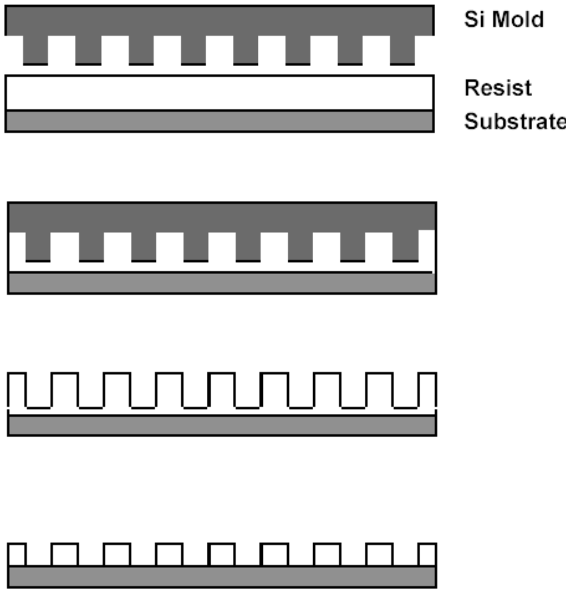
Photolithography vs.
Soft Lithography

國立中興大學
National ChungHsing University

Hard Nanoimprinting Lithogrpahy

NIL Process



(1) Press in mold

(2) Heat up mold and substrate

(3) Mold separation after cooling

(4) O_2 RIE

- Sub-10nm feature size
- Large area (4-8 in.)
- High throughput
- Low cost

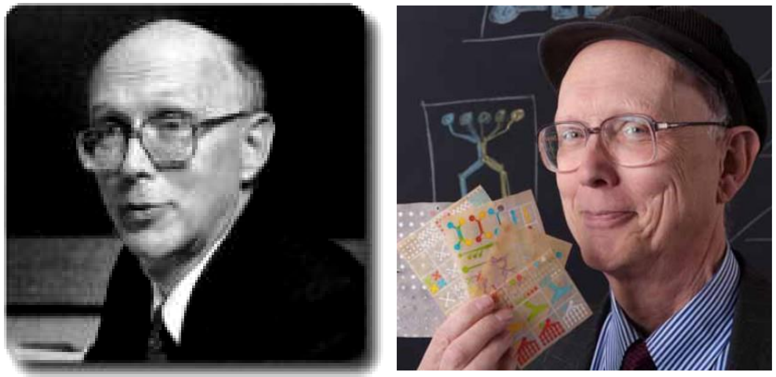
Nanonex NX-2000 Nanoimprinter

Up to 4" wafer

Sub-100 nm resolution

Up to 300°C, 600 psi, UV

“Soft” Lithography



George M. Whitesides
http://gmwgroup.harvard.edu/
Father of Soft Lithography

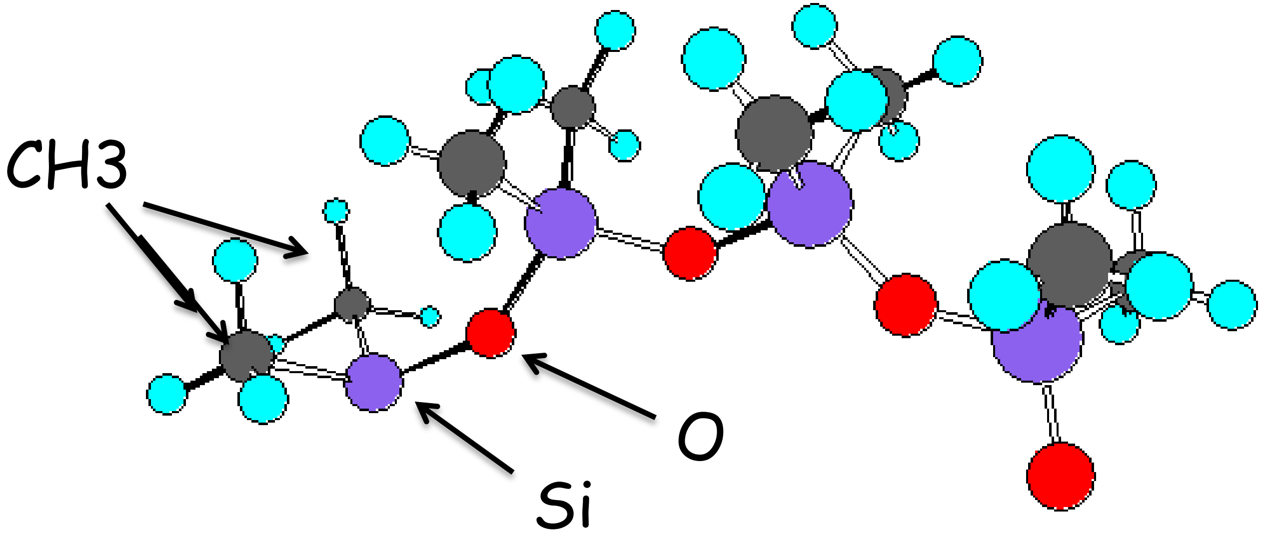
Reviews:

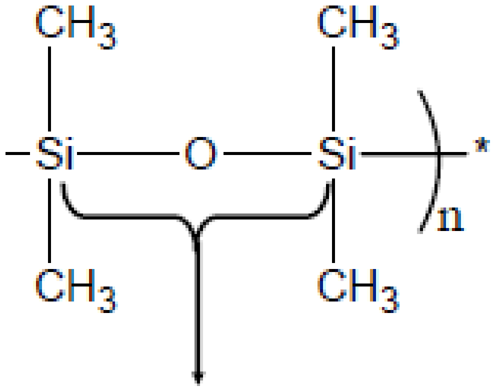
1. Whitesides, G. M., *Angew. Chem. Int. Ed.* (1998).
2. Whitesides, G. M., *Chem. Rev.* (1999).

- Low-cost, non-lithographic method to complement photolithogrpahy.
- Use a patterned elastomer such as poly(dimethylsiloxane) (PDMS) as a ***mask***, ***stamp*** or ***mold***.
- Embrace chemical concepts of self-assembly, templating and crystal engineering, with soft lithographic techniques of microcontact printing and micromolding.
- Shape materials over different length scales from 1 nm to 500 mm.
- Pattern two- and three-dimensional structures on planar and curved surfaces.
- Important in MEMS and biological applications.

The Core Material of Soft Lithography

Poly(dimethylsiloxane) (PDMS)





$$-\left(\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\right)_n-*$$

Very bendable
(135° - 180°)

Polycondensation Reaction:

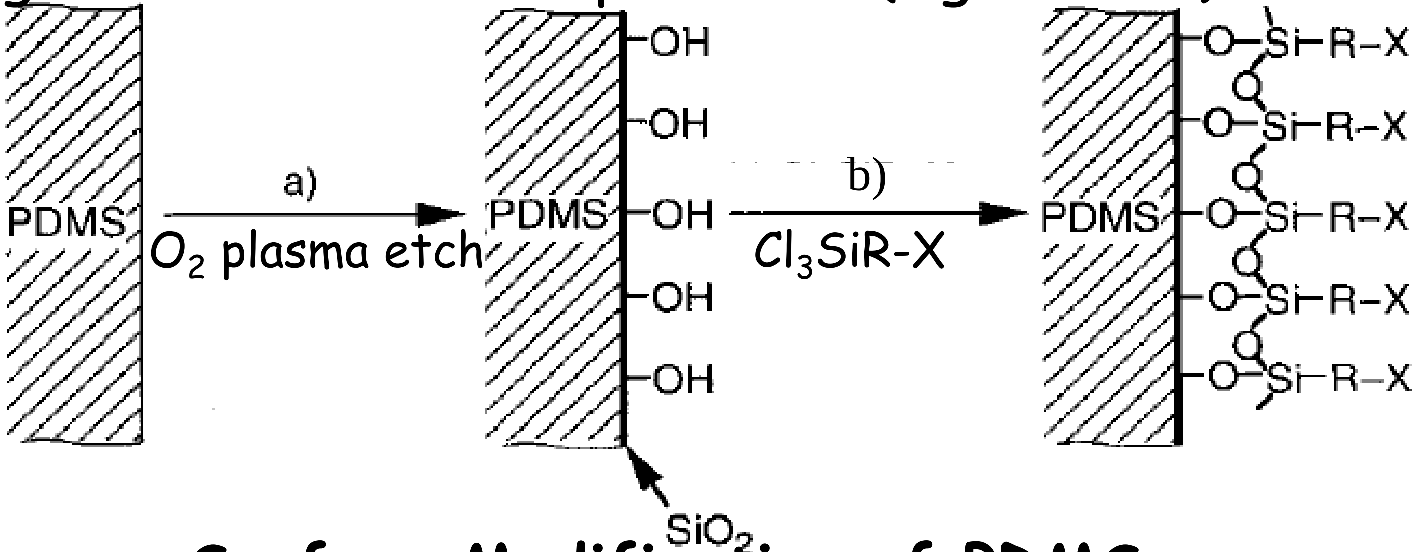
$$2\mathrm{HOSi(Me)_2OH} \longrightarrow \mathrm{HO(Si(Me)_2O)_2OH} + \mathrm{H_2O}$$

$$2\mathrm{HO(Si(Me)_2O)_2OH} \longrightarrow \mathrm{HO(Si(Me)_2O)_4OH} + \mathrm{H_2O}$$

Unique Properties of PDMS

Unique Properties:

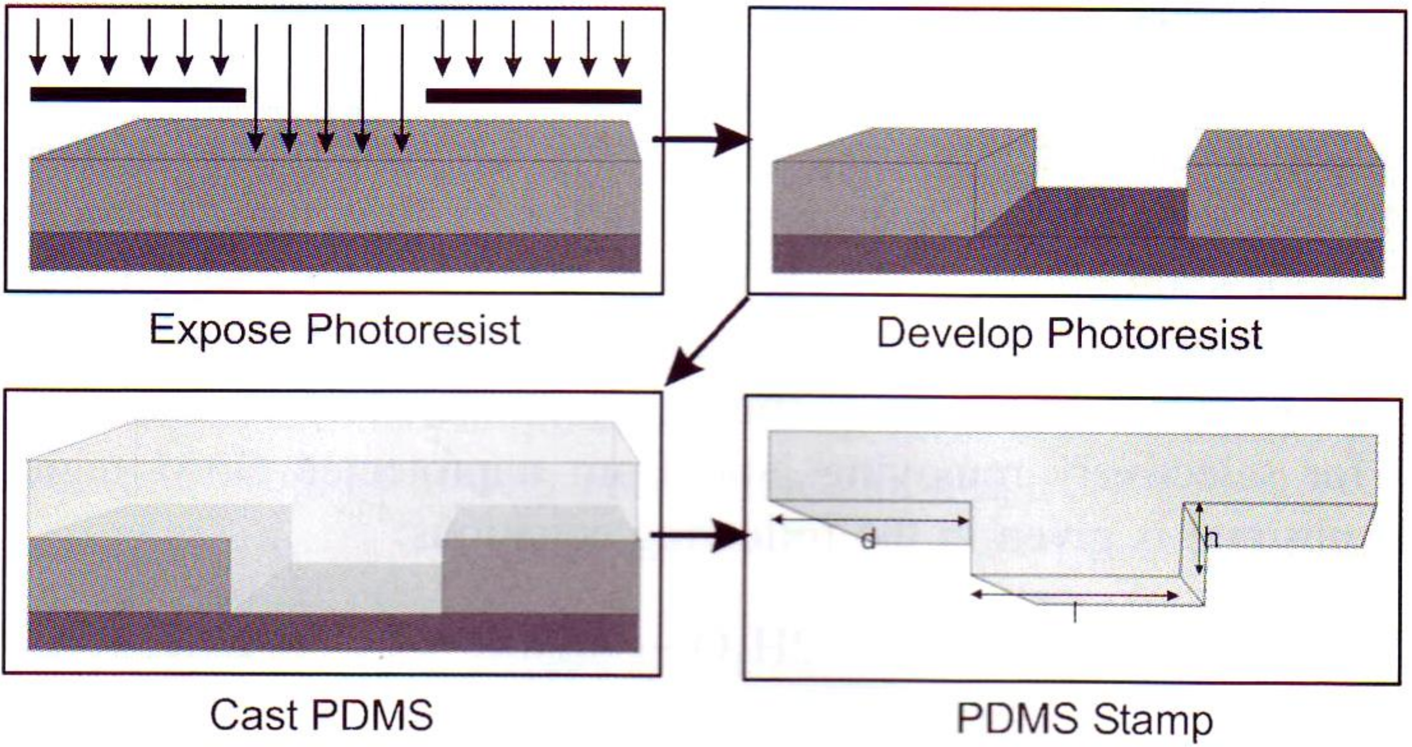
- High flexibility and optically transparent
- High gas permeability
- Low surface energy (21.6 $\times 10^{-3}$ J/m^2)
- Conformal contact to almost all surfaces
- Low glass transition temperature (Tg ~ 146K)



Surface Modification of PDMS

The Science of Soft Lithography

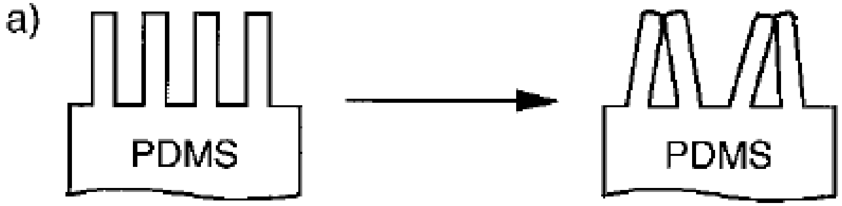
$CF_3(CF_2)_6(CH_2)_2SiCl_3$ treatment



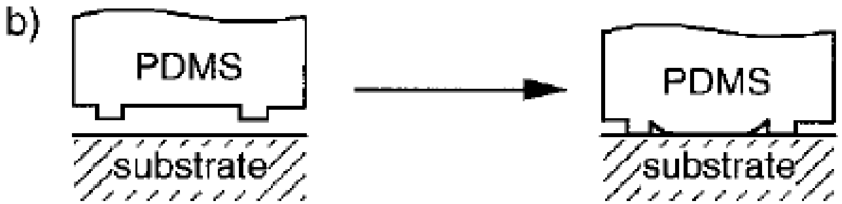
- h: 0.2-20 μm
- d: 0.5-200 μm
- l: 0.5-200 μm

Deformation/Distortion of Relief Structure

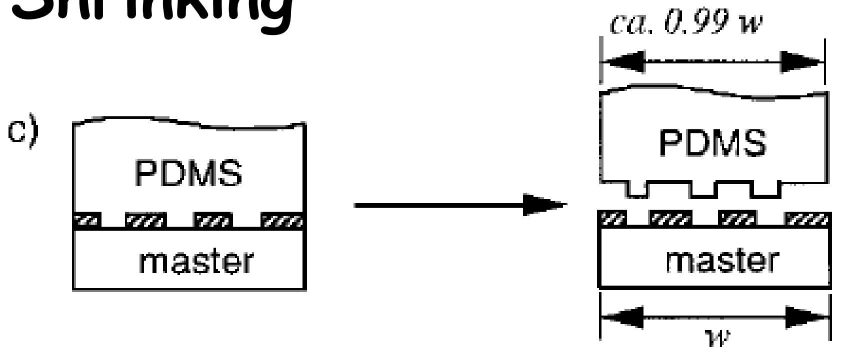
Pairing



Sagging

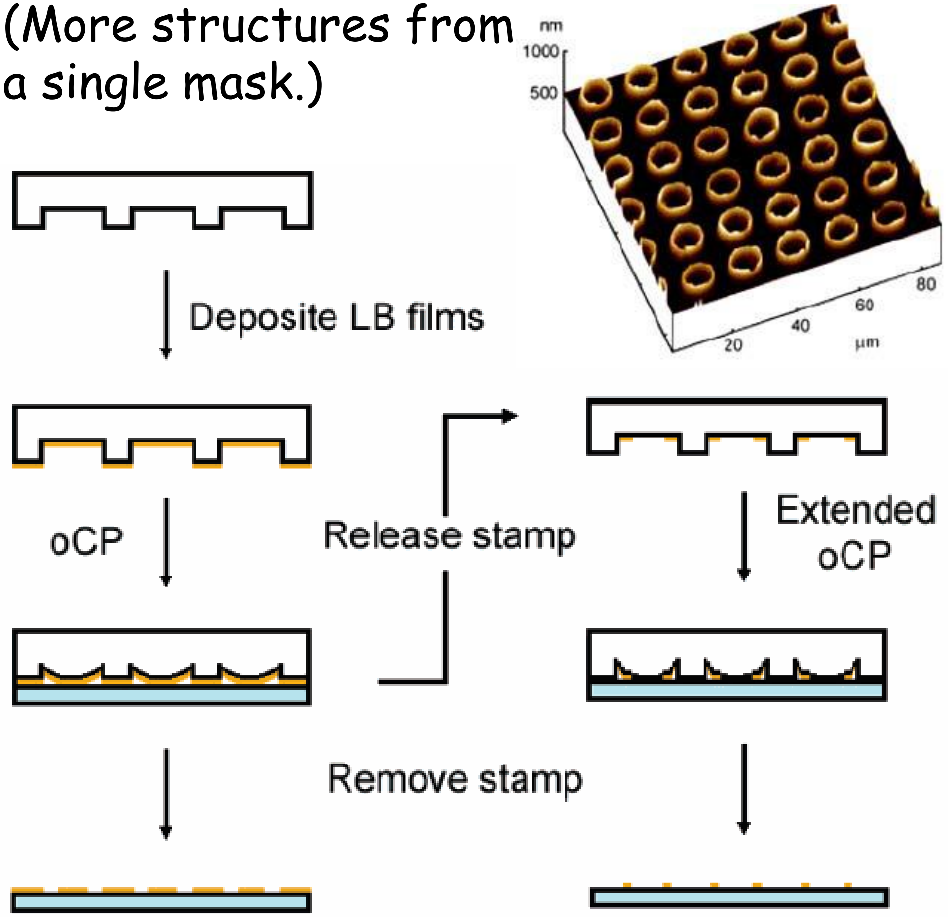


Shrinking



Sometimes, deformation is good.

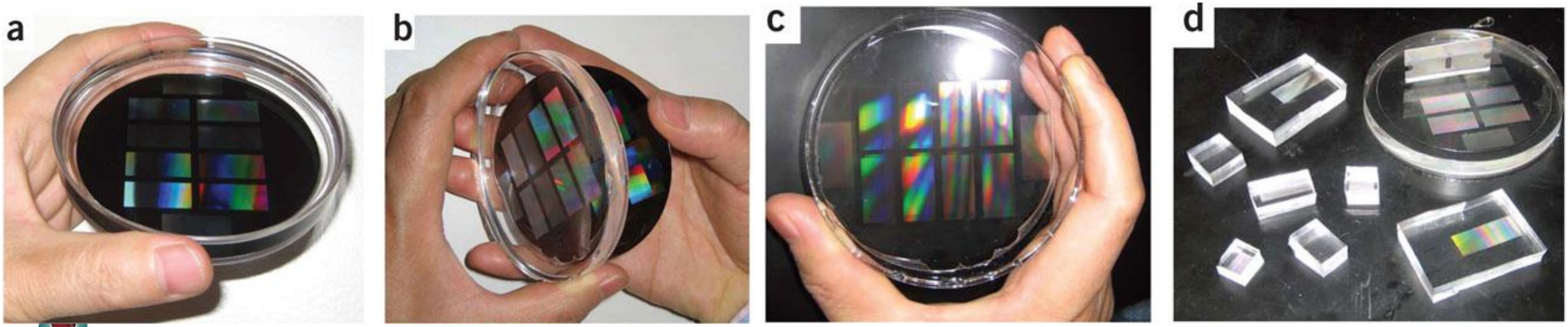
(More structures from a single mask.)



