

APPLICATIONS OF POLYMERS IN NANOTECH/NANOFAB

Polymers are at the forefront of many current approaches to nanofabrication, so we will whiz through a quick overview of some of the currently investigated approaches to fabrication 10—100nm

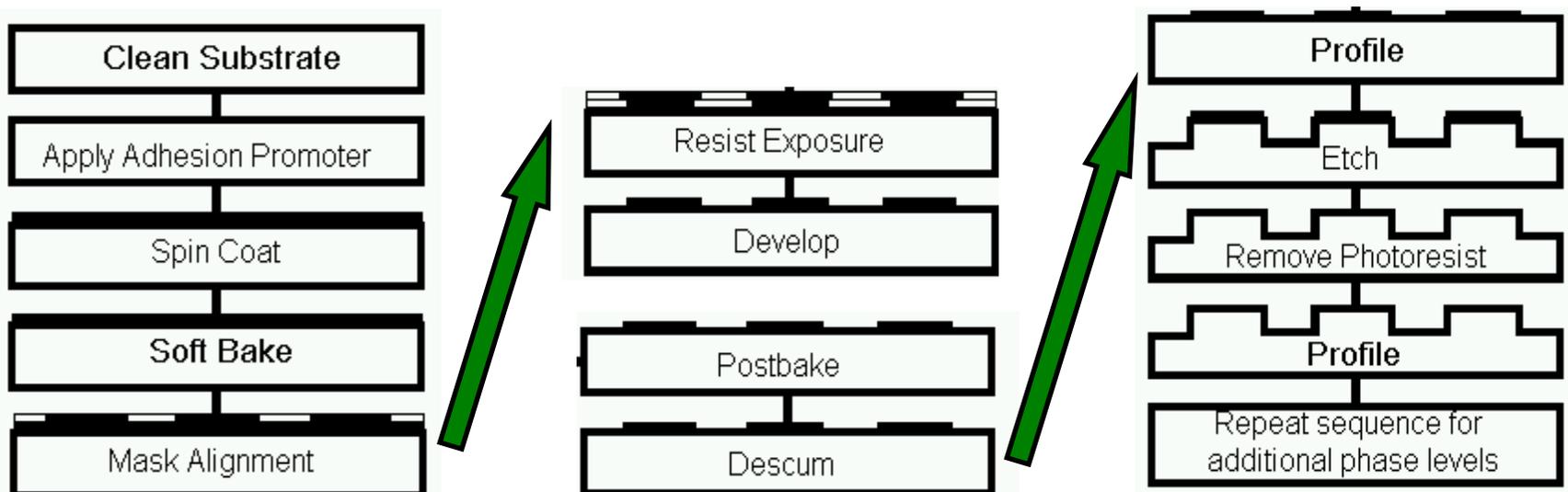
What we will do in this 'Applications' section of Polymers :

- 1) Practical advantages and drawbacks of organic self-assembly (SA)
- 2) Guiding self-assembly with a $h\nu$ -free master (Soft Lithography)
- 3) Completely mask-free methods based on self-assembly
- 2) Strategies for extending the length-scale of small-molecule SA

BOTTOM UP FABRICATION

Challenges of Traditional Mask Lithography using Photons:

- 1) Inherent diffraction limit (*strategies: lower wavelength, near field*)
- 2) Thermodynamic instability (*strategies: ultra-clean fab environment \$*)
- 3) Large number of steps (*strategies: highly parallel fabrication \$\$*)

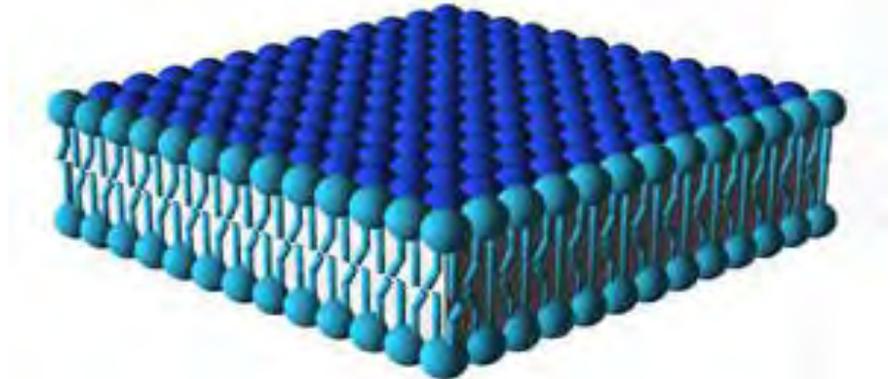


BOTTOM UP FABRICATION

Advantages of Self-Assembled Organics to Control / Exploit:

- 1) Small natural size-scale (*challenge: too small in many cases*)
- 2) Thermodynamic minimum (*challenge: if so, then usually reversible*)
- 3) Steps sequential (*challenge: control over final state of assembly*)

The key difference between
'top down' and 'bottom up' :



existing
pieces

controlled fab

desired
structure

natural fab

designed
pieces

BOTTOM UP FABRICATION

The Motif of Self-Assembly Approaches Summarized:

To exploit natural and existing mechanisms of structure formation by supplying cleverly-designed starting materials to a system, and then allowing that system to proceed to a thermodynamic equilibrium with desired product as the end result.



Demonstration of principle:

Assembly of a simple, functioning 12-
component electronic logic device by
stirring a large array of components in
aqueous solution for 1 minute

George Whitesides, Harvard University

BOTTOM UP FABRICATION

The 2 fundamental general problems to overcome with self-assembly:

#1) Natural methods assemble controlled structures on a LOCAL frame of reference at the meso sizescale. We usually want structures indexed to a GLOBAL reference, with LONG-RANGE order and control.

#2) In order to exploit the process, we have to understand the process

There are two basic approaches to solve #1:

A) Guide the patterning process mechanically (physically) using masters

B) Guide the patterning optically (non-contact, external) using light

SOFT LITHOGRAPHY

A) Guiding a pattern mechanically (physically) using a master:

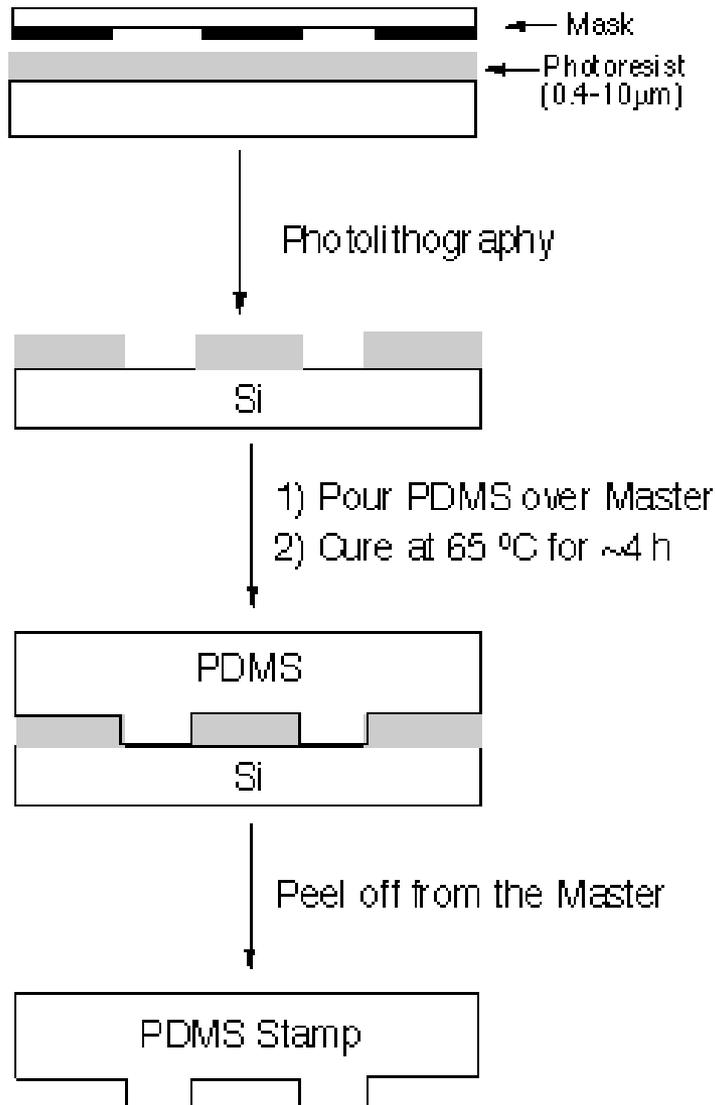
A traditional photo-lithographic pattern is used in JUST 1 STEP, then polymer self-assembly for the rest of the process, for defect tolerance, fabrication ease, parallel processing, and small sizescale:

Some representative methods of 'Soft Lithography' (photo free)

- 1) Replica Molding (to make n copies from 1 photo-lith master)
- 2) Micro-Contact Printing (pattern transfer by direct contact)
- 3) Micro-molding (using fluid dynamics to form structure *in situ*)

Soft Lithography is based on elastomeric polymers which can transfer a pattern from a master to a large number of copies, for 1 layer fab.

REPLICA MOLDING (REM)



Standard photolithography is used to produce a master on Si from a mask

A monomer, oligomer, or other pre-polymer (or polymer solution) is poured over the mask to conform to features

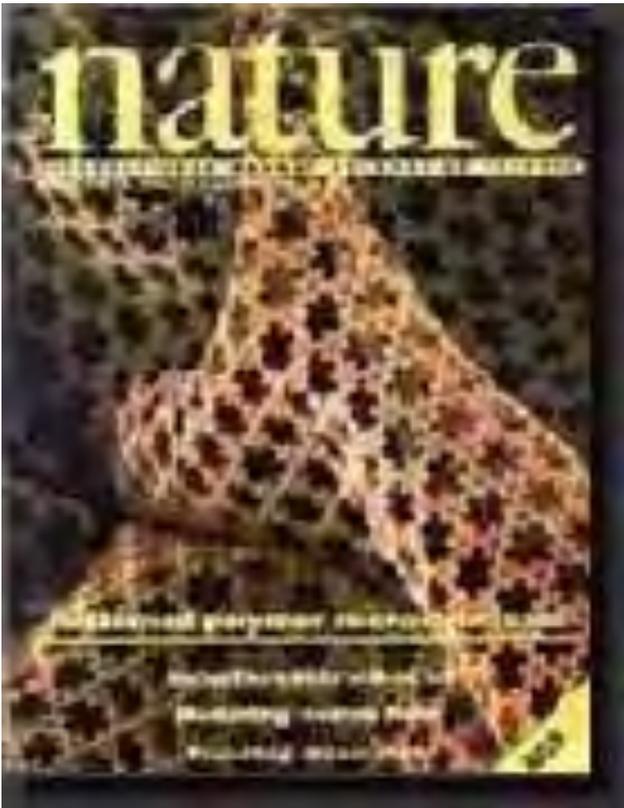
The resulting polymer needs a T_g below processing temperature (such as PDMS) after curing by heat or UV light

The elastomeric PDMS is removed from the original, leaving no residue and holding the negative of the surface

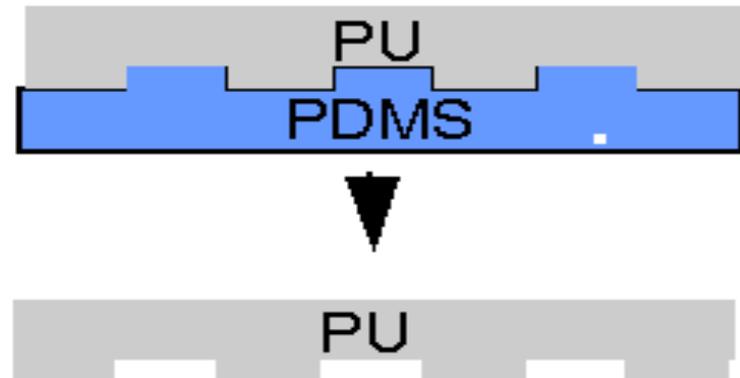
REPLICA MOLDING (REM)



The original master can be used many times, with PDMS poured and peeled off repeatedly, with good stability



This PDMS negative can then act as mask to reproduce the original, with a high Tg polymer such as poly(methyl methacrylate) PMMA, or polyurethane

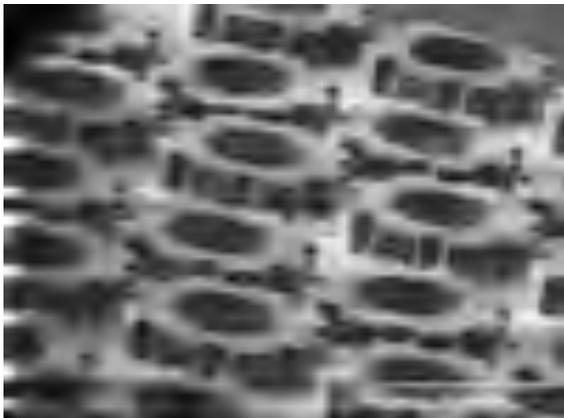


REPLICA MOLDING (REM)



