Making Things Small: using Polymers in Nanofabrication for Applications from Microelectronics to Biotechnology

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Cornell Nanofabrication Facility
Cornell High Energy Synchrotron Source

Funding & Interactions

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Nanobiotechnology Center
Office of Naval Research
Semiconductor Research Corporation
International Sematech

Chrysalis
EIT
Intel
IBM
KRATON
Praxair

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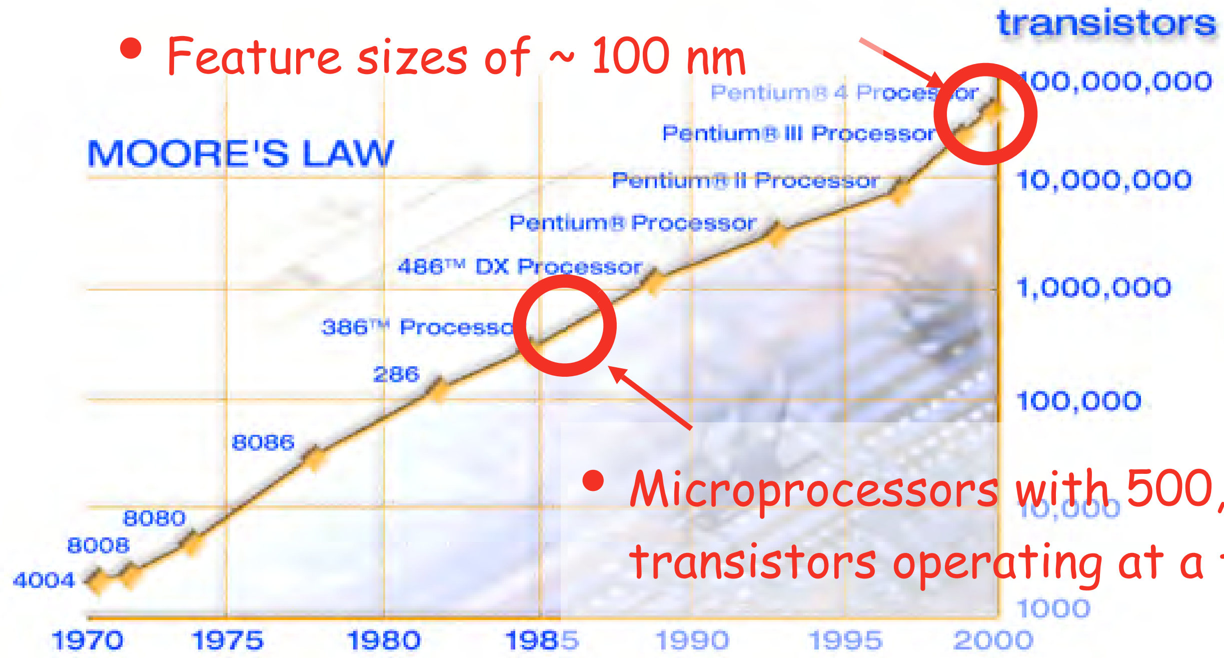
Smaller is Better

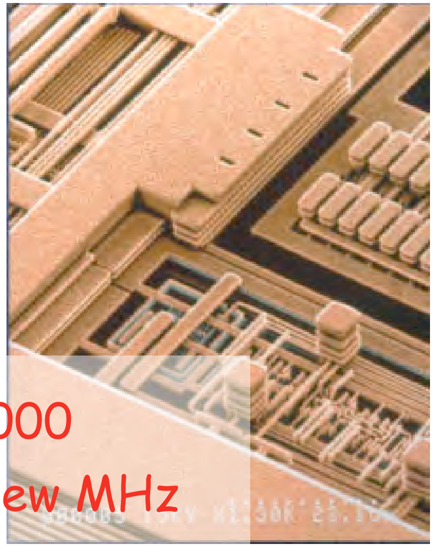
Moore's Law after 40 Years

- Now few GHz
- Feature sizes of ~ 100 nm



- Microprocessors with 500,000 transistors operating at a few MHz
- Feature sizes of ~ 0.5 μm

http://www.intel.com/research/silicon/mooreslaw.htm

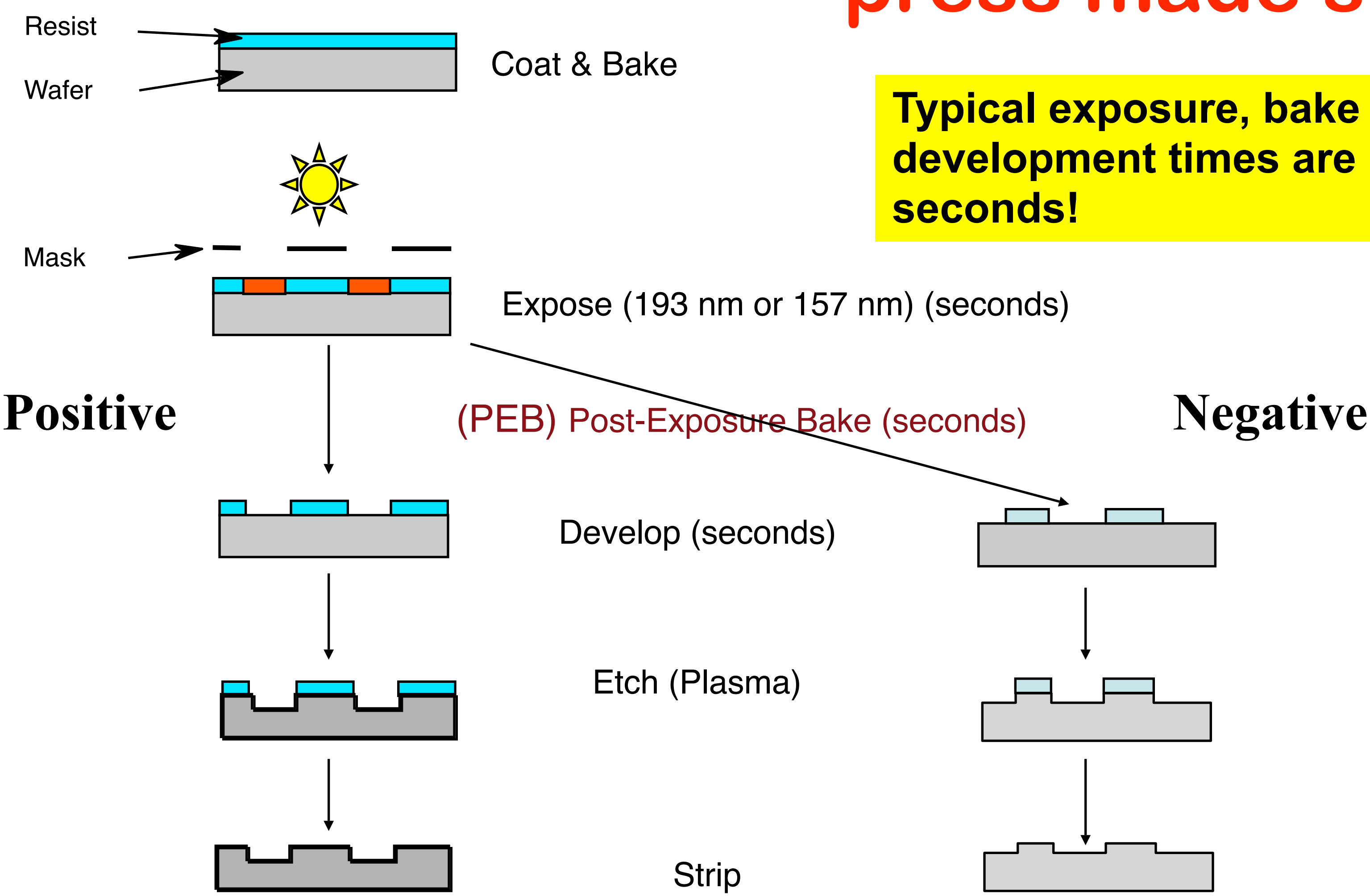


http://www.chips.ibm.com/gallery/p-n2.html

Chemically
Amplified Photoresist

Lithography: the printing press made small

Typical exposure, bake and development times are in seconds!