(*Nano Lett.* **4**, 1657, 2004)

Five Components of Soft Lithography

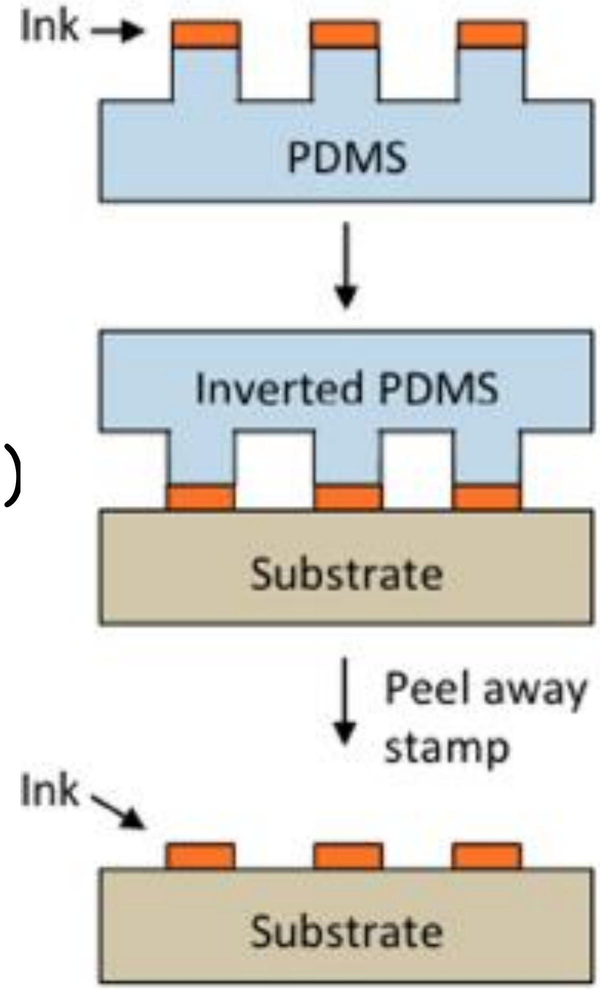
Soft Lithography	**Resolution**
• Microcontact printing (μCP)	35 nm
• Replica molding (REM)	~2 nm
• Microtransfer molding (μTM)	1 μm
• Micromolding in capillaries (MIMIC)	1 μm
• Solvent-assisted micromolding (SAMIM)	60 nm

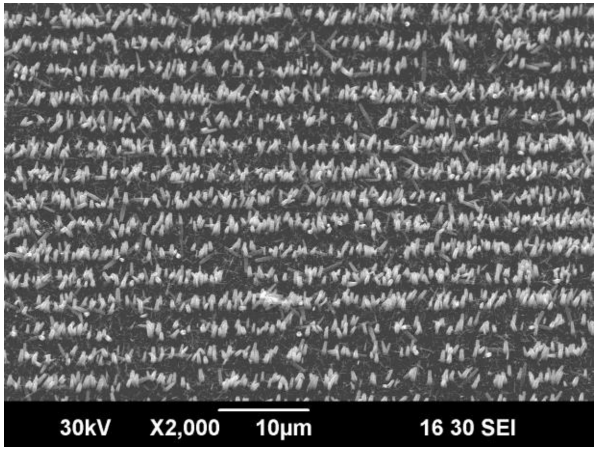


Five Components of Soft Lithography

Soft Lithography

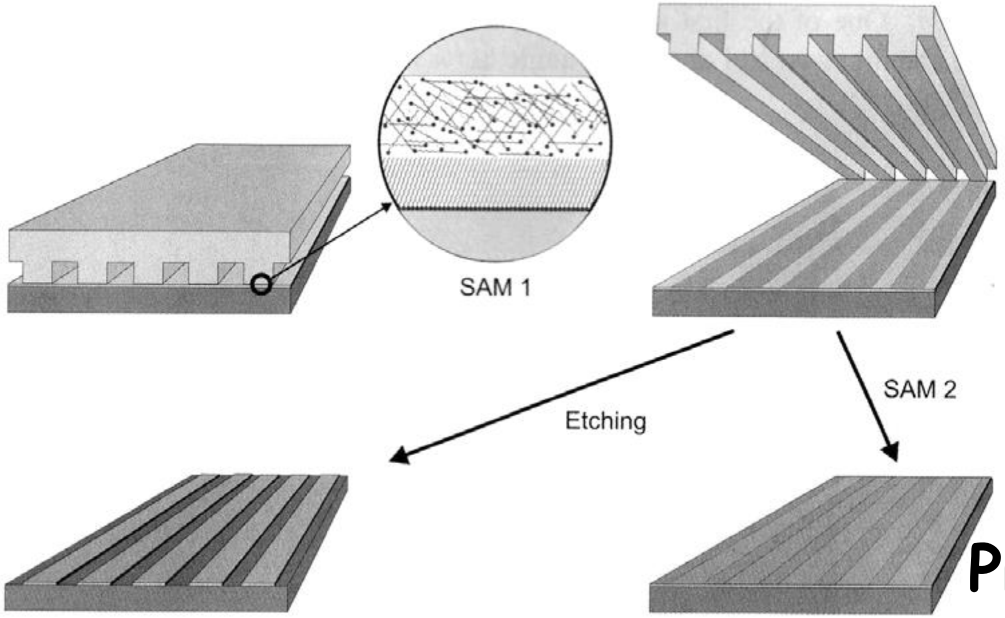
- **Microcontact printing (μCP)**
- Replica molding (REM)
- Microtransfer molding (μTM)
- Micromolding in capillaries (MIMIC)
- Solvent-assisted micromolding (SAMIM)



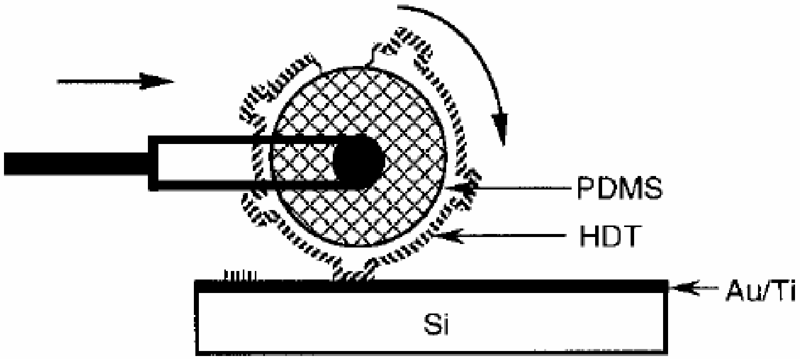


Patterned ZnO Nanowires

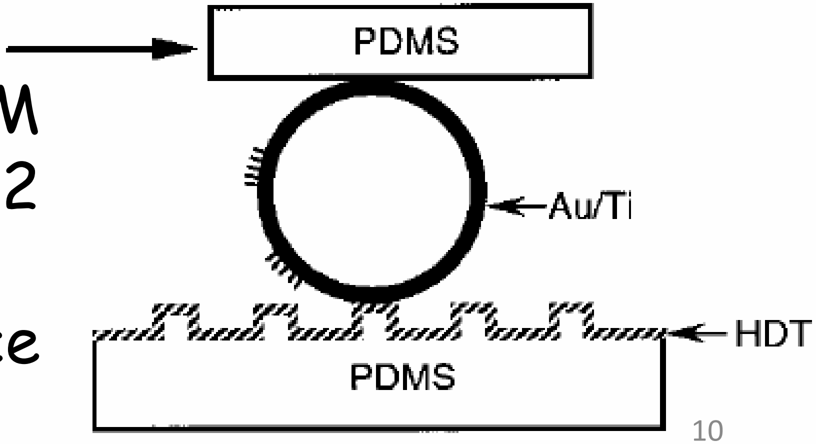
Principles of Microcontact Printing



Roll-to-Roll Printing



Printing on Nonplanar Surface



- Dip PDMS stamp in ~2 mM alkanethiol ethanol solution for 1-2 minutes.
- Press PDMS stamp on gold surface for 10-20s.

Five Components of Soft Lithography

Soft Lithography

- Microcontact printing (μCP)
- Replica molding (REM)
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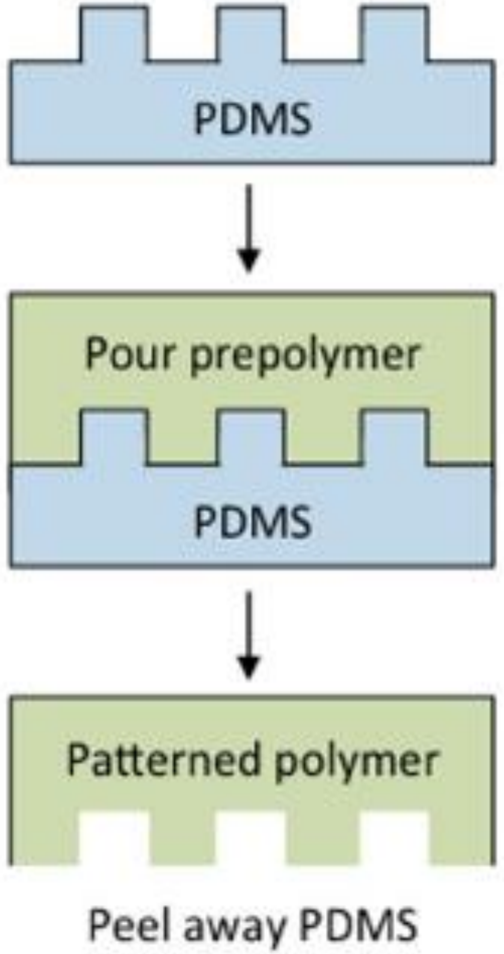
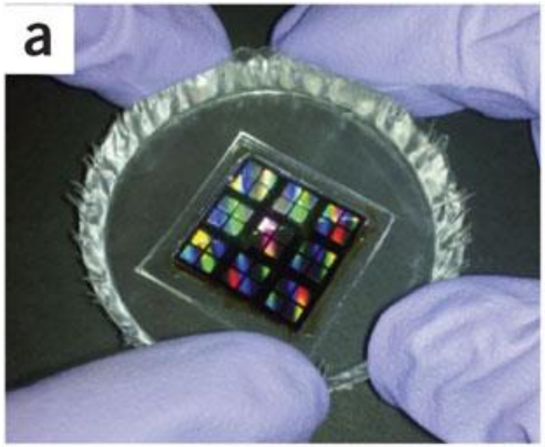
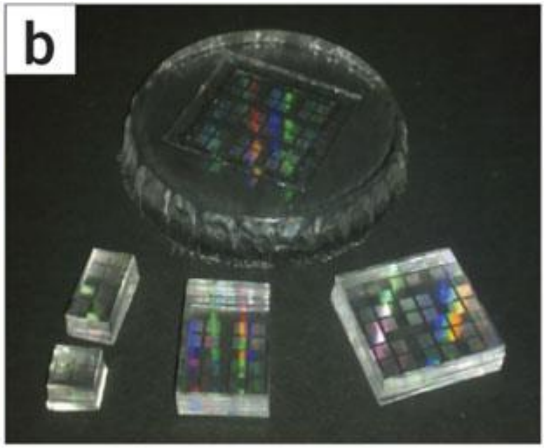


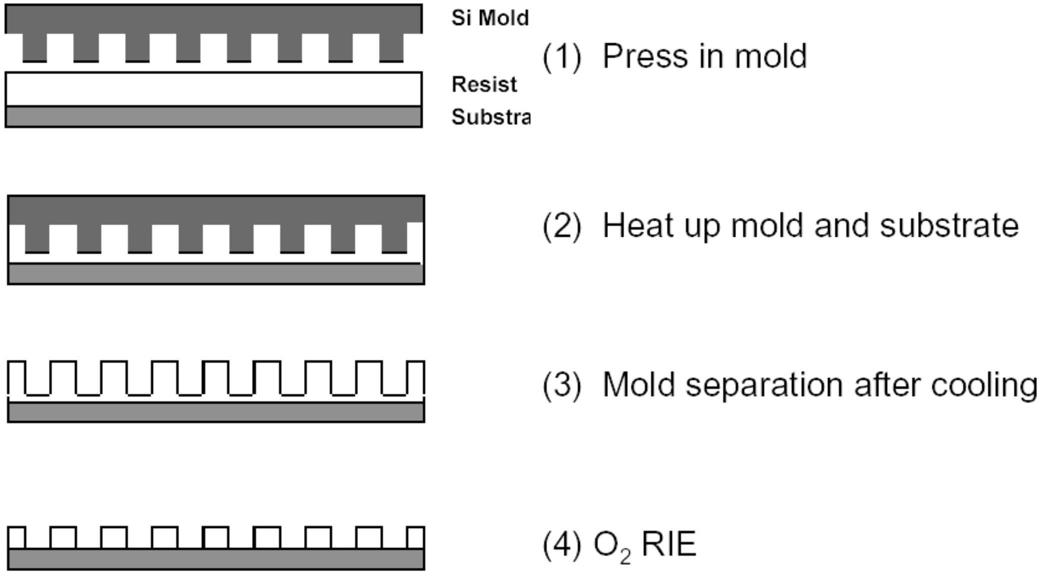
Peel away PDMS



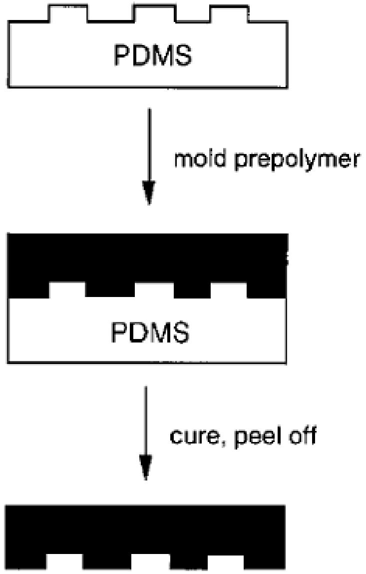


“Soft” Replica Molding

“Rigid-Mask” Molding



“Soft-Mask” Molding

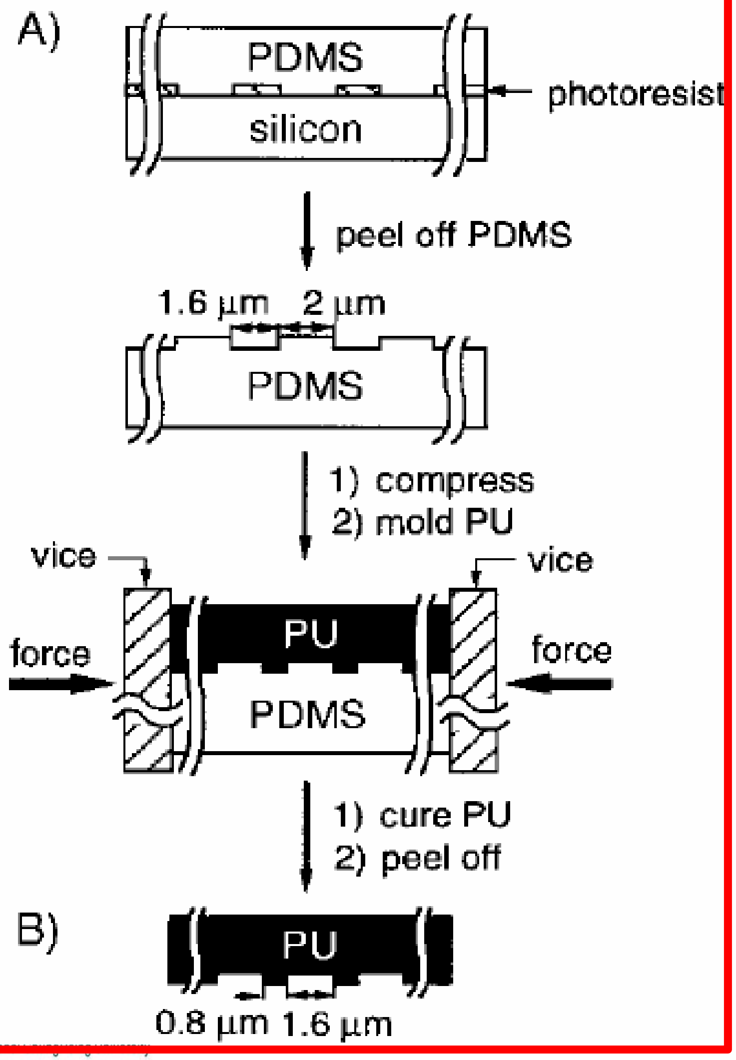


Advantages of soft-mask molding:

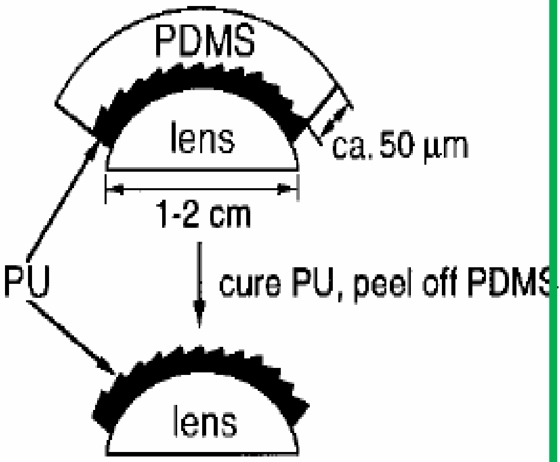
- The elasticity and low surface energy of the elastomeric PDMS mold allows it to be released easily.
- PDMS mold also enables manipulating the size and shape of features present on the mold by mechanical deformation.

Manipulating PDMS Molds

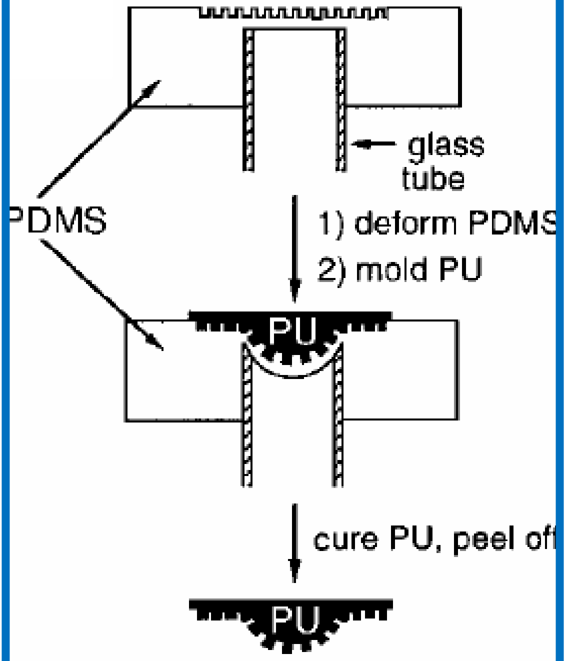
Mechanical Compression



Bending



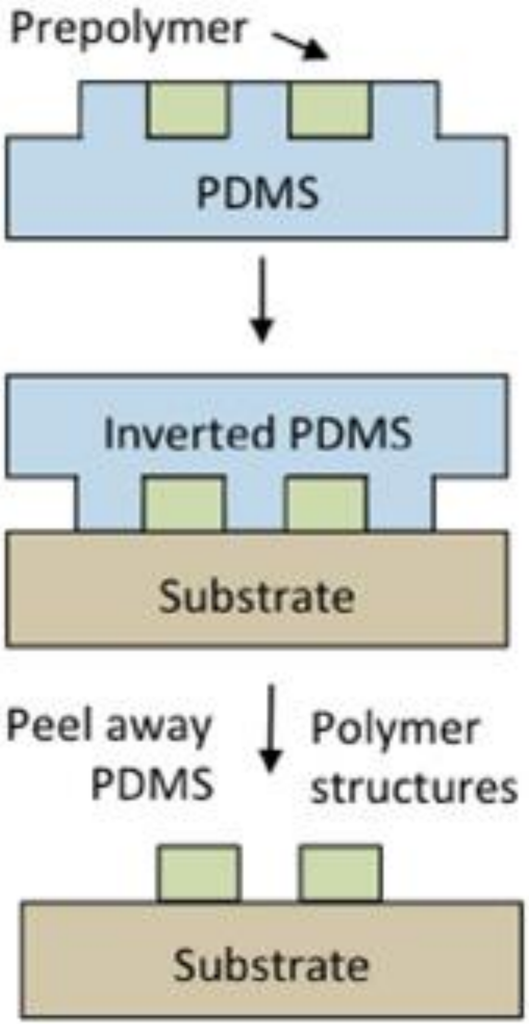
Stretching

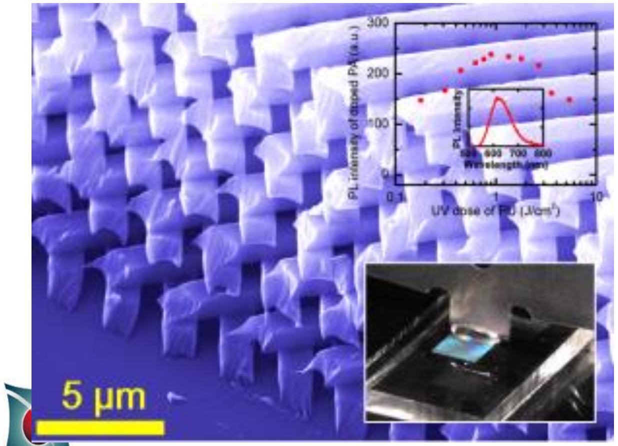


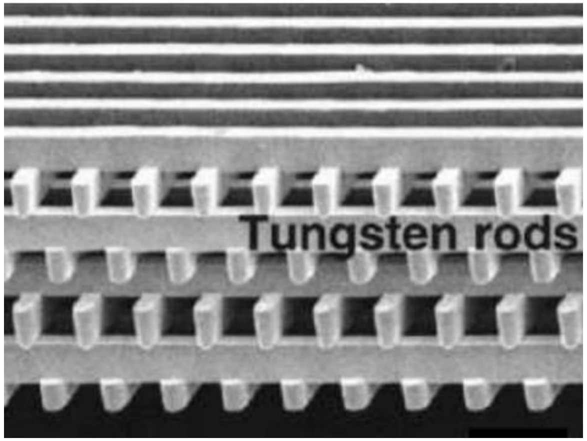
Five Components of Soft Lithography

Soft Lithography

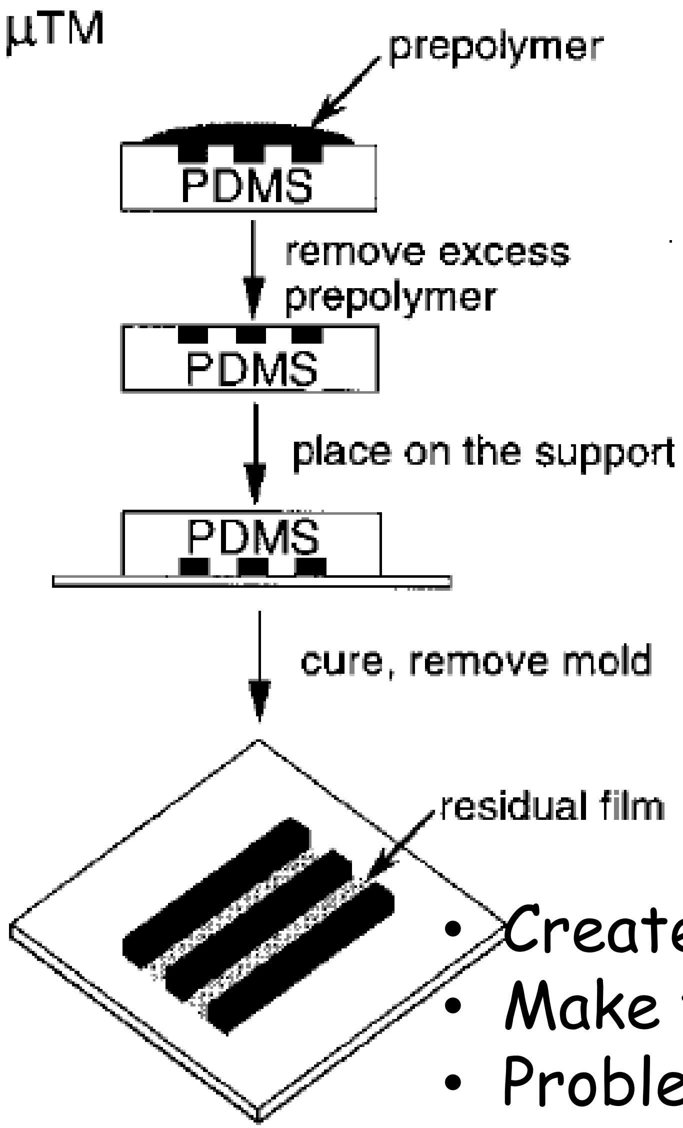
- Microcontact printing (μCP)
- Replica molding (REM)
- Microtransfer molding (μTM)
- Micromolding in capillaries (MIMIC)
- Solvent-assisted micromolding (SAMIM)

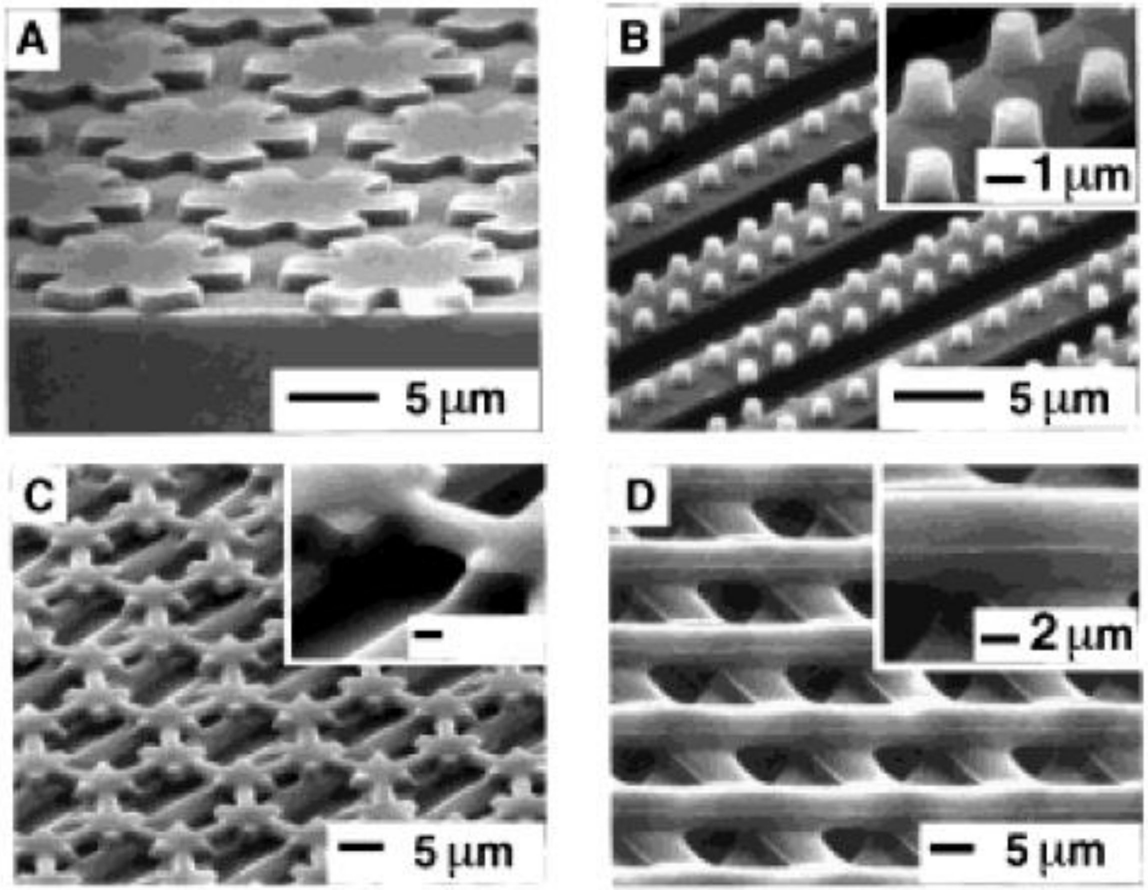






Microtransfer Molding (μTM)





- Create microstructures on nonplanar surfaces.
- Make three-dimensional microstructures.
- Problem: residual film.