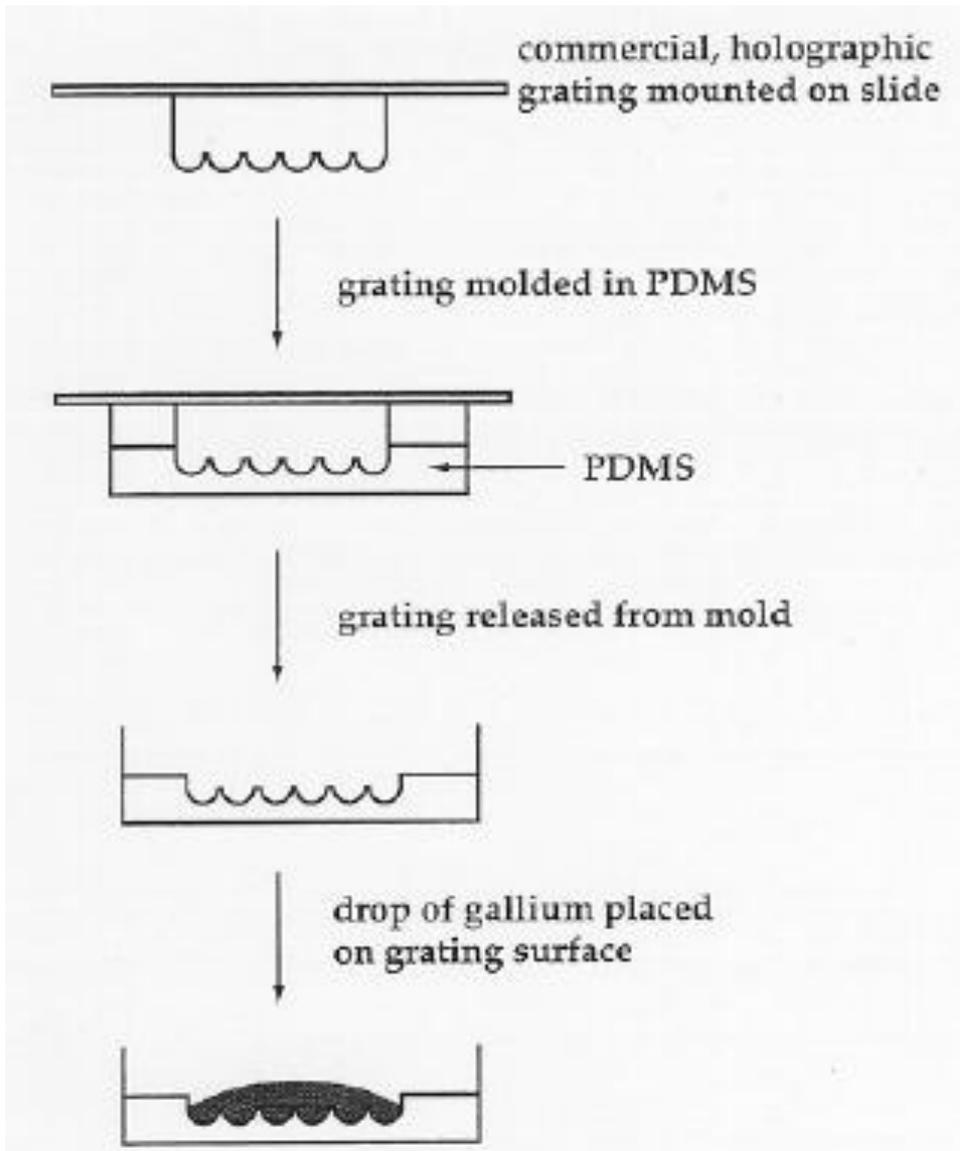
The elastomeric properties of the PDMS can also be used to stretch or compress the sizescale, from 180nm of a waveguide to 40nm (Xia, U. Wash.)

The drawbacks of this compression are introducing more fabrication steps (reproducible compression limit ~25%)



also liftoff surface energies in small systems can exceed the PDMS surface energy (~22 dyn/cm), which increases wear, limiting number of reproductions

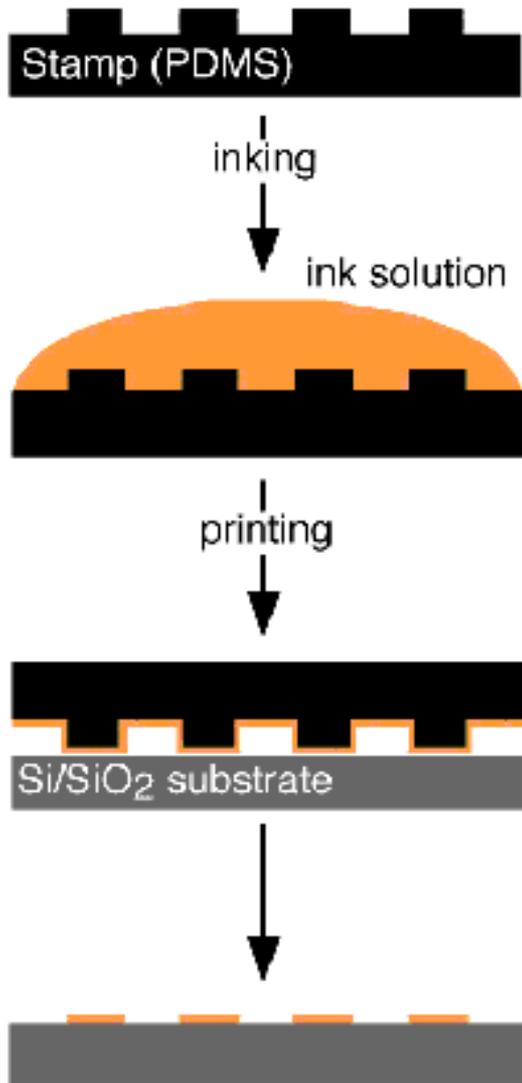
REPLICA MOLDING (REM)



One clever side application however is to use slight expansion and compression for mechanically switchable elastic optical applications

Here, optical elements are formed **INSIDE** the PDMS using liquid metals (Hg or Ga) which conform to the cavity and act as adaptive optics for beam steering and focus

MICRO CONTACT PRINTING (μ CP)

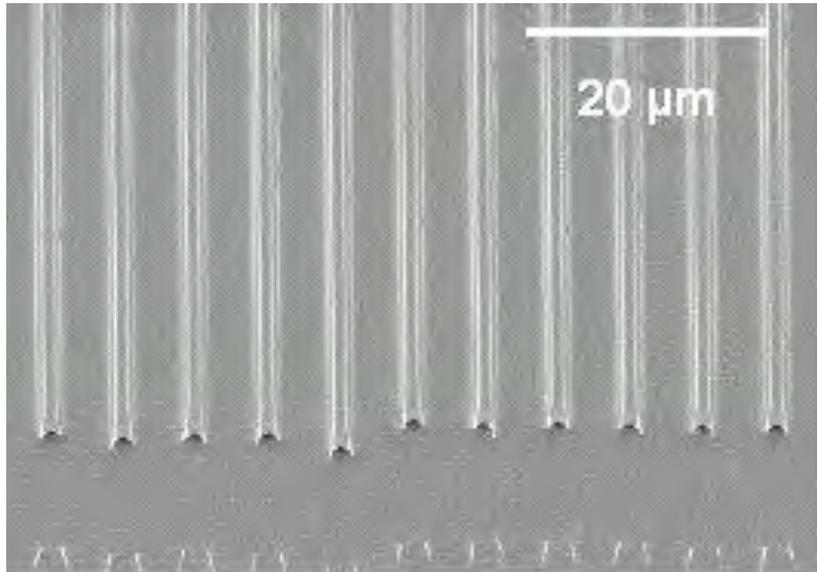
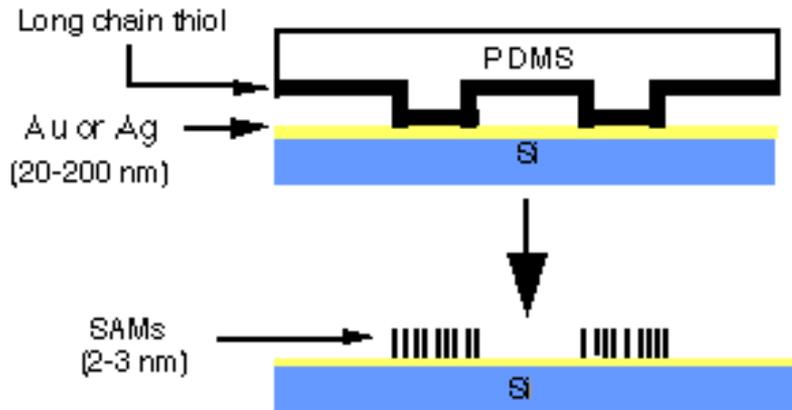


The PDMS masks can also be applied as flexible stamps, inked with adsorbing or assembling molecules, and then used as small rubber contact stamps

The chemical ink covers all surfaces, but Surface relief patterns transfer only molecules in direct contact. 5nm is sufficient, with 200nm spaces.

Inks can be adsorbing polymers, reactant compounds, or self assembling monolayers based on silanes or thiols

MICRO CONTACT PRINTING (μ CP)

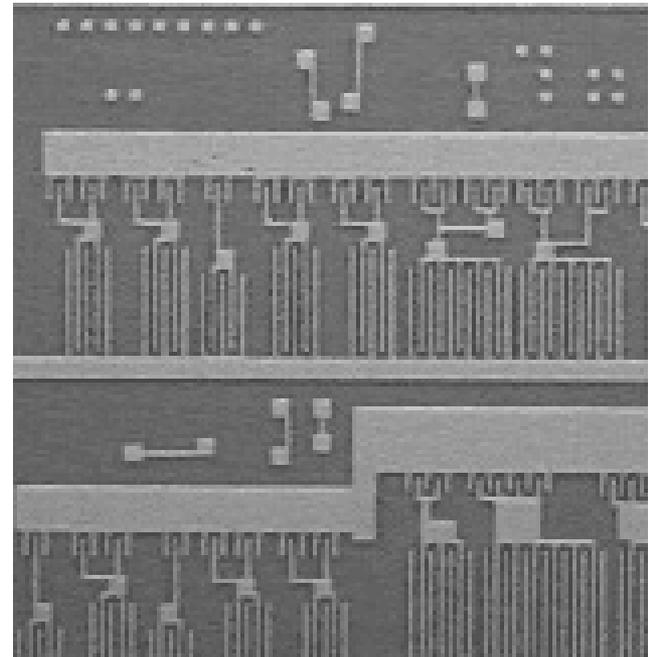
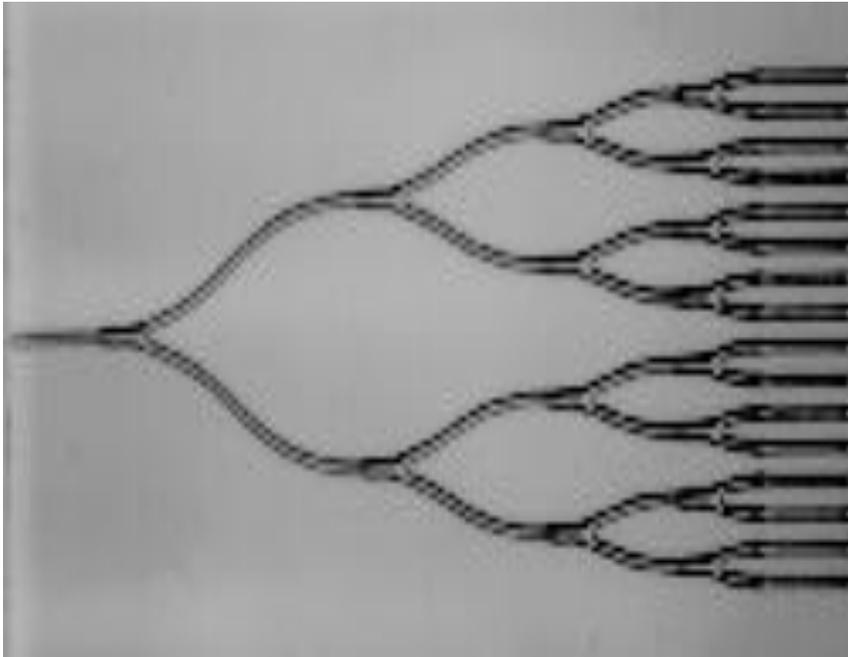


Alkane thiols with tailored headgroups provide versatile and powerful chemical control over subsequent patterning, such as polymer adsorption, photoresists, vapour deposition of inorganics, etching, electroplating of metals...

PDMS Stamps can deposit controlled patterns within 10nm over many square cm, and have been demonstrated for features down to 35nm (etching of grooves on gold)

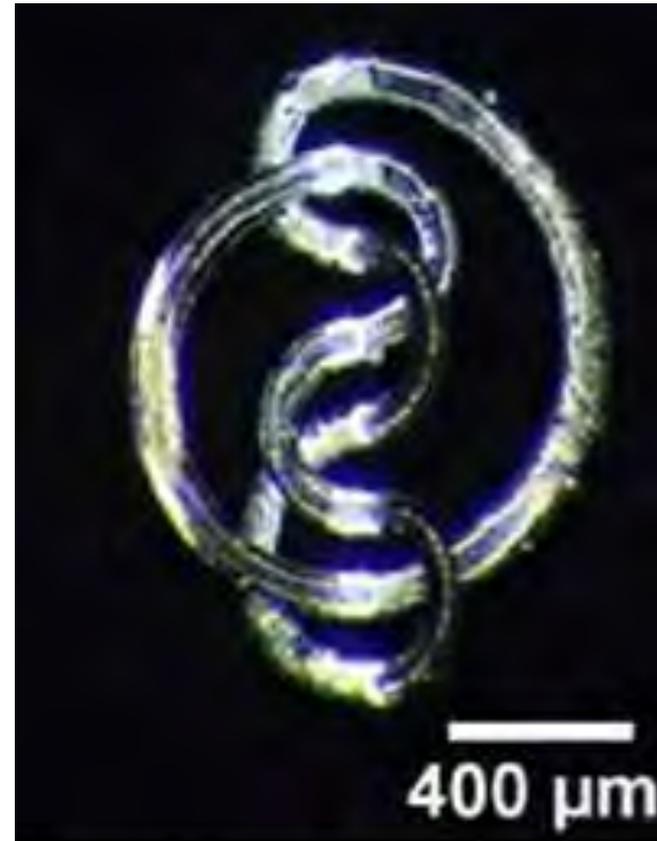
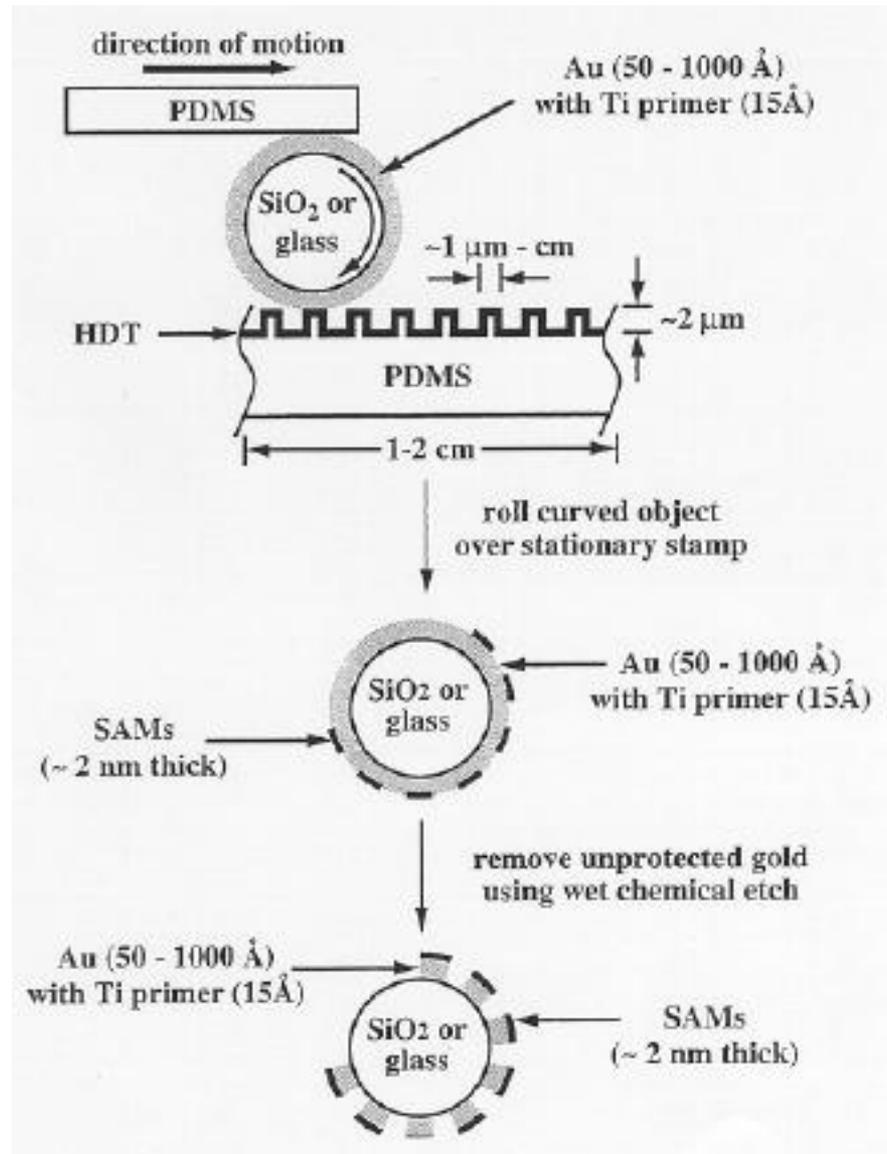
MICRO CONTACT PRINTING (μ CP)

