IM2655 Nano Materials and Nanotechnology

Bottom-up Fabrication Strategies

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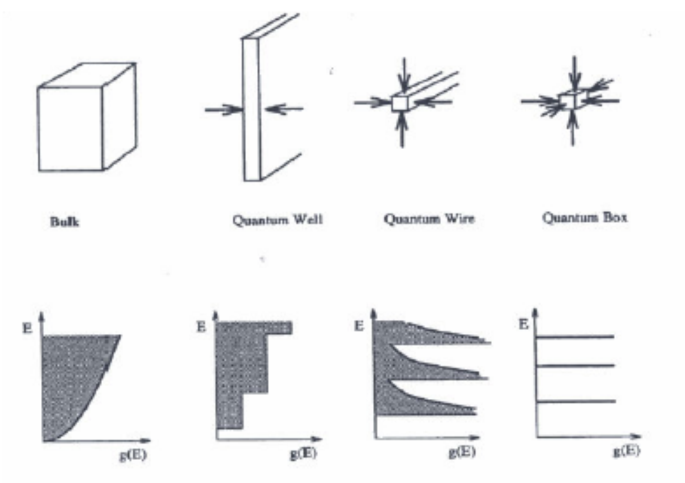
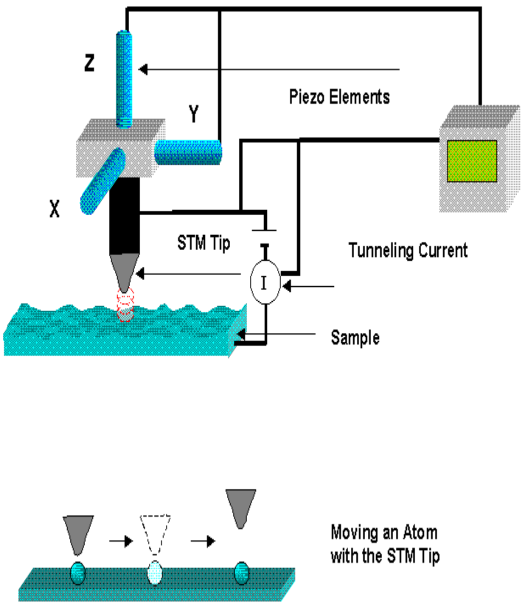
Energy States

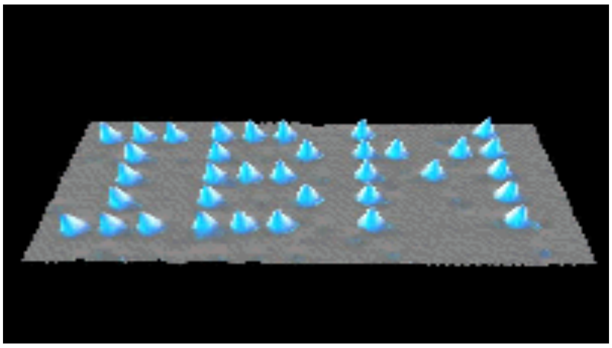
* *Energy states of electrons for bulk, quantum well, wire and dots*

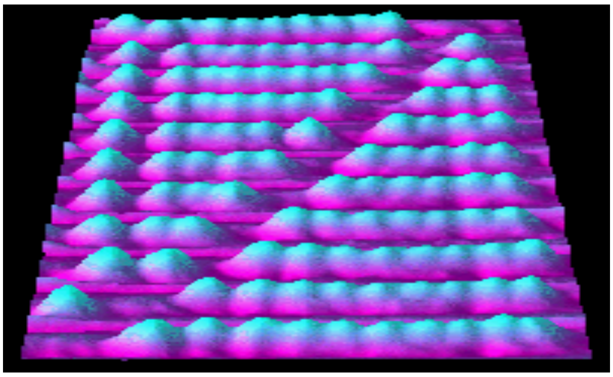


Change in the density of states, g(E), as the number of confining dimensions is increased.

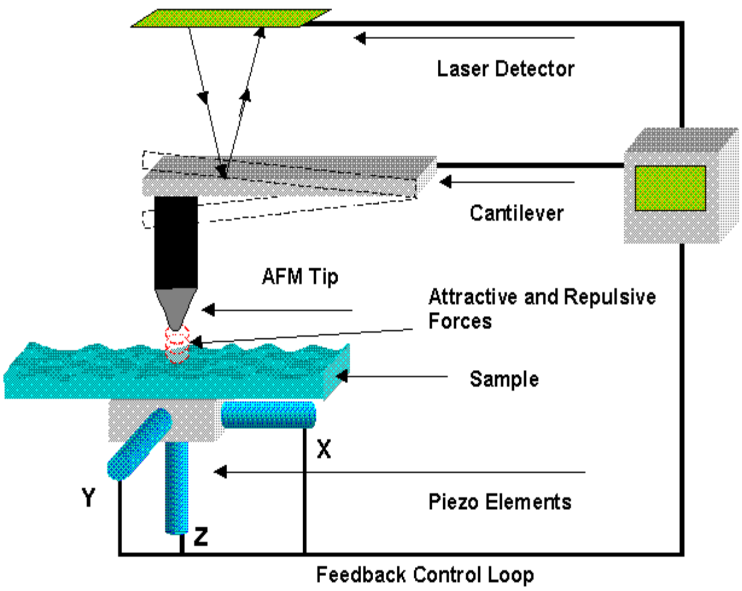
Scanning Tunneling Microscope (STM)

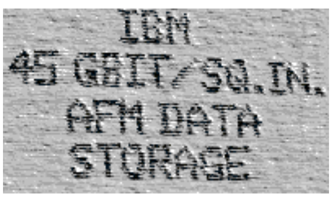






Atomic Force Microscope (AFM)



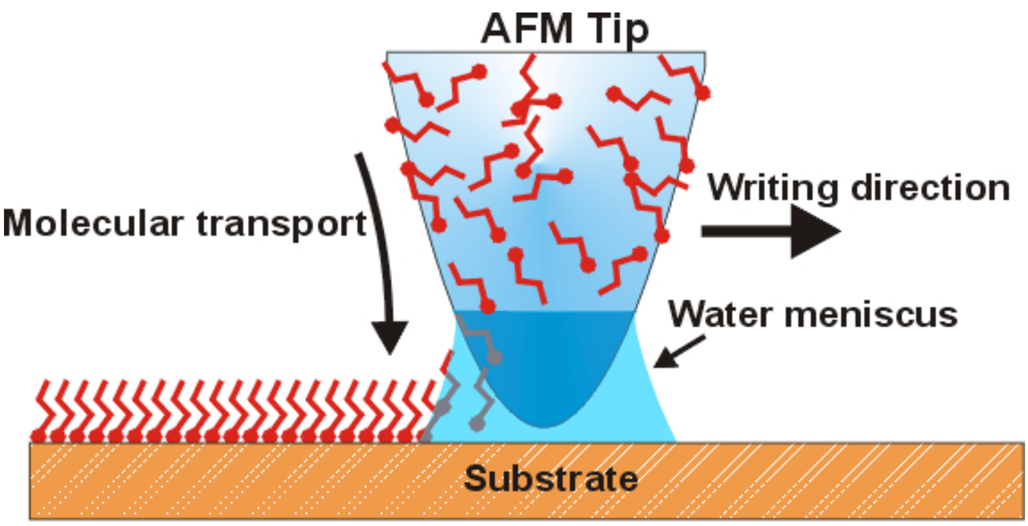


This 45xGBIT(109)/In2, image was written with an AFM tip, and took ≈ 1 minute to write with a conventional AFM.