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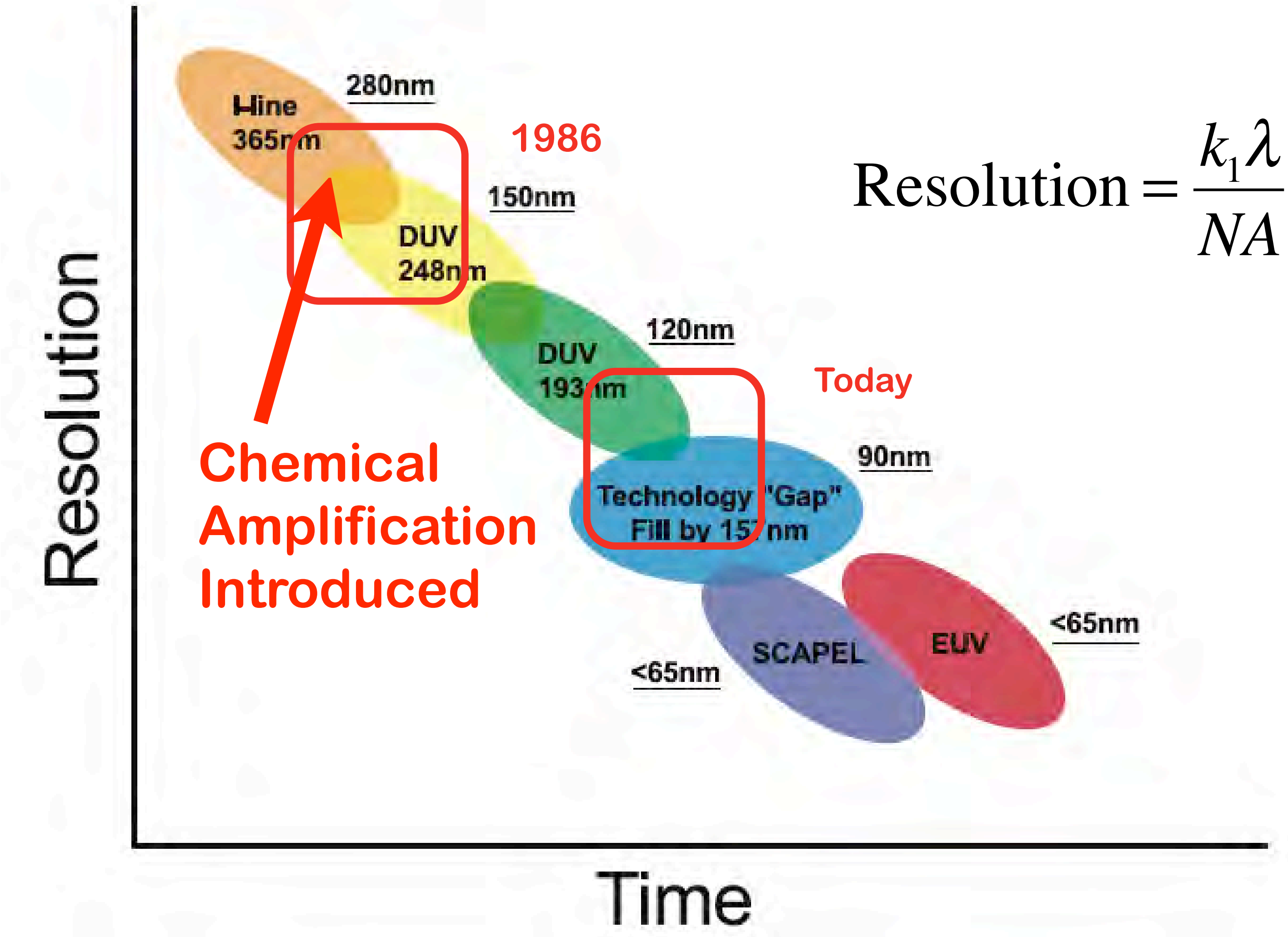
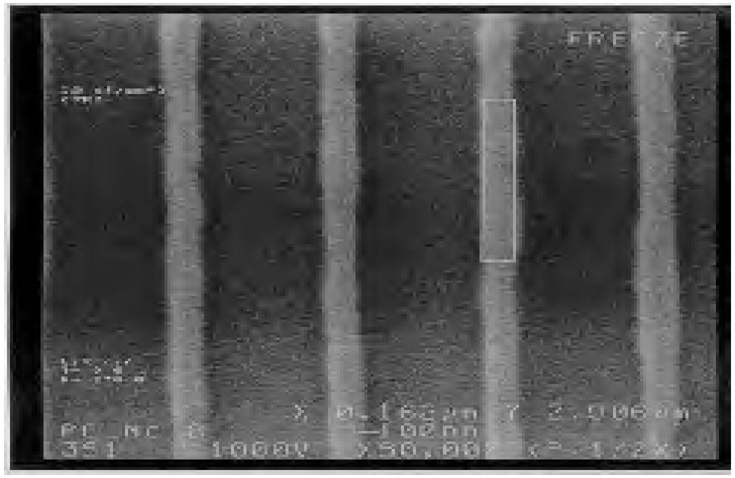
The March to Smaller Dimensions

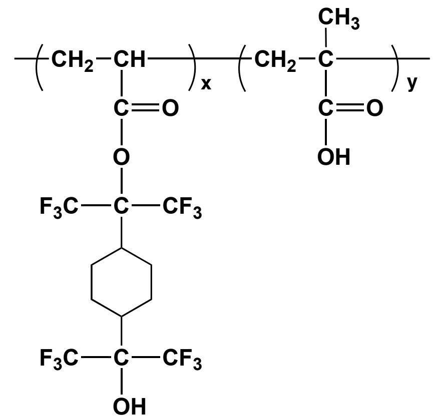


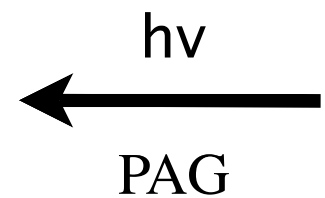
$$\text{Resolution} = \frac{k_1 \lambda}{NA}$$

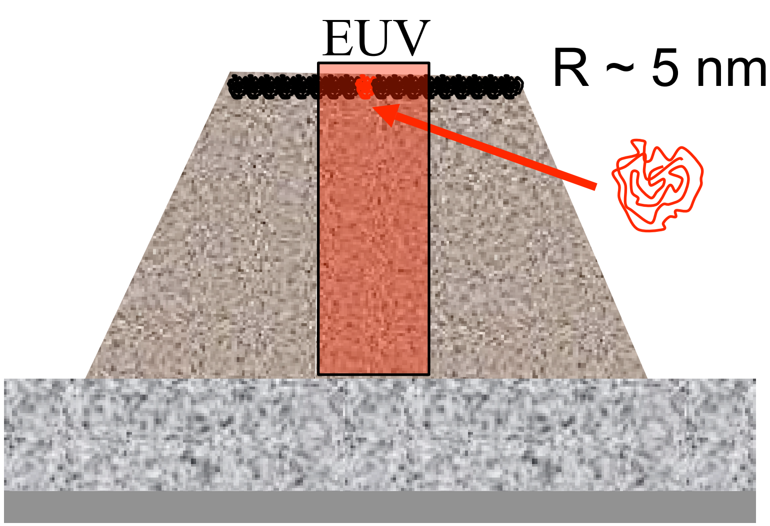
157 nm Lithography

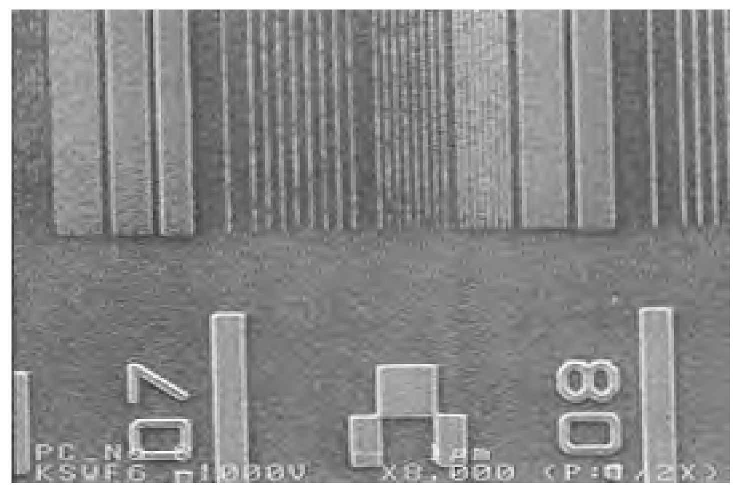


130 nm 1:5 L/S





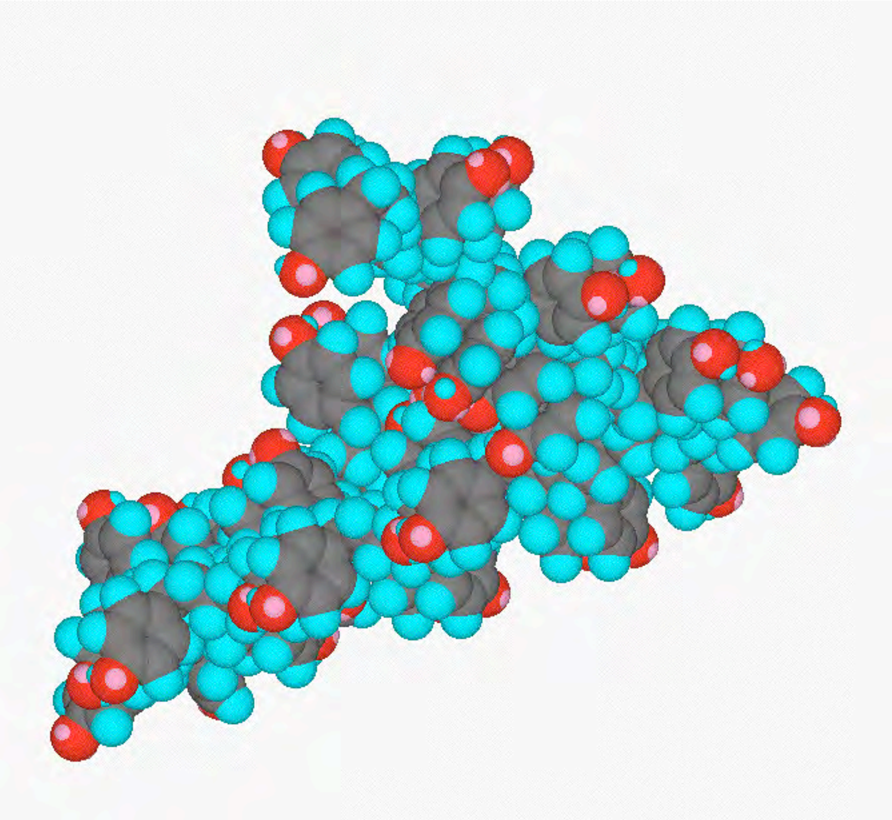




80 nm L/S

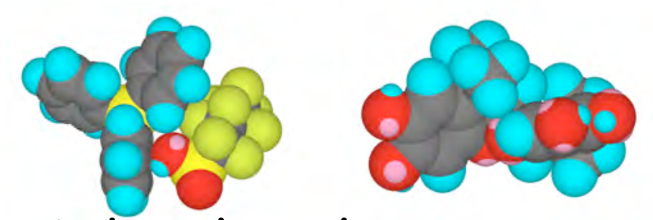
Y. C. Bae, C. K. Ober et al."Tailoring Transparency of Imageable Fluoropolymers at 157 nm by Incorporation of Hexafluoroisopropyl Alcohol to Photoresist Backbones", *Chem Mater.*, (2002), 14(3), 1306-1313.