Complex architectures are possible from any master, as long as it's limited to a single layer to be deposited on a Au or Si coated flat surface



The Limitation: This produces one layer well, but only a *single* layer.

CURVED surfaces are also amenable to micro-contact printing, opening the way to the third dimension through unfolding complex topologies

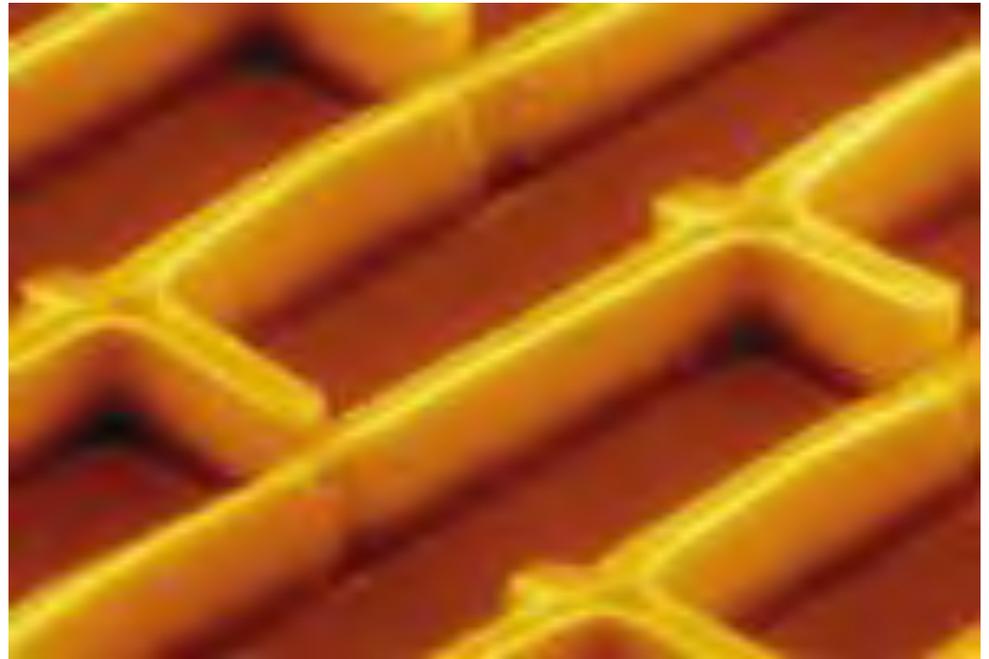
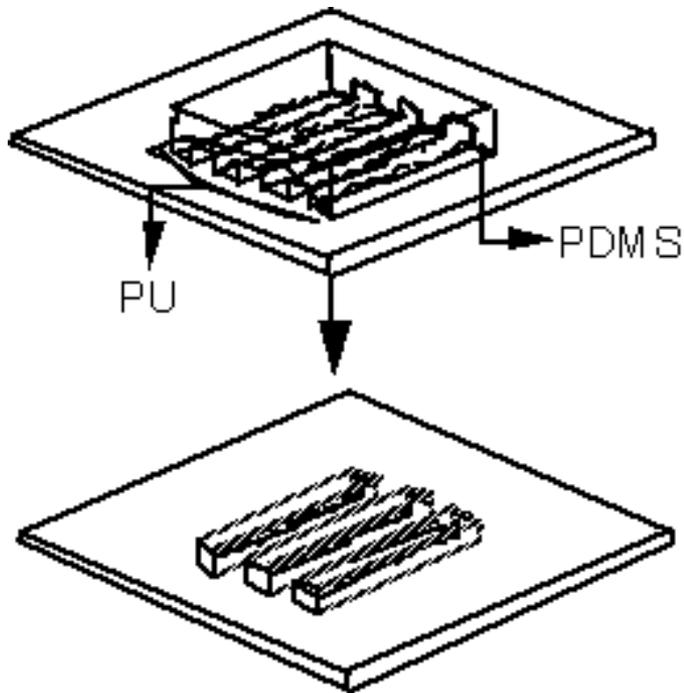


These miniature metal knots were created by precisely printing a flattened pattern on a pair of parallel glass tubes.

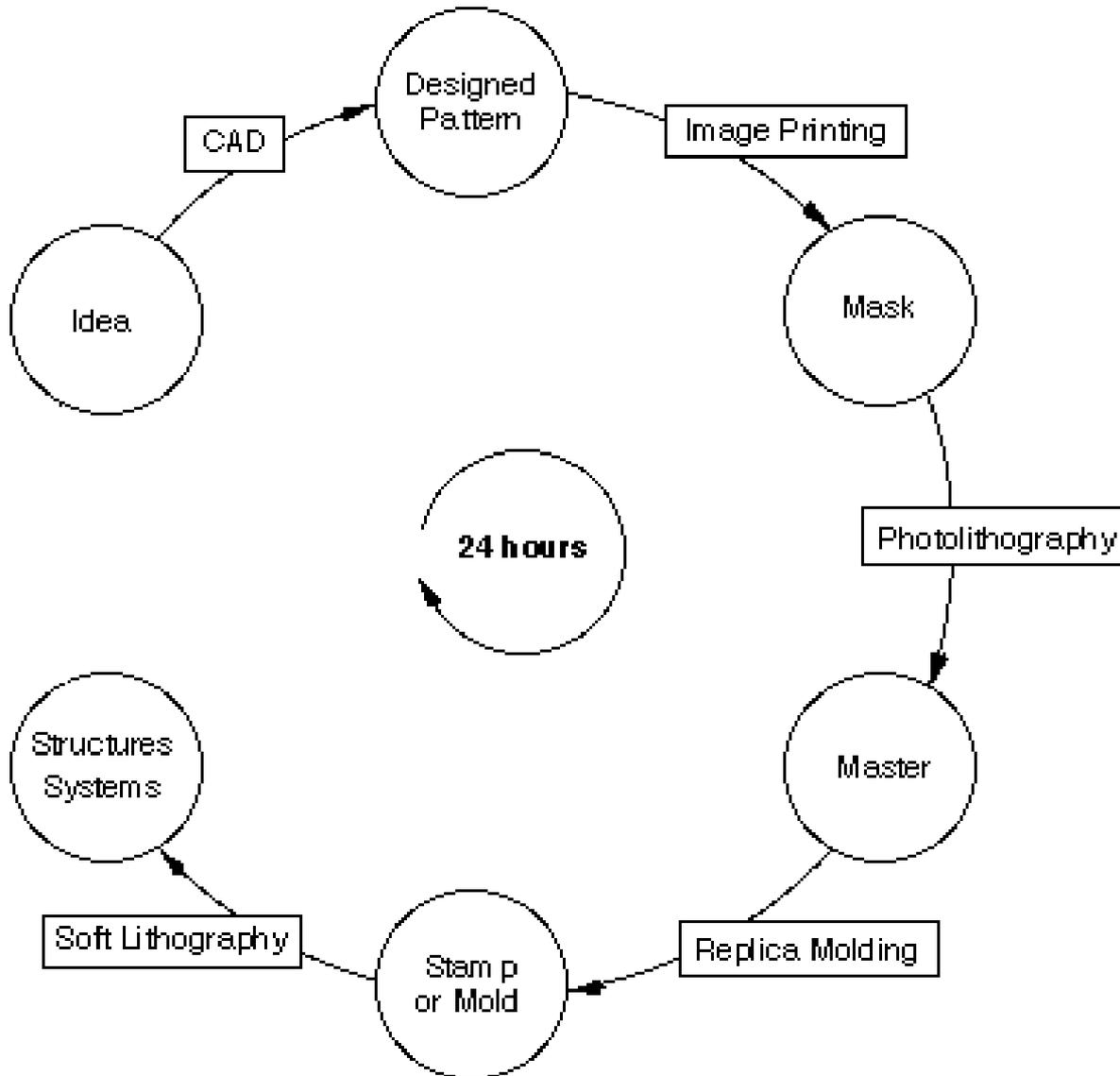
Source: Harvard University

MICRO CONTACT MOLDING

Here, liquid pre-polymer flows into channels by capillary action, hardens over time, and with mask removal the desired structures are left behind



BOTTOM UP FABRICATION



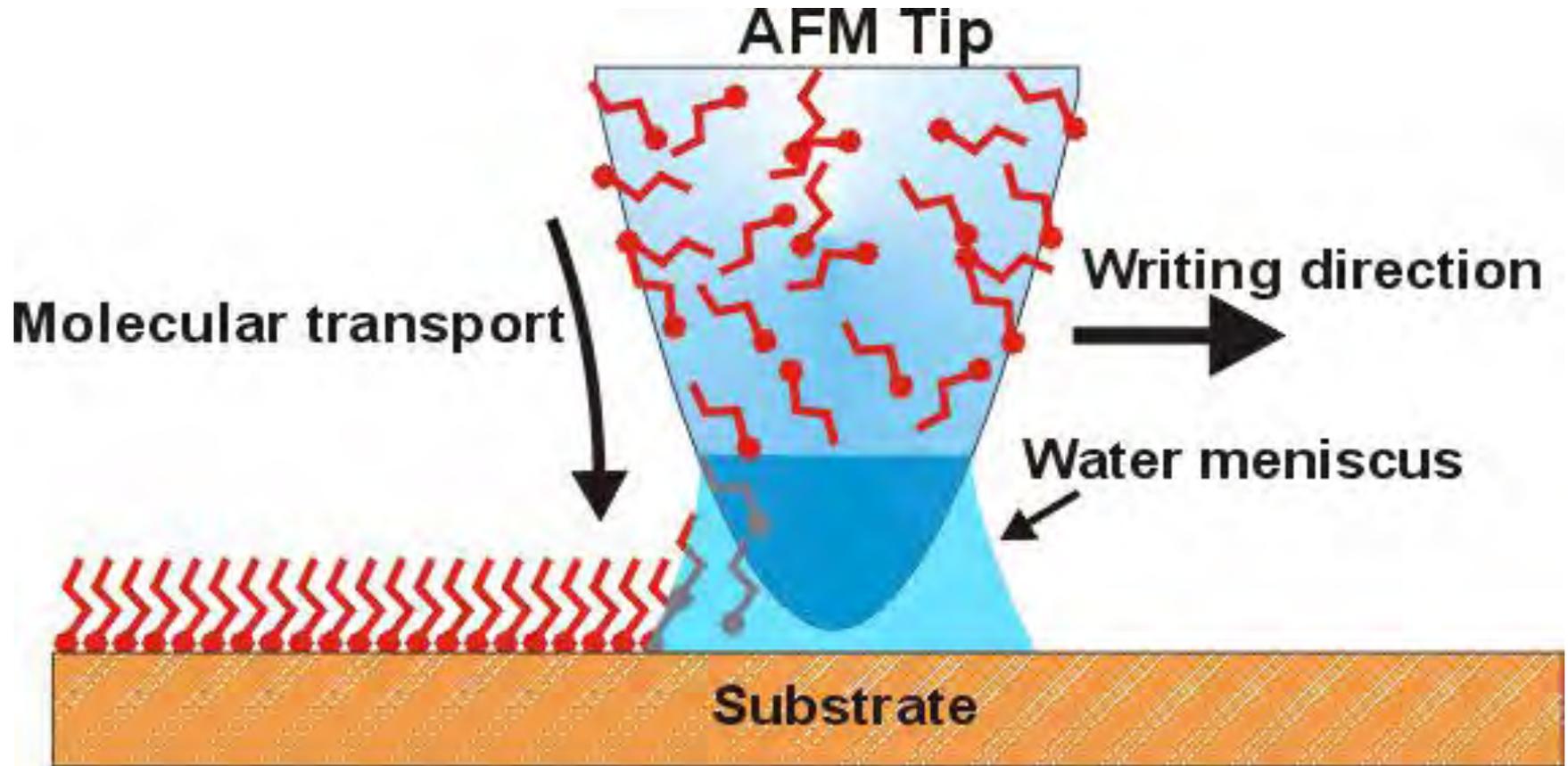
The result ? :

The timescale to produce new design nanostructures has gone from ~6 months to less than 24h, and now much can even be done with a standard inkjet printer