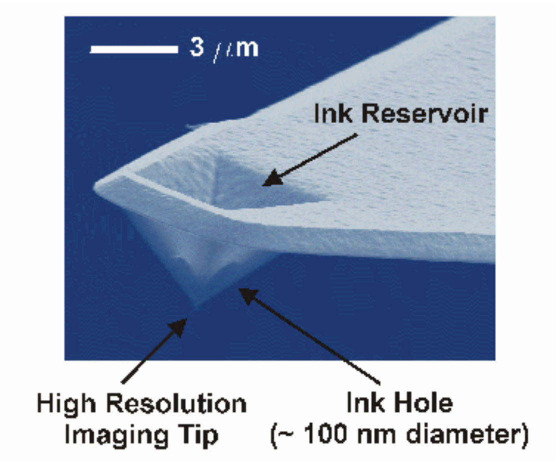
BOTTOM-UP FABRICATION STRATEGIES

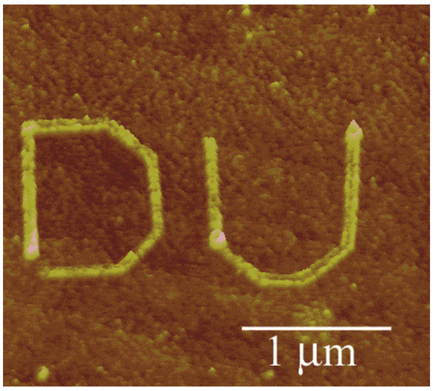
MASK-FREE FABRICATION

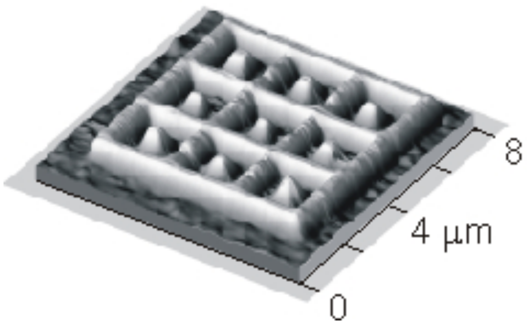
Deposition of a trail of liquids from an AFM tip represents a small ink pen

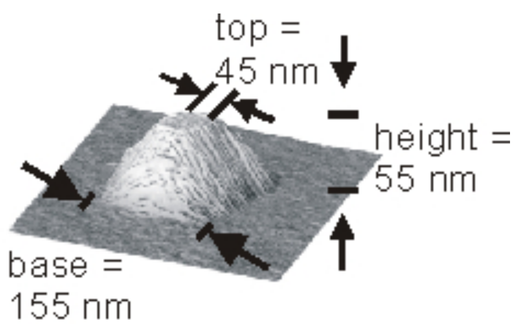


BOTTOM UP FABRICATION









As soon as I mention this, people tell me about miniaturization, and how far it has progressed today. They tell me about electric motors that are the size of the nail on your small finger. And there is a device on the market, they tell me, by which you can write the Lord's Prayer on the head of a pin. But that's nothing; that's the most primitive, halting step in the direction I intend to discuss. It is a staggeringly small world that is below. In the year 2000, when they look back at this age, they will wonder why it was not until the year 1960 that anybody began seriously to move in this direction.

Richard P. Feynman, 1960

Nanomovies-1

- http://video.google.com/videoplay?docid=-2022170440316254003
- http://video.google.com/videoplay?docid=3921652881104153368&q=nanosystems&total=17&start=0&num=10&so=0&type=search&plindex=5
- Nanomanufacturing
- http://www.youtube.com/watch?v=9yuTM_EOtHY&feature=related

National Cancer Institute

- http://nano.cancer.gov/learn/understanding/video_journey.asp

Nanomovies-2

KQED-Quest

- http://www.youtube.com/watch?v=S4CjZ-OkGDs

NanoBots

- http://www.youtube.com/watch?v=oCMVTykWIno
- http://www.youtube.com/watch?v=P7zw9fvfBZI&feature=related

Nanotechnology and drug delivery

- http://www.youtube.com/watch?v=ybK5TIGNNFA&feature=related

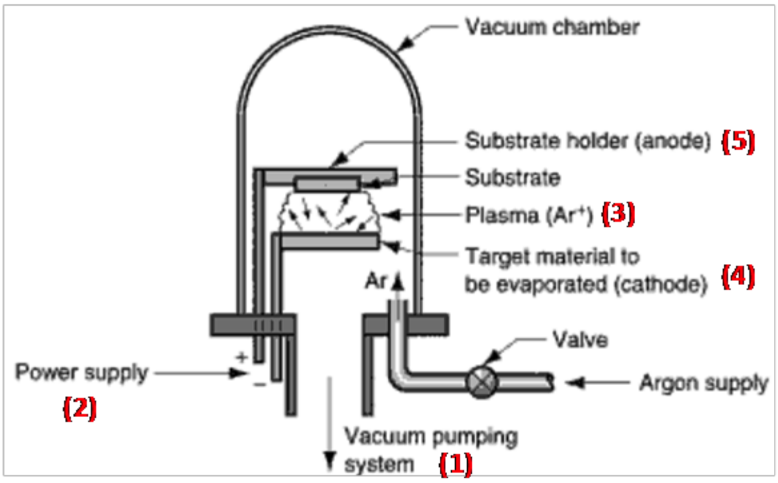
Bottom-Up Strategies Continued

Sputtering

1) Sputtering principle

=> Physical deposition technique

Schematic of a sputtering system:



a) A vapor phase is generated by bombarding the source material with plasma generated ions.

b) The vapor is transported from the source to the substrate.

c) The vapor is condensed to a solid film on the substrate surface.

Chemical Vapor Deposition

-Chemical Vapor Synthesis (CVS): is a process for making fine solid particles by the vapor-phase chemical reactions of precursors.

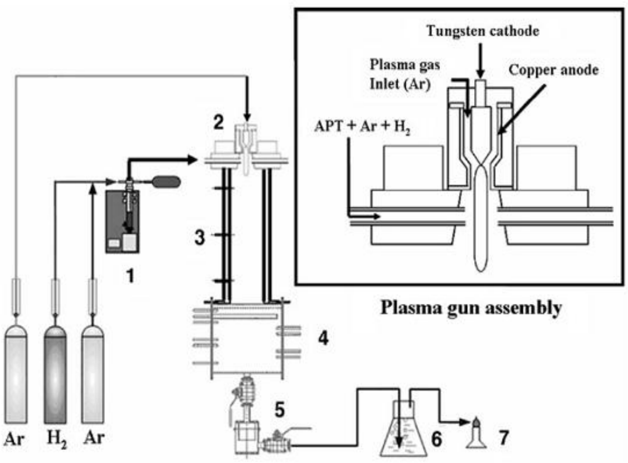


Fig. 1 Schematic diagram of the plasma reactor system:

(1) powder feeder for APT
(2) Plasma gun
(3) Cylindrical reactor
(4) Cooling chamber
(5) Powder collector
(6) Scrubber
(7) Bunsen burner

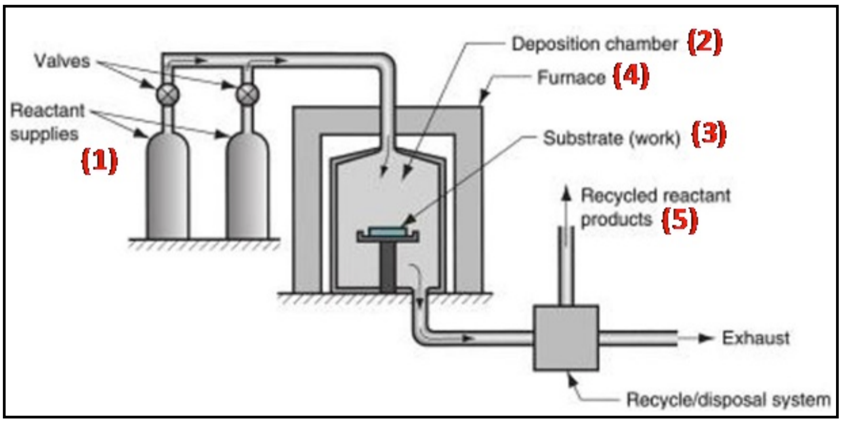
Taeong Ryu, et al. "Chemical vapour synthesis (CVS) of tungsten nanopowder in thermal plasma reactor." 27. (2009): 149-154.