Molecular Size



Poly(hydroxy styrene), DPn = 50

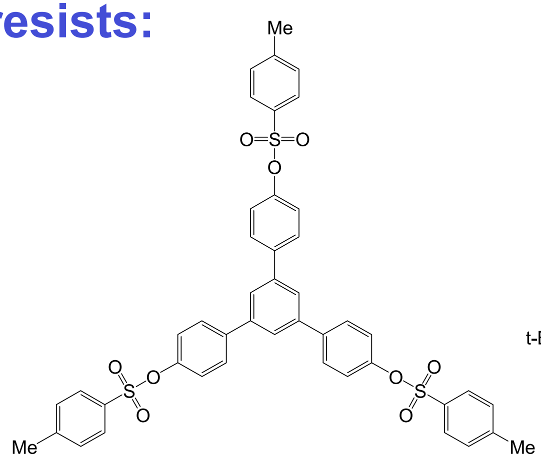
- Molecular glasses can possess substantially smaller size
- Many of same features as polymer
- More uniform distribution of resist additives

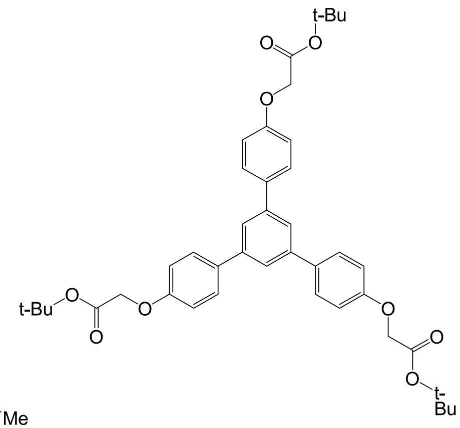


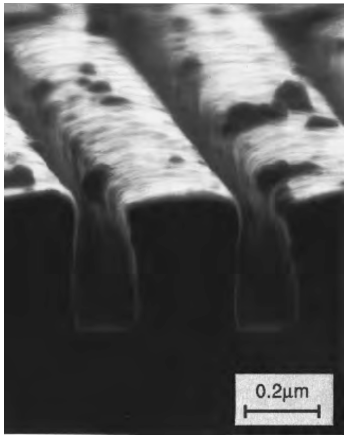
Molecular glass resist components

E-beam Molecular Glass Resists

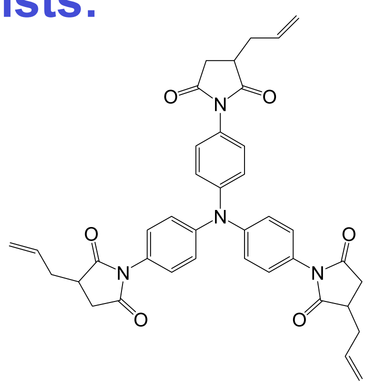
Positive-tone resists:

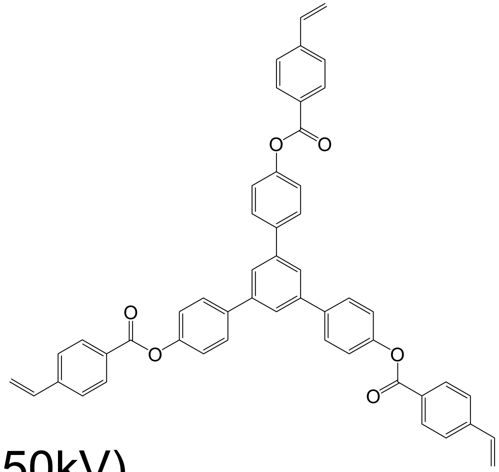


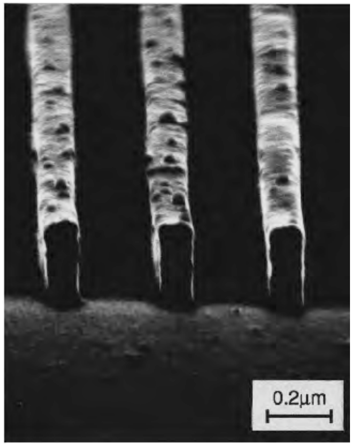




Negative-tone resists:





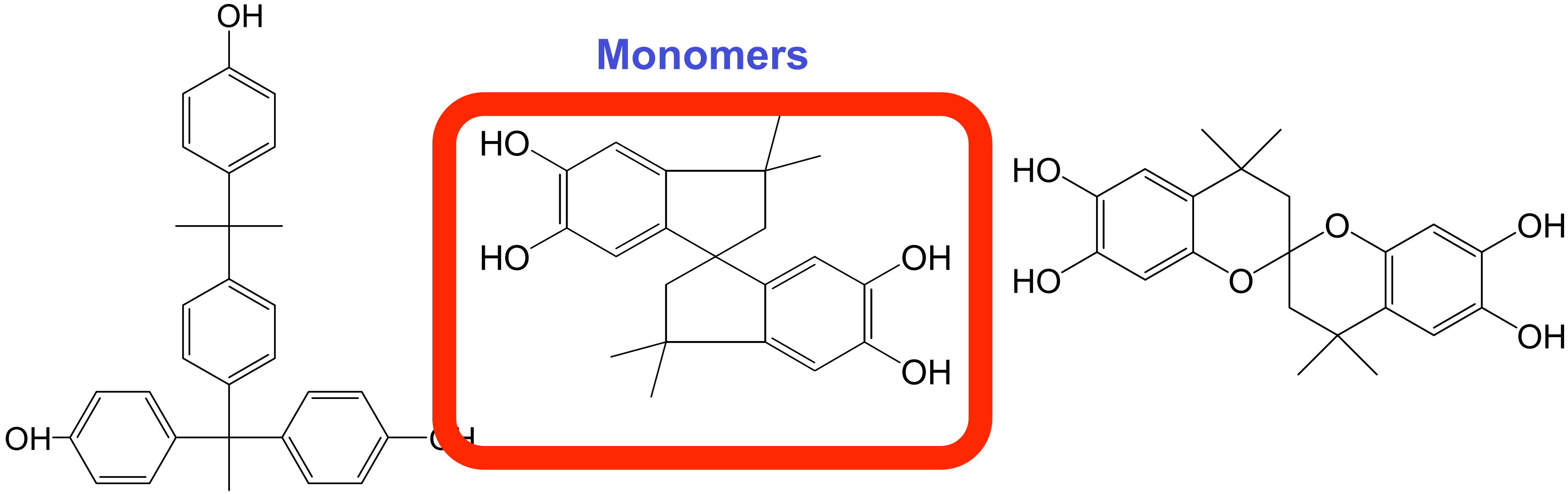


- High dosage (12 ~ 14 mC/cm^2 @ 50kV)

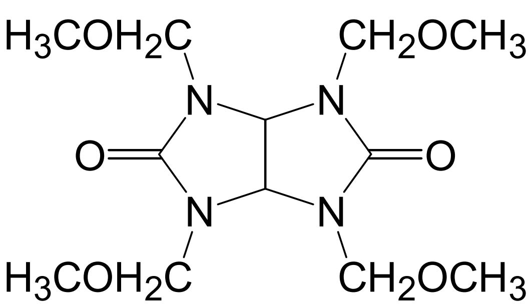
Kadota, T.; Yoshiiwa, M.; Kageyama, H.; Wakaya, F.; Gamo, K.; Shirota, Y. *Proceedings of SPIE* **2002**, *4345*, 891-899

Negative-tone Molecular Glass Resist - Components

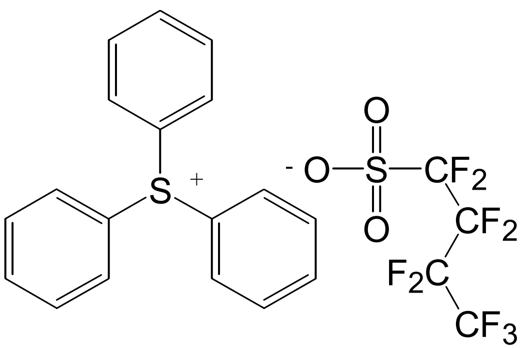
Monomers



TMMGU Crosslinker



Photoacid Generator



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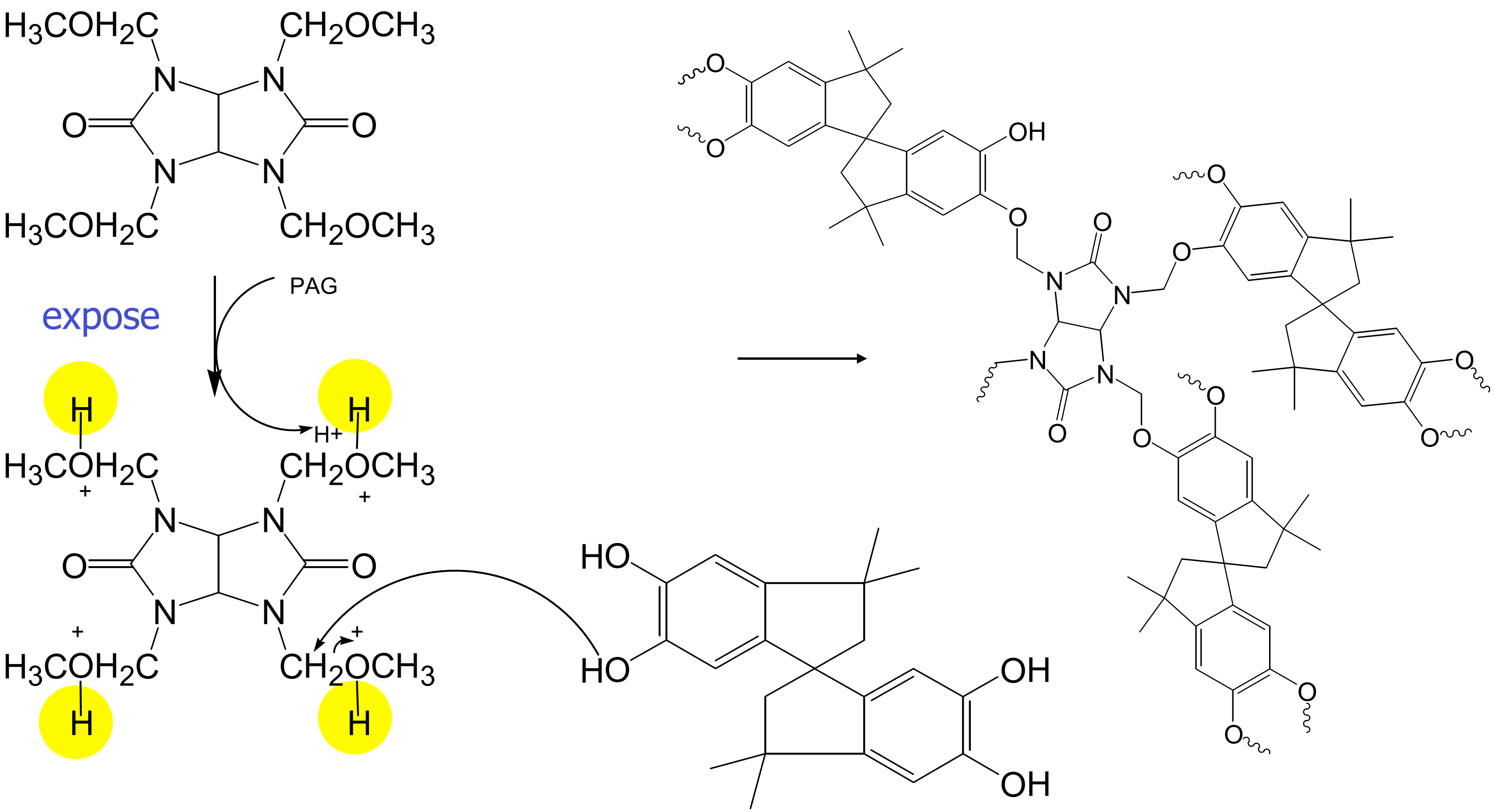
Negative-tone Molecular Glass Resist - Chemistry