Five Components of Soft Lithography

Soft Lithography

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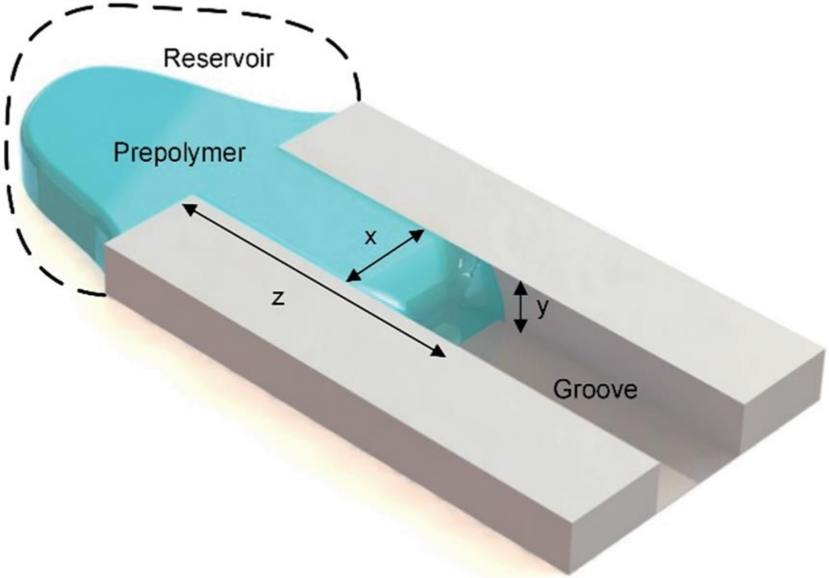
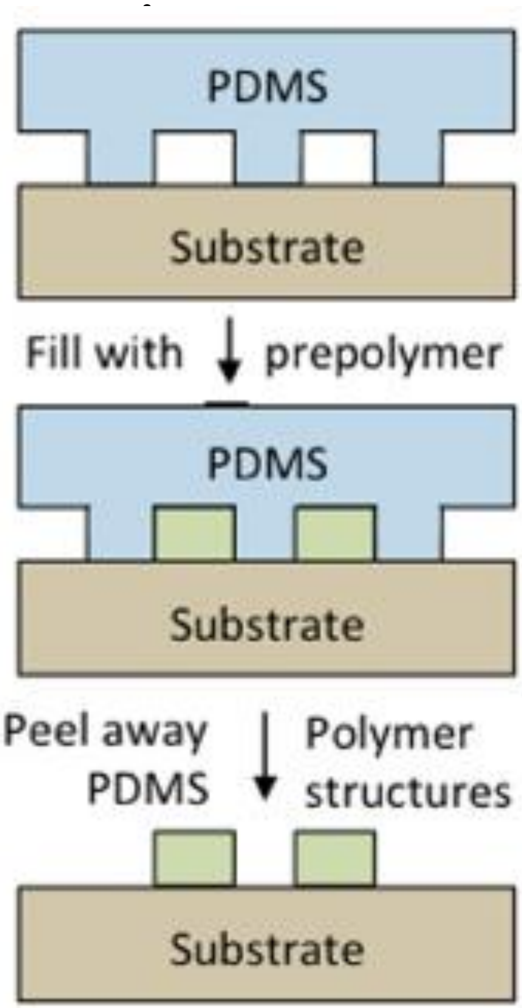
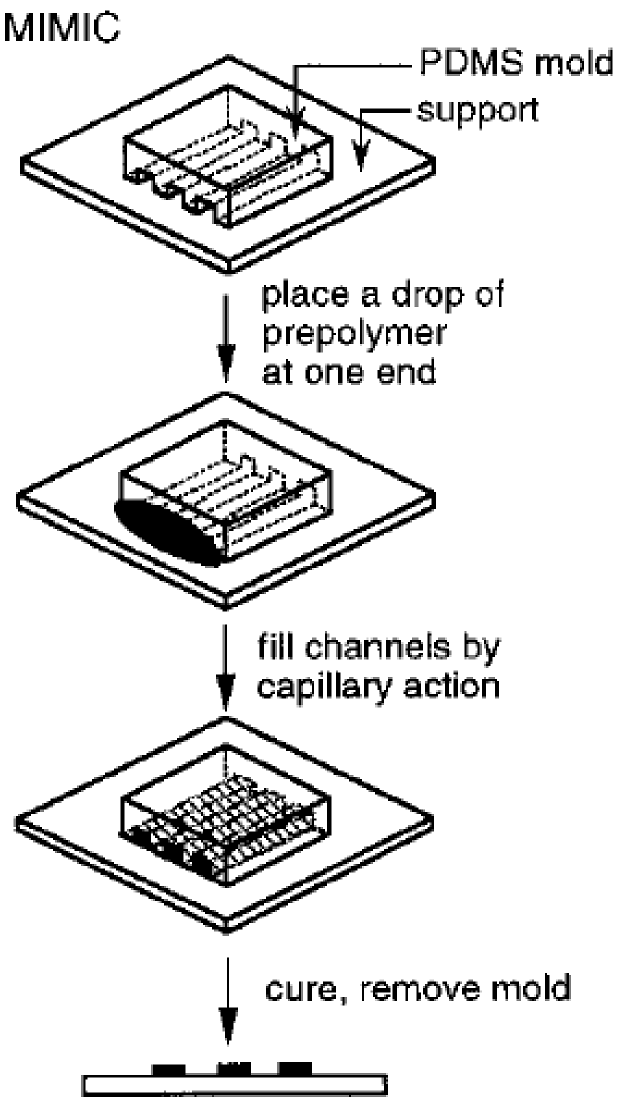
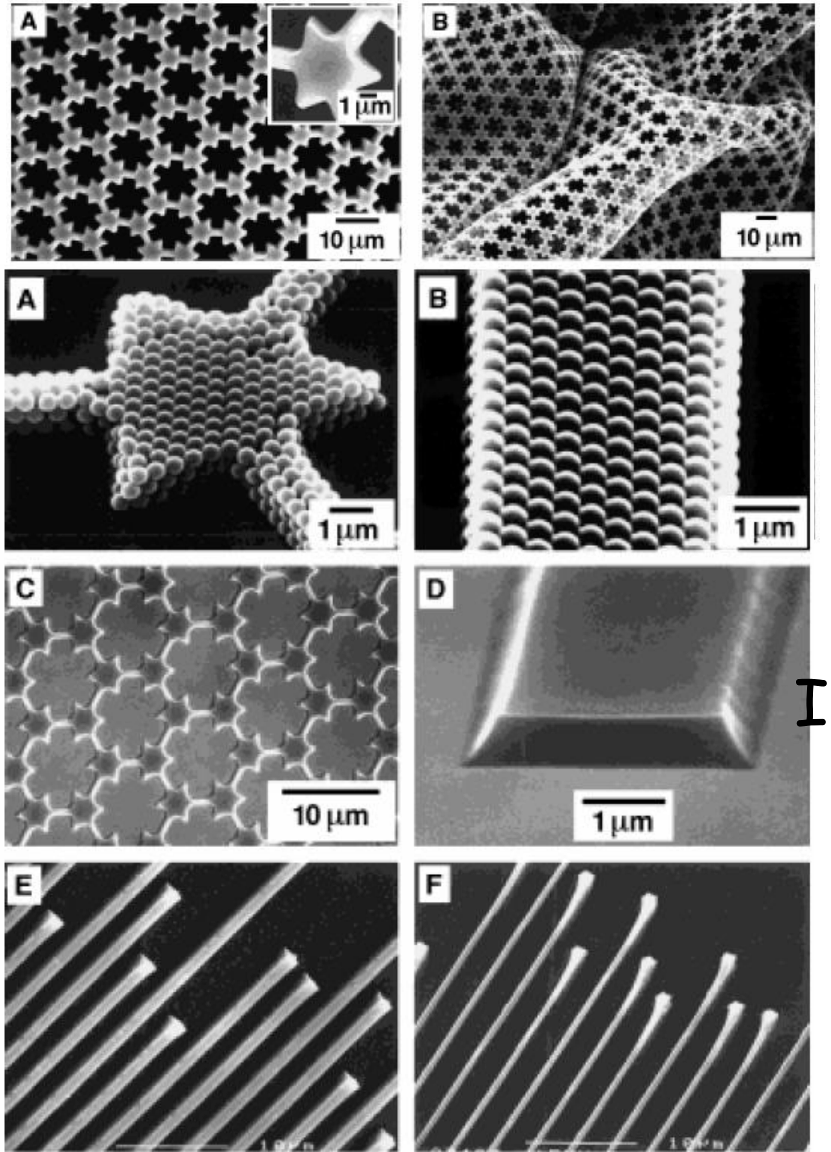




Micromolding in Capillaries (MIMIC)





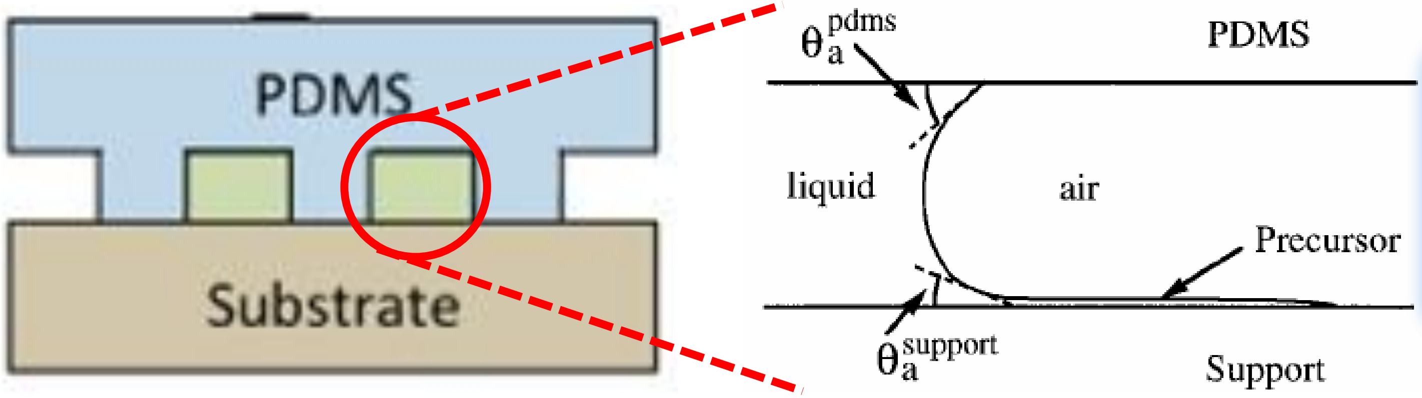
PMMA

Colloids

Inorganic salt

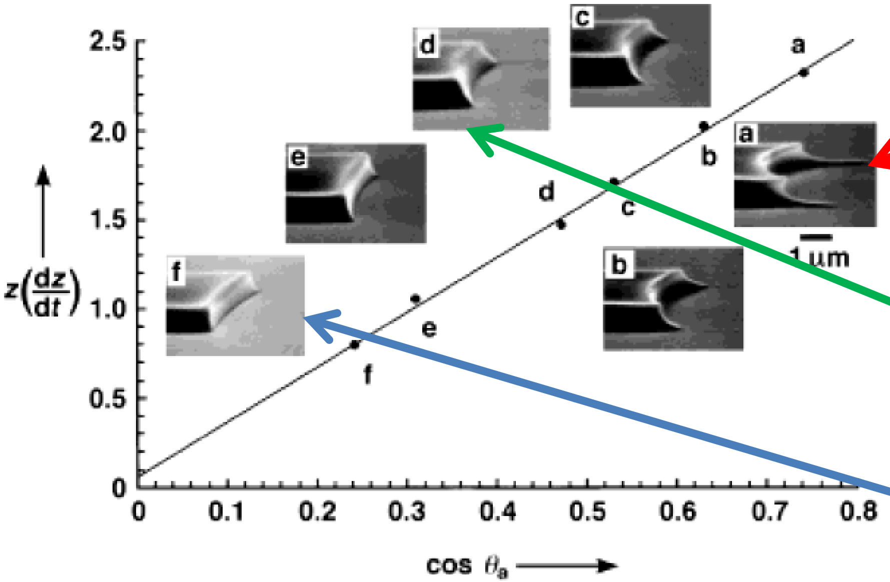
ZrO_2

Principles of Micromolding in Capillaries



most always

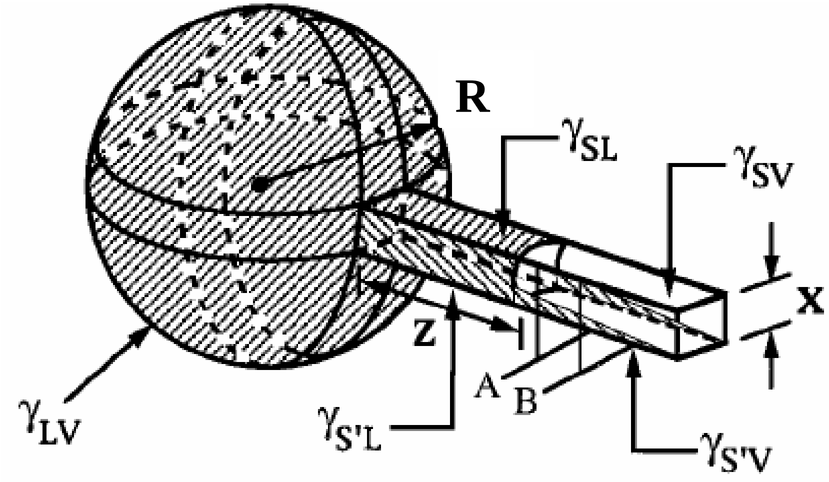
$\theta_a^{pdms} > \theta_a^{support}$



- Small $\theta_a^{support}$: slipping film.
- Intermediate $\theta_a^{support}$: slipping films with shoulders.
- Large $\theta_a^{support}$: wedge flow

Gold substrate with different prepolymers

Rate of Capillary Filling



Rate of capillary filling:

Hydraulic radius

contact angle

$$\boxed{\frac{dz}{dt} = \frac{R\gamma_{LV}\cos\theta}{4\eta z} = \frac{R(\gamma_{SV} - \gamma_{SL})}{4\eta z}}$$

interfacial free energy

viscosity

Square capillary: $R = x^2 z/(4xz)$

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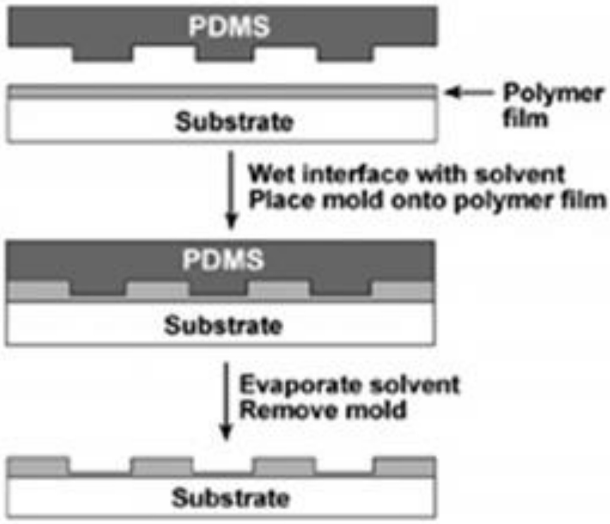
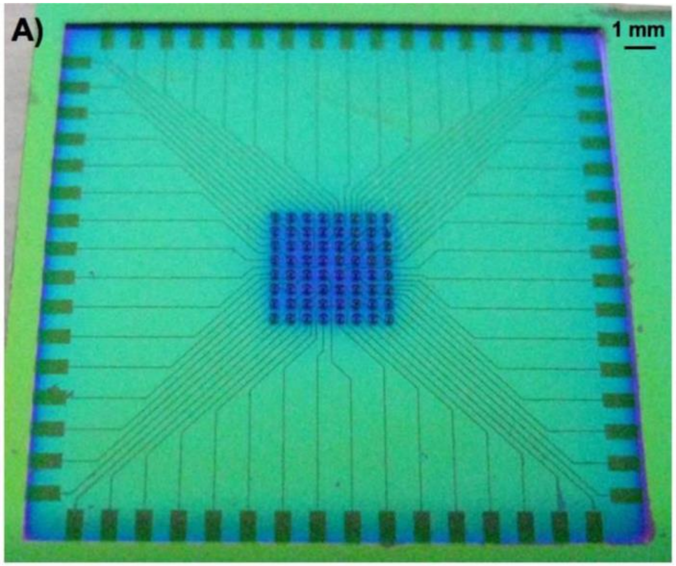
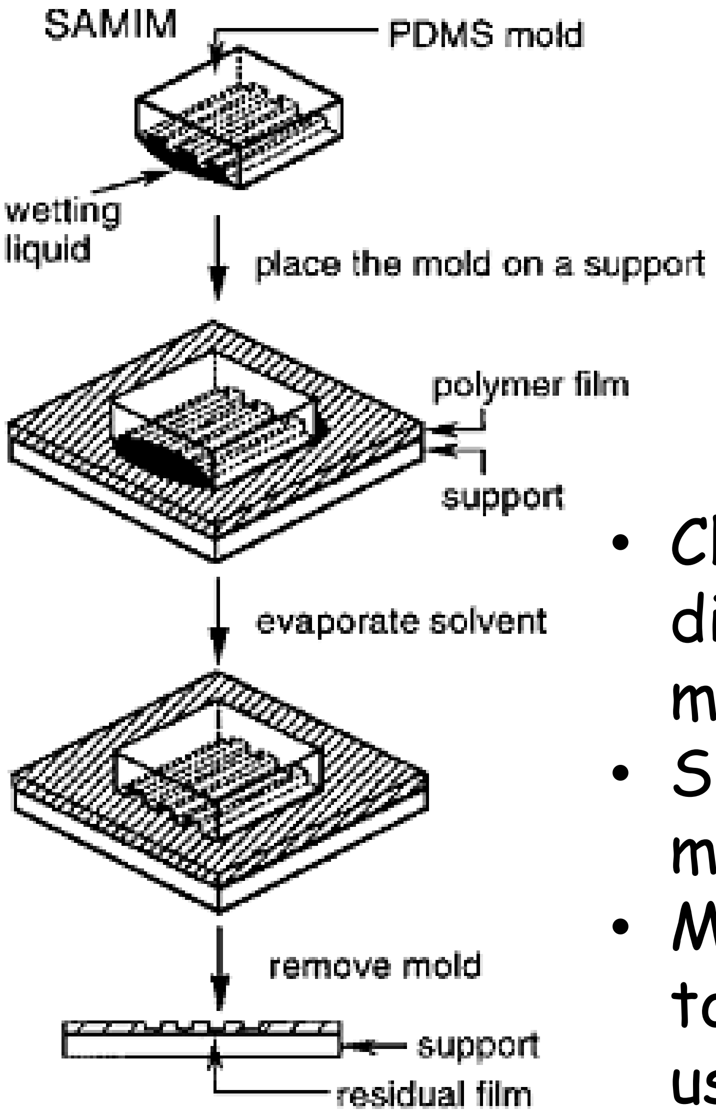
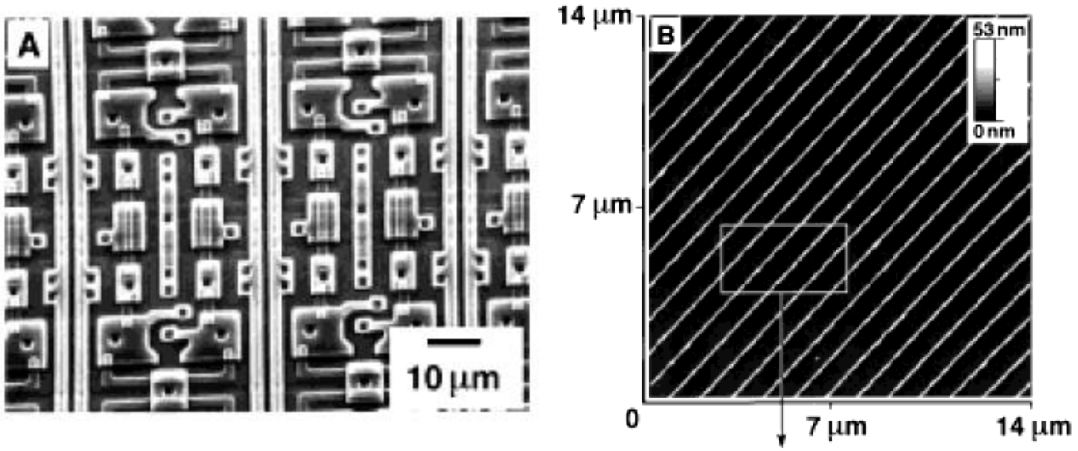