Atomic Layer Deposition

1) Chemical Vapor Deposition Principle

=> Chemical deposition technique. (ALD belongs to CVD techniques).

Typical chemical vapor deposition reactor :

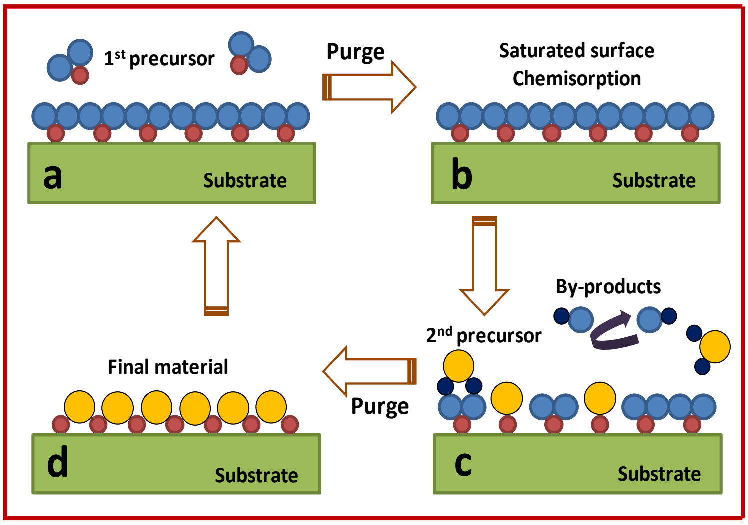


Atomic Layer Deposition

2) Atomic Layer Deposition Principle

❖ **ALD principle**: separating the reaction that occurs in a CVD reactor into 2 half-reactions that will take place alternatively.

Schematic of the cyclic atomic layer deposition process:



Atomic Layer Deposition

3) Application to the ZrO_2 deposition (1/2)

❖ Possible precursors:

- Metal Halide $ZrCl_4$
- Metal Amide $Zr-(N-R)_4$
- Alkoxide $Zr-(O-R)_4$

❖ Successive half-reactions:

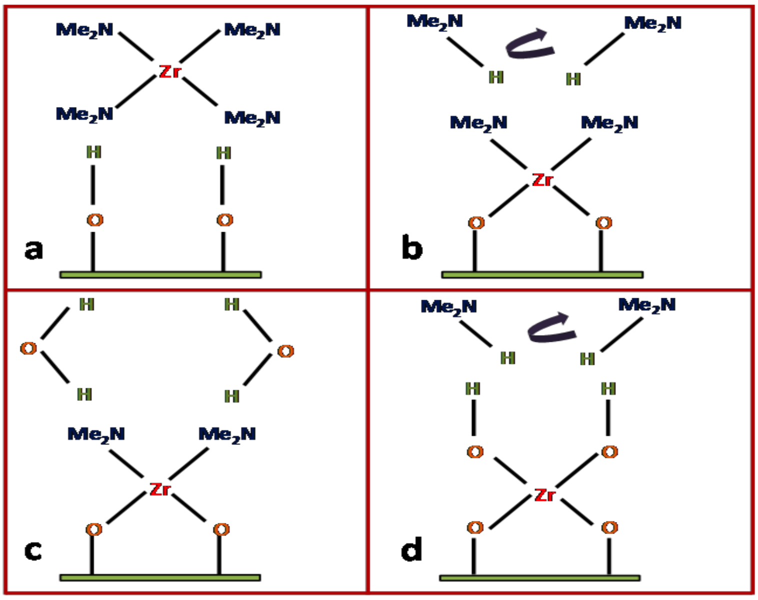
$$ZrCl_{4(g)} + 2OH_{(surface)} = ZrCl_2O_{2(g)} + 2HCl_{(g)}$$

$$ZrCl_2O_{2(g)} + 2H_2O_{(g)} = Zr0_2(OH)_{2(surface)} + 2HCl_{(g)}$$

Atomic Layer Deposition

3) Application to the ZrO_2 deposition (2/2)

❖ ALD cycle using alternatively $Zr-(N-R)_4$ andH_2O precursors:

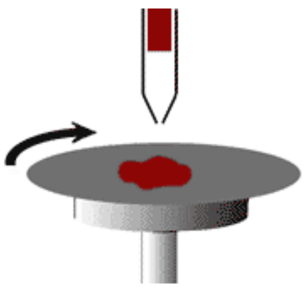


Sol Gel process and Spin coating

1) Sol-Gel principle applied to the deposition of HfO_2 films (1/2)

=> Chemical deposition technique.

❖ **Spin-coating** already widely used for microelectronics thin films deposition.



Sol Gel process and Spin coating

1) Sol-Gel principle applied to the deposition of HfO_2 films (2/2)

Manufacturing process (J. Tardy and al. (2007):

❖ **Hf-based alkoxide** dissolved in **Ethanol**, with **Acetylacetone.**

$Hf(OC_2H_5)_4$ C_2H_6O $C_5H_8O_2$

❖ **Hydrolysis: Solution is exposed to water vapor:**

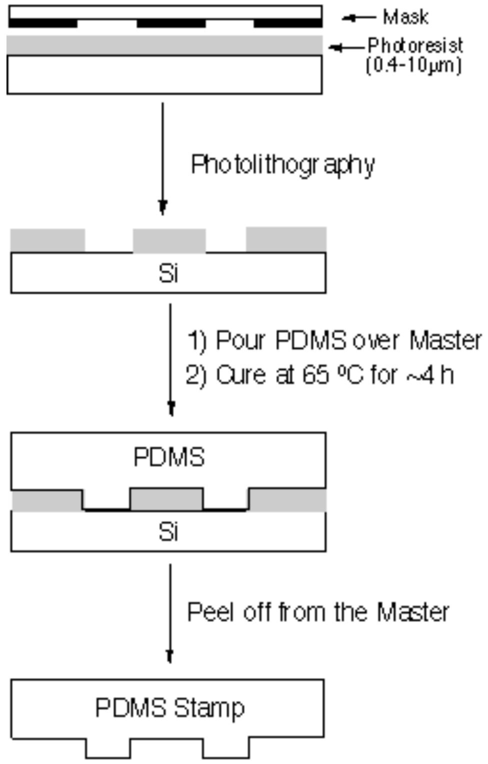
$$Hf(OC_2H_5)_4 + x * H_2O \rightarrow Hf(OC_2H_5)_{4-x}(OH)_x + x * C_2H_5OH\ , \qquad 0 \le x \le 3$$

=> Formation of the **Sol.**

❖ **Then:**

- Sol is deposited on the substrate using spin-coating technique (high rotation speed: 3000-5000 rpm).
- Dried at 100°C for 10mn (Condensation) **=>** Creates **HfO_2 Xerogel**.
- Annealing at T>400°C to increase film density.