Soluble monomer

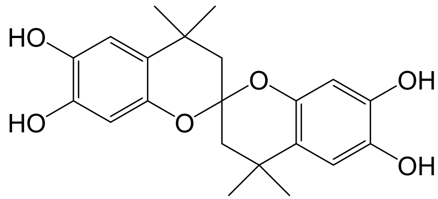
Insoluble cross-linked oligomer

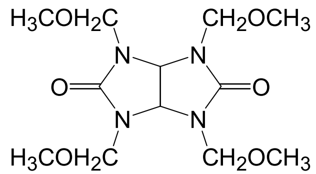


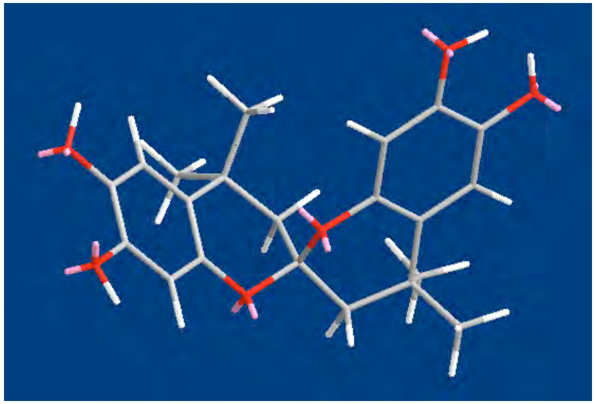
unexposed

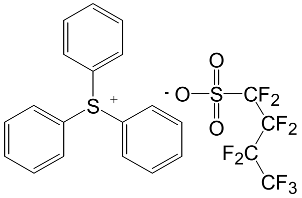
exposed

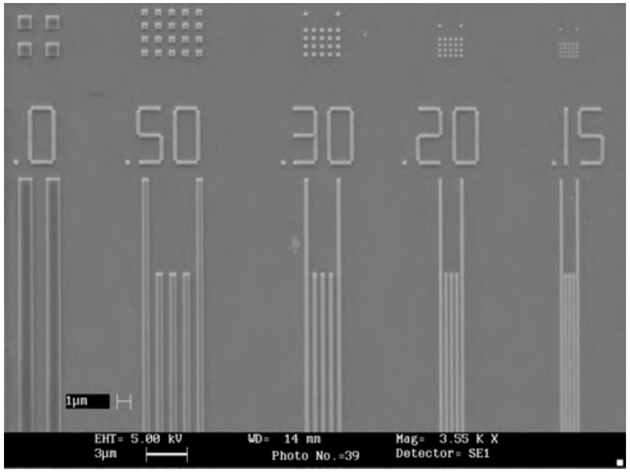
E-beam Patterned Molecular Glass Resist



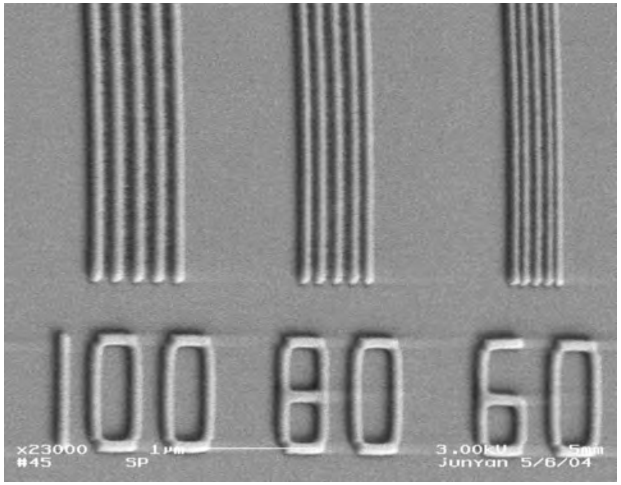








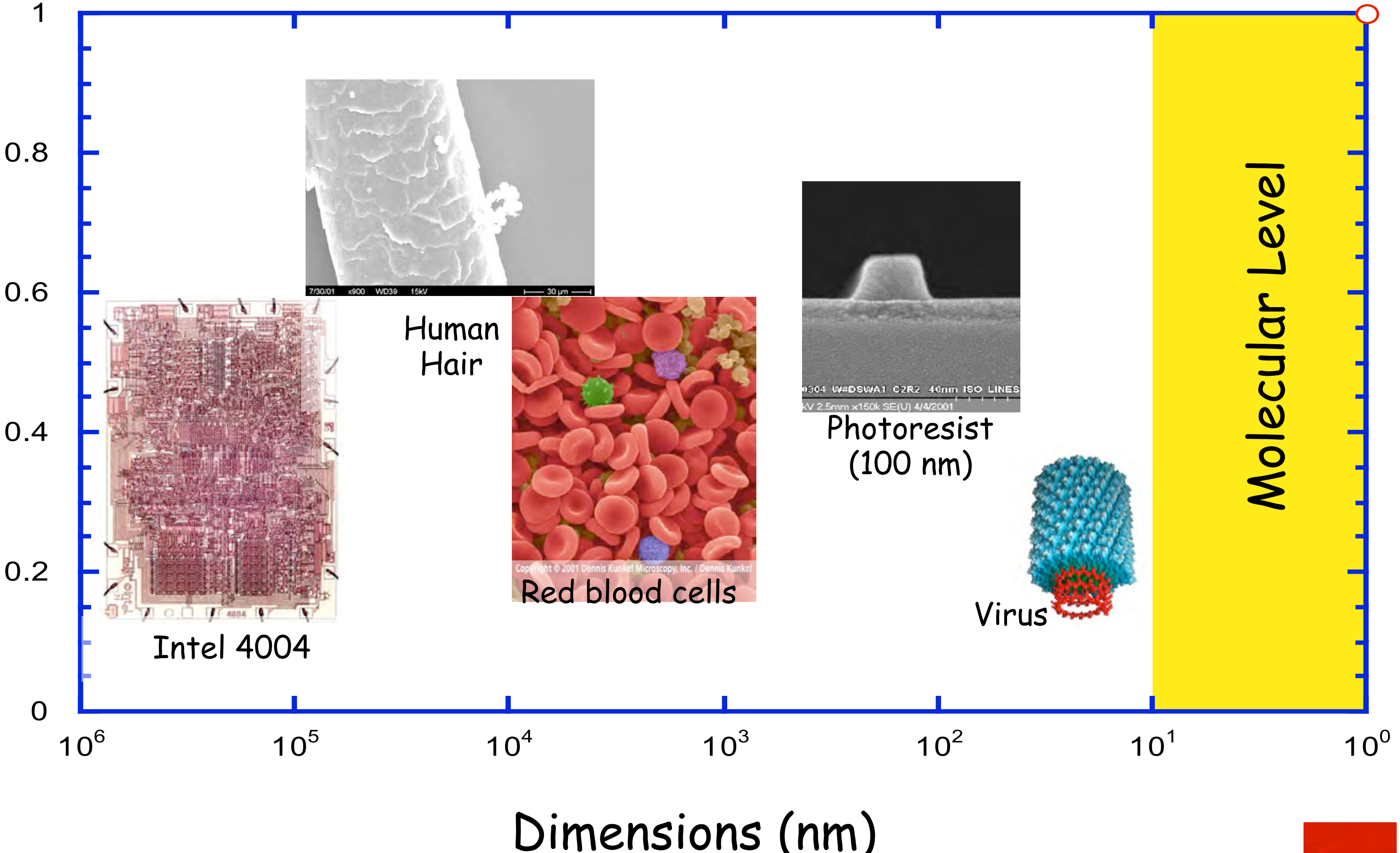
60µC/cm² @100kV



Dose range 60 – 240 µC/cm² @100kV
60 nm pattern image at 180µC/cm² @100kV

15 wt% TMMGU
5 wt% TPS Nonaflate
PAB: 115ºC, 60s
PEB: 115ºC, 60s
Development: 0.026N TMAH, 10s

A Matter of Scale



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Attogram Mass Detection Using a Resonant Nanomechanical Oscillator

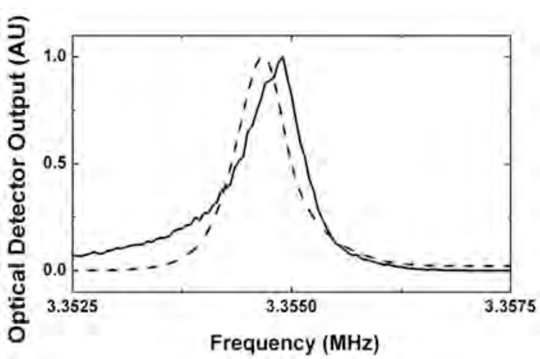
Note 50 nm diameter Au dot

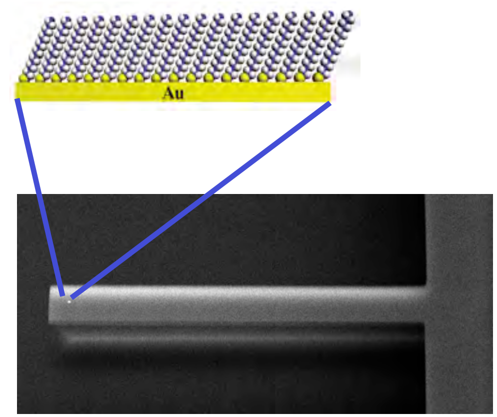
Si cantilever (5 µm scale bar)

B. Ilic, H. G. Craighead, S. Krylov, W. Senaratne, C. Ober, P. Neuzil, *Journal of Applied Physics*, **95**, 3694 (2004).