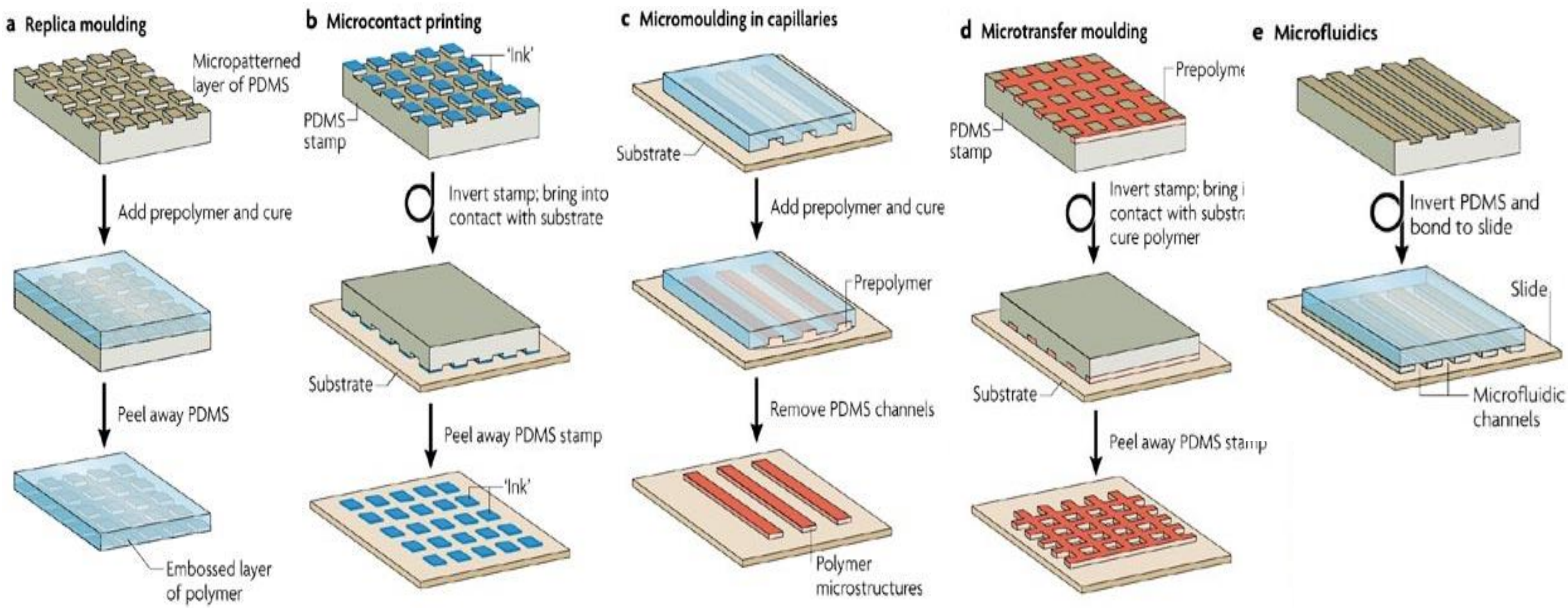
Solvent-Assisted Micromolding (SAMIM)

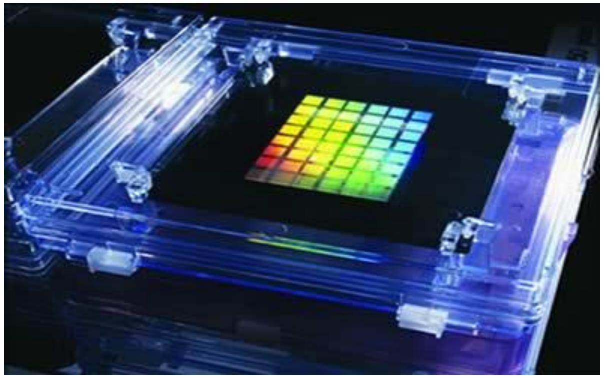


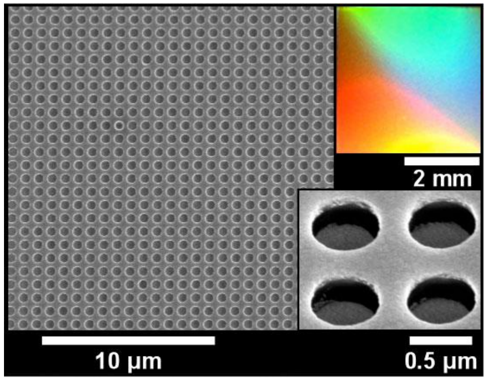


- Choice of solvent is critical – rapidly dissolve or swell polymer, but not PDMS mold.
- Solvent – high vapor pressure and a moderately high surface tension.
- Methanol, ethanol, acetone are good; toluene and dichloromethane can not be used.

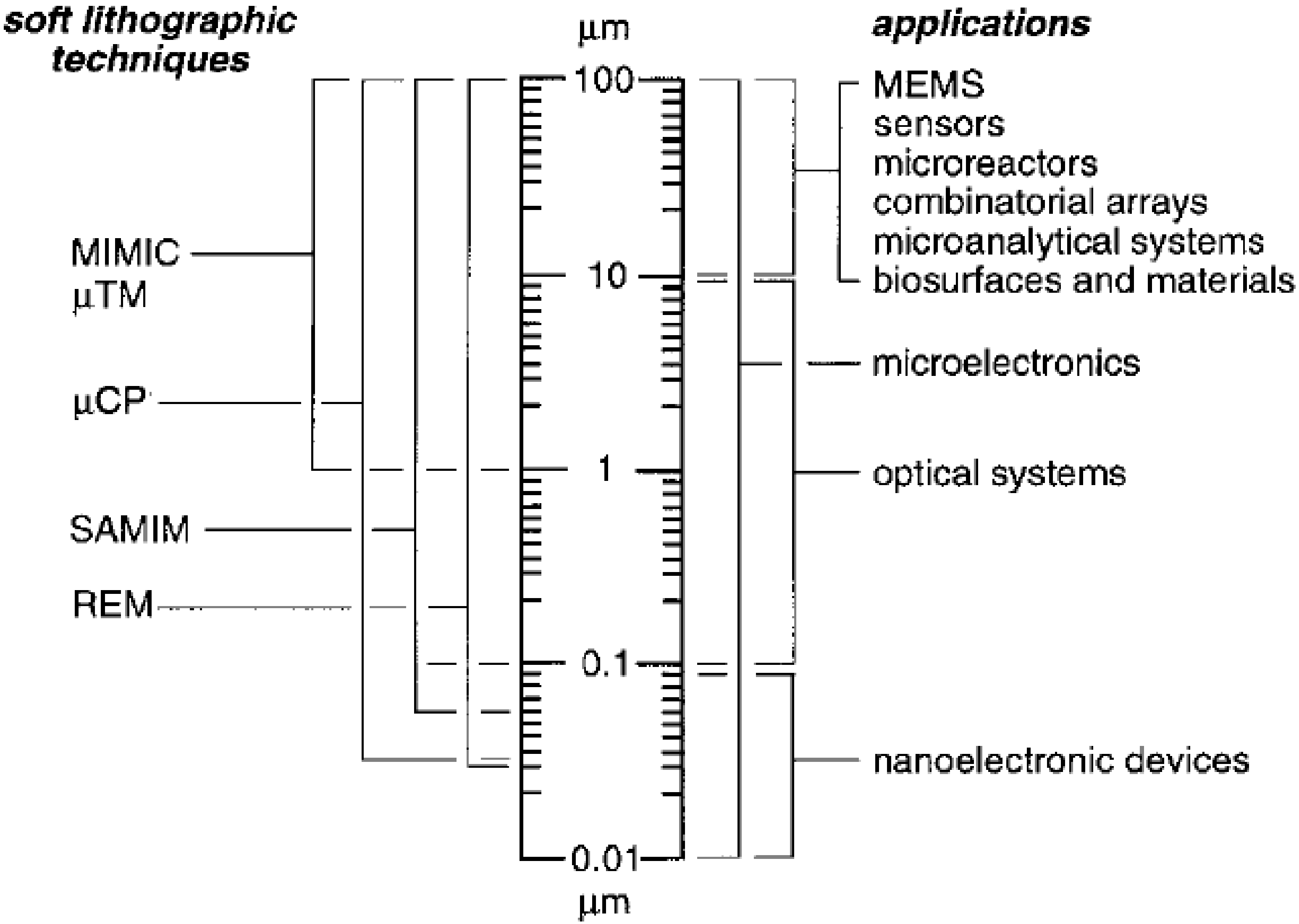
Five Components of Soft Lithography







Applications of Soft Lithography



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Photolithography vs. Soft Lithography

	Photolithography	Soft Lithography
Definition of patterns	Rigid photomask (patterned Cr supported on a quartz plate)	Elastomeric stamp or mold (a PDMS block patterned With relief features)
Materials that can be patterned directly	Photoresist (polymers with photosensitive additives) SAMs	SAMs Unsensitized polymers (epoxy, PU, PMMA, PPV, etc.) Polymer precursors Colloidal materials Sol-gel materials Organic and inorganic salts Biological macromolecules
Minimum feature size	ca. 60 nm	1 - 100 nm

Advantages of Soft Lithography

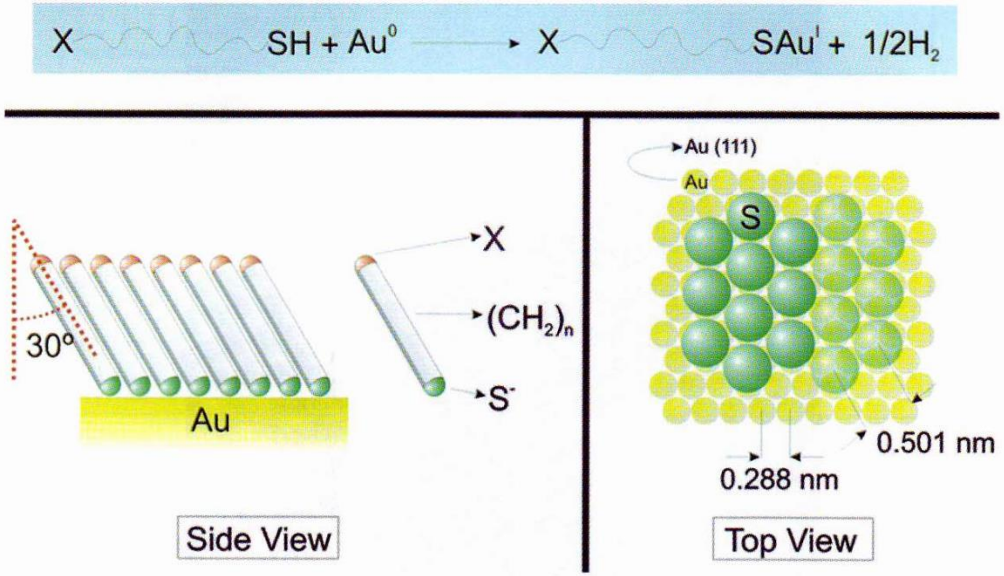
- Convenient, inexpensive, accessible to chemists, biologists, and material scientists.
- Basis in self-assembly tends to minimize certain types of defects.
- Many soft lithographic processes are additive and minimize waste of materials.
- Isotropic mechanical deformation of PDMS mold or stamp provides routes to complex patterns.
- No diffraction limit; features as small as 30 nm have been fabricated.
- Nonplanar surfaces (lenses) can be used as substrates.
- Generation and replication of 3D topologies or structures are possible.
- Optical transparency of the mask allows through-mask registration and processing.
- Good control over surface chemistry, very useful for interfacial engineering.
- Applicable to manufacturing: production of indistinguishable copies at low cost.

Disadvantages of Soft Lithography

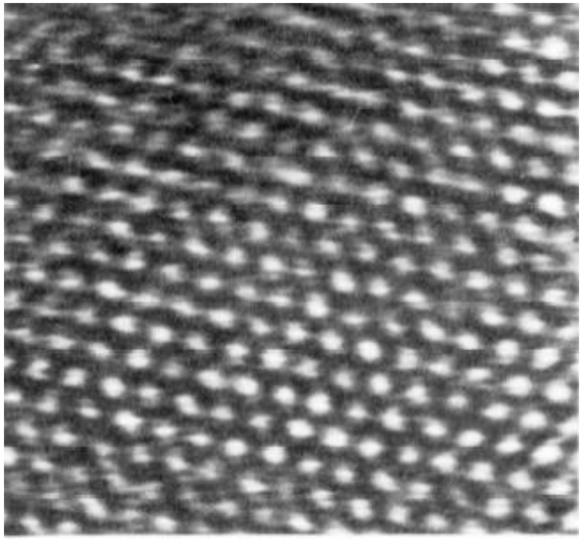
- Patterns in the stamp or mold may distort due to the deformation (pairing, sagging, swelling, and shrinking) of the elastomer used.
- Difficulty in achieving accurate registration with elastomers (<1 μm).
- Compatibility with current integrate-circuit processes and materials must be demonstrated.
- Defect levels higher than photolithography.
- μCP works well with only a limited range of surfaces; MIMIC is slow; REM, μTM, and SAMIM leave a thin film of polymer over the surface.

Self-Assembled Monolayers (SAMs)

Oxidative addition:



Hexanethiolate SAM On Au (111)

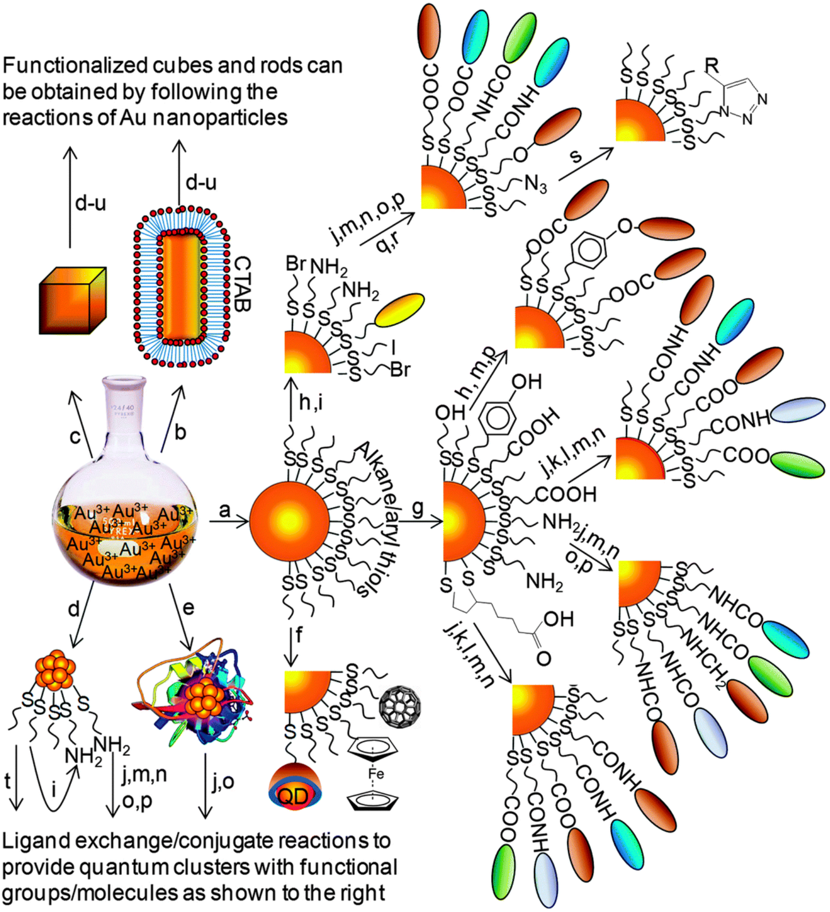


(J. Am. Chem. Soc. 114, 1222, 1992)

- The real power of SAMs stems from the ability to chemically tailor the terminal X groups of the alkanethiolate.
- Surface organic chemistry allows controlling surface wettability, adhesion, corrosion, etch protection, chemical and electrochemical reactivity, etc.

Substrates and Ligands that Form SAMs

Substrate	Ligand or Precursor	Binding
Au	RSH, ArSH (thiols)	RS–Au
Au	RSSR′ (disulfides)	RS–Au
Au	RSR′ (sulfides)	RS–Au
Au	RSO_2H	RSO_2–Au
Au	R_3P	R_3P–Au
Ag	RSH, ArSH	RS–Ag
Cu	RSH, ArSH	RS–Cu
Pd	RSH, ArSH	RS–Pd
Pt	RNC	RNC–Pt
GaAs	RSH	RS–GaAs
InP	RSH	RS–InP
SiO_2, glass	$RSiCl_3$, $RSi(OR')_3$	siloxane
Si/Si–H	$(RCOO)_2$ (neat)	R–Si
Si/Si–H	$RCH{=}CH_2$	RCH_2CH_2Si
Si/Si–Cl	RLi, RMgX	R–Si
metal oxides	RCOOH	$RCOO^- \cdots MO_n$
metal oxides	RCONHOH	$RCONHOH \cdots MO_n$
ZrO_2	RPO_3H_2	$RPO_3^{2-} \cdots Zr^{IV}$
In_2O_3/SnO_2 (ITO)	RPO_3H_2	$RPO_3^{2-} \cdots M^{n+}$

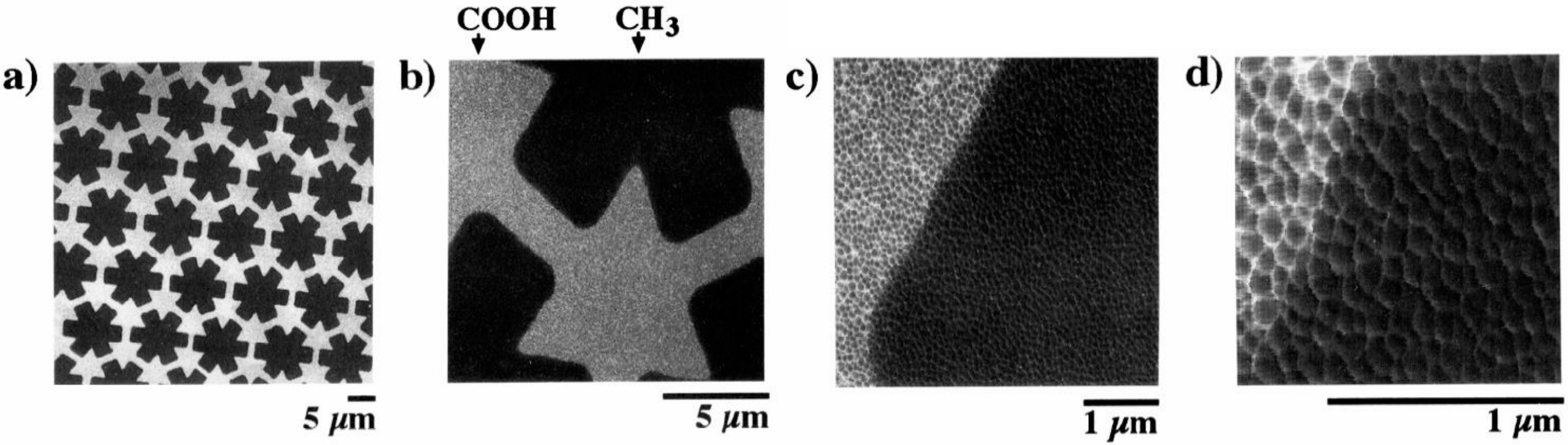


Functionalized cubes and rods can be obtained by following the reactions of Au nanoparticles

Ligand exchange/conjugate reactions to provide quantum clusters with functional groups/molecules as shown to the right

SAMs with Different Head Groups

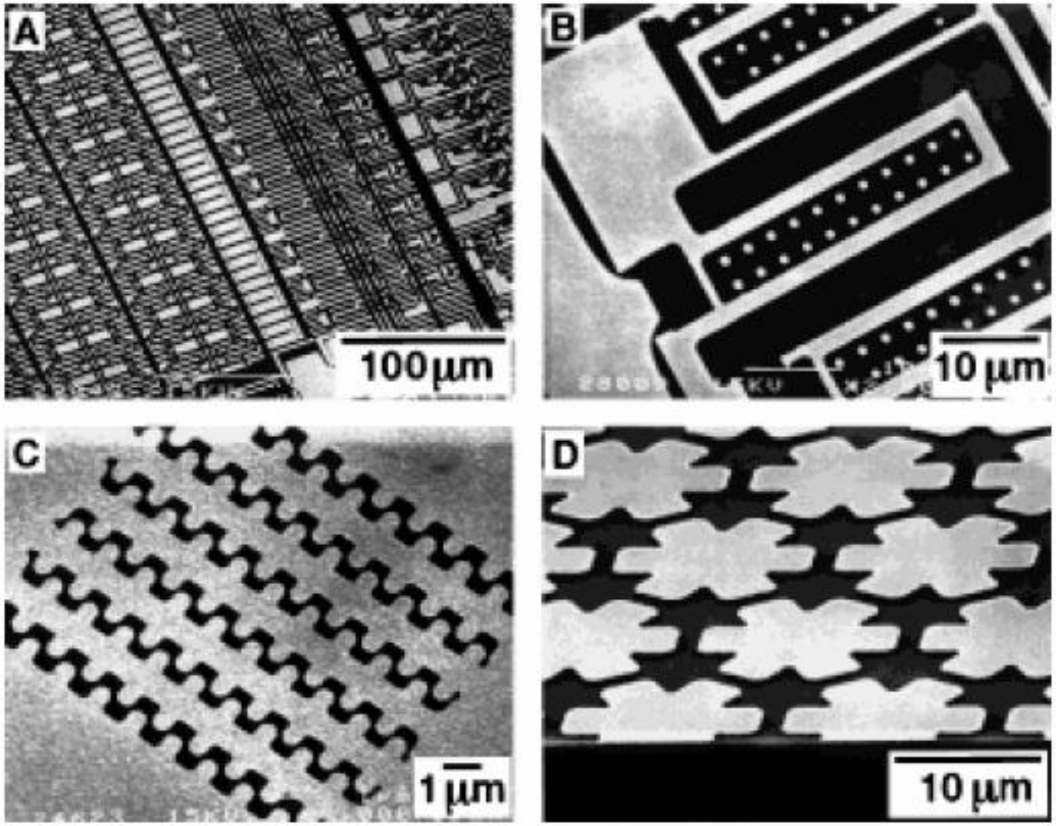
Lateral Force Microscope (Contact Mode AFM)



- μCPed $HS(CH_2)_{15}CH_3$ followed by adsorption of $HS(CH_2)_{15}COOH$.
- The contrast arose from differences in the fractional force between the AFM tip and the surface in each region.