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

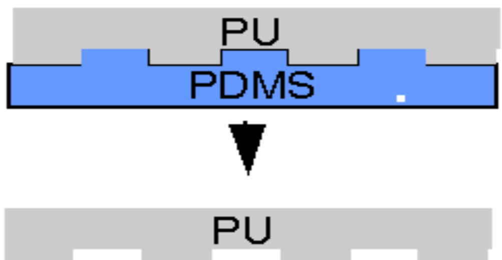
The resulting polymer needs a Tg below processing temperature (such as PDMS) after curing by heat or UV light

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

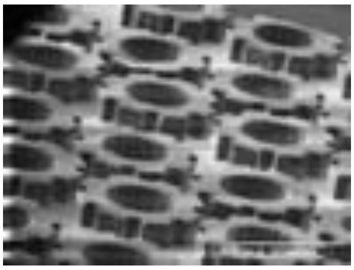
Replica Molding (REM)

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)

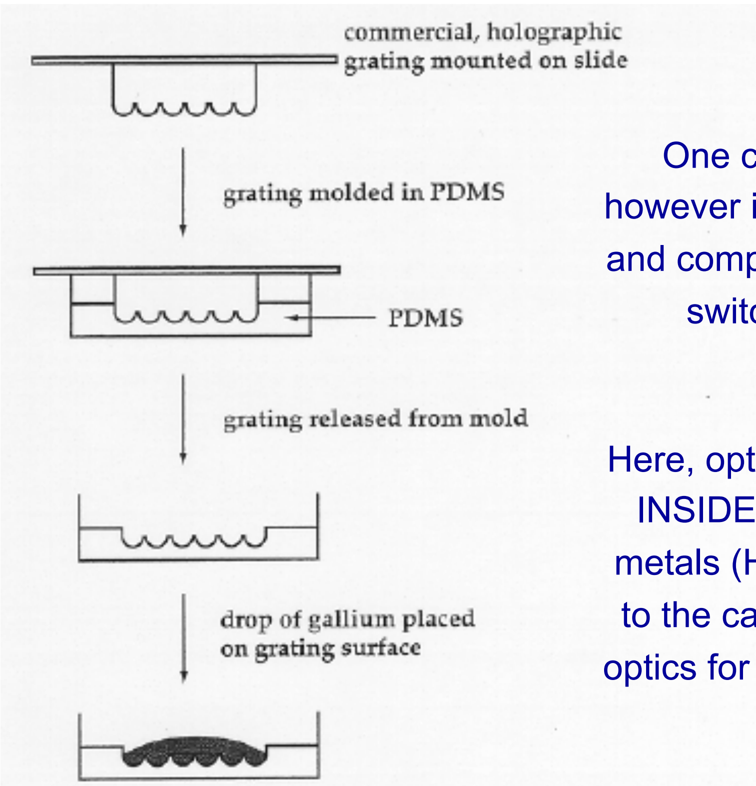


The elastomeric properties of the PDMS can also be used to stretch or compress the sizescale, from 180nm of a waveguide to 40nm (Xia, U. Wash.)

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

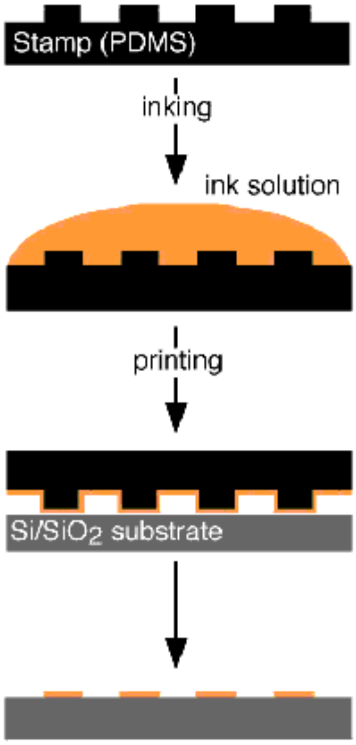
Replica Molding (REM)



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

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 (µCP)

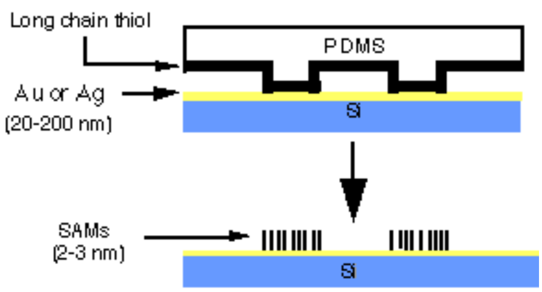


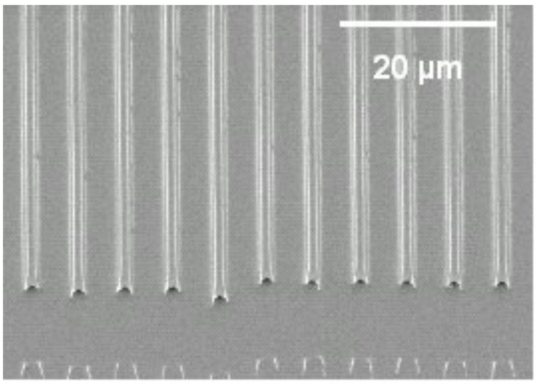
The PDMS masks can also be applied as flexible stamps, inked with adsorbing or assembling molecules, and then used as small rubber contact stamps

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 (µCP)



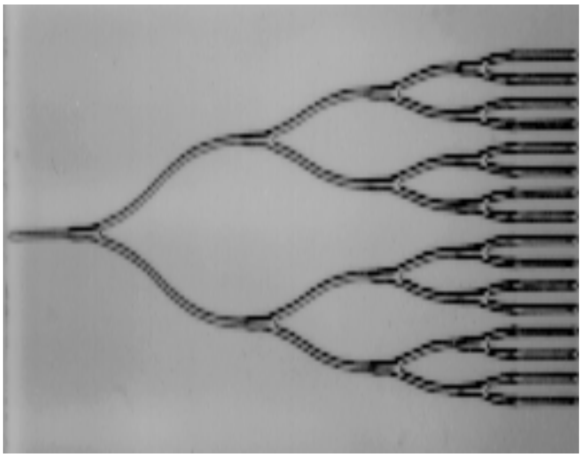


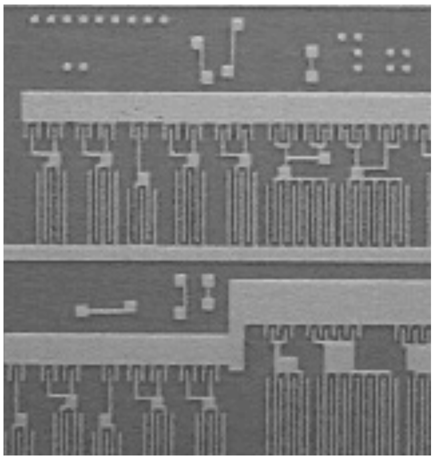
Alkane thiols with tailored headgroups provide versatile and powerful chemical control over subsequent patterning, such as polymer adsorption, photoresists, vapour deposition of inorganics, etching, electroplating of metals…

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 (μCP)