See also: http://www.advancedphysics.org

SAM on metal dot (~6 ag) shifts resonant frequency of oscillator





Measured frequency spectra before (solid line) and after (dashed line) the adsorption of the thiolate on a 50nm diameter Au dot. The 125 Hz shift corresponds to 6.3 attograms (6.3×10^{-18} g) . The corresponding scanning electron micrograph of the NEMS oscillator is shown on the right.

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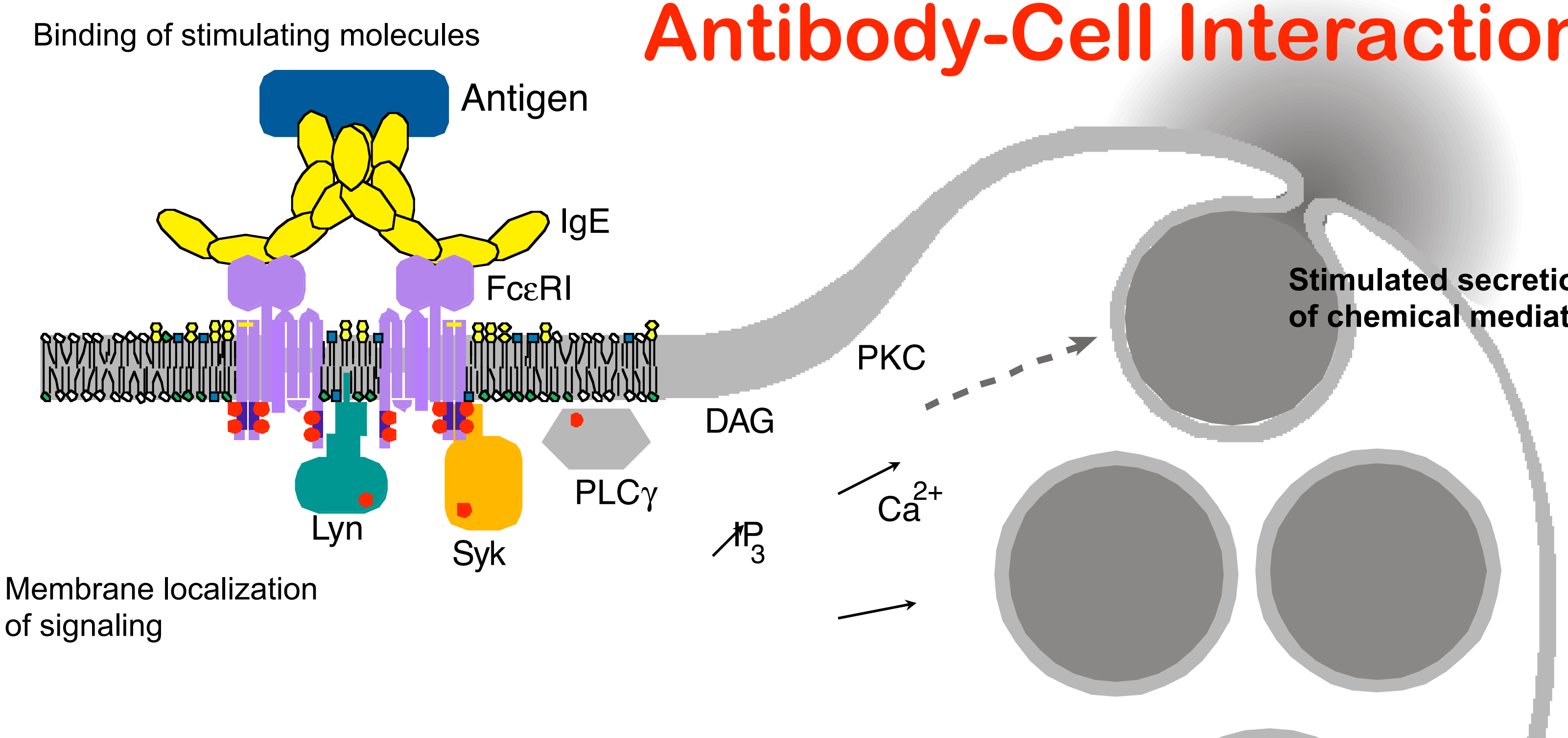
Lithography and Biology: Studying Antibody-Cell Interactions



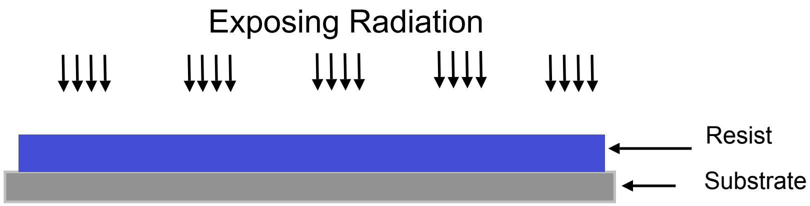
<u>NanoMicro Scale</u>:

a) Antigen receptors crosslinking by defined ligands (10-100 nm)

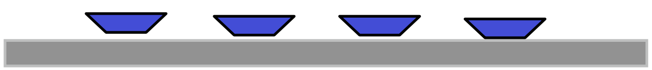
b) Localization of cellular response processes (0.1 - 1 μm)

Courtesy of Barbara Baird and Dave Holowka Lab

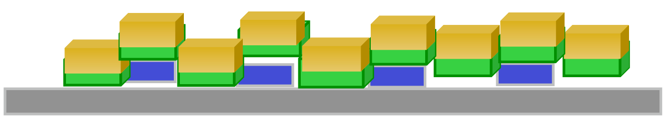
Patterning at Relevant Length Scales



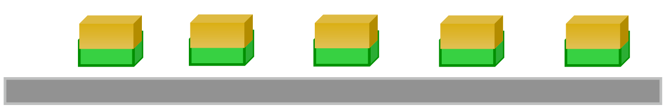
Resist
exposure



Resist Development



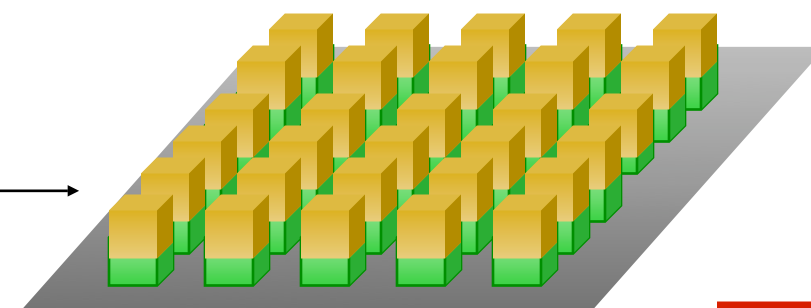
Film Deposition e.g. metal evaporation
10 nm Ti / 50 nm Au



Resist Removal (lift off)

- Pattern using resist
- Positive tone ablative processing
- Lift off processing
- Modify with SAM

As small as 0.3 μm x 0.3 μm
with 25% gold



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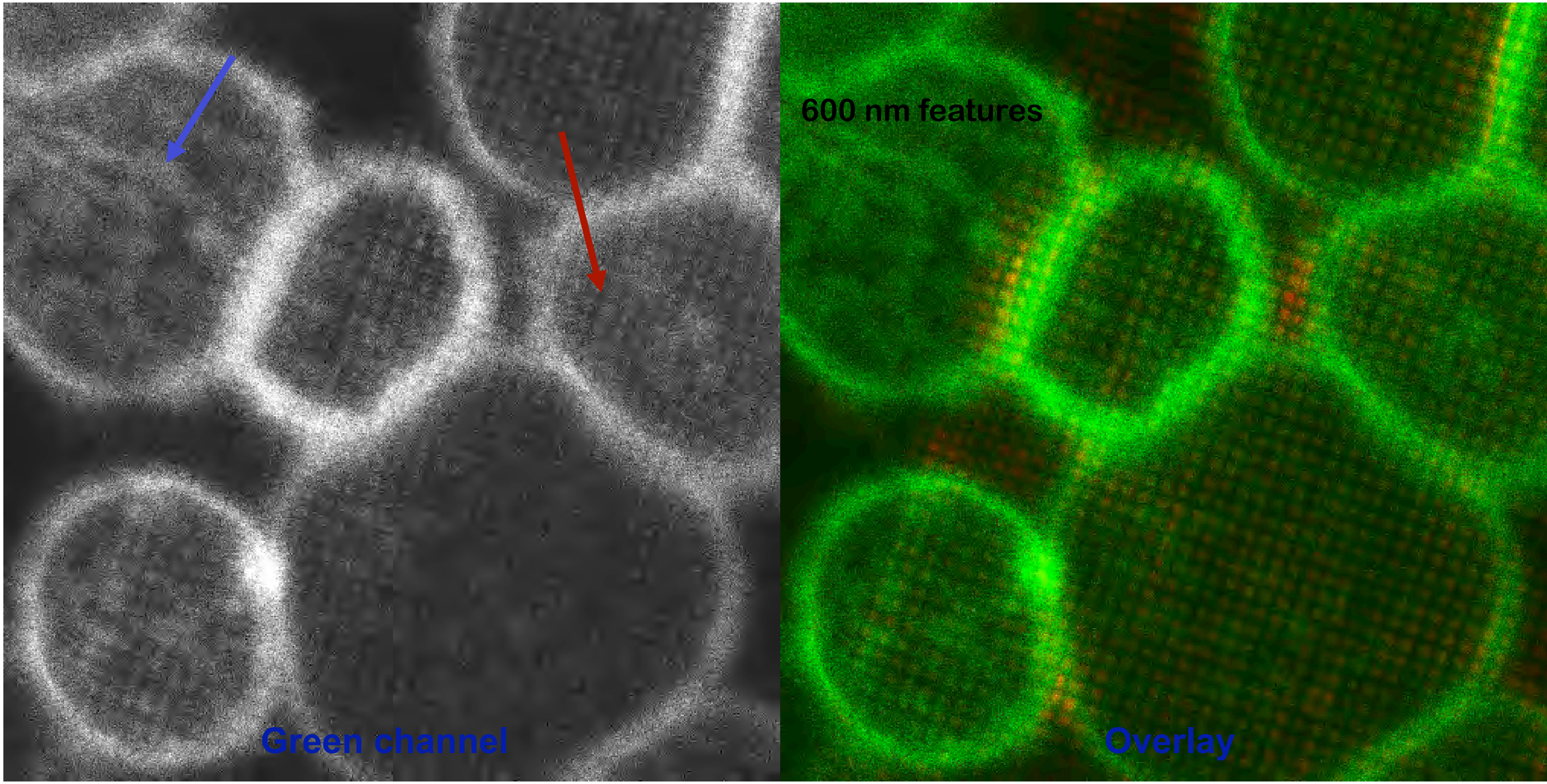
IgE-R Crosslinking on Patterned Ligand-SAMs