(*Langmuir* 11, 825, 1995)

Patterned SAMs as Ultrathin Resists in Selective Wet Etching

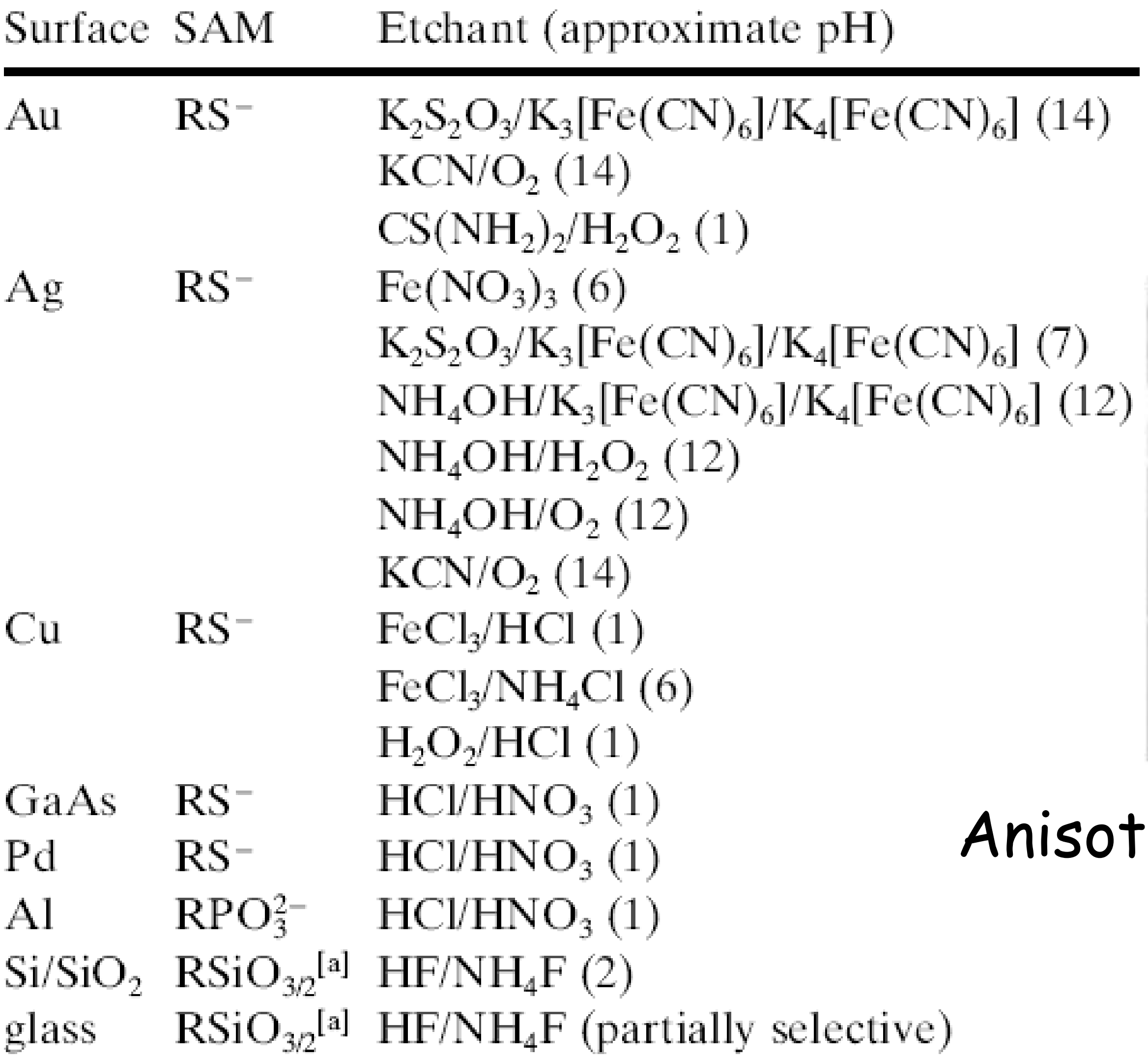


Representative Au wet-etch chemistry:

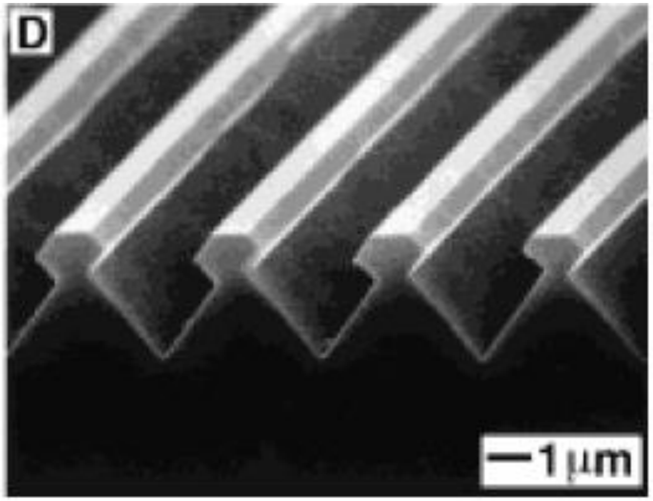
$$4Au + 8CN^- + O_2 + 2H_2O \longrightarrow 4[Au(CN)_2]^- + 4OH^-$$

$$Au + 2CN^- + [Fe(CN)_6]^{3-} \longrightarrow [Fe(CN)_6]^{4-} + [Au(CN)_2]^-$$

Etchants Used with Patterned SAMs



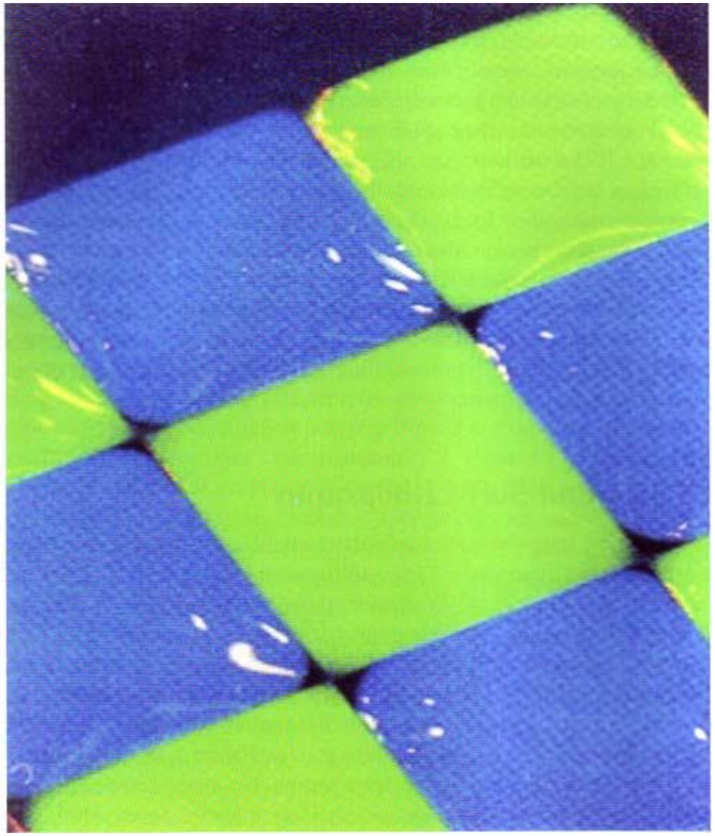
Surface	SAM	Etchant (approximate pH)
Au	RS^-	$K_2S_2O_3/K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (14)
		KCN/O_2 (14)
		$CS(NH_2)_2/H_2O_2$ (1)
Ag	RS^-	$Fe(NO_3)_3$ (6)
		$K_2S_2O_3/K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (7)
		$NH_4OH/K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (12)
		NH_4OH/H_2O_2 (12)
		NH_4OH/O_2 (12)
		KCN/O_2 (14)
Cu	RS^-	$FeCl_3/HCl$ (1)
		$FeCl_3/NH_4Cl$ (6)
		H_2O_2/HCl (1)
GaAs	RS^-	HCl/HNO_3 (1)
Pd	RS^-	HCl/HNO_3 (1)
Al	RPO_3^{2-}	HCl/HNO_3 (1)
Si/SiO_2	$RSiO_{3/2}$[a]	HF/NH_4F (2)
glass	$RSiO_{3/2}$[a]	HF/NH_4F (partially selective)



Anisotropic etching of Si (100)

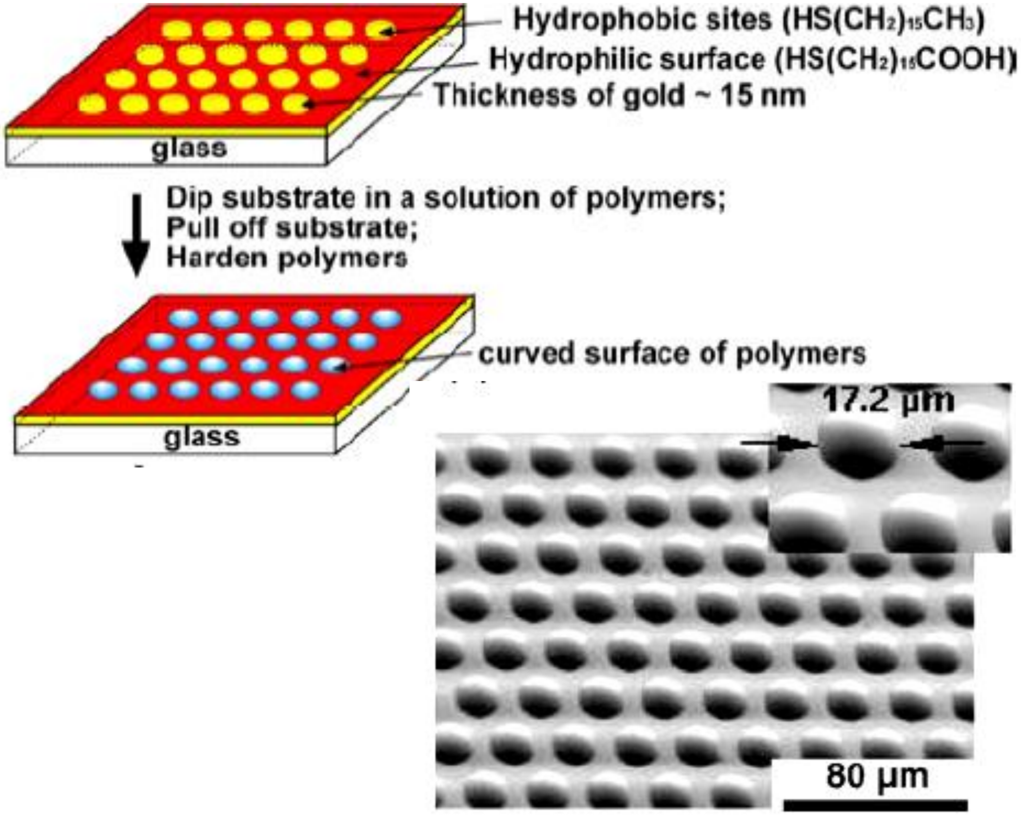
Patterning Wettability

Condensation Figures



Square drops of water held by surrounding hydrophobic lines.

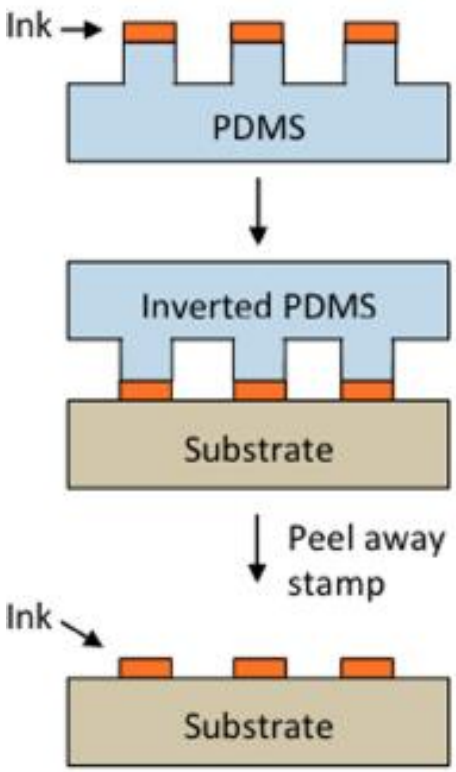
Microlens Arrays

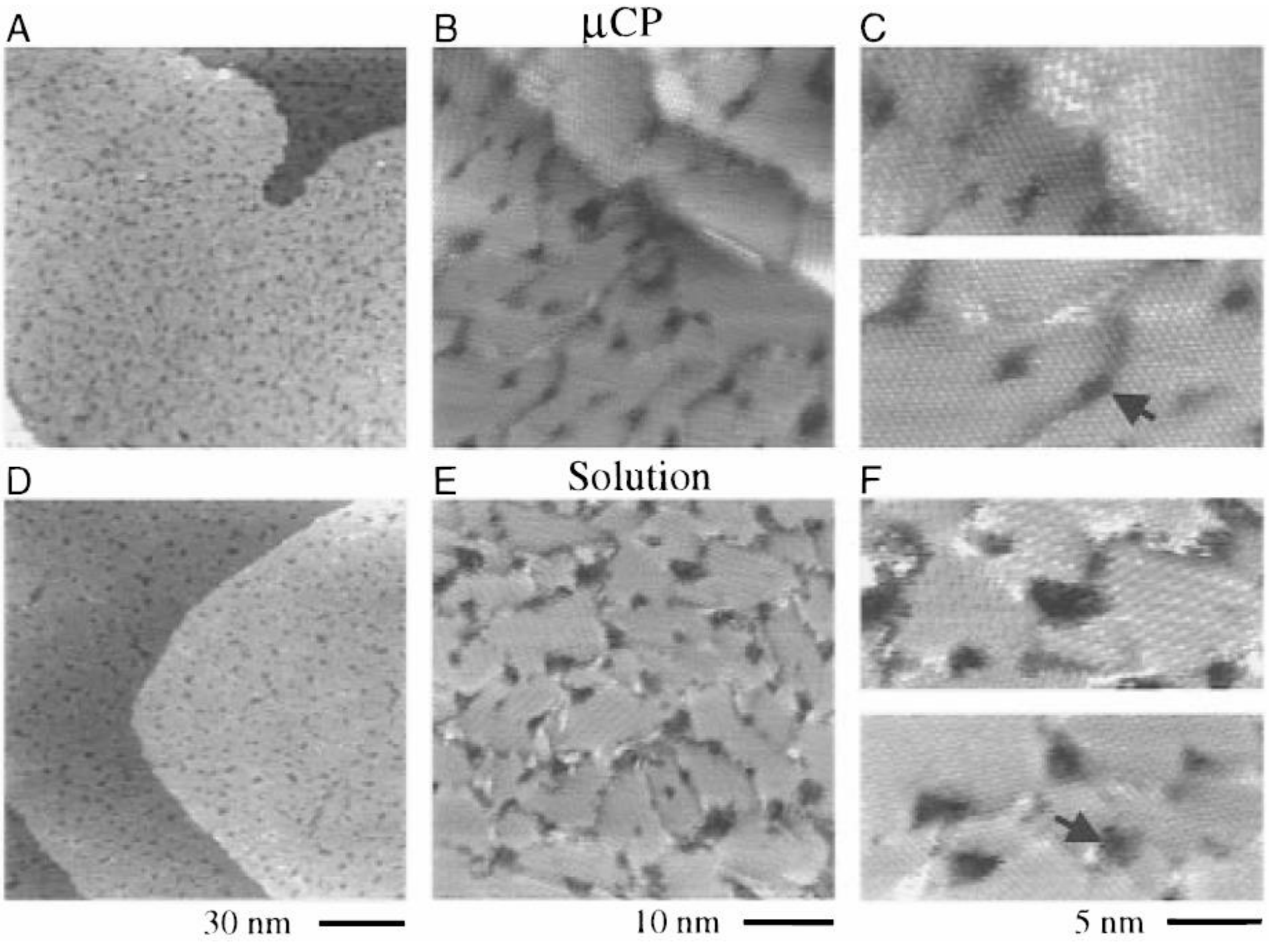


Polyurethane precursors selectively wet patterned hydrophobic regions

SAMs Formed by μCP vs. Adsorption

μCP

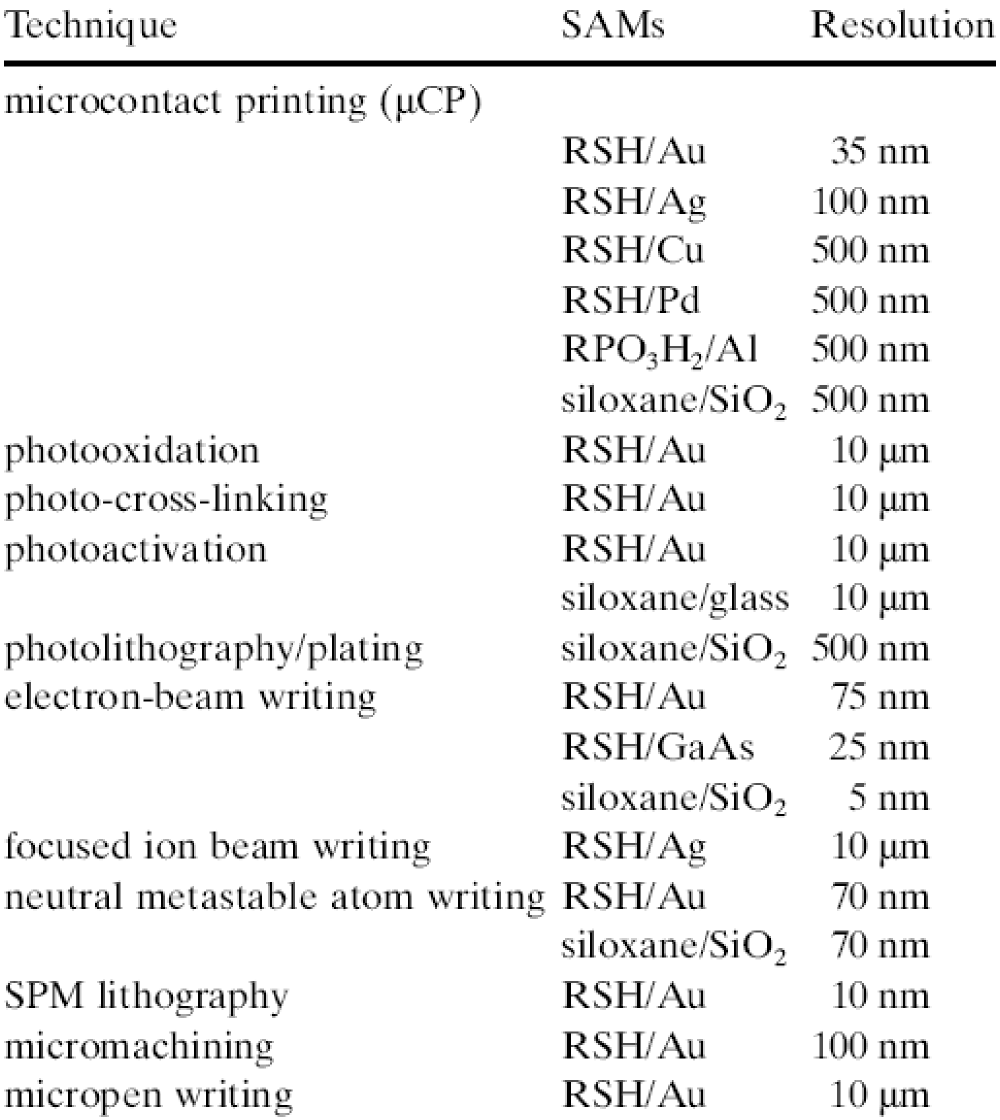




Similarity between μCP and adsorption from solution.