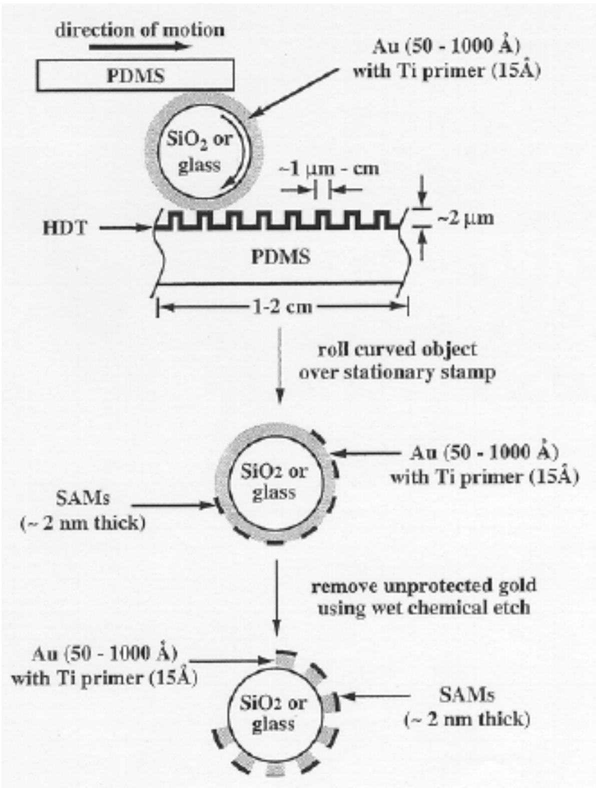
Complex architectures are possible from any master, as long as it's limited to a single layer to be deposited on a Au or Si coated flat surface

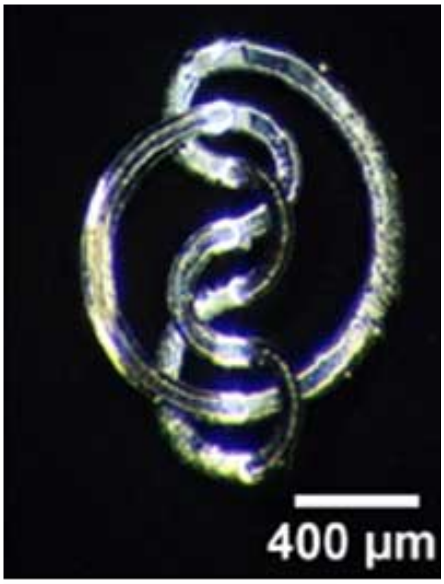




The Limitation: This produces one layer well, but only a *single* layer.

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



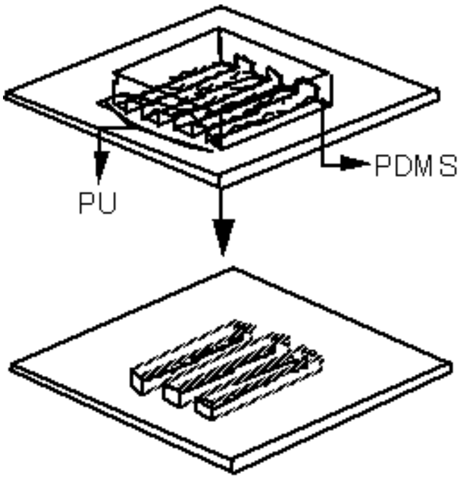


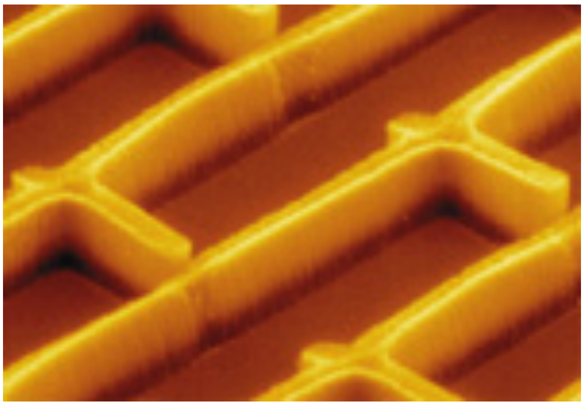
These miniature metal knots were created by precisely printing a flattened pattern on a pair of parallel glass tubes.

Source: Harvard University

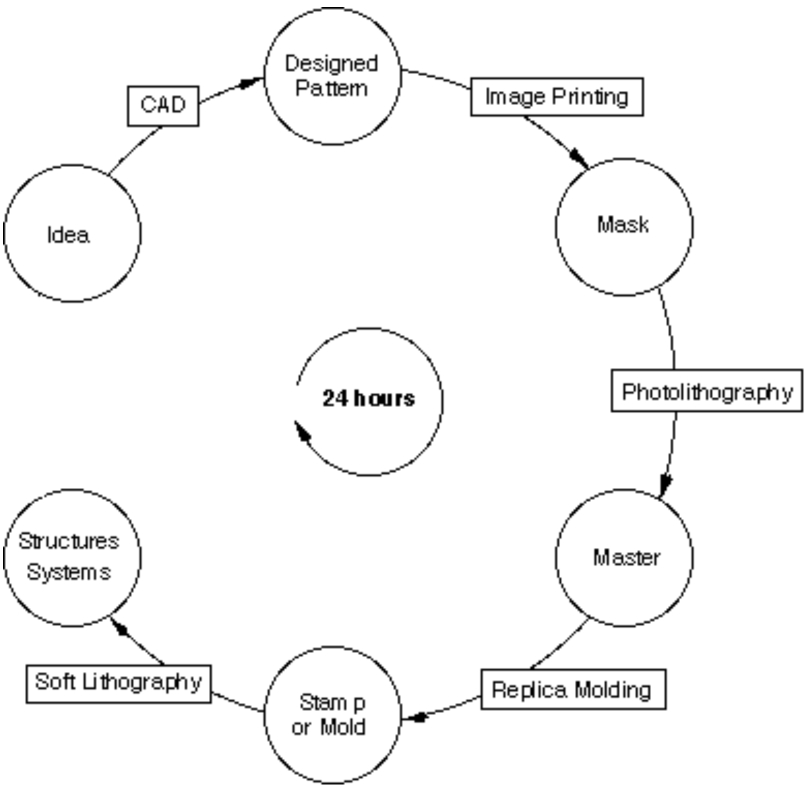
Micro Contact Molding

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





Bottom Up Fabrication



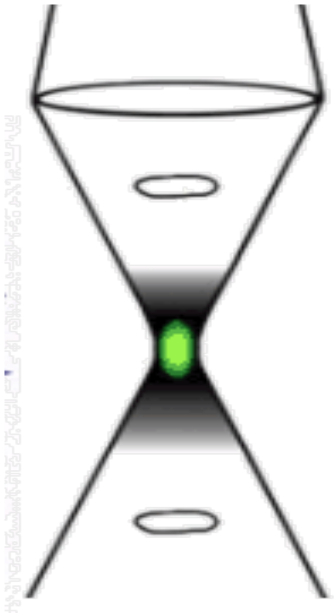
The result ? :

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)