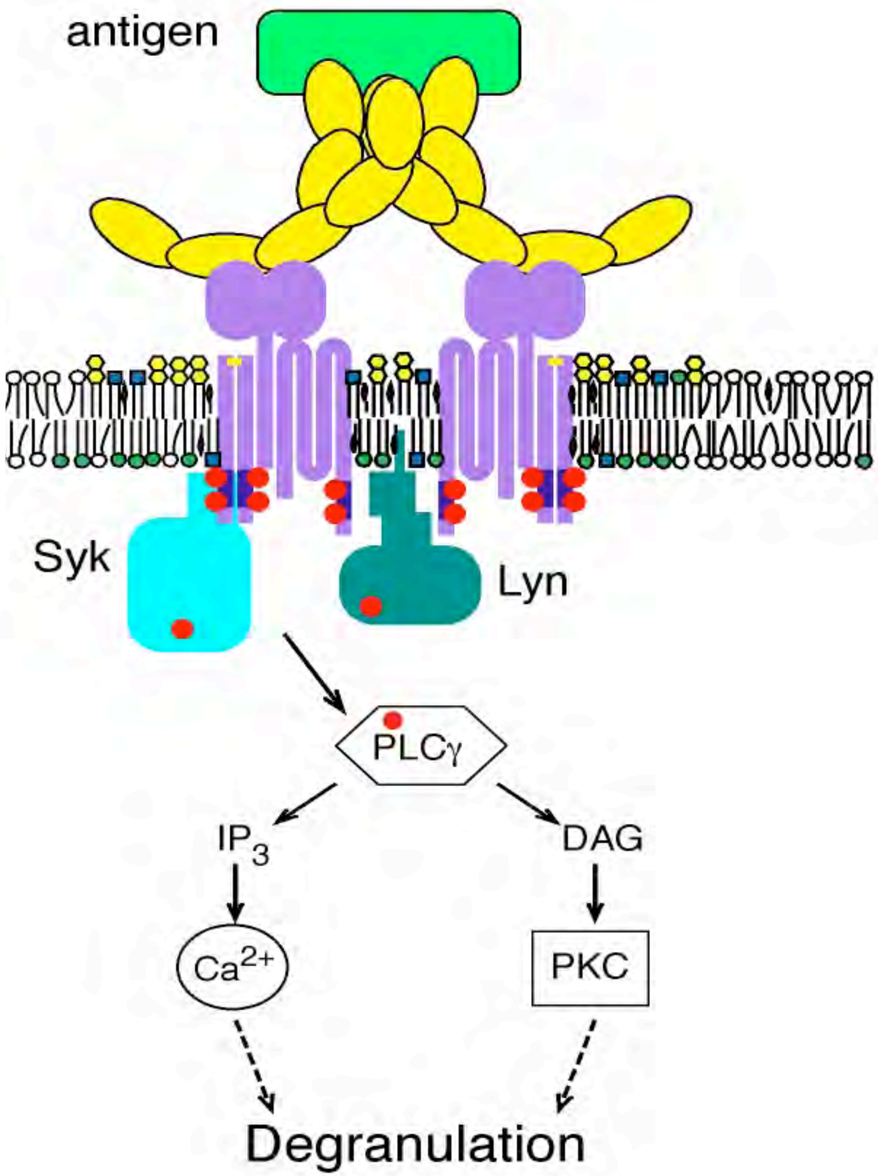
IgE-R are crosslinked by ligands on the surface observed by visualizing co-localization of the fluorescently labeled IgE on mast cell receptors

Receptor Mediated Transmembrane Signaling

Out

Cell Membrane

In

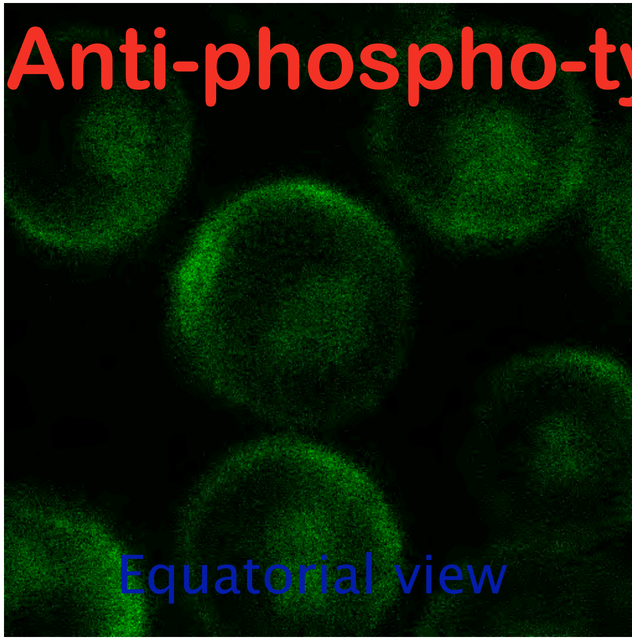


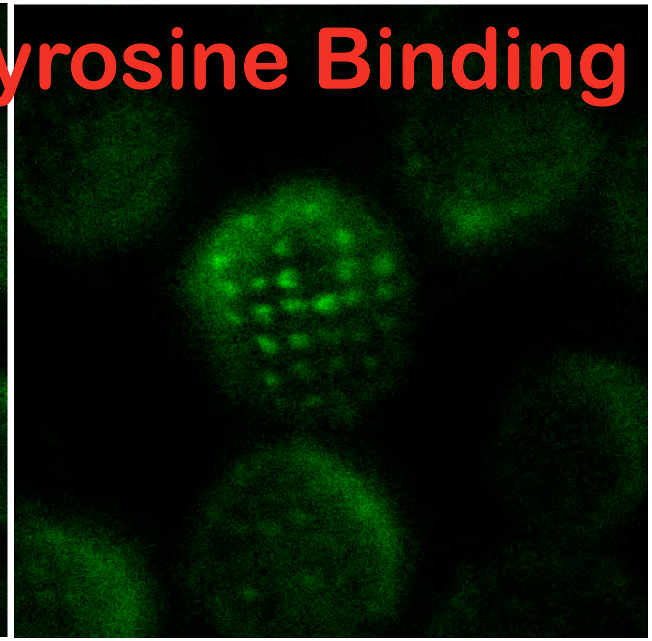
IgE-R are crosslinked by antigen on the surface

IgE-R must couple with Lyn kinase on the inner leaflet of the cell membrane in order to initiate cell membrane coupling

Signaling pathways proceed, leading to cellular degranulation

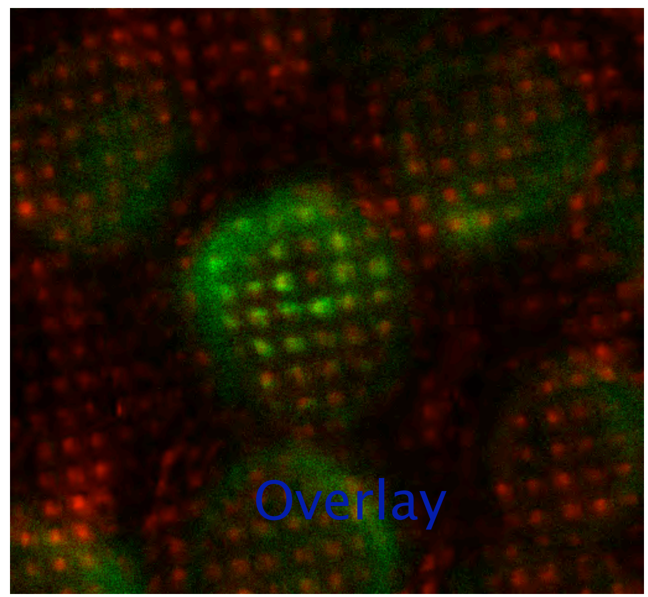
Anti-phospho-tyrosine Binding





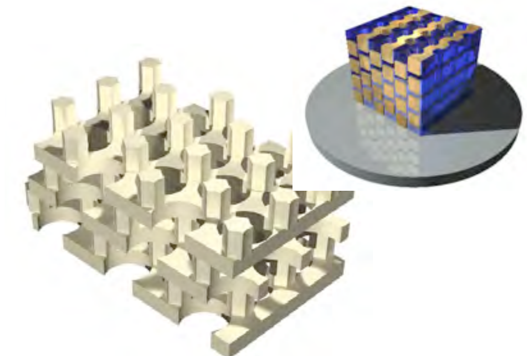
Primary antibody binding to the phosphorylated tyrosine residues on the inner leaflet of the plasma membrane.
Alexa 488 labeled secondary antibody used for detection