(J. Am. Chem. Soc. 119, 3017, 1997)

μCP vs. other SAMs Patterning Techniques



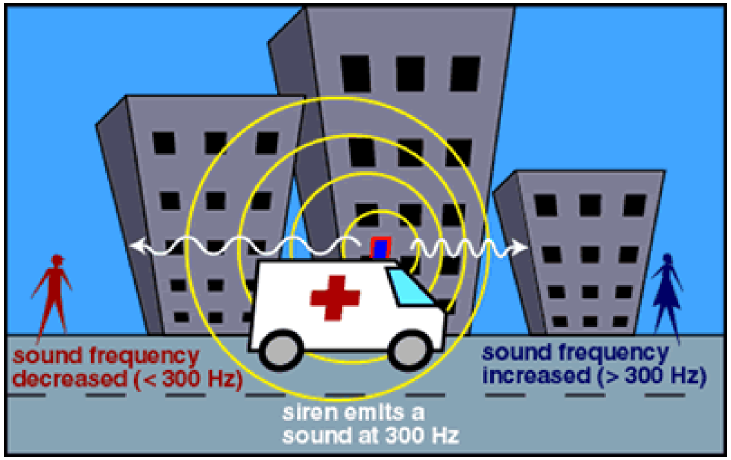
Technique	SAMs	Resolution
microcontact printing (μCP)		
	RSH/Au	35 nm
	RSH/Ag	100 nm
	RSH/Cu	500 nm
	RSH/Pd	500 nm
	RPO_3H_2/Al	500 nm
	siloxane/SiO_2	500 nm
photooxidation	RSH/Au	10 μm
photo-cross-linking	RSH/Au	10 μm
photoactivation	RSH/Au	10 μm
	siloxane/glass	10 μm
photolithography/plating	siloxane/SiO_2	500 nm
electron-beam writing	RSH/Au	75 nm
	RSH/GaAs	25 nm
	siloxane/SiO_2	5 nm
focused ion beam writing	RSH/Ag	10 μm
neutral metastable atom writing	RSH/Au	70 nm
	siloxane/SiO_2	70 nm
SPM lithography	RSH/Au	10 nm
micromachining	RSH/Au	100 nm
micropen writing	RSH/Au	10 μm

Invisible Materials

國立中興大學
National ChungHsing University

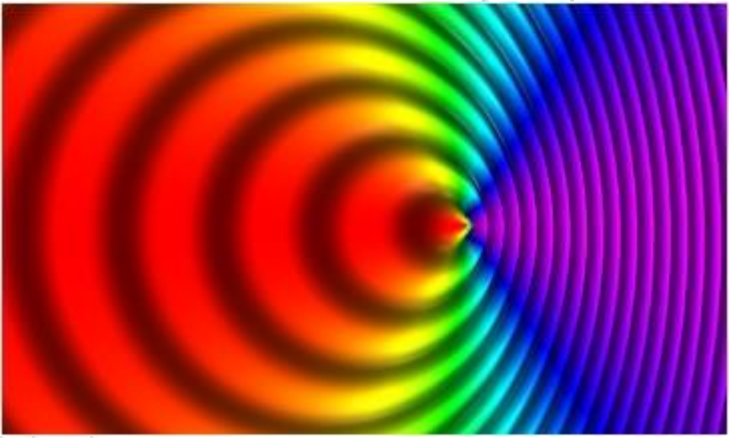

på hela världen åt
resia
Vi har flyttat 121 meter ditåt

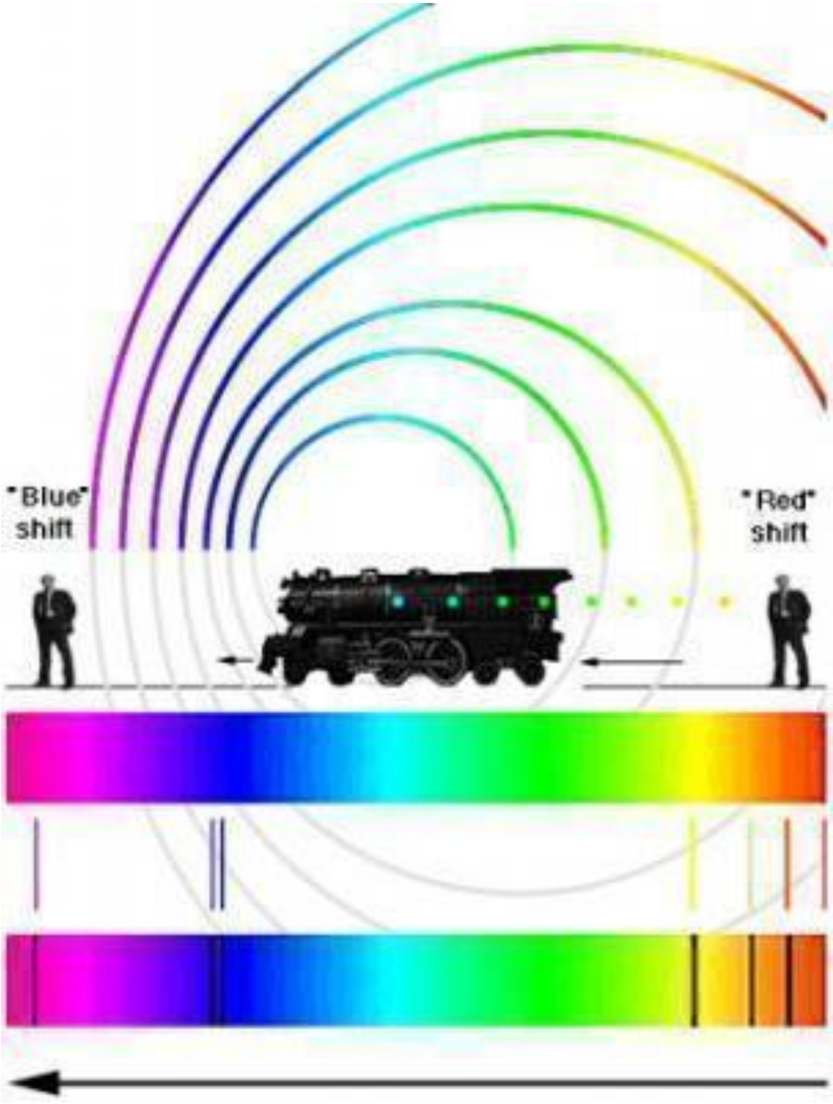
Doppler Effect



Doppler Effect

$$f_o = f_s \left(\frac{v \pm v_o}{v \mp v_s}\right)$$



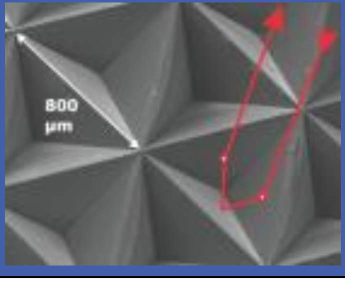


Run! Run! The Flash Run!

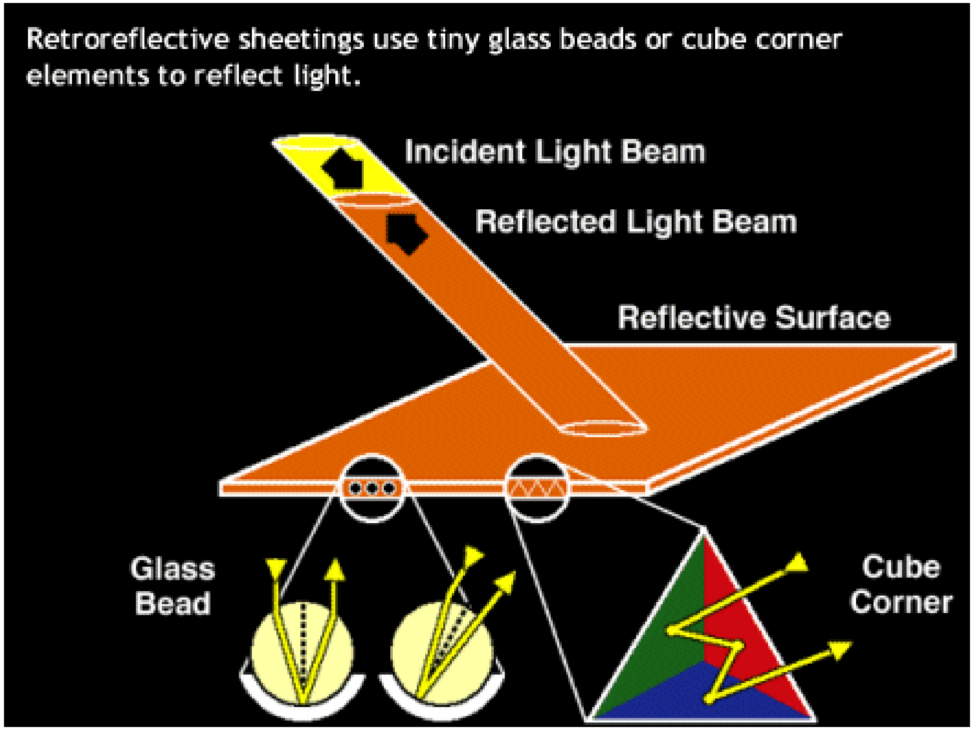

No Reason
Coca-Cola


Enjoy!
Coca-Cola

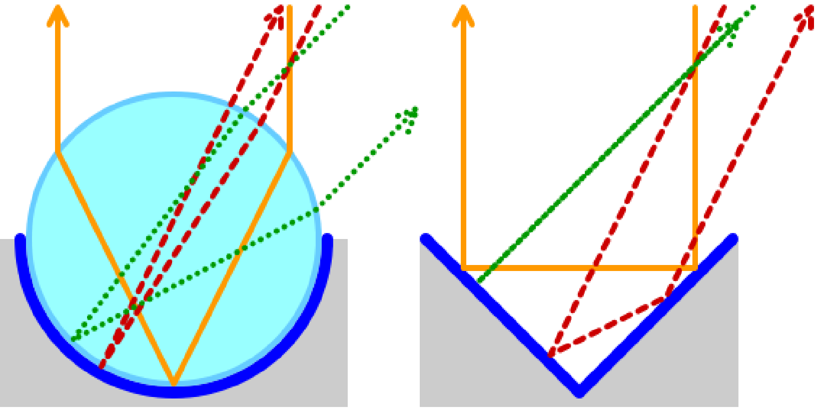
Retroreflective Coatings

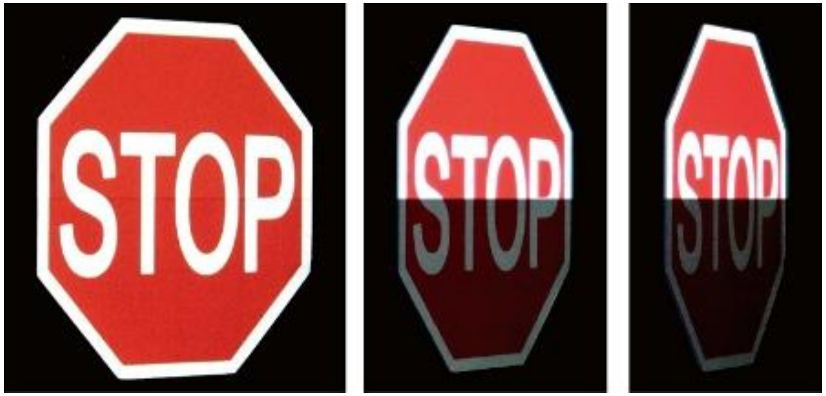


Retroreflection Mechanism

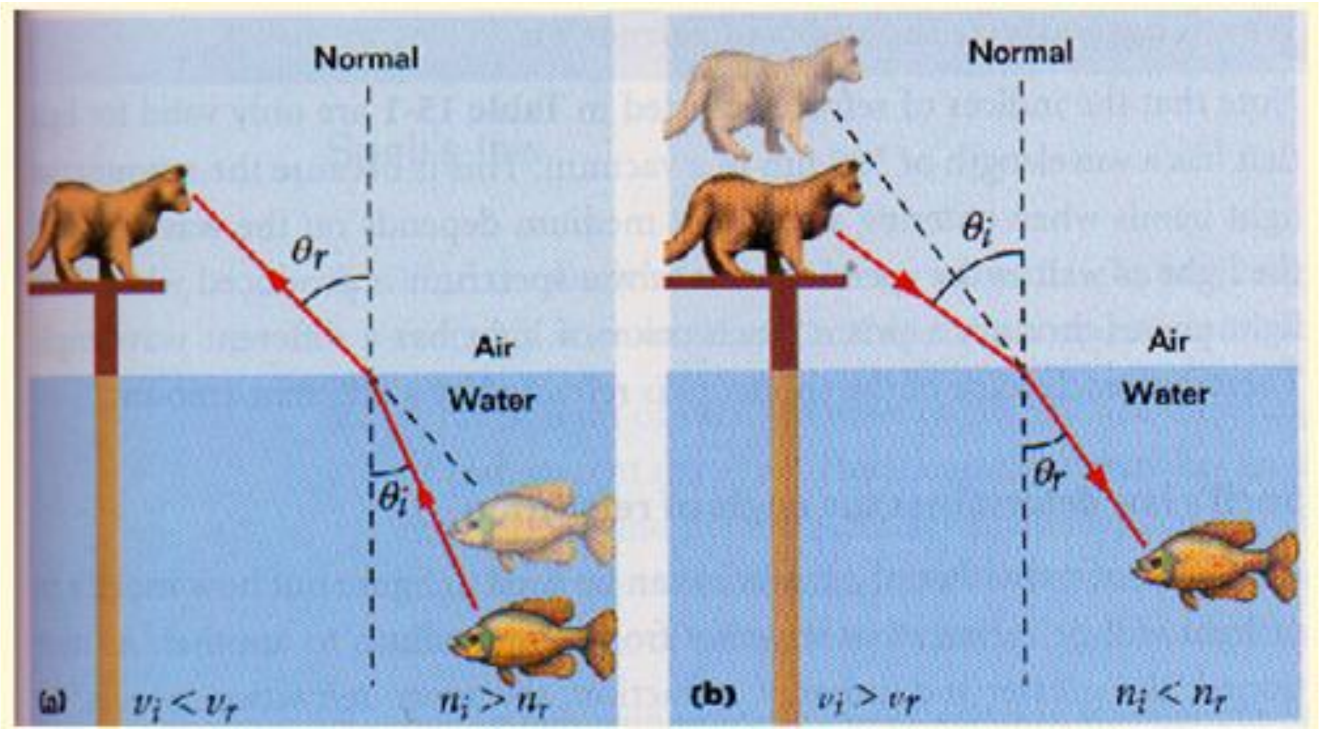


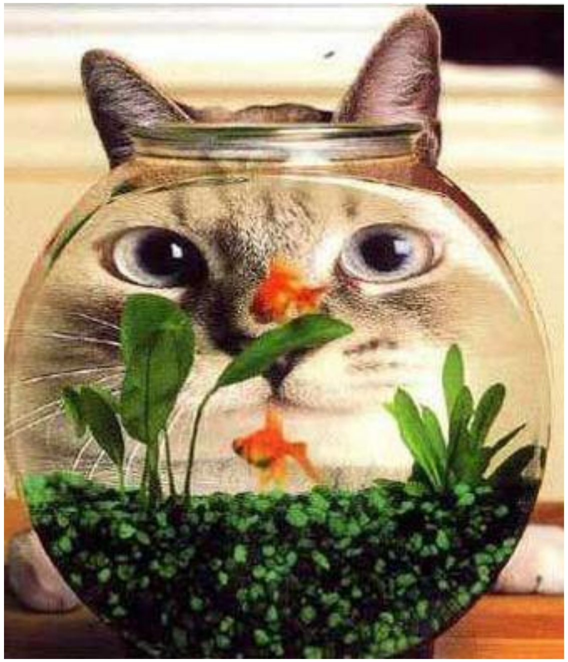
Retroreflective sheetings use tiny glass beads or cube corner elements to reflect light.





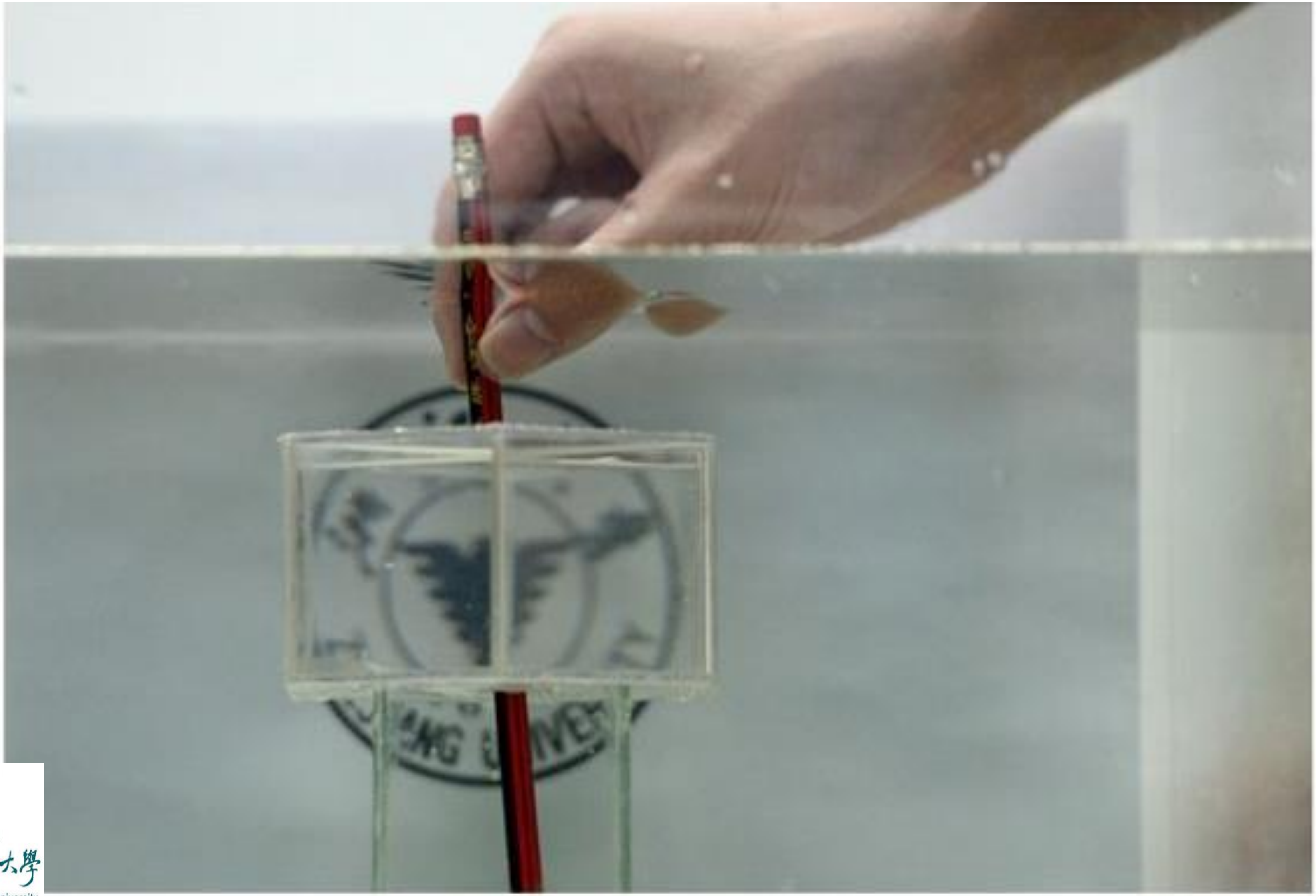
The Cat and The Fish



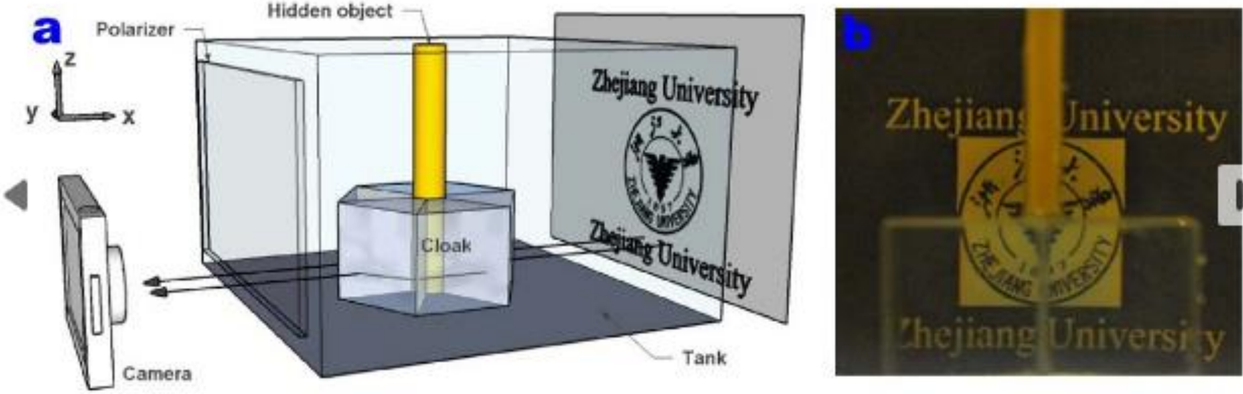


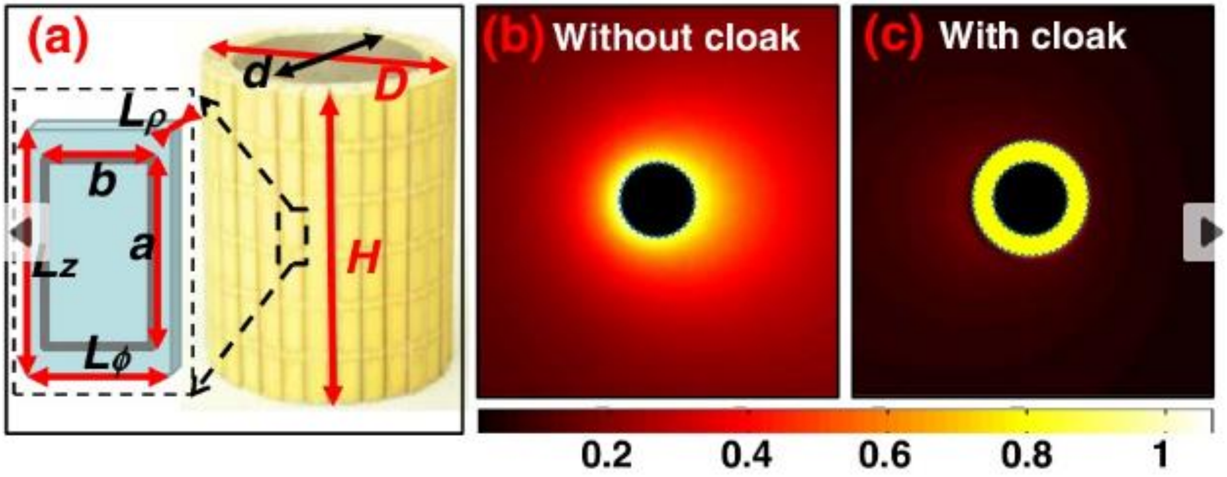
The light is refracted toward the normal when it passes into a denser medium.