Light to define Patterns

using a locally-defined chemical reactions by a free-space 2-photon process



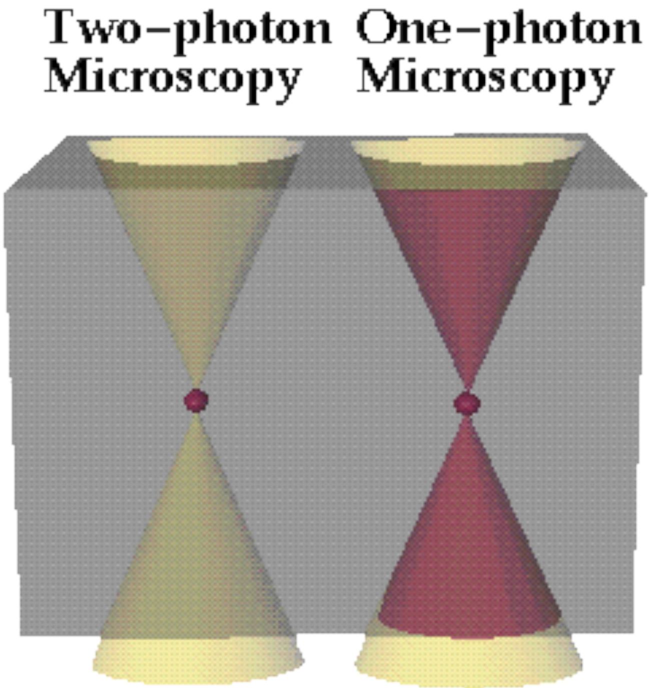
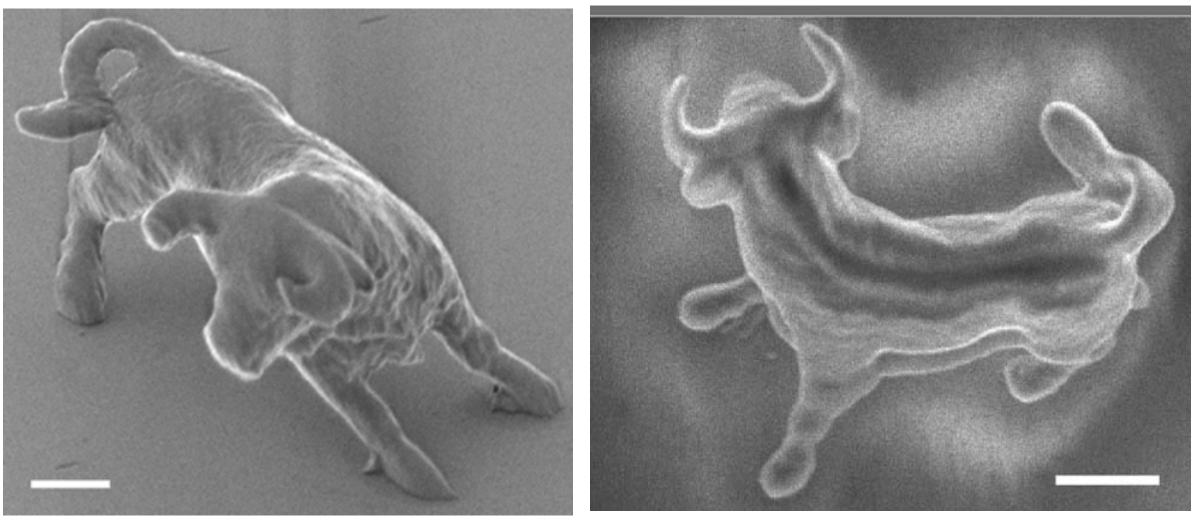


Photo-Polymerization

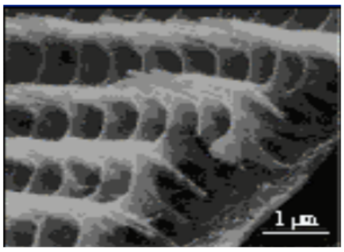
acrylate monomer is mixed with AIBN azo initiator, and undergoes photo-induced free radical polymerization locally, by a deep red 2 photon process



2 microns

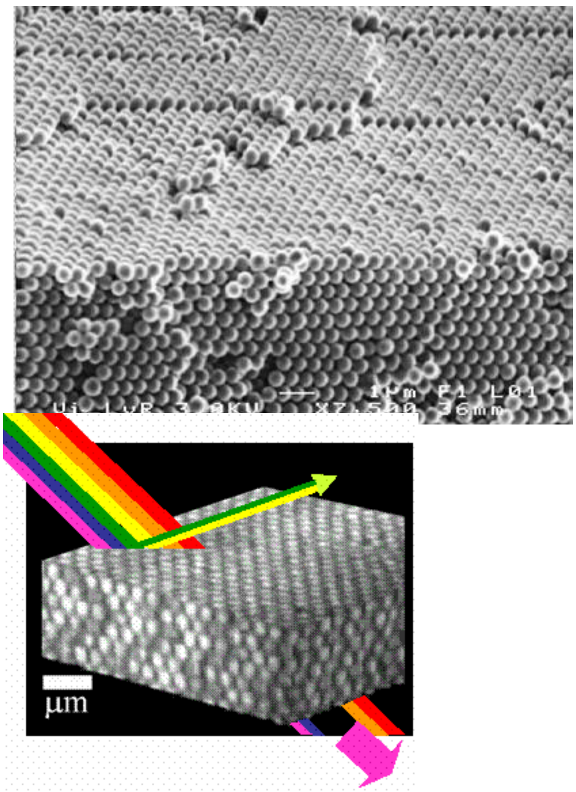
Many colourful displays in nature: Rainbows, butterfly,
Results from diffraction, scattering, reflection, refraction
by micro or nano structures

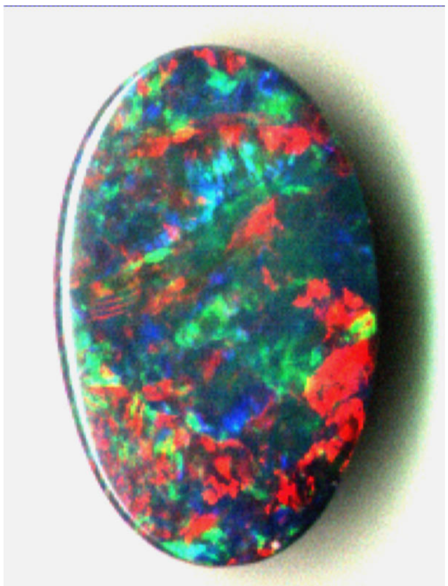
Adonis Blue Butterfly



SEM of wing scale

Opals





Photonic properties

- The position of the first order Bragg peak (λ) is related to the effective refractive index of the material (n_{eff}), the sum of the refractive index components, and the lattice parameter (d_{111}) and the angle of incidence θ by the expression;

$$\lambda = 2d_{111} \{ (n_{eff})^2 - \sin^2 \theta \}^{1/2}$$

$$\text{where } n_{eff} = f\, n_{SiO2} + f'\, n_{infill} + f''\, n_{air}$$

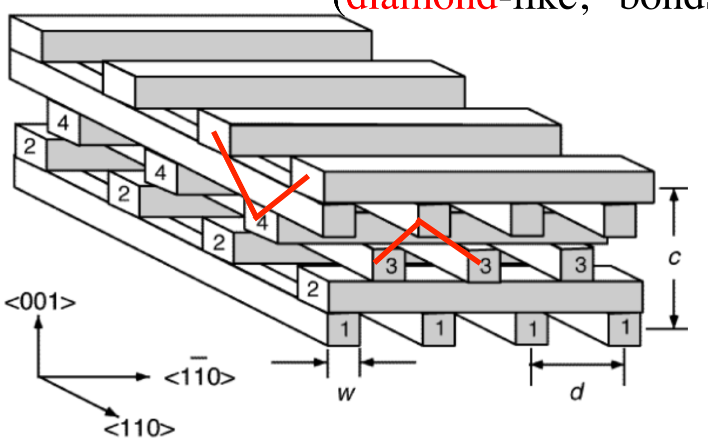
- infilling the voids within an opal structure with a material of high refractive index such as GaAs, increases the n_{eff} and shifts the Bragg peak to higher wavelength.