1 μm features



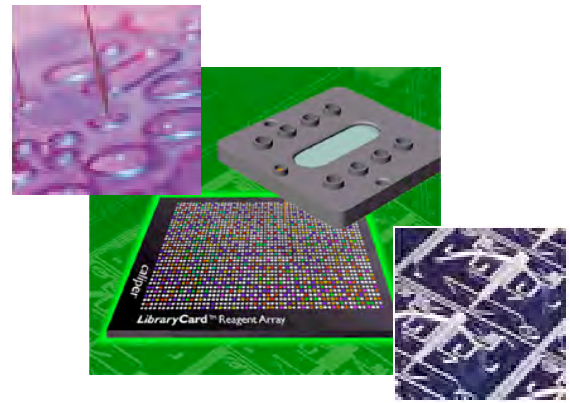
3D Lithography

Photonic Bandgap Structures



http://ab-initio.mit.edu/photons/3d-crystal.html#2000

Microfluidics



http://www.calipertech.com/products

Tissue engineering

Bone growth and tissue implant

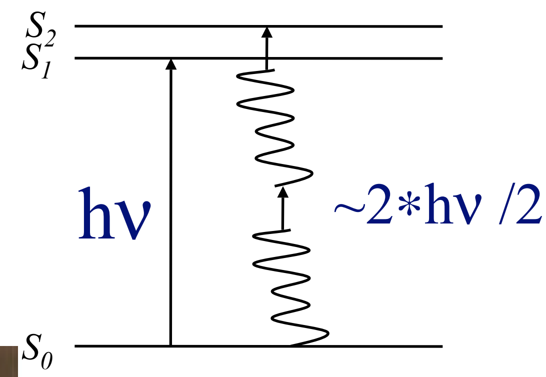
MEMS

http://home.earthlink.net/~trimmerw/mems/many_pic.html

And much more …

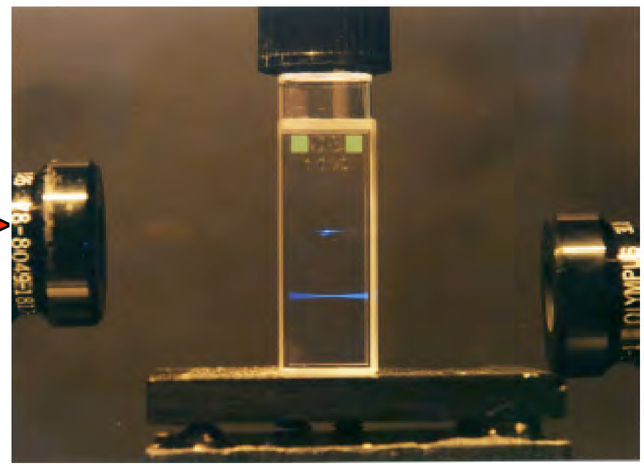
Two-Photon Excitation

Photoactive material which normally absorbs a single photon of energy hν can also simultaneously absorb two photons of energy around hν/2.



Two-photon excitation

One-photon excitation



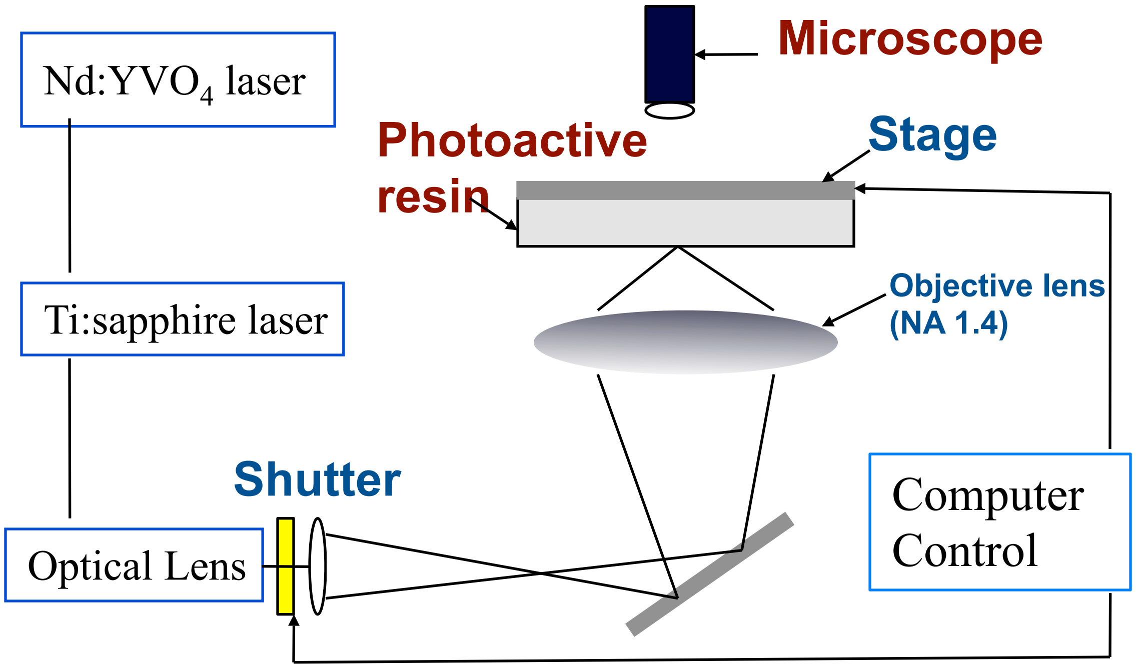
$$TPA \propto \delta I^2$$

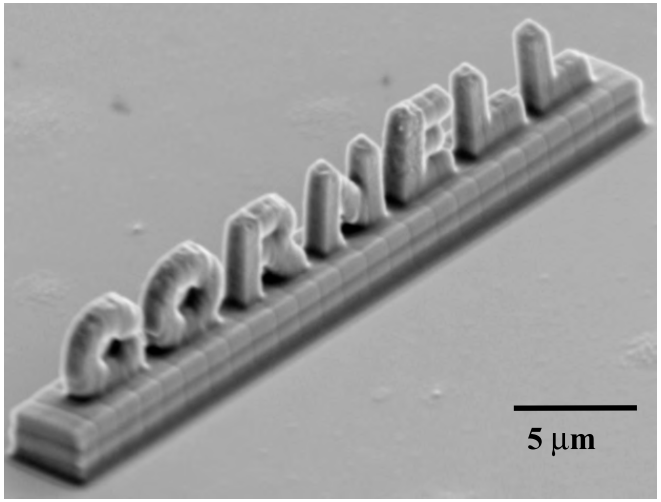
$$I \sim \frac{1}{z^2}$$

$$\Rightarrow TPA \sim \frac{1}{z^4}$$

Excited volume ~ 0.05 μm^3

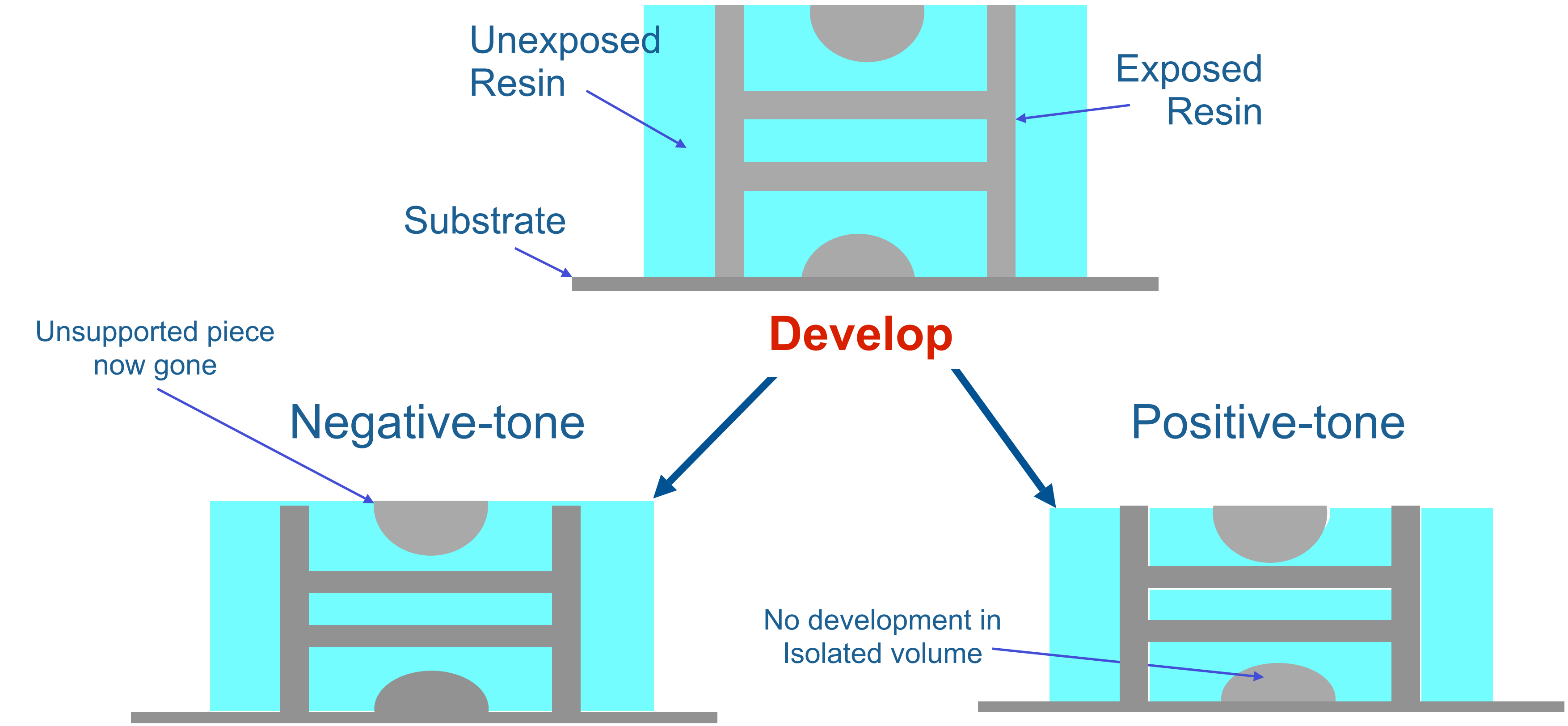
Two-photon Microfabrication





- x,y,z stage control enables 3D patterning
- Sub-micron resolution capable of forming miniature features