Invisible Cloak by Zhejiang University

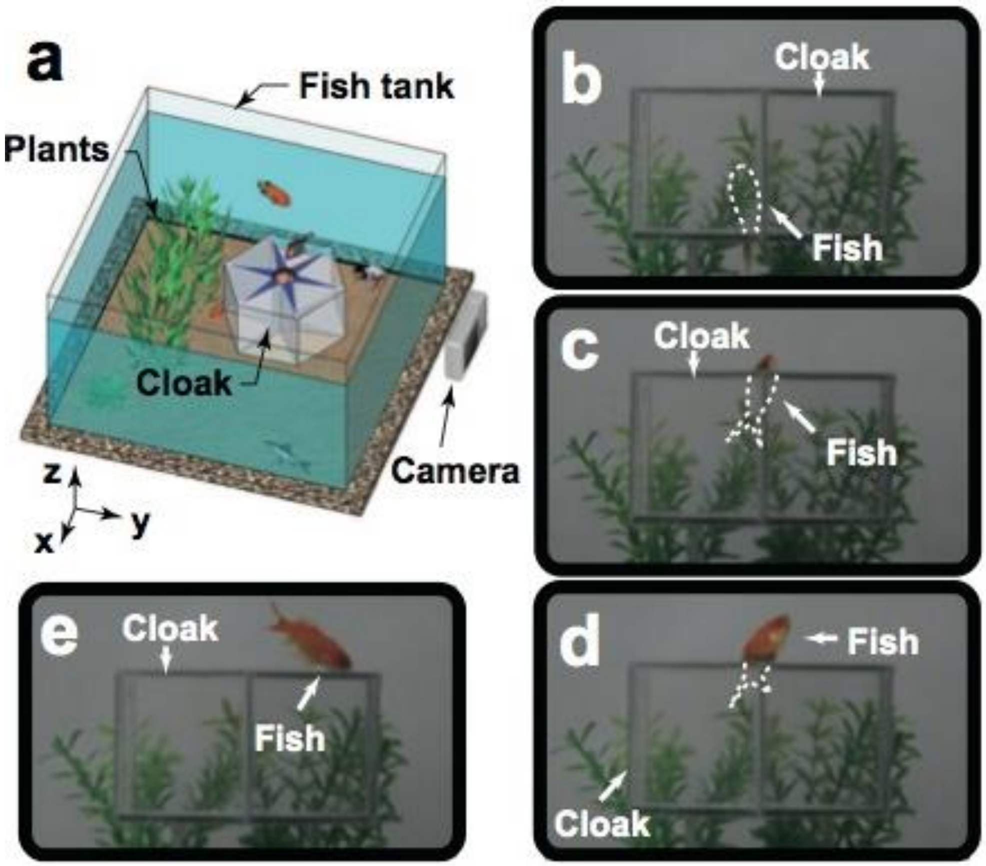


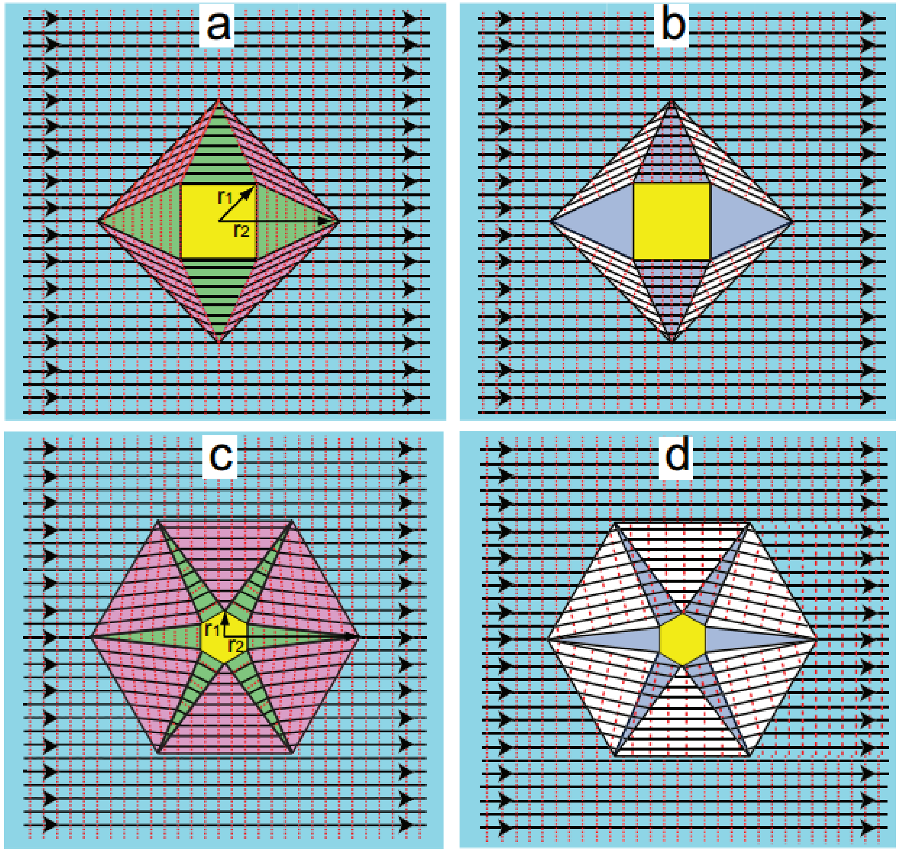
Invisible Cloak by Zhejiang University





Invisible Cloak by Zhejiang University

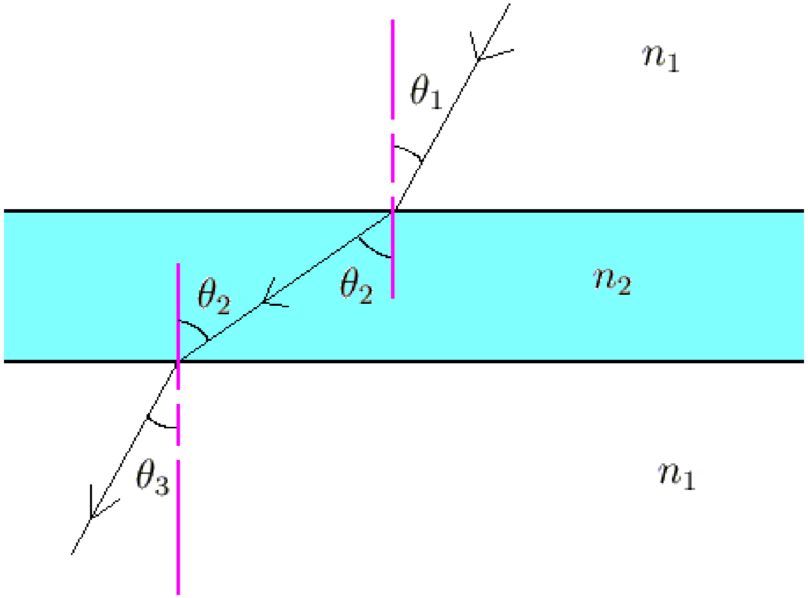




Snell's Law of Refraction

Snell's Law of Refraction

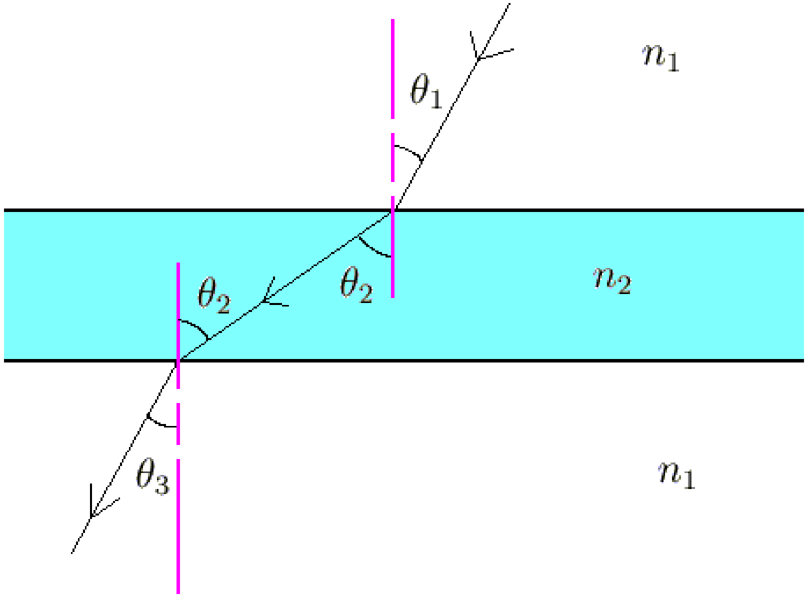
$$n_1 \sin\theta_1 = n_2 \sin\theta_2$$



國立中興大學
National ChungHsing University

Invisible Cloak Effect

What heppens if "n_2" is < 0 ???



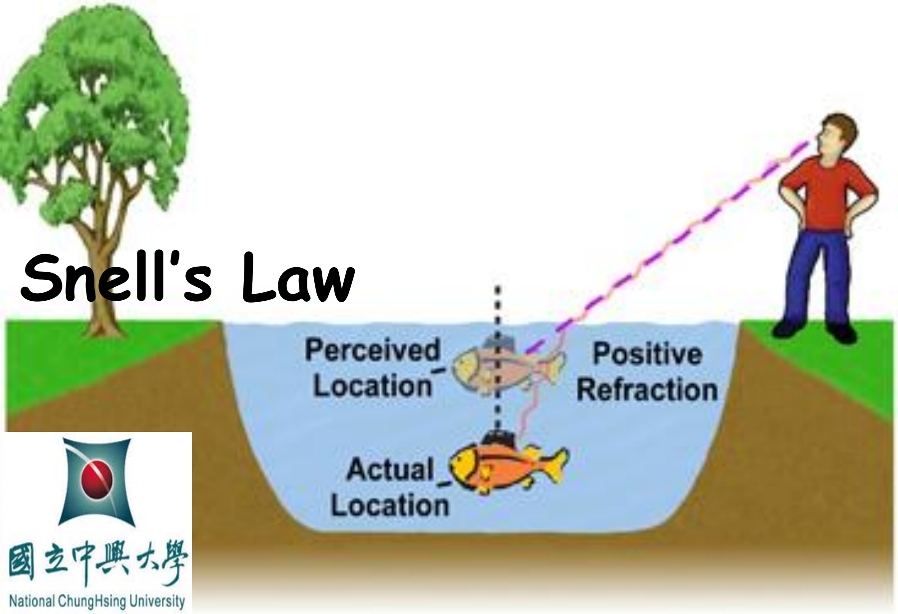
Harry Potter's invisible cloak

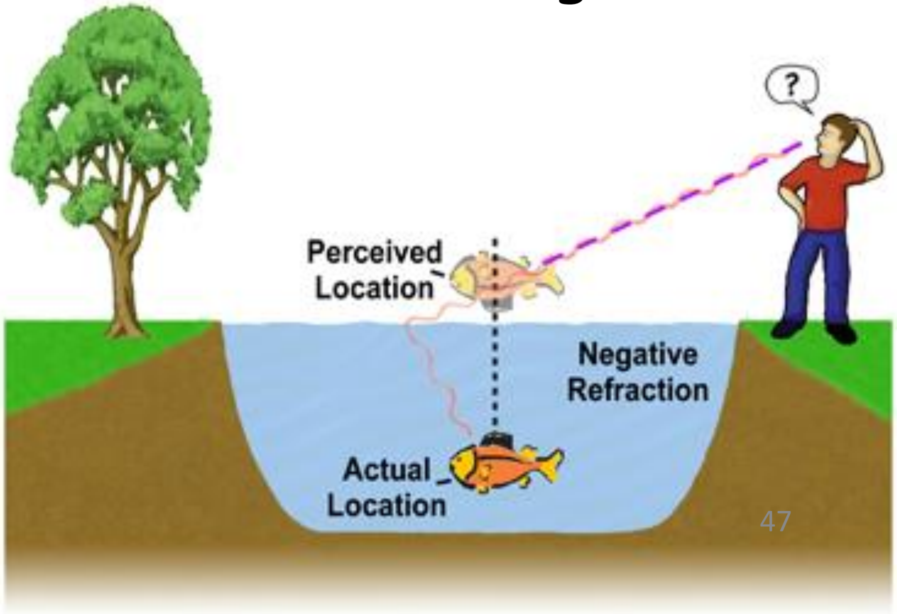
Metamaterials

Negative Refractive Index (n is < 0)

1. Two components:(S. Tretyakov)
    1) Negative permittivity
    2) Negative permeability
2. Novel metals based chiral structures (J. Pendry)
3. Applications:
    Invisible cloak; Invisible vehicles; Invisible coatings

Snell's Law

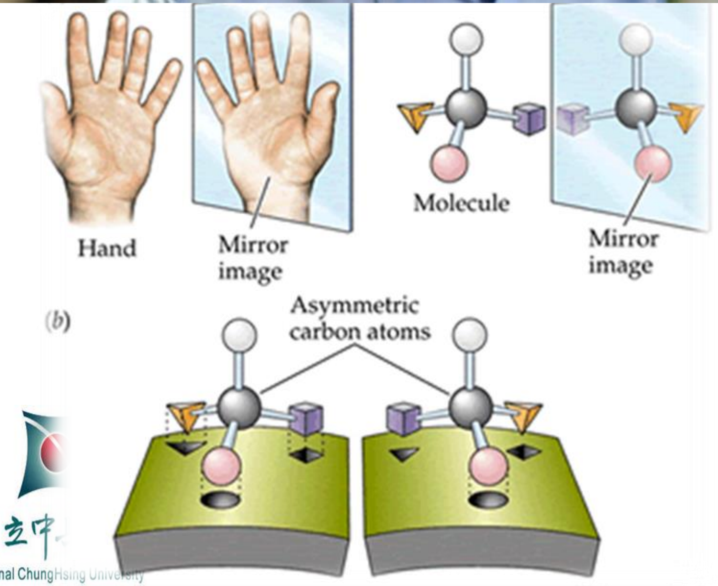


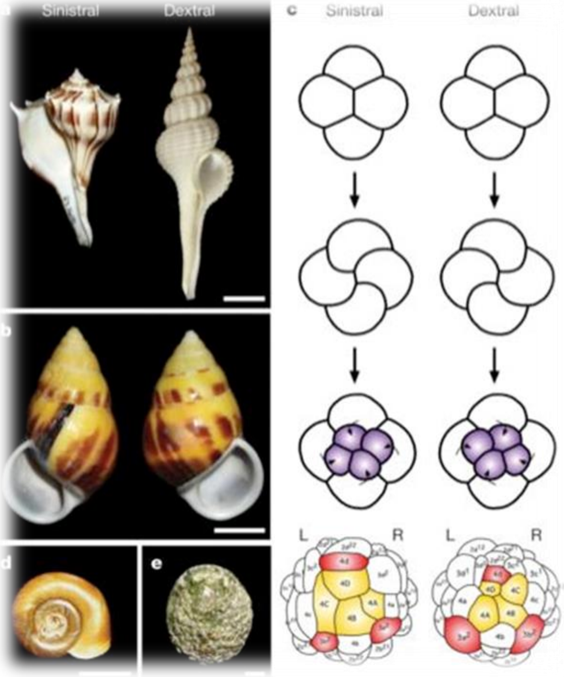


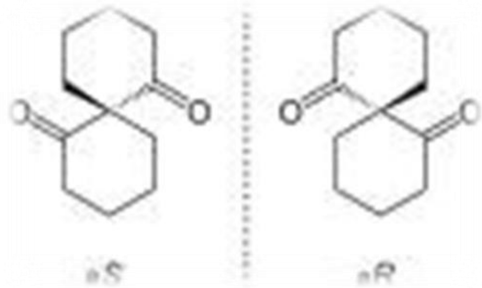
Chiral Structures

Newton Medal Winner (2013)
John Pendry, Imperial College London

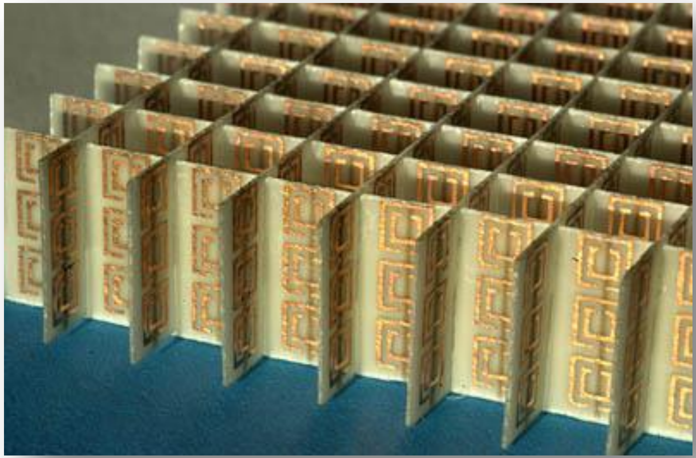
Chirality:
An object that can not be superimposed on its mirror image







Metamaterials by Mask Etching

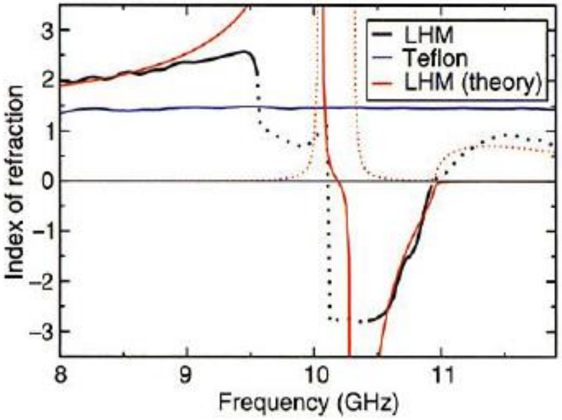


Permeability

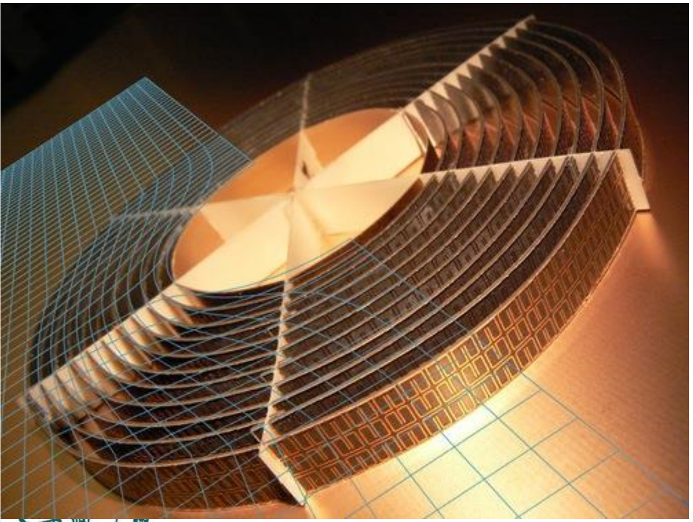
$$\frac{\mu(\omega)}{\mu_0} = 1 - \frac{\omega_{mp}^2 - \omega_{mo}^2}{\omega^2 - \omega_{mo}^2 + i\gamma\omega}$$

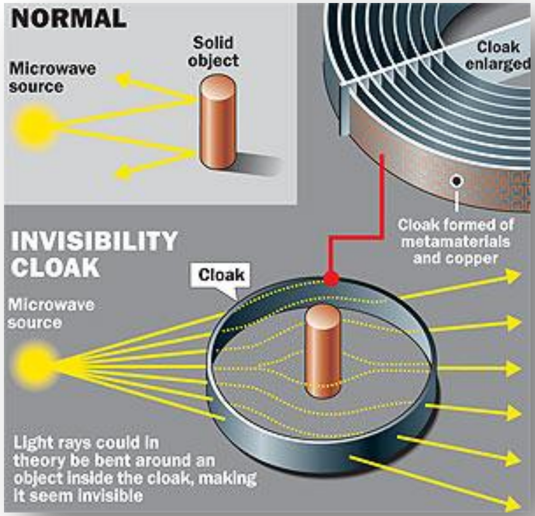
Permittivity

$$\frac{\varepsilon(\omega)}{\varepsilon_0} = 1 - \frac{\omega_{ep}^2 - \omega_{eo}^2}{\omega^2 - \omega_{eo}^2 + i\gamma\omega}$$



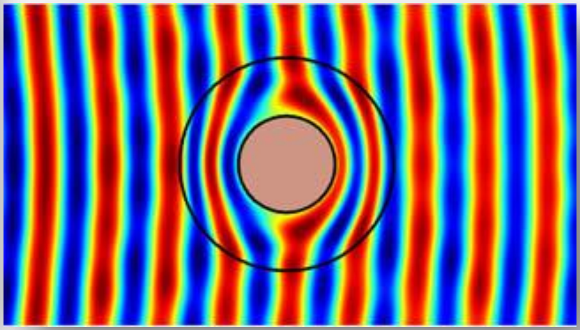
Copper mm-sized split rings





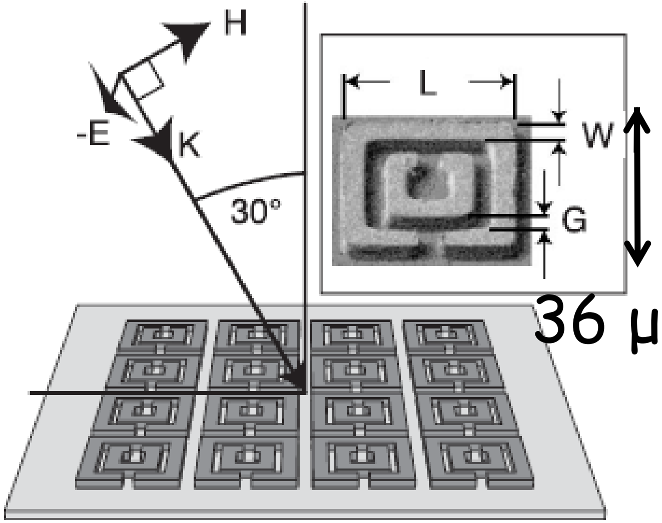
Light rays could in theory be bent around an object inside the cloak, making it seem invisible

1. Microwave Region
   (>100 micrometer)
2. GHz

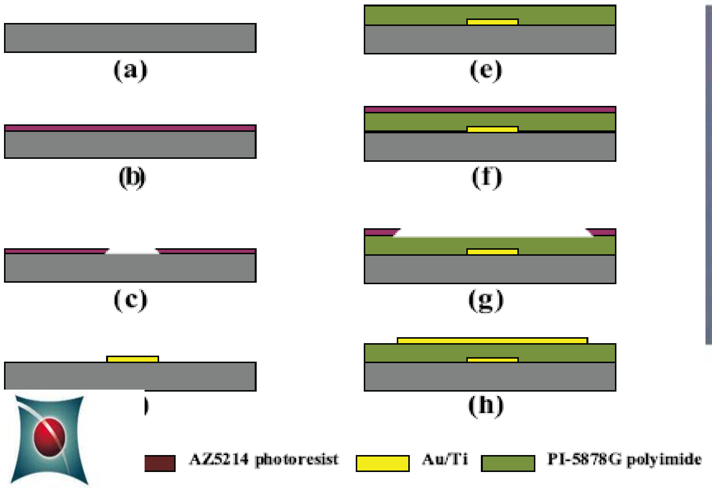


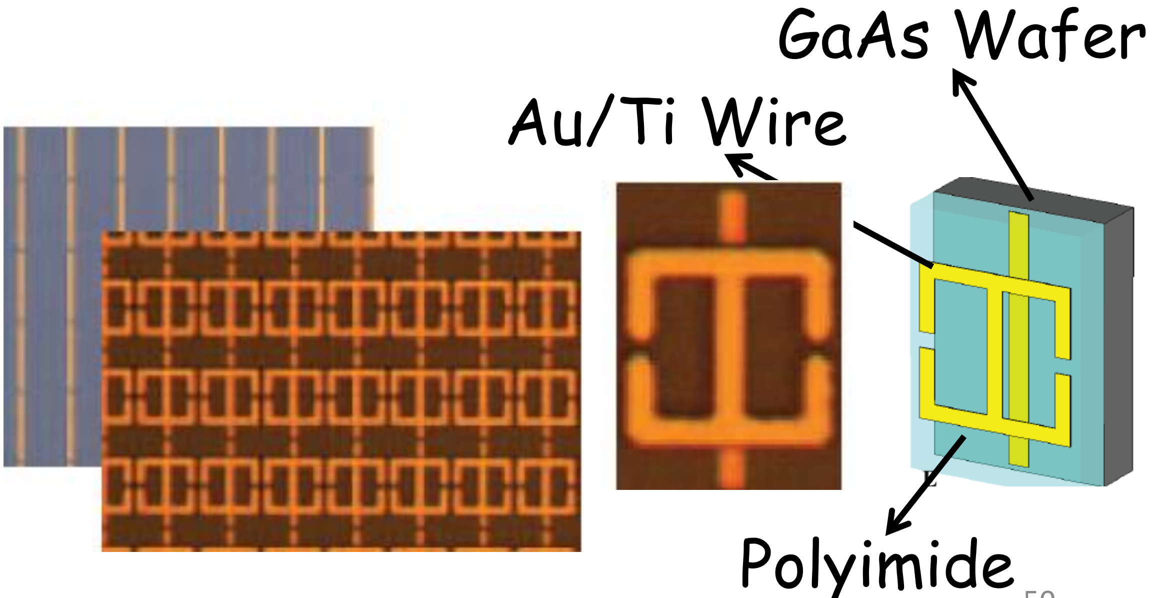
D. Smith et al., *Science*, 292, 77 (2001)

Micrometer Scale Metamaterials



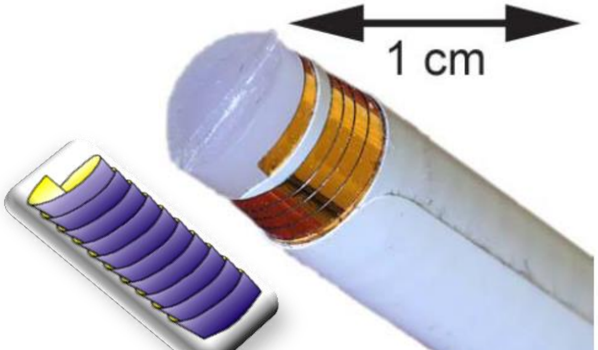
1. Negative reflective index at near-IR region.
2. THz
3. Small features results in higher frequency & narrowband wavelength.