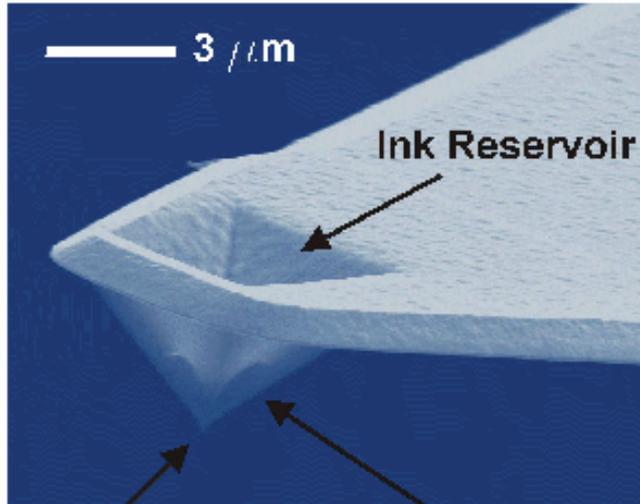
(but we still need a mask at some step)

MASK-FREE FABRICATION

Deposition of a trail of liquid from an AFM tip represents a small ink pen



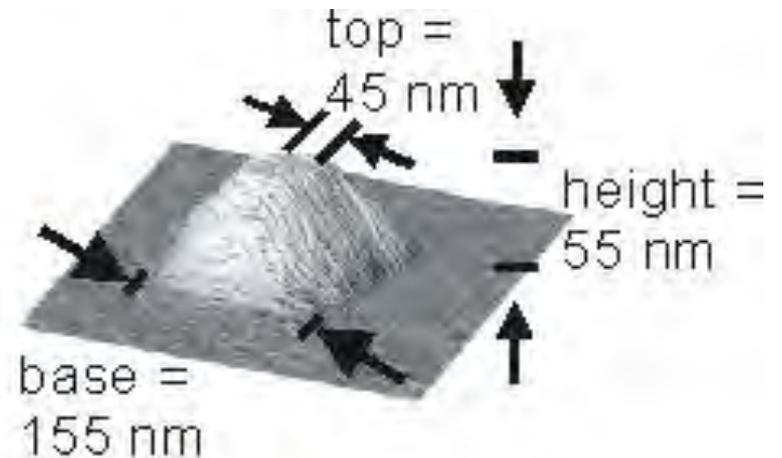
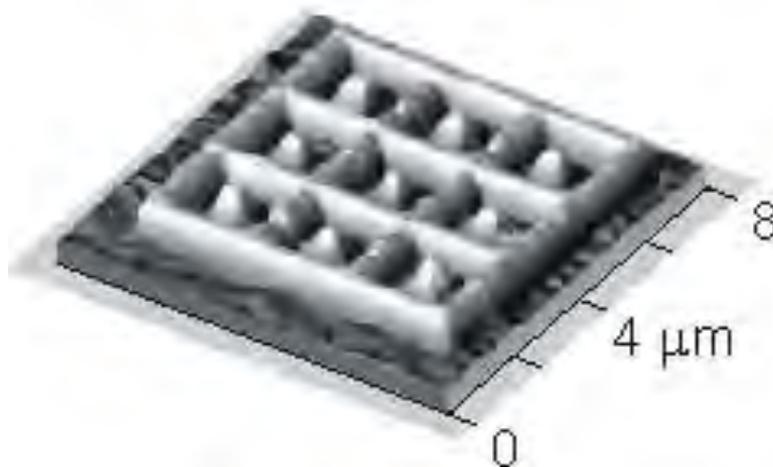
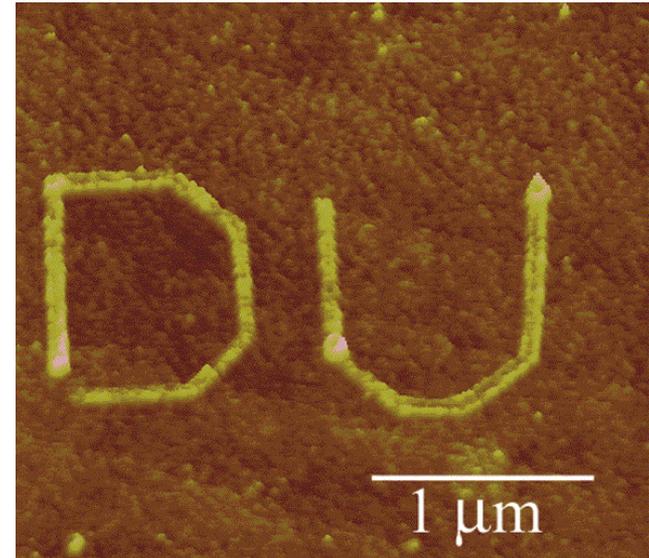
BOTTOM UP FABRICATION



High Resolution Imaging Tip (~ 100 nm diameter)

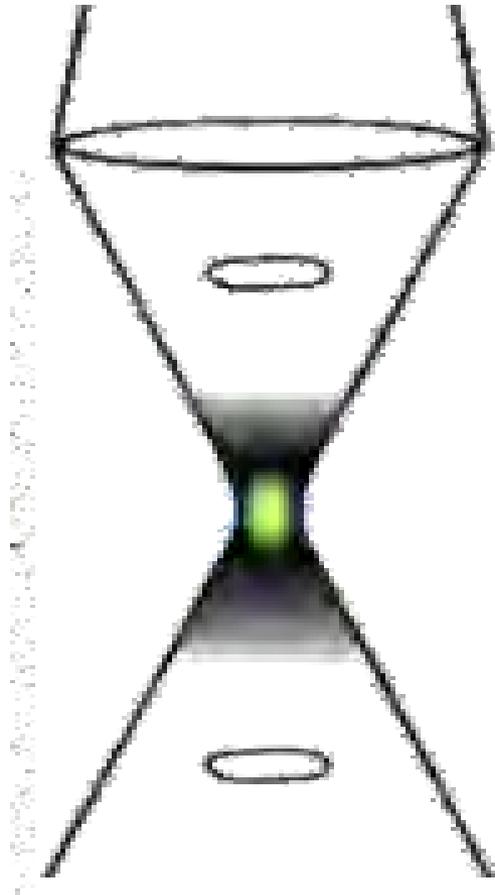
Ink Hole

(~ 100 nm diameter)



LIGHT TO DEFINE PATTERNS

using a locally-defined polymerization by a free-space 2-photon process



Two-photon Microscopy **One-photon Microscopy**

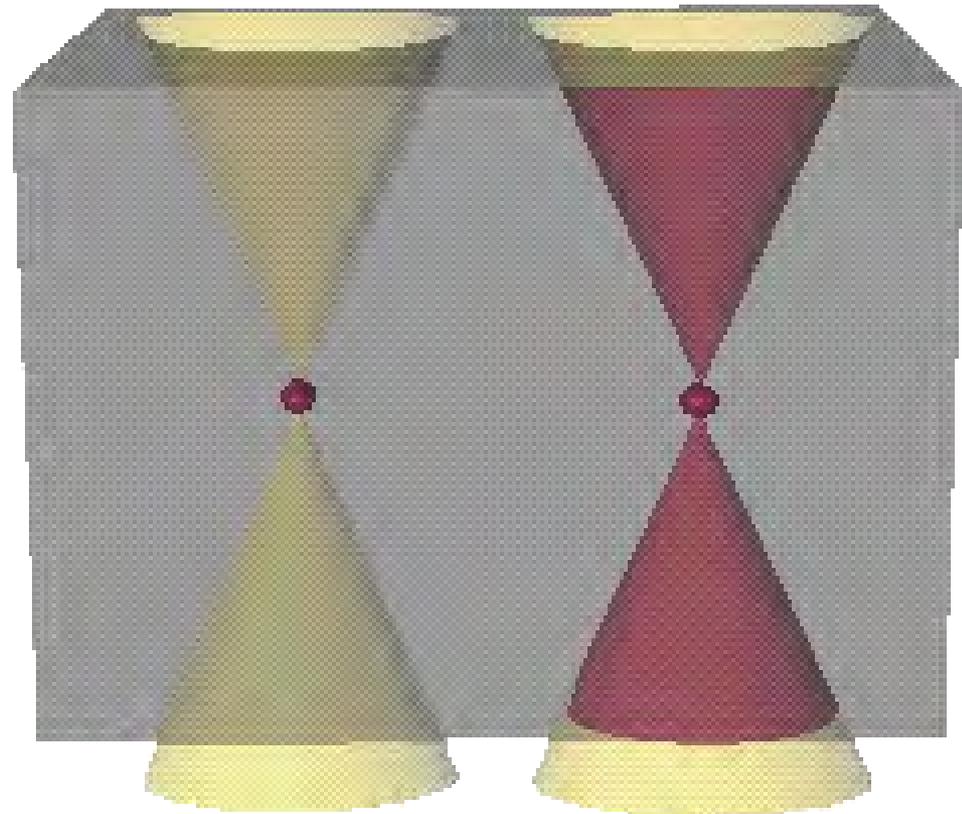
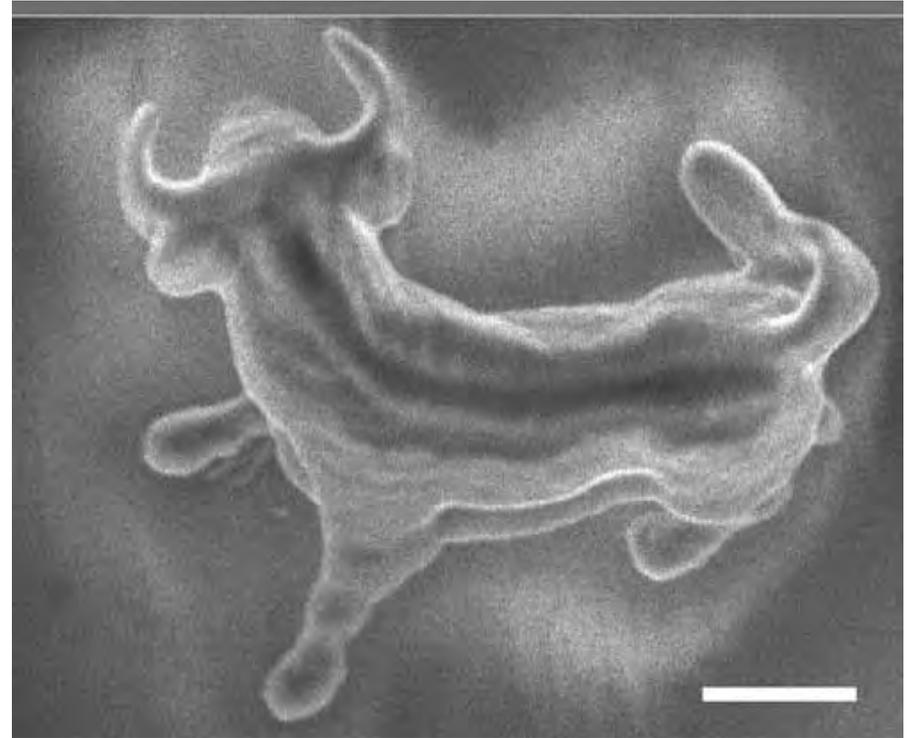
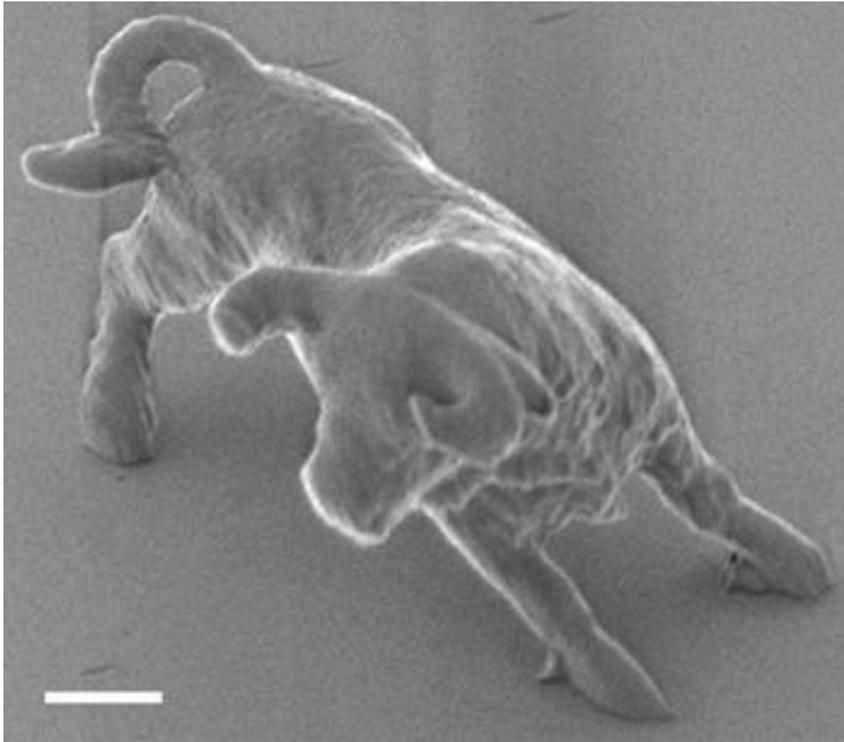


PHOTO-POLYMERIZATION

acrylate monomer is mixed with AIBN initiator, and undergoes photo free radical polymerization locally, by a deep red 2 photon process



2 microns

POLYMERS for OPTICS, ELECTRO-OPTICS, & PHOTONICS

Polymeric materials for optics, electro-optics, and photonics can be classified usefully according to their application, as:

1) **PASSIVE MATERIALS:** where the polymer serves as a benign host for information transmission and ROM storage (for eg: optical fibres, waveguides, and cladding layers)

2) **ACTIVE MATERIALS:** where the polymer is tailored to respond quickly to electric or optical fields for switching (for eg: high-speed read/write storage, optical routing)

POLYMERS for OPTICS, ELECTRO-OPTICS, & PHOTONICS

For either application, our design and synthesis goals are the same—to produce polymers which are efficient and effective:

- *easy and cheap* to synthesize, characterize, and process.
- *versatile* so that properties can be tuned and optimized.
- *compatible* with surfaces and interfaces of existing devices
- *stable* over time, temperature, and a range of environments

Optics is the guiding and control of light properties using materials.