Positive and Negative-tone 3D Systems



Free standing fine scaffolds

Interconnected fine channels
Surface openings

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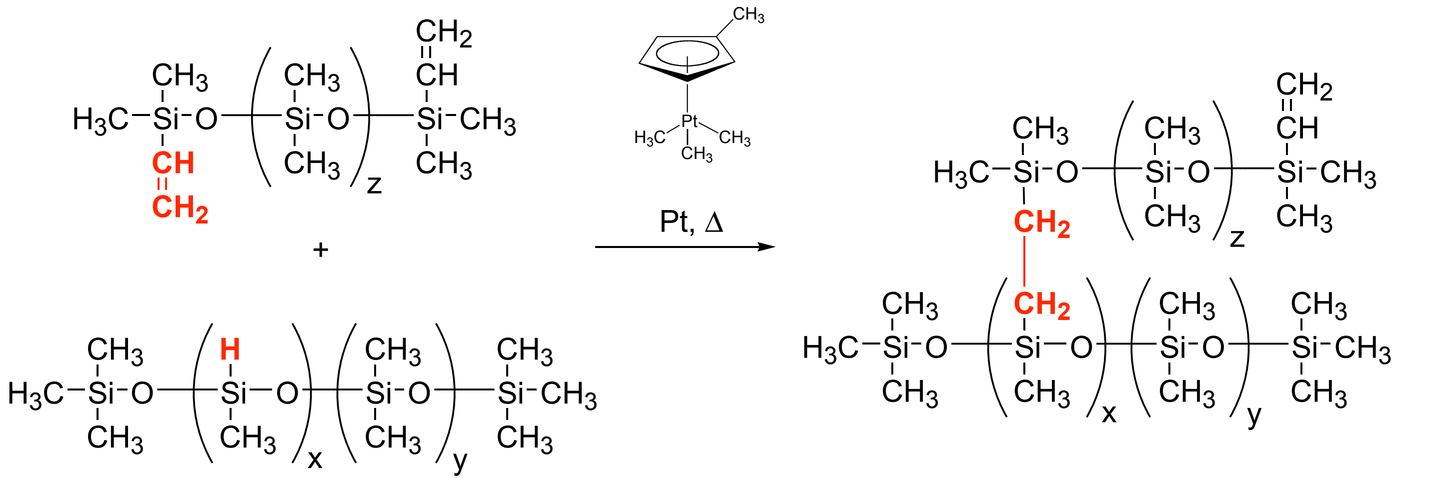
PDMS Microstructures by Two-Photon Microfabrication



- Platinum catalyzed hydrosilylation yields poly(dimethylsiloxane) elastomer
- Photohydrosilylation catalyst used for UV cure for coatings
- No byproducts – dimensional stability
- PDMS can be deformed reversibly and repeatedly without permanent distortion or relaxation of features

C. Coenjarts and C. K. Ober, "Three Dimensional 2-Photon Microfabrication of Silicone Elastomers", *Chem. Mater, (Communication);* 2004 16(26); 5556-5558.

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PDMS Microstructures by Two-Photon Microfabrication

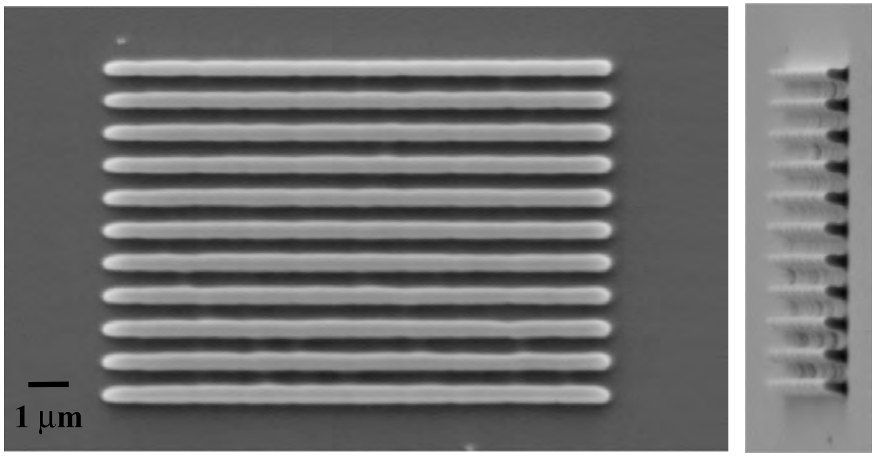
- Material has never been exploited in a photoimaging/stereolithography application
- Photoinitiator has never been used with two-photon irradiation

Two-Photon Absorption Sensitivity

- 0.7 wt% photoinitiator in Sylgard 182
- 710 nm
- 1.8 – 3.0 mW

Image Development

- Require a solubility difference between cured and uncured
- PDMS swells in organic solvents but is undamaged (due to elastomeric nature)
- Ethyl acetate rinse



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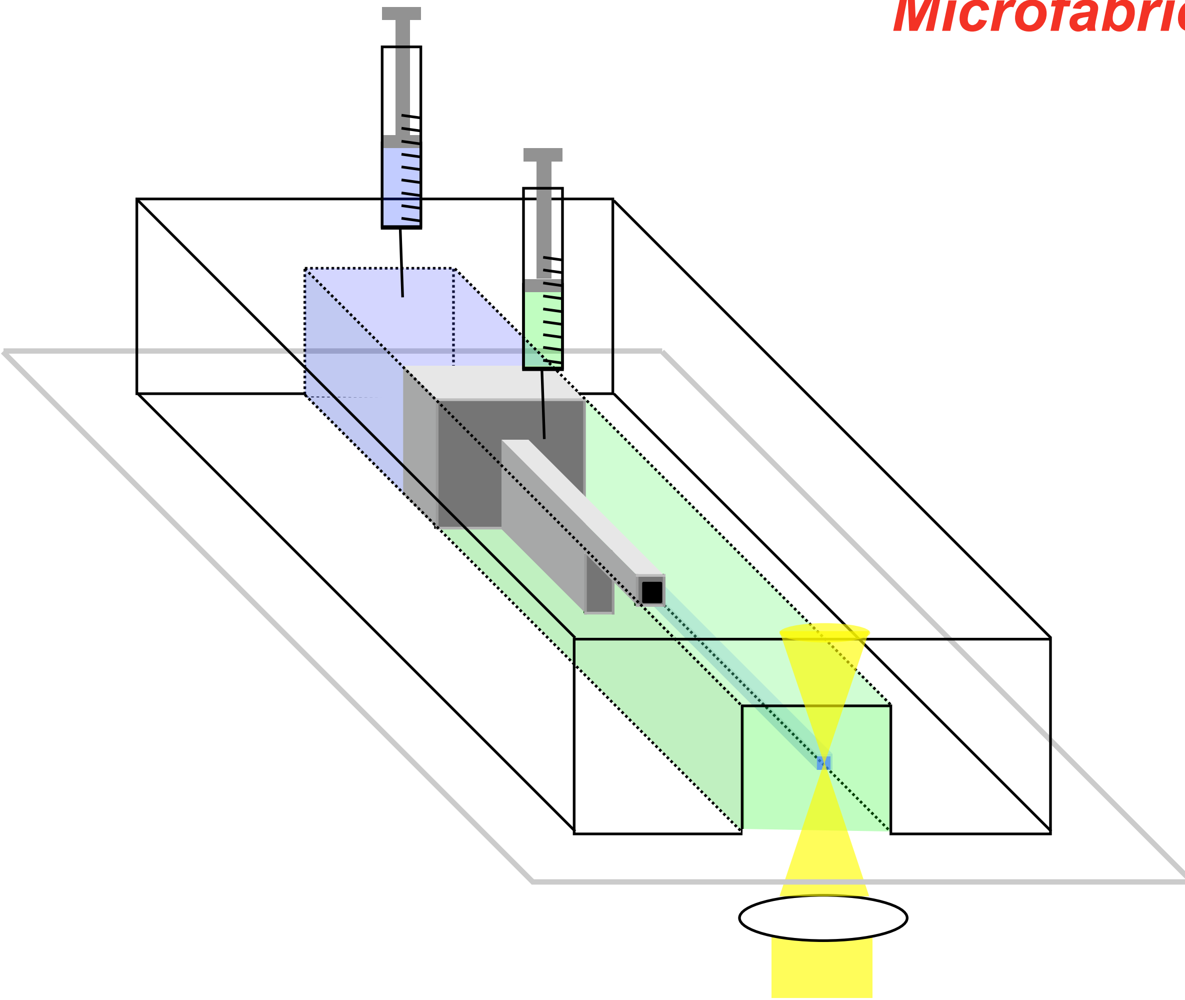
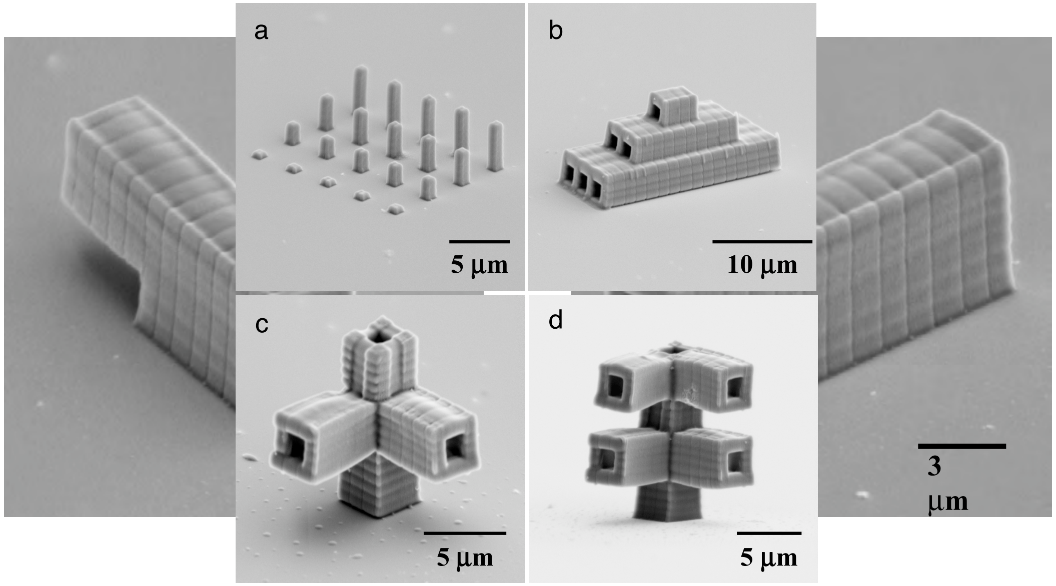
Microfluidic Continuous Flow Mixer by Two-Photon Microfabrication



- time-resolved analysis of hydrodynamically focused stream

Microcapillary Fabrication



- 3.9 mW, 100 ms/pixel, 100x 1.35 NA objective

- first attempt at PDMS microcapillary fabrication
- low NA fabrication requires an increase in sensitivity

Summary

- Capability of lithography to make very small structures continues to improve
- Use of 2-photon lithography permits the creation of intricate 3D structures
- These processes and convergence with self-assembly will provide numerous opportunities in the development of intricate, molecular level structures