- Cost of ownership less than other nanofabrication techniques – environmental benefits
- Patterning into: resists, metals, organics, functional materials
- Must understand surfaces and interfaces

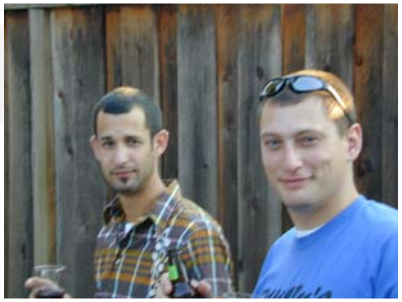
Carter Research Group

From Left: Mike Mahdavi, Matthew Fagan, Damla Koylu, Dr. Sarav Jhaveri, and Prof. Carter.

Dr. Isaac Moran

Dr. Matthias Beinhoff

Not shown:
Janet Magerlein
Burcin Erenturk
Dalton Cheng
Dylan Donnovan (Elizabethtown C)
Dominik Maschke (U. Mainz)



Drs. Tim von Werne & Erik Hagberg

Acknowledgments

- NSF Materials Research Science and Engineering Center (DMR 0213695)
- NSF DMR Polymers (DMR 0606391)
- NSF NSEC CHM (DMI-0531171)
- The Nanoimprint Lithography Laboratory recently established at the University of Massachusetts Amherst is supported by a grant from the NSF Major Research Instrumentation (MRI) program (DMR-0606391)
- IBM Corporation
- 3M Non-Tenured Faculty Award