Electro-Optics is using materials to mediate the communication between electrons and photons, or using E fields to control optical properties

Photonics is the processing and conveying of information using photons instead of electrons. ie: electronics substituting the electrons.

Question 1) Why Photonics? (what's wrong with electronics ?)

Traditional electronics successfully merged the conductance of metals with the inorganic electric transistor (1947) to produce a nearly perfect communications processing platform

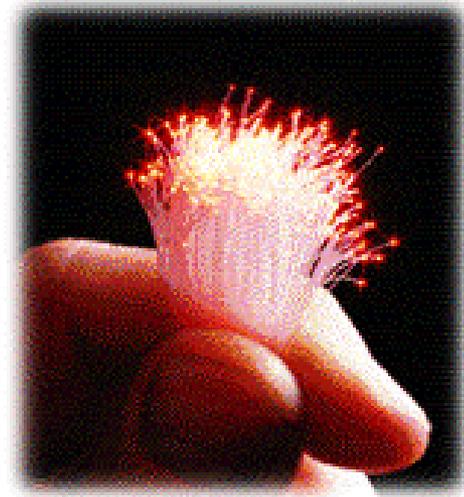


electrons in; electrons out (+ some heat), and one at a time.

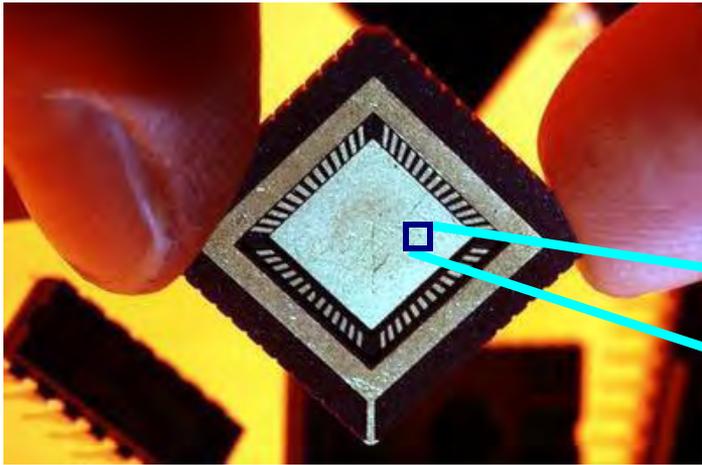
It's the *heat* and the *one-at-a-time* parts which can cause problems.

Question 1) Why Photonics? (what's better about photonics ?)

Photonics, in contrast, uses photons the same way, exploiting the advantages of many more 'coding variables', low heat loss in a material, and superimposability

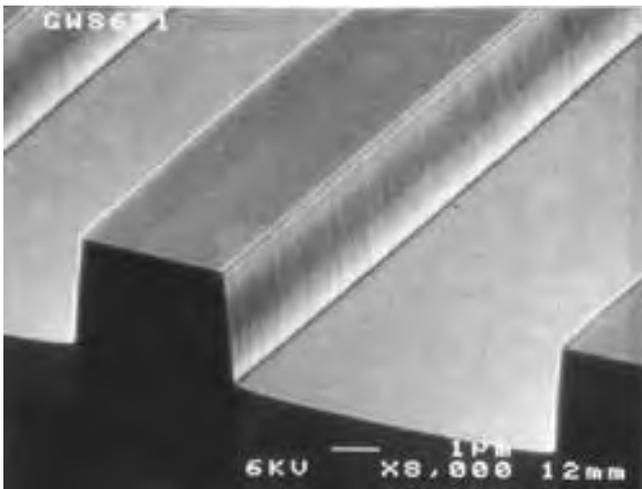
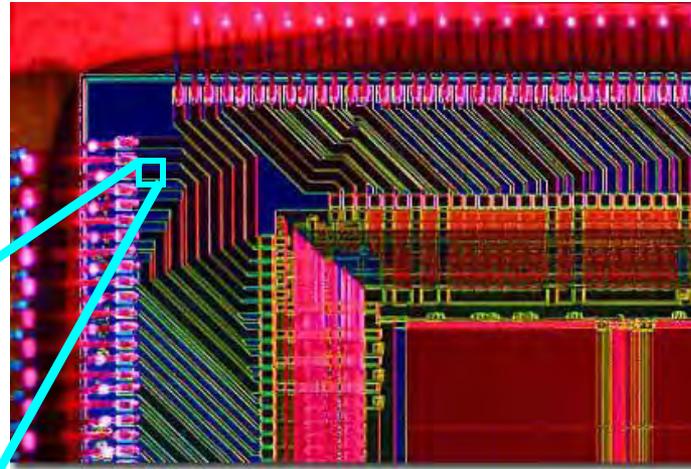


distinguishable photons in; distinguishable photons out, with little heat, no cross-talk, and a vast new set of architectures available. Variables include wavelength and polarization state.



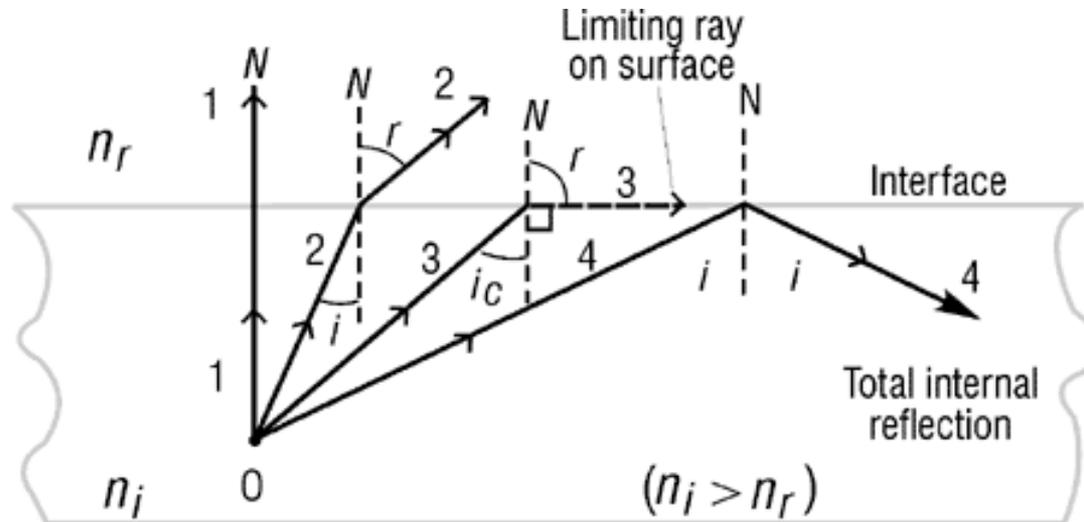
PASSIVE optical materials can be either *short path* (~mm), or *long path* (~km) distances. The polymer properties required for each are much different.

Centimetre 
Millimetre 
Micrometre 



Short Path materials are primarily for on-chip signal transport, and require the ability to be patterned somehow, and be stable to temperature and over time once placed

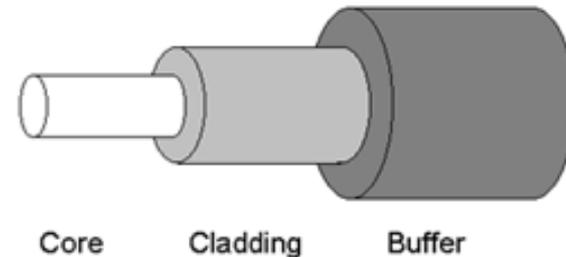
Long Path PASSIVE materials (optical fibres) rely on the same principle of total internal reflection, but now the main concern is the absorptive material losses over long distances, and the mode of propagation



For confinement of light in dimensions similar to that of the wavelength, there are only certain allowed quantum solutions to the propagation of the wave through the fibre, called *MODES*. 0, 1, 2, 3 ...

Amorphous polymers have an advantage of flexibility (so that they can be larger diameter when bending), processability, and durability.

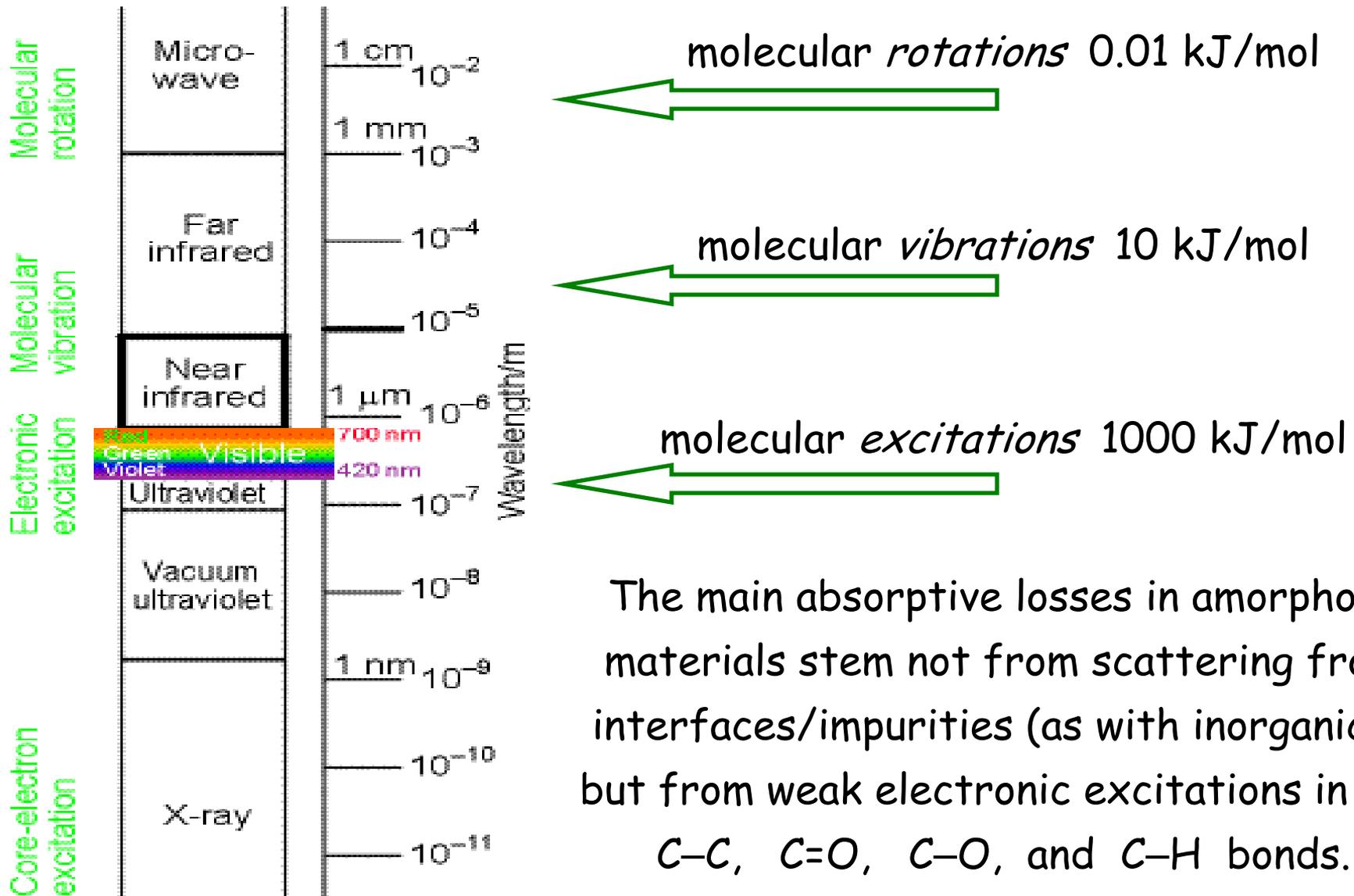
The main challenge to be overcome is the interaction between organic bonds and the light being transmitted



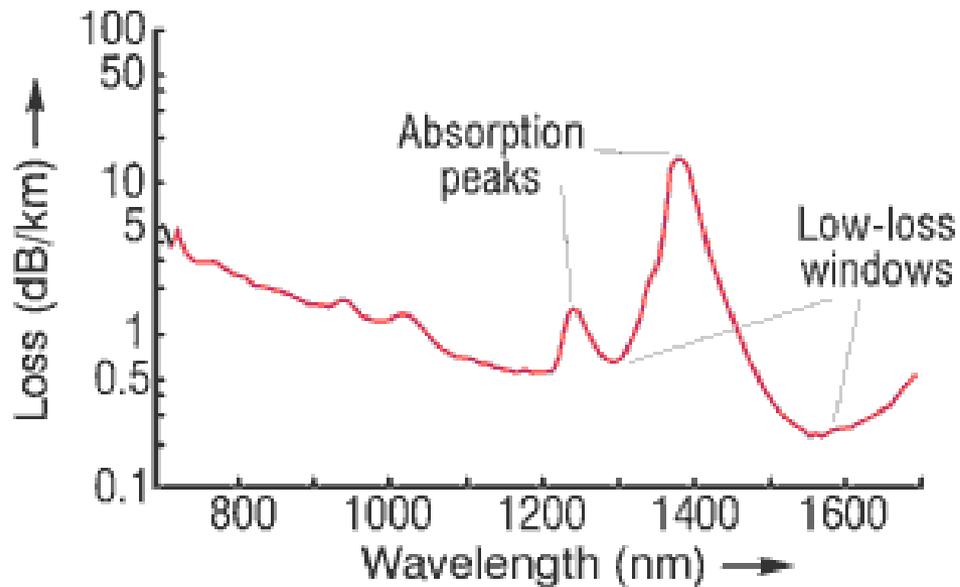
The ability of polymers to be molecularly tailored then allows us to address this problem synthetically, in the fume hood, an approach that would be prohibitively difficult with inorganic glasses.

Some of the best waveguiding materials are acrylates such as PMMA. Low loss is a function of few interfaces, and low electronic absorbance.