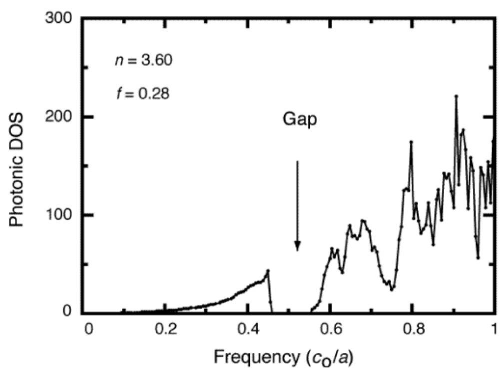
an earlier design:
(& currently more popular)

The Woodpile Crystal

[K. Ho *et al*., *Solid State Comm*. **89**, 413 (1994)] [H. S. Sözüer *et al*., *J. Mod. Opt*. **41**, 231 (1994)]

(diamond-like, “bonds”)





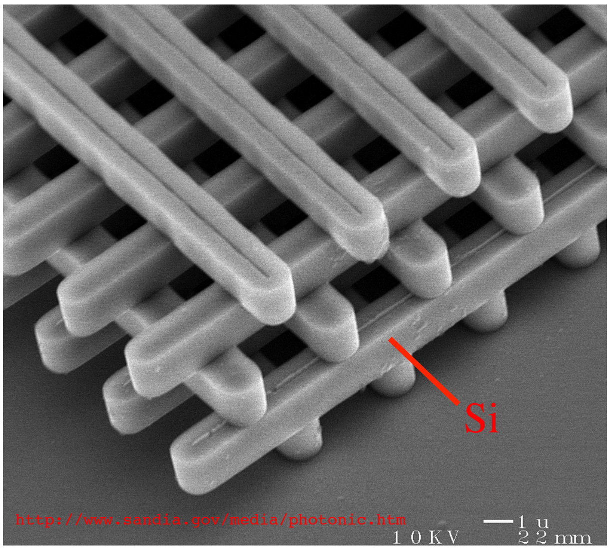
Up to ~ 17% gap for Si/air

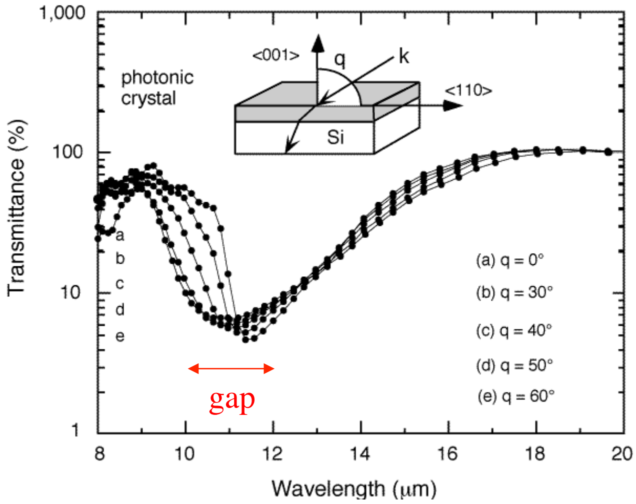
[Figures from S. Y. Lin *et al*., *Nature* **394**, 251 (1998)]

1.25 Periods of Woodpile

(4 "log" layers = 1 period)

[S. Y. Lin *et al.*, *Nature* **394**, 251 (1998)]





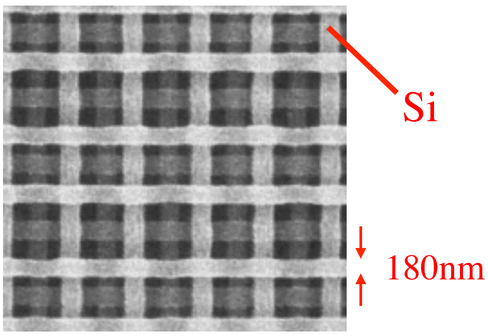
"UV Stepper:" e-beam mask at ~4x size
+ UV through mask, focused on substrate

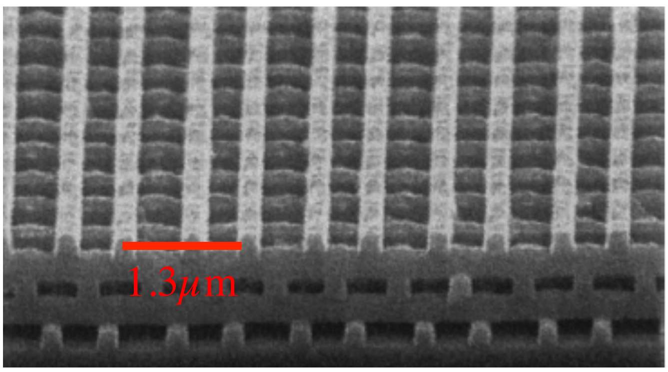
Good: high resolution, mass production Bad: expensive ($20 million)

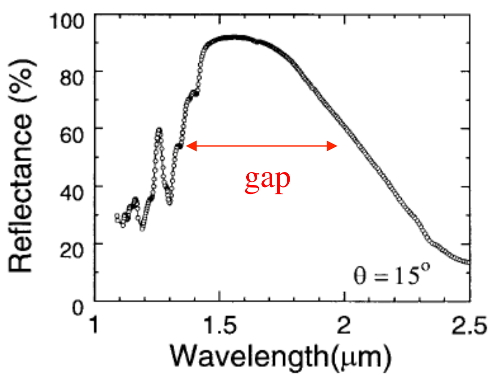
1.25 Periods of Woodpile @ 1.55μm

(4 "log" layers = 1 period)

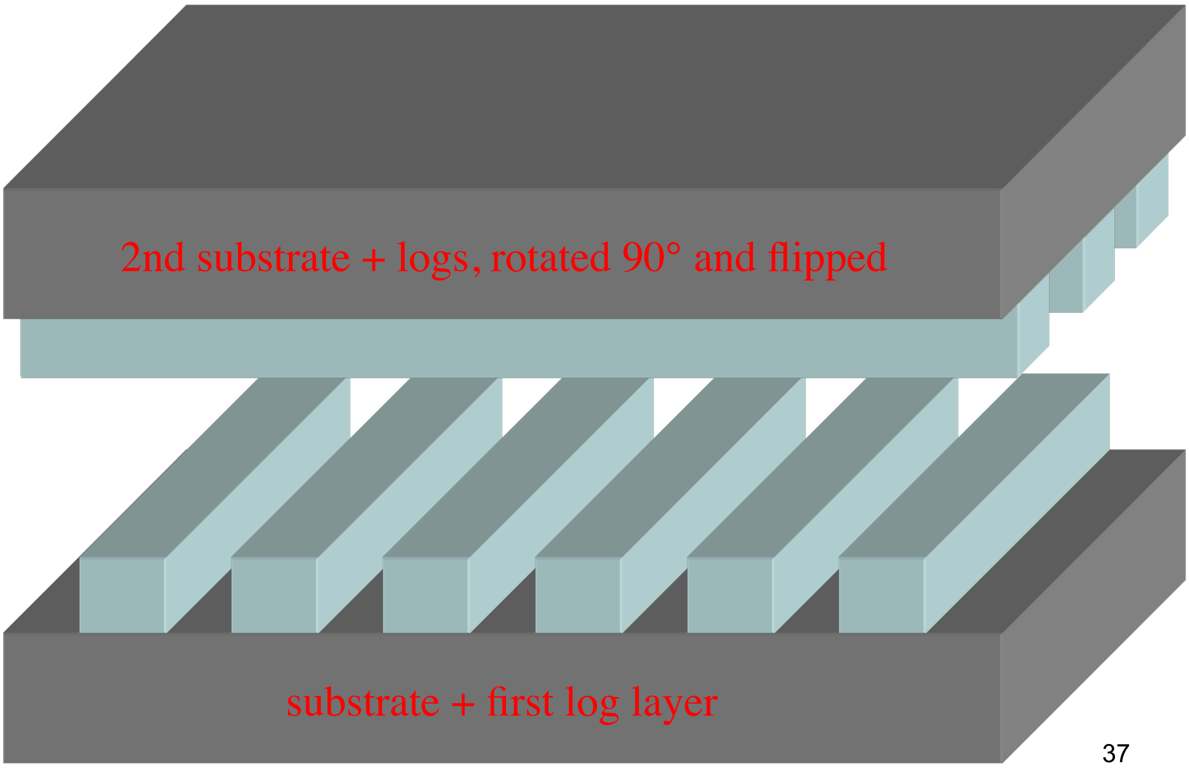
[S. Y. Lin *et al.*, *Nature* **394**, 251 (1998)]