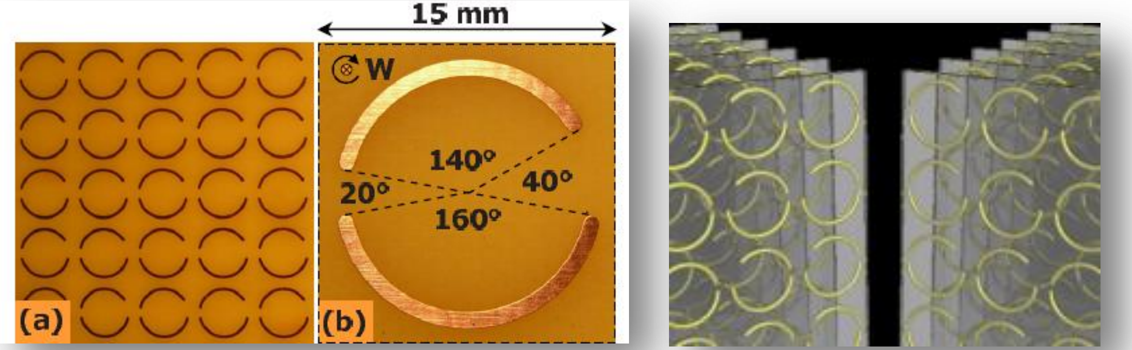


Padilla et al., *Science*, 313, 1495 (2006); *Optics Express*, 16, 7181 (2008)

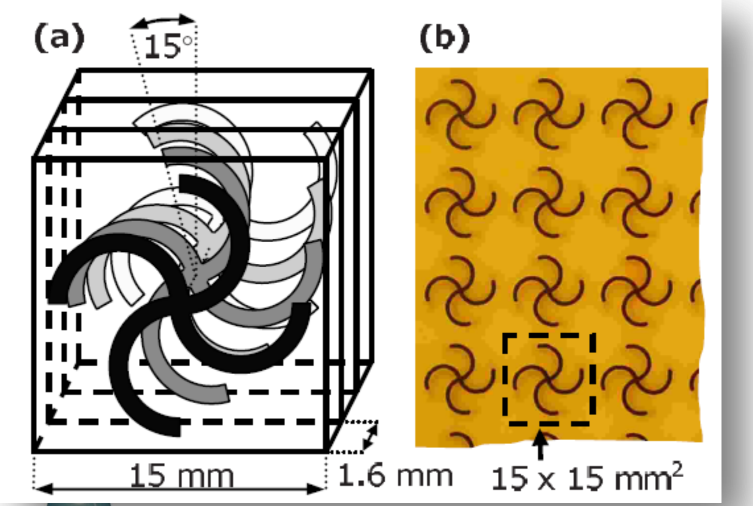
Spiral Metamaterials



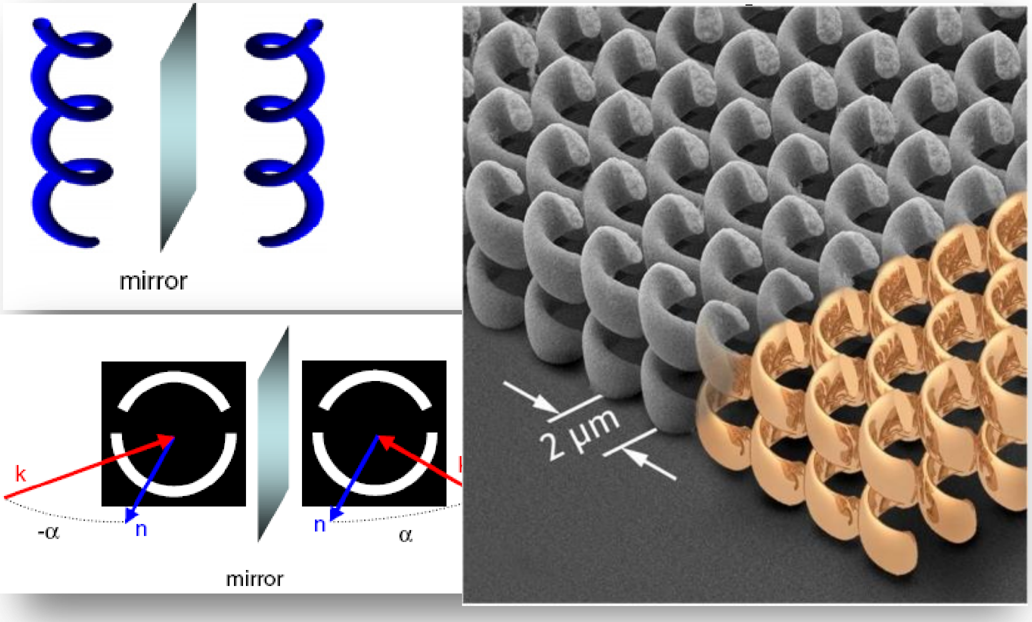
J. Pendry et al., *Science* (2004)



N. Zheludev et al., *Appl. Phys. Lett.* (2009)

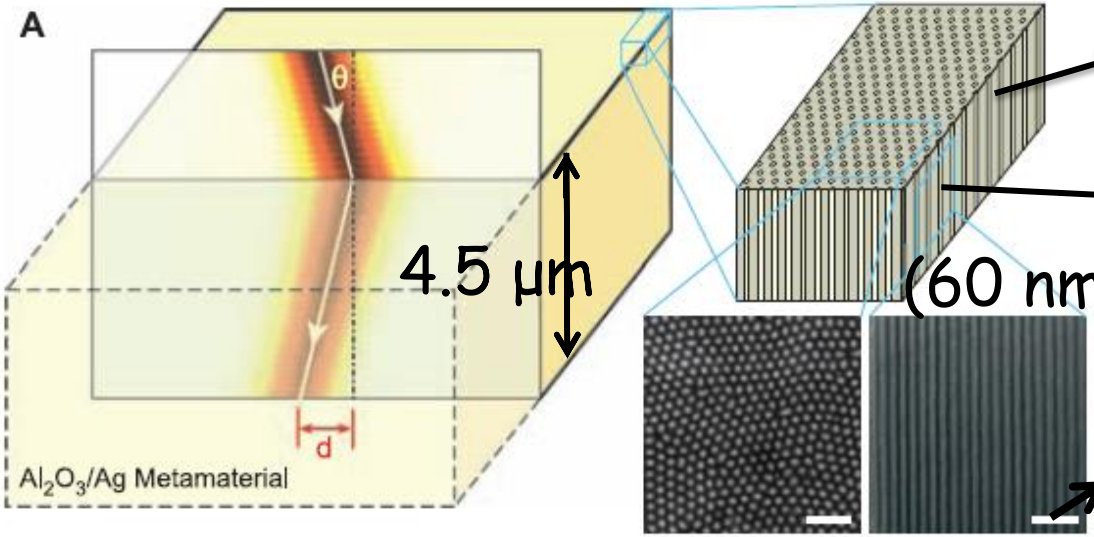


N. Zheludev et al., *Phys. Rev.* (2007)



E. Plum et al., *J. Opt.* (2008)

Metamaterials by Anodization

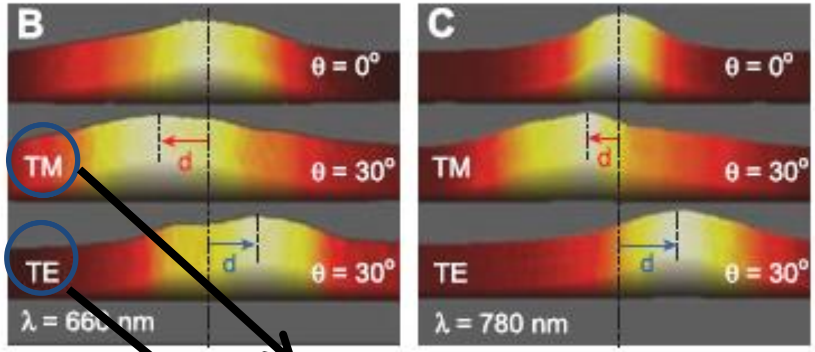


4.5 μm

Al_2O_3

Ag Wires
(60 nm wire dia., 110 nm spacing)

500 nm

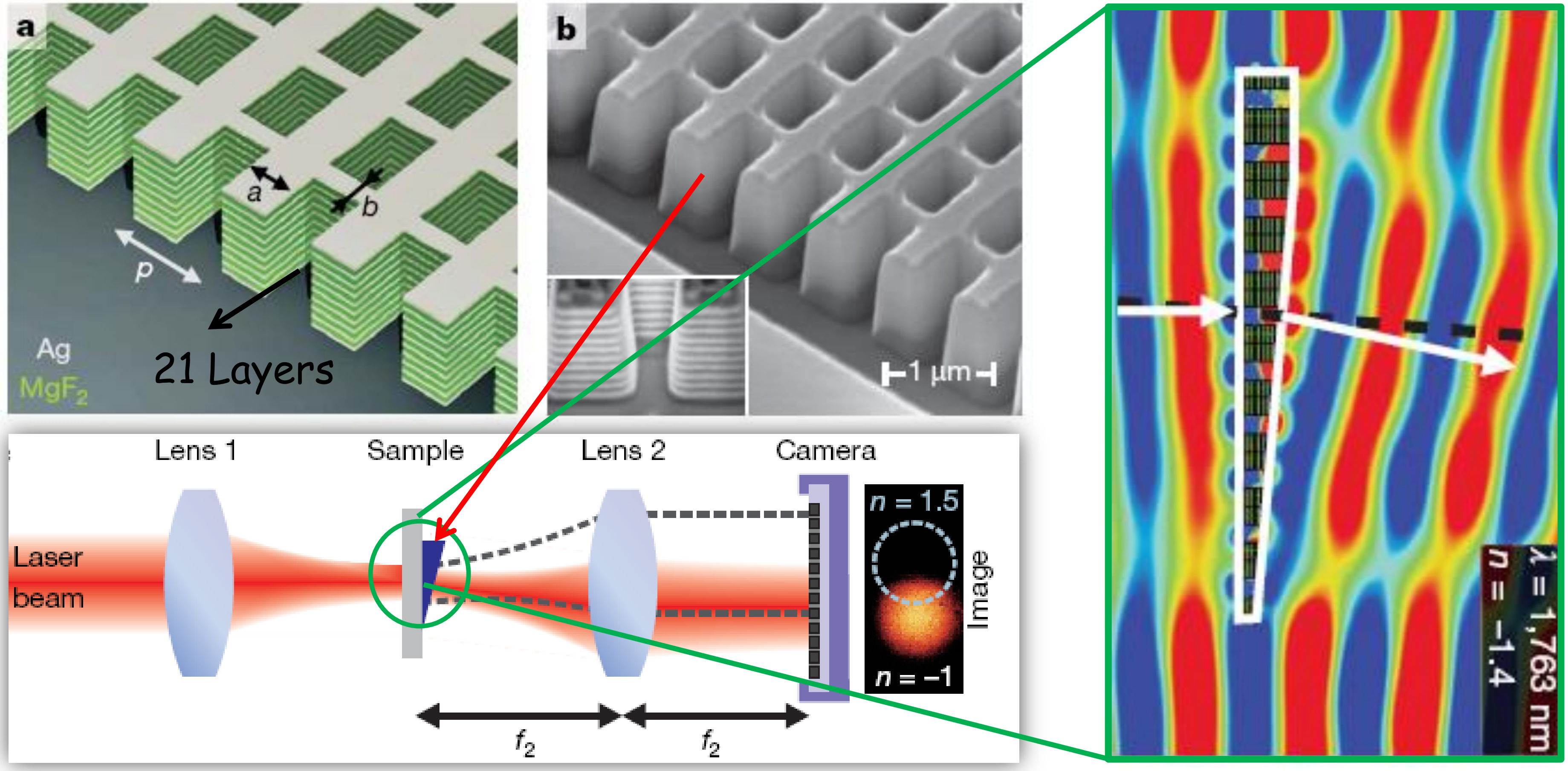


TM → transverse magnetic
TE → transverse electric

1. Negative R. I. at IR Region
2. Limitations
   1) 2 D
   2) Strong energy losses
   3) Fabrication difficult
   4) Limit band of frequency
   5) Angle dependent

X. Zhang et al., *Science*, 321, 930 (2008); *Nature Materials*, 8, 568 (2009)

Metamaterials by FIB Milling 1

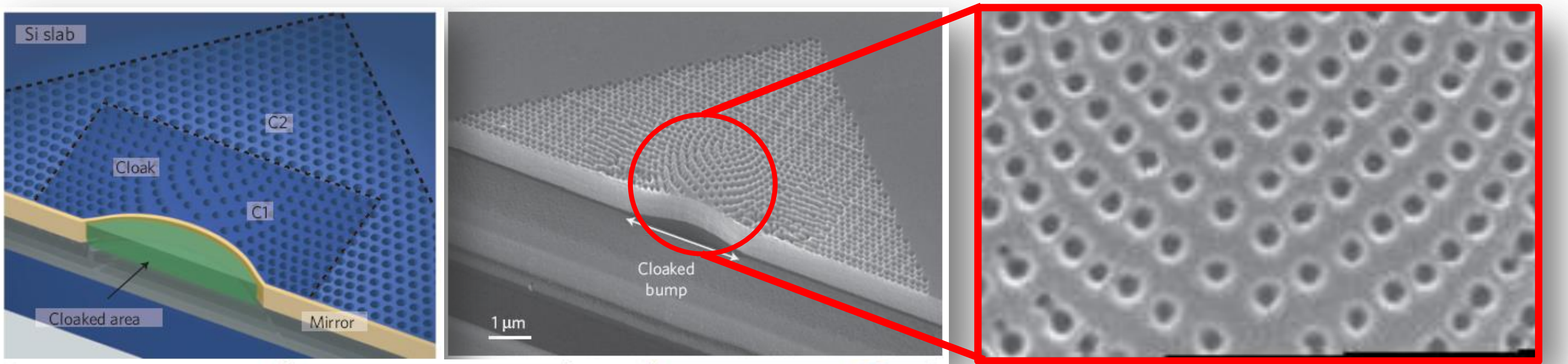


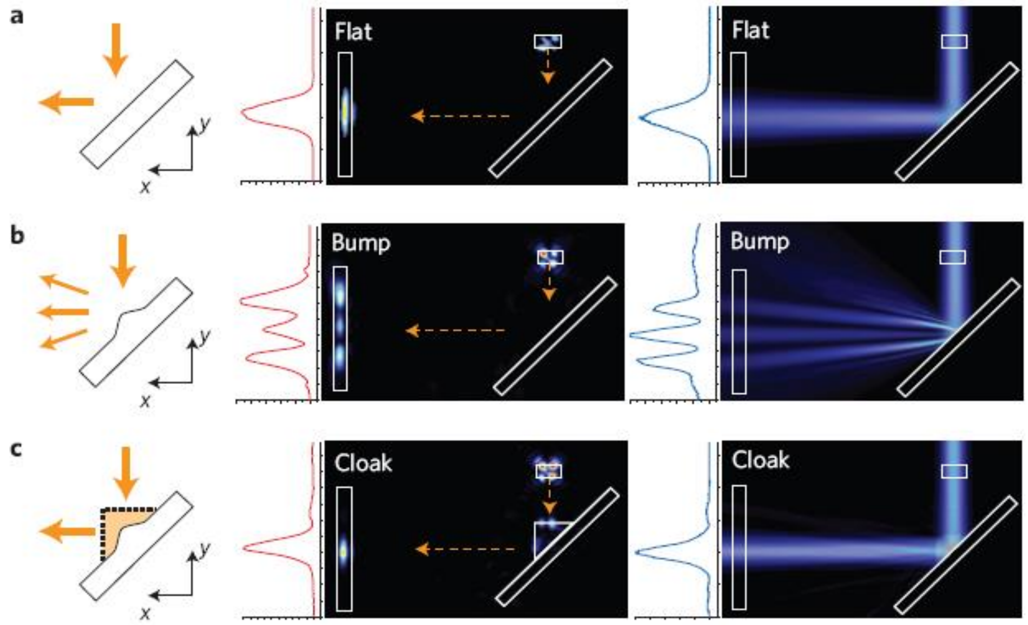
1. 3D structures,
2. R. I. shifts in microwave region (Fabry-Pe´rot effect).

X. Zhang et al., *Nature*, 07247, 1 (2008)

Metamaterials by FIB Milling 2

Imitate reflection of flat surface on dielectric substrate

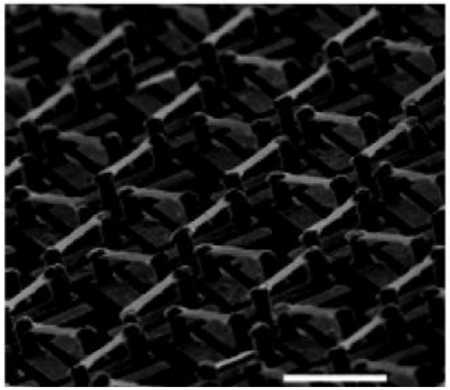


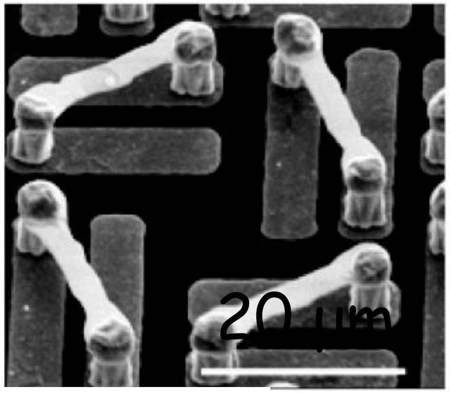


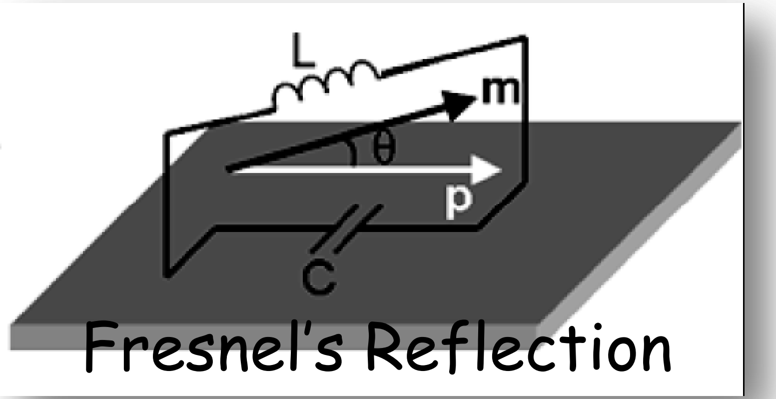
1. Hole (110 nm) arrays
2. Low energy loss
3. Broadband wavelength
   (1400 nm ~ 1800 nm)

X. Zhang et al., *Nature Materials*, 8, 568 (2009)

Circularly Polarized Wave Metamaterials







Fresnel's Reflection

$$\begin{pmatrix}D_x\\ D_y\end{pmatrix} = \varepsilon_0\varepsilon\begin{pmatrix}E_x\\ E_y\end{pmatrix} + \frac{i}{c_0}\begin{pmatrix}\xi & \xi_{12}\\ -\xi_{12} & \xi\end{pmatrix}\begin{pmatrix}H_x\\ H_y\end{pmatrix},$$

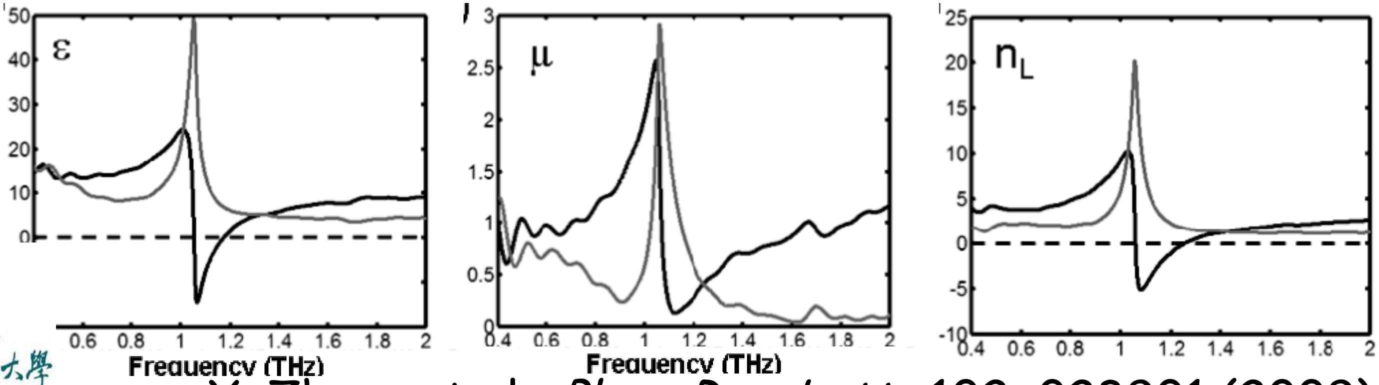
$$\begin{pmatrix}B_x\\ B_y\end{pmatrix} = \frac{i}{c_0}\begin{pmatrix}-\xi & \xi_{12}\\ -\xi_{12} & -\xi\end{pmatrix}\begin{pmatrix}E_x\\ E_y\end{pmatrix} + \mu_0\mu\begin{pmatrix}H_x\\ H_y\end{pmatrix},$$

$$(n_{L/R} \mp \xi)^2 = \varepsilon\mu - \xi_{12}^2,$$

Permittivity

Permeability

Refractive index



X. Zhang et al., *Phys. Rev. Lett.*, 102, 023901 (2009)