Transparency 'windows' are governed by the energy of the bonds :

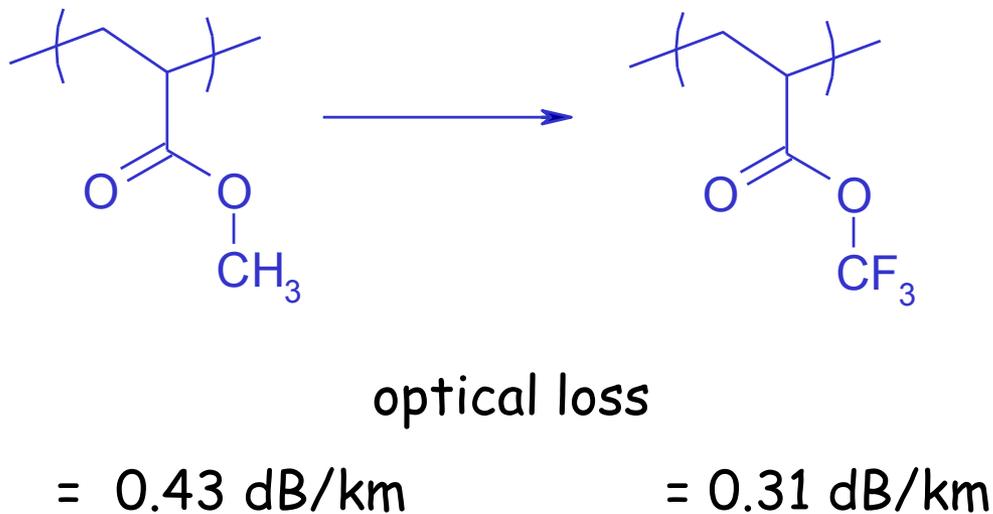


The main absorptive losses in amorphous materials stem not from scattering from interfaces/impurities (as with inorganics), but from weak electronic excitations in the C-C, C=O, C-O, and C-H bonds.



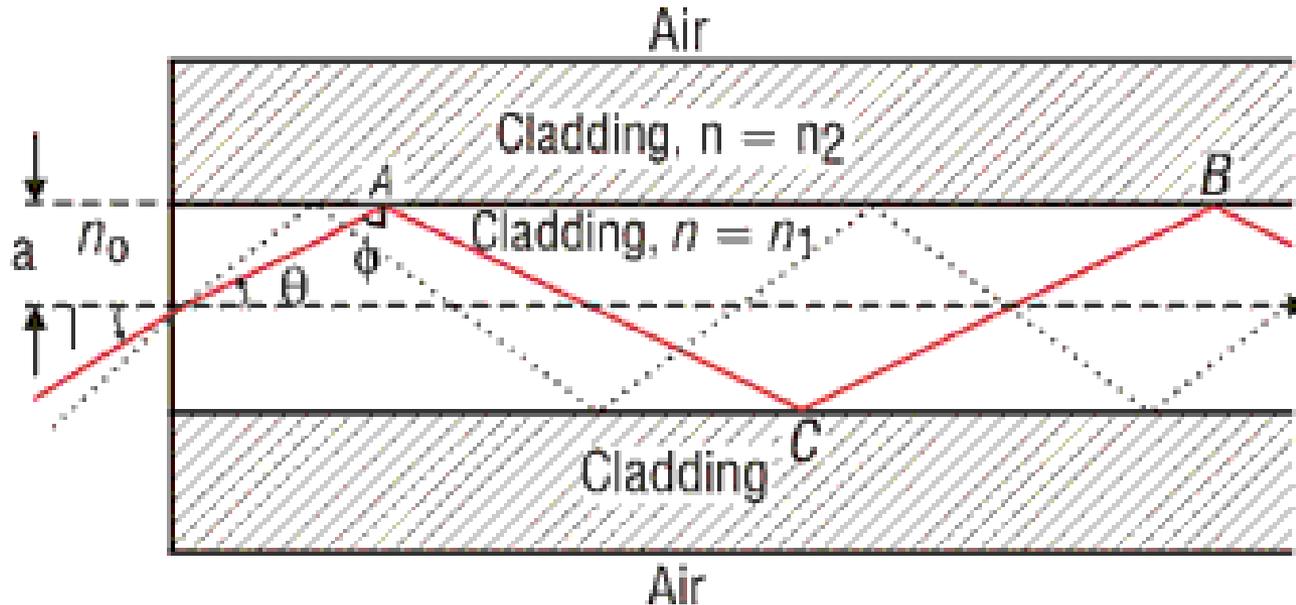
Even the best window available however, at (1.54 microns), for PMMA still adds up significantly with path lengths of many km

A Synthetic Strategy? Try and minimize the contributions of the vibrational mode excitation, by lowering the bond energy



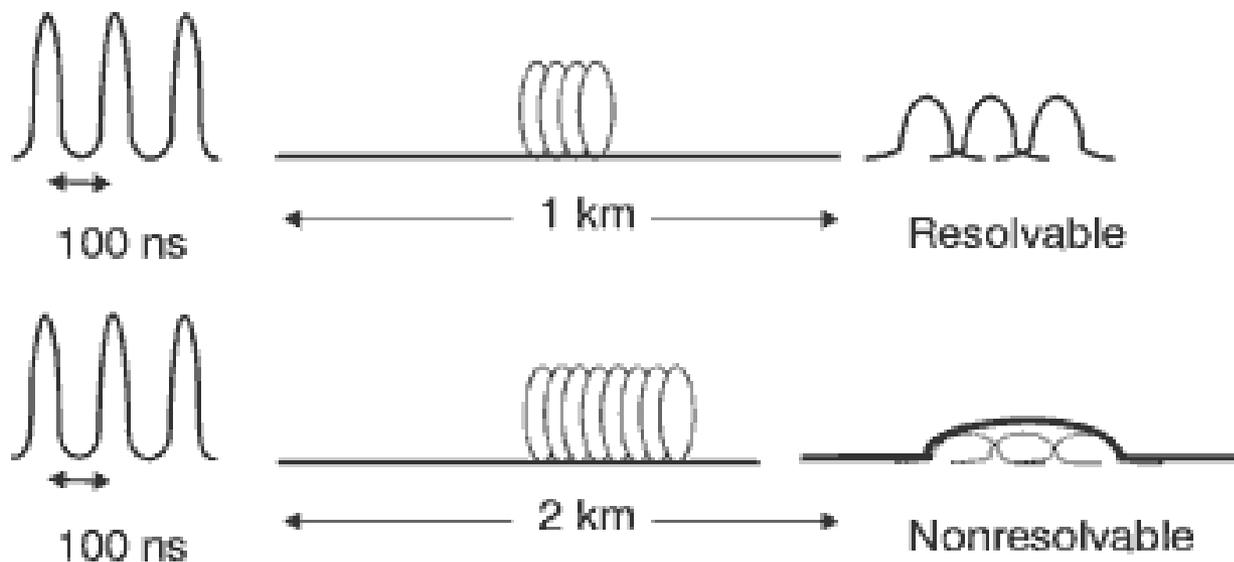
Ross and L. Newsome,
Macromolecules
1996, 29, 2374.

The second main concern with passive *long path* optical fibres is the MODE of light propagation through the material — the solution to the usual quantum mechanical confinement problem



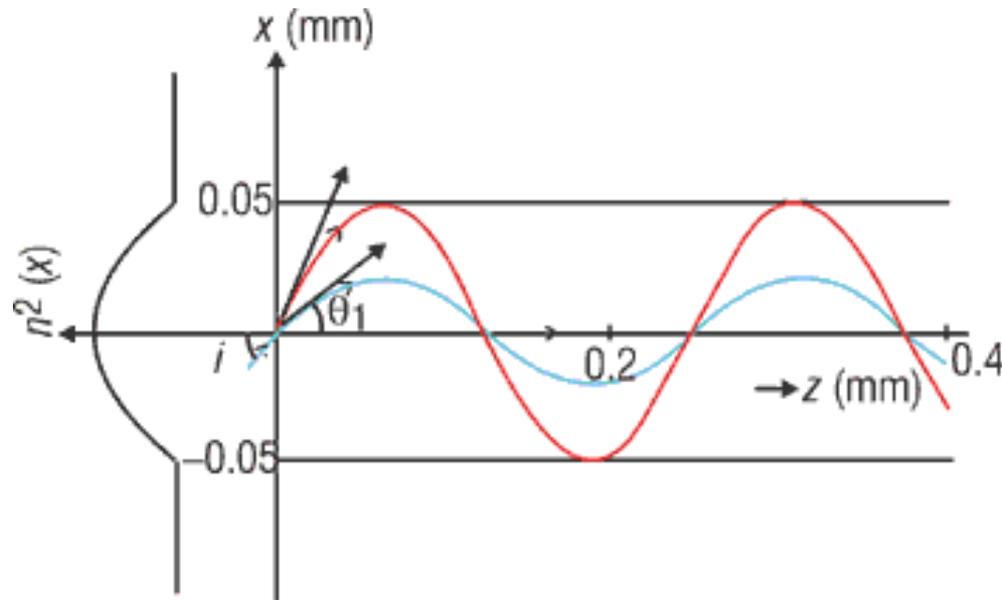
there is a natural spread of 'arrival times' at the other end, between paths with more reflections, and paths with fewer. This means that light of the same wavelength which departs at the same instant (but propagating with different modes), arrives in a distribution.

This Mode propagation distribution means that there is a natural spread of 'arrival times' at the other end, between paths with more reflections, and paths with fewer, which interferes with pulse-coded communication:



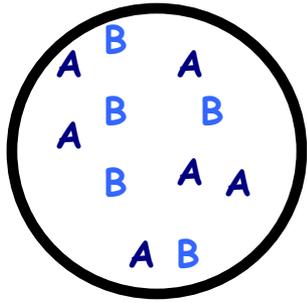
The result is an unwanted broadening of the once-sharp signal. A synthetic solution is again proposed, based on an optical 'trick' that is impossible to apply to inorganics, but possible with polymers:

In contrast to step-index fibres, we can keep the propagation of various input angle photons 'in step' by bending the light through a refractive index that is **GRADED** across the fibre :

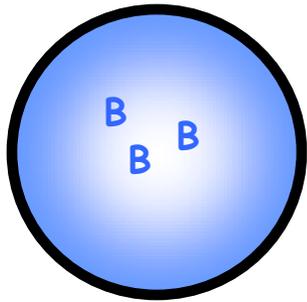


Y. Koike, *Applied Optics* **1996**, 35, 28.

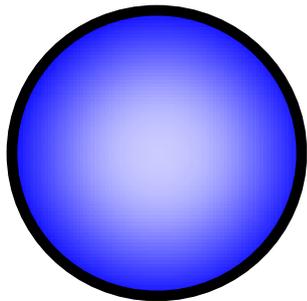
Nice theory, but is it practical to make? A clever and elegant solution was proposed for synthesis of copolymers from different index-of-refraction monomers, using different reactivity ratios between mers.



One starts with a hollow PMMA tube, which is filled with the monomers m_A and m_B , which have higher and lower n values respectively. Polymerization is carried out by a UV lamp through the PMMA shell.

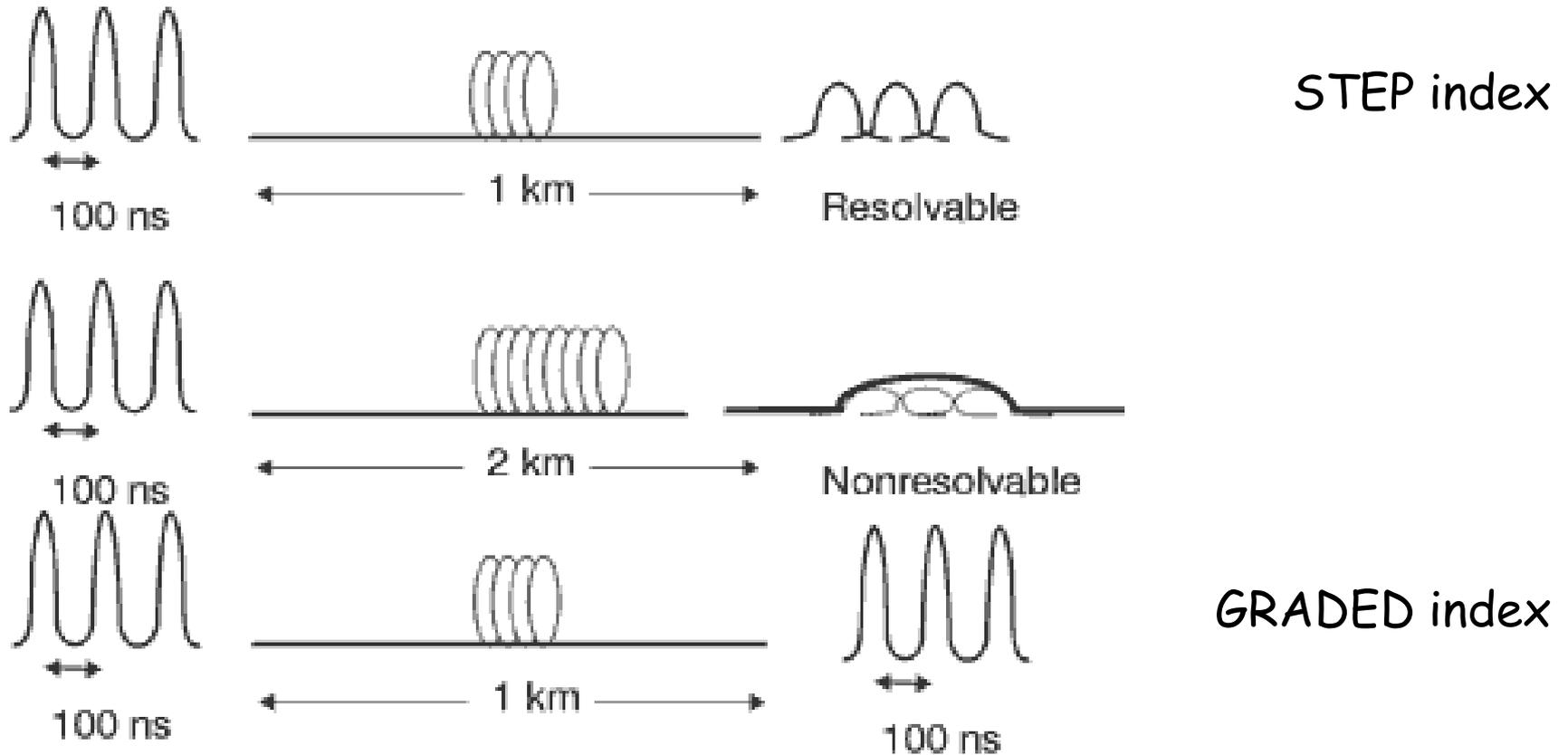


A and B co-monomers are further tailored so that the two reactivity ratios are dissimilar, which leads to increased incorporation of A near the tube walls where the photo-initiation light is strongest



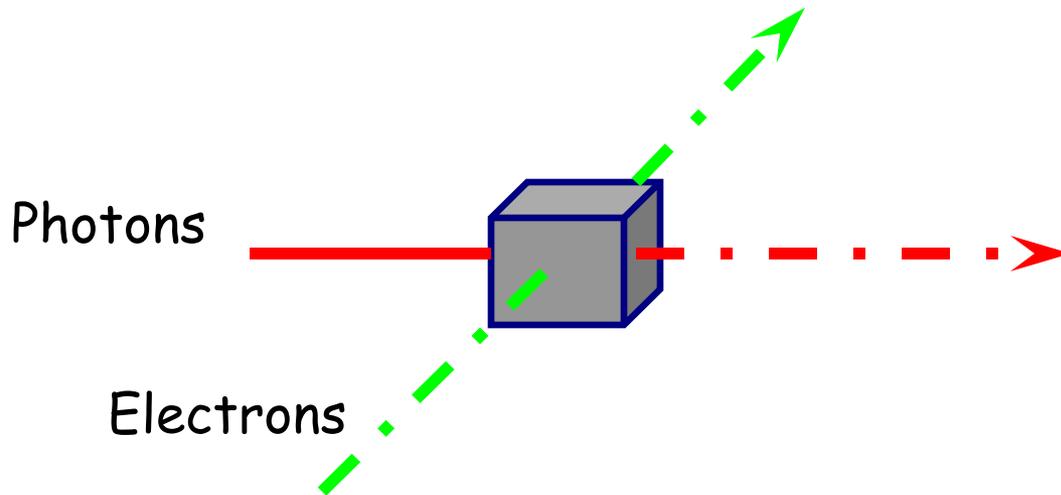
As monomer A gets used up near the outer edges of the tube, monomer B (with the lower refractive index) is incorporated in a higher proportion in the middle of the tube, towards the end of the reaction.

The Graded Index Polymer Fibres can then Mode Match efficiently, and travel of many hundreds of km is possible retaining resolvability.



ACTIVE MATERIALS can be classified by *what* is used to produce optical changes (electrons or other photons), and whether these changes are reversible (for use as re-writable storage) or irreversible (WORM)

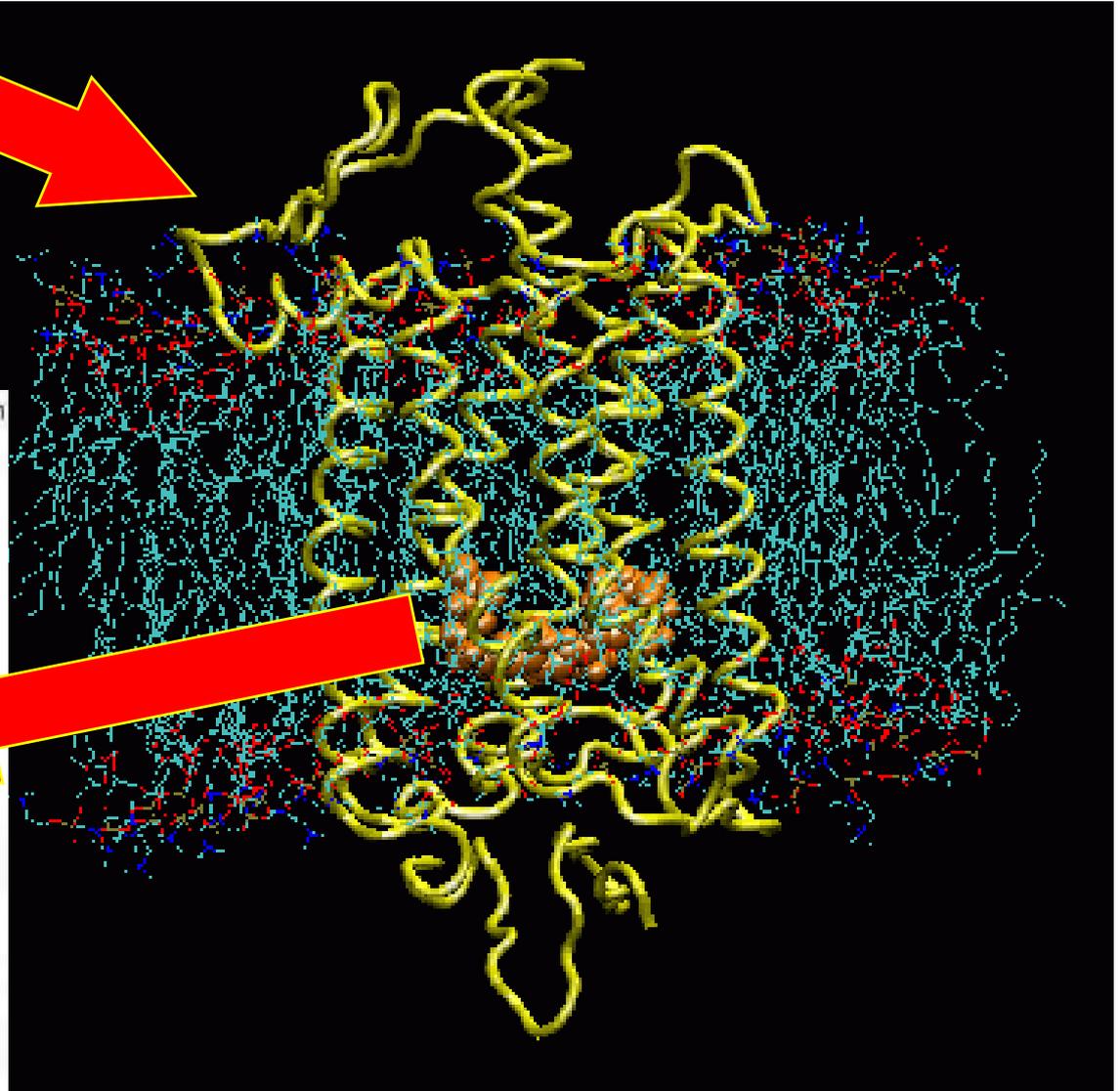
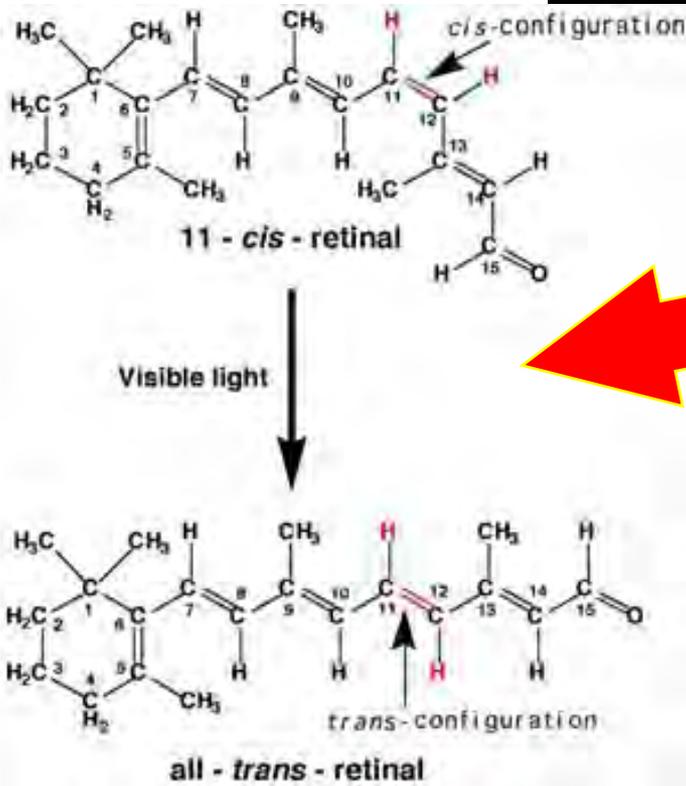
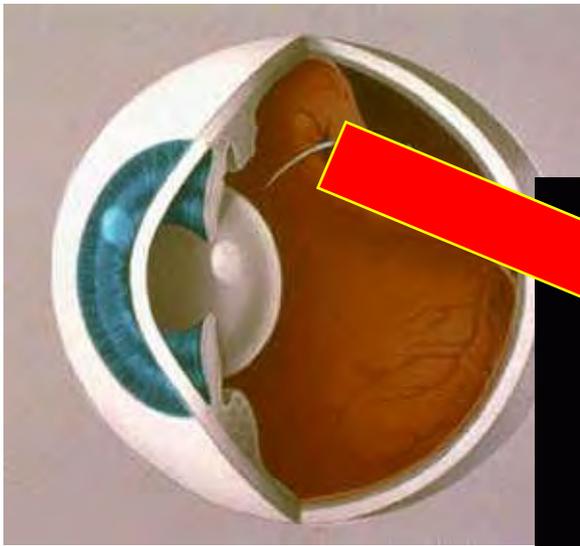
Electrical-Optical (EO) switching allows information coded as electron packets to be transferred without error to packets of photons

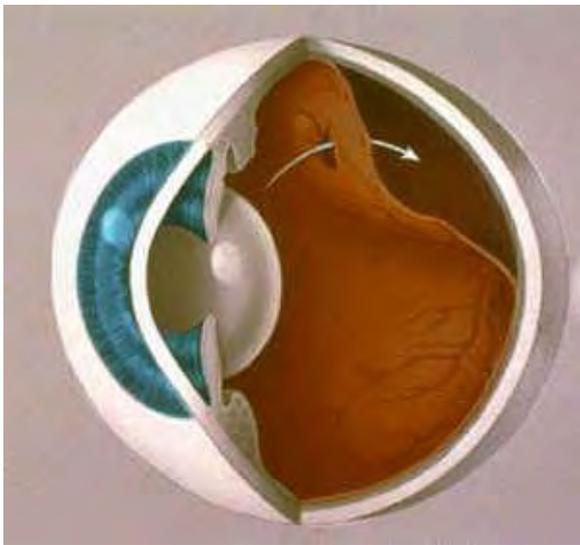


Thus, we need a material which can change its optical properties VERY quickly (nanoseconds) and repeatedly (10^{16}), by an electrical signal.

PHOTOSWITCHES change their physical properties reversibly with light

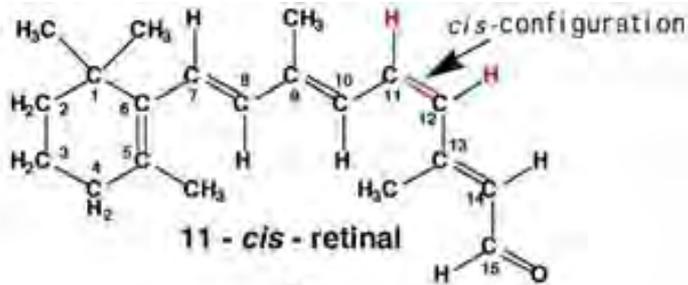
Self-Assembled Reversible Photo-Switch



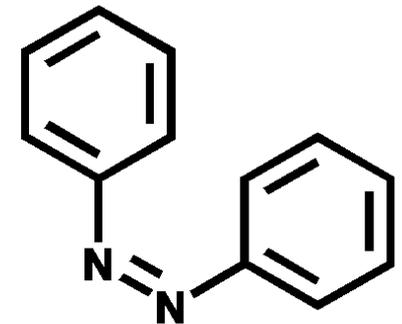
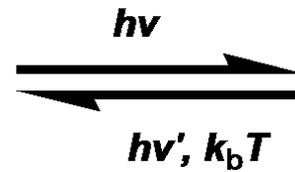
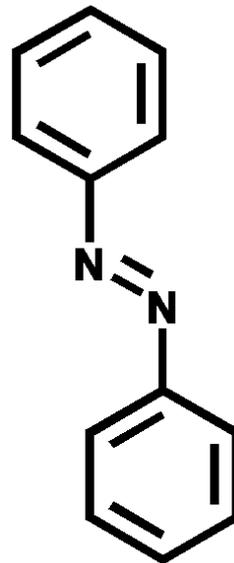
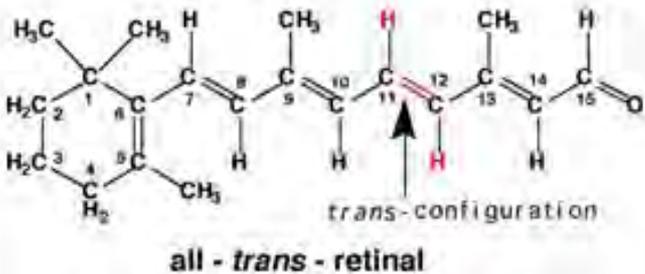


Simple mimics of retinal in rhodopsin is azobenzene, spiropyran, DTE, or PNQ embedded in a self-assembled polyelectrolyte structure.

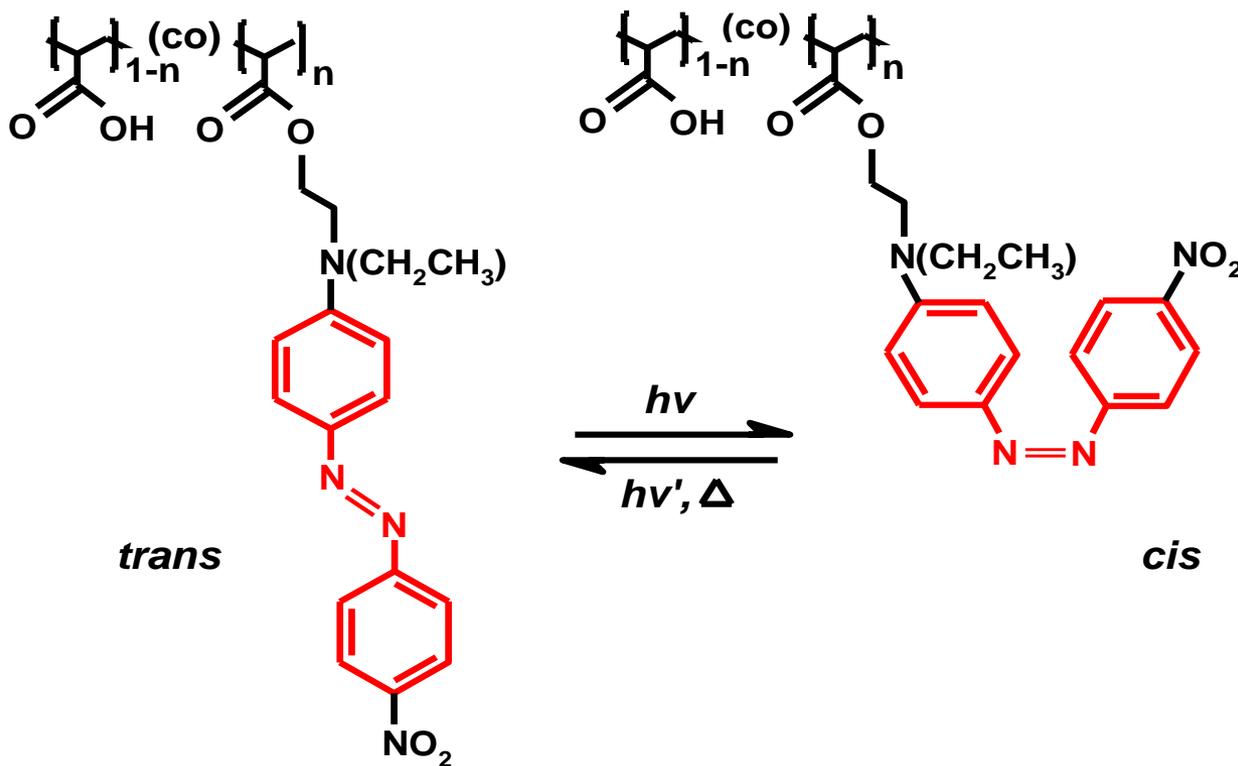
The Azo chromophore is best, as it can be switched quickly, reversibly, and repeatedly with high quantum yield.



Visible light



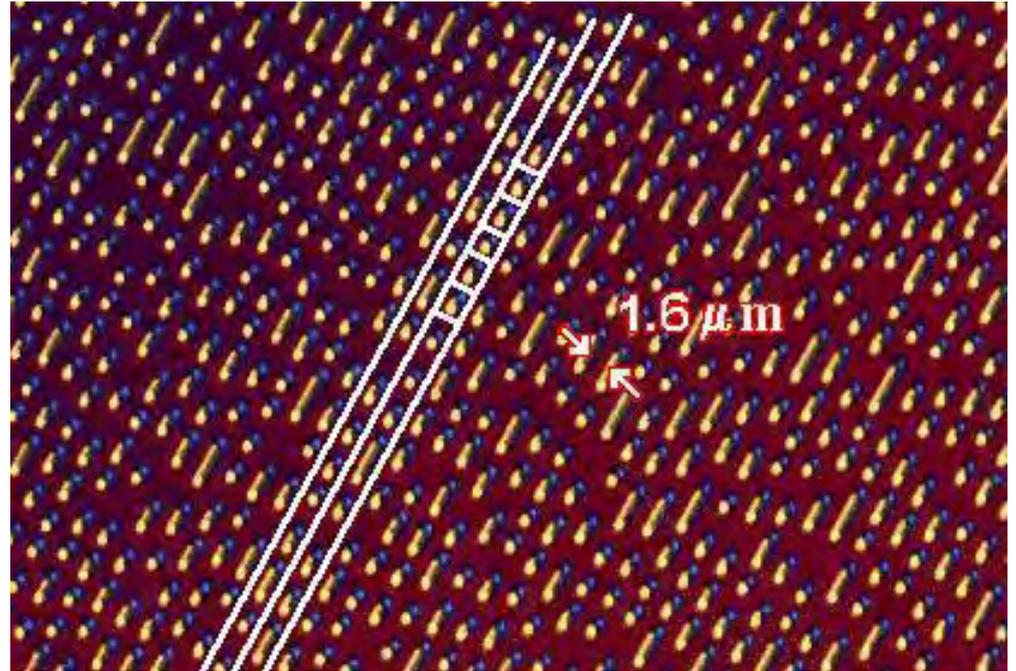
Azobenzene chromophores can be doped into polymers (cheaper), but this causes dispersion, stability problems due to crystallization and phase segregation over time. Much better to incorporate directly:



The two different forms of azobenzene polymers can exhibit very different optical and physical properties, and can be switched with light on the picosecond timescale. The *cis* form is unstable however, and always reverts back to the *trans* form, sooner or later.

Optical Information Storage: a) Write Once, Read Many times (WORM)

Not much elegance required, just a polymer layer that can change optical properties very quickly and significantly to another state that's stable.

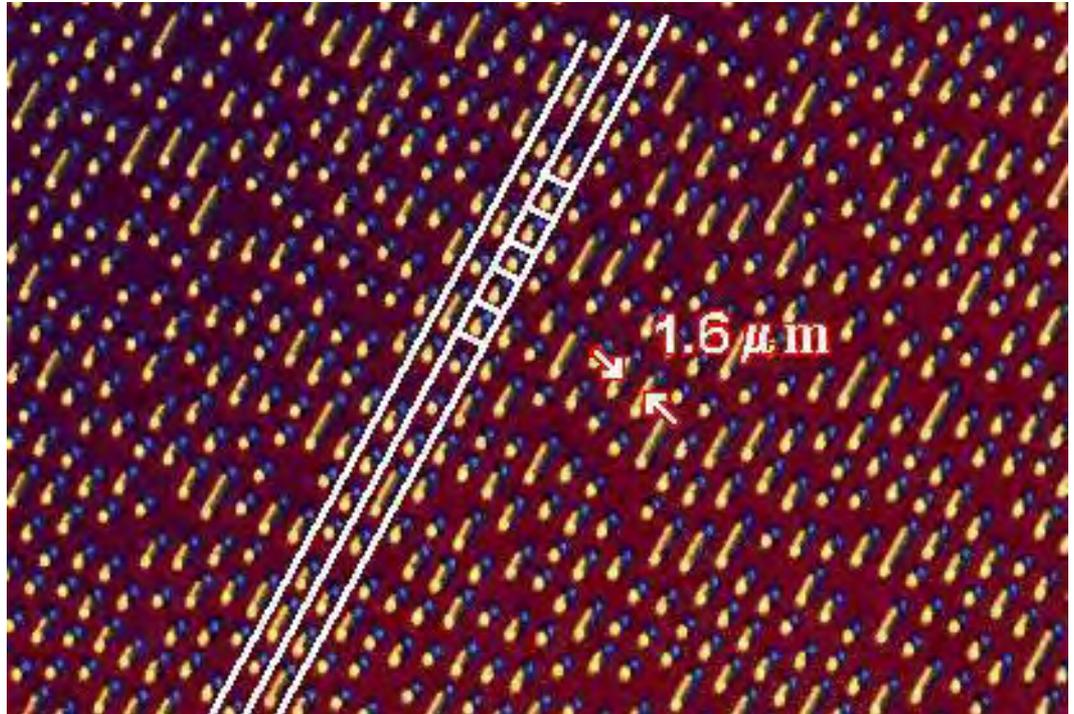


'Burning' a CD is a fair description, with a thin polycarbonate layer on aluminum locally melted by a focused writing laser to make a bit

The focusing optics and heat diffusion rates limit the size of these bits to approx: 0.7 microns x 4 microns, with 1.6 microns between tracks.

With each total bit area $1.3 \times 10^{-6} \text{ mm}^2 = 800,000$ bits per square mm, or at 8 bits per byte = $100,000$ bytes/ mm^2 . With a total available disk area of ~ 14 square inches, = 9000 mm^2 , the number of bytes/ mm^2 times the size in mm^2 gives an estimate of the total capacity of a CD:

$$\begin{aligned} 100 \text{ kb/mm}^2 \times 9000 \text{ mm}^2 \\ &= 900,000 \text{ kb} \\ &= 900 \text{ Mb (megabytes).} \\ &\text{(theoretical maximum)} \end{aligned}$$



There is much space used for checking the information however, and other forms of software 'overhead', so available space only = ~ 650 Mb

We don't need much in the way of polymer science for this however...

What IS really tricky is ACTIVE MATERIALS which are reversible.

b) Reversible Optical Storage, for re-writable compact disks

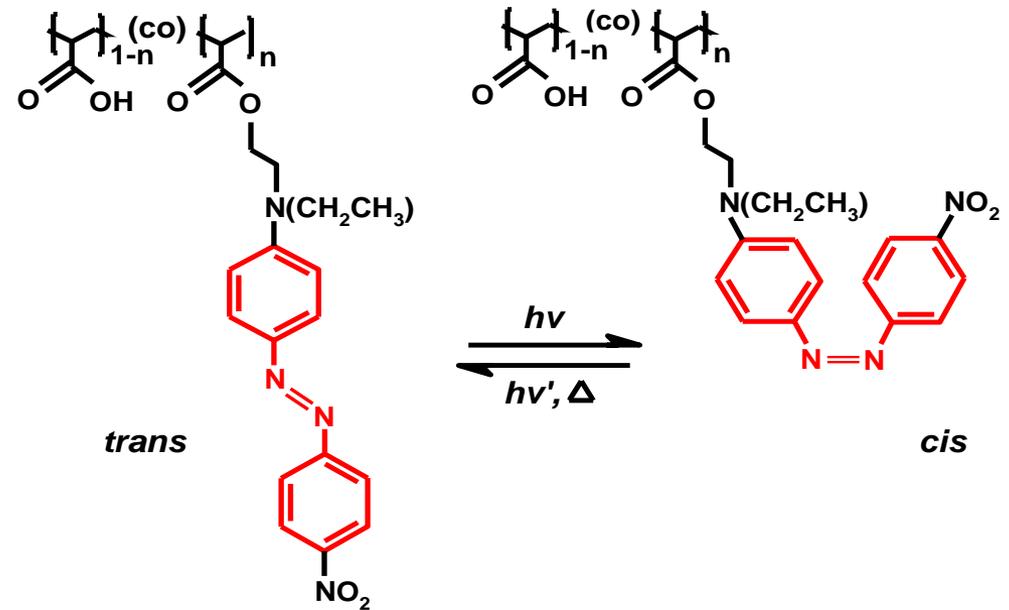
Here, we DO need to make clever use of polymer properties to allow a photoswitchable property to be fast and significant, but also reversible.

How quickly? Our 650 Mb CD has 5,200,000,000 bits.

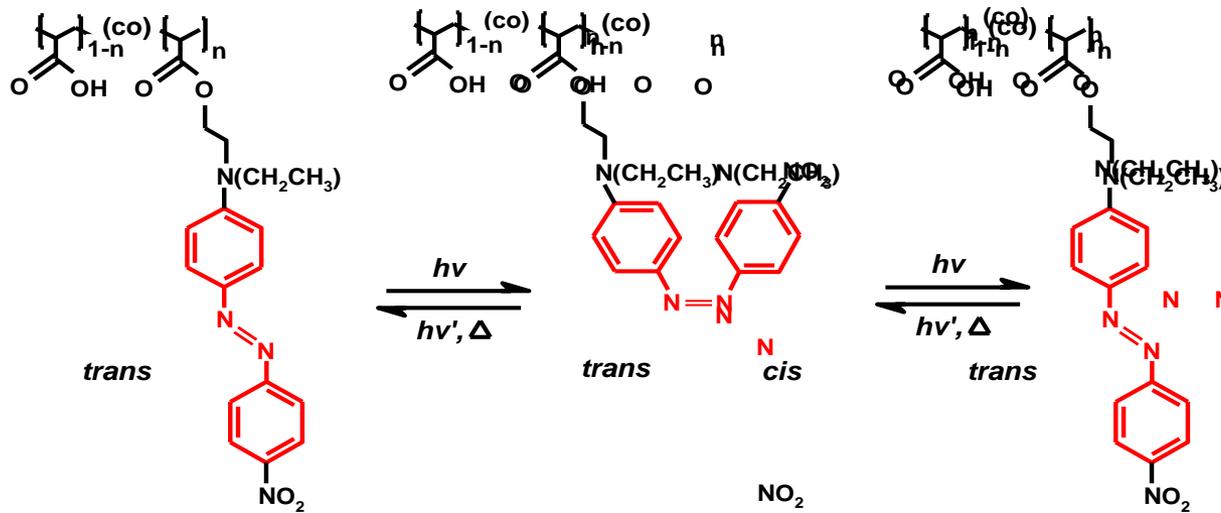
To write a CD in a minute is ~ 0.00000007 seconds/bit = 10 nanosec/bit.

In principle, a photoswitch like azobenzene would work.

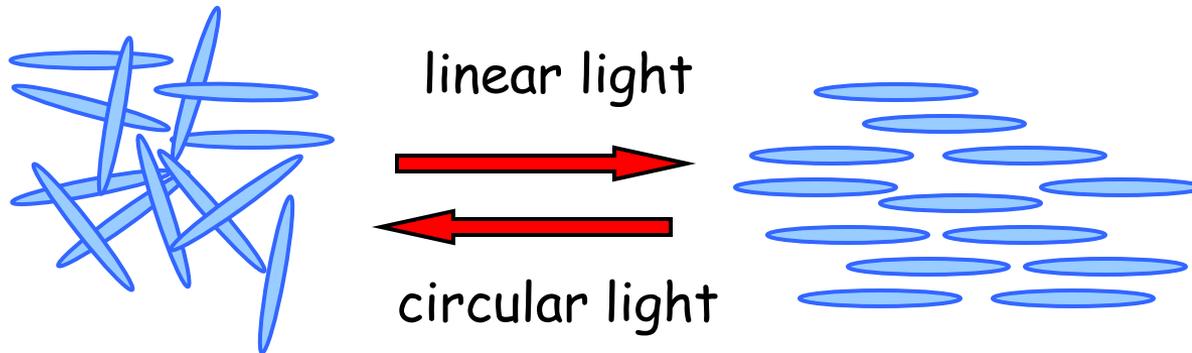
In practice, the cis isomer is not stable enough at room temperature (or more).
(but there are certain apps)



What one CAN do however is to take advantage of a variation of this optical storage, to re-align the azo chromophores to write localized and reversible birefringence, with all azobenzene groups in the *trans* state



With a full cycle
 $trans \rightarrow cis \rightarrow trans$
 now, orientation of
 $trans$ is used to
 encode information,
 not the two isomers.



Using polarized light
 (linear or circular),
 random vs. oriented
 bits can be written,
 erased, and re-read.
 (whole circuits too)