Woodpile by Wafer Fusion



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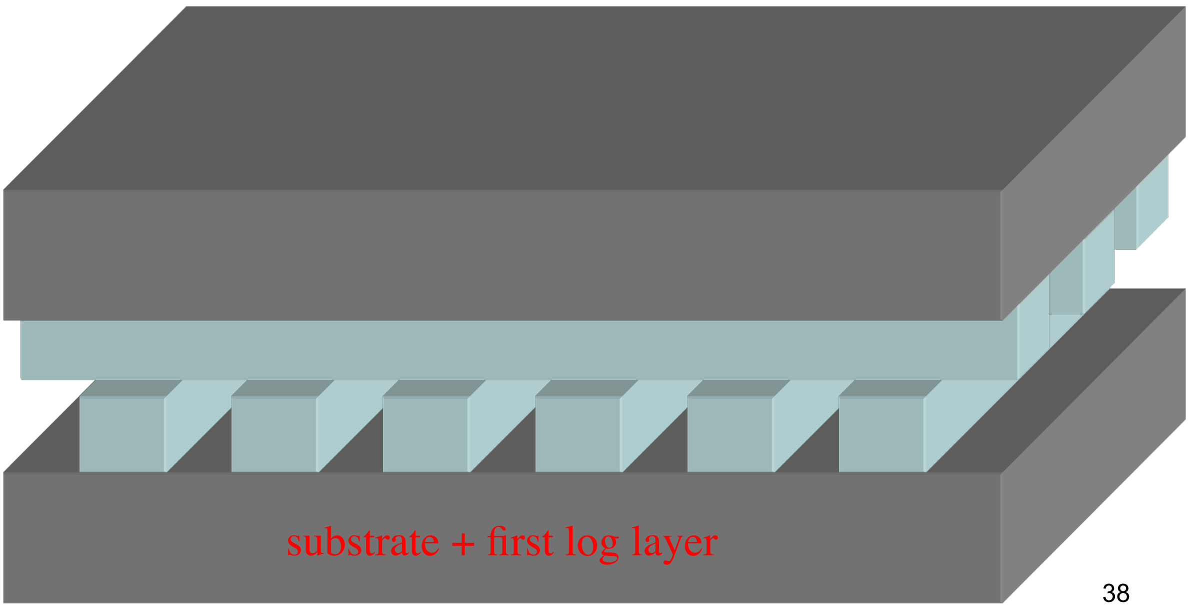
[S. Noda *et al*., *Science* **289**, 604 (2000)]

Woodpile by Wafer Fusion

fuse wafers together…



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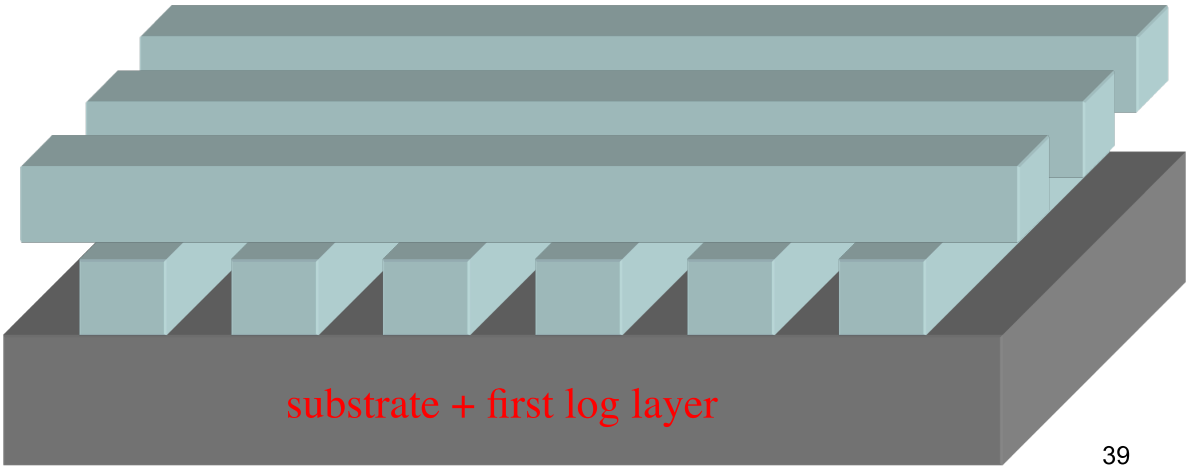
[S. Noda *et al*., *Science* **289**, 604 (2000)]

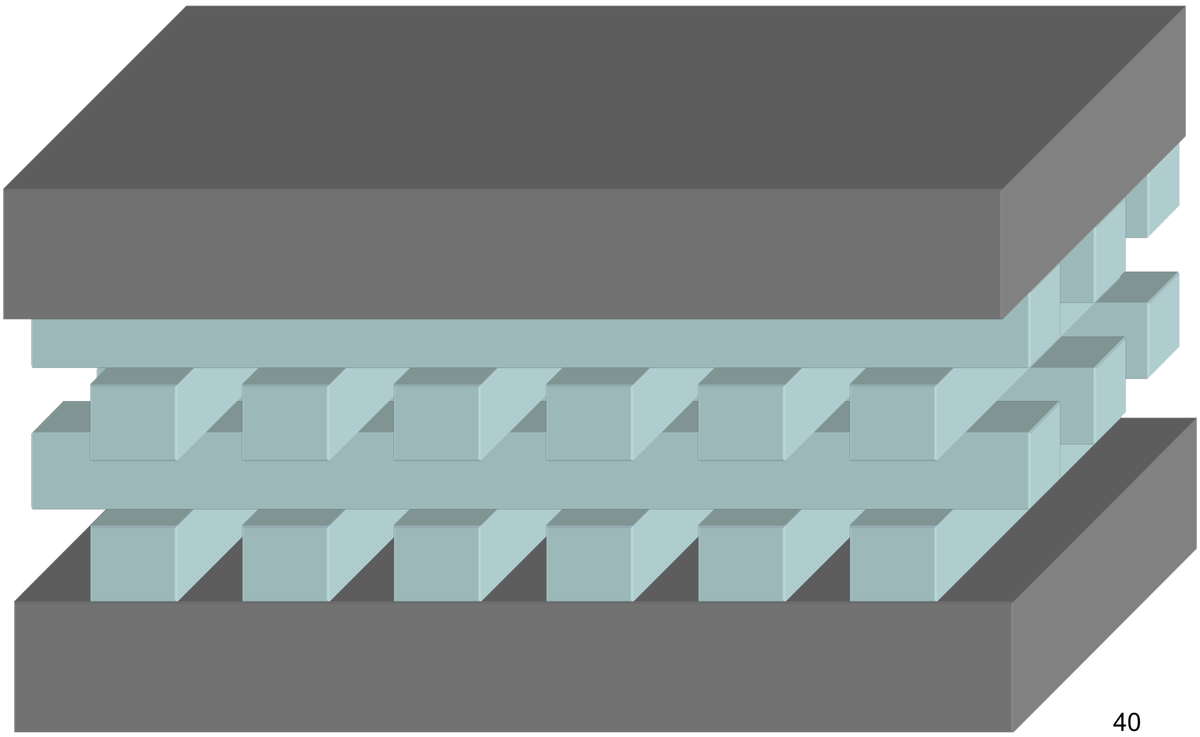
Woodpile by Wafer Fusion



[S. Noda *et al.*, *Science* **289**, 604 (2000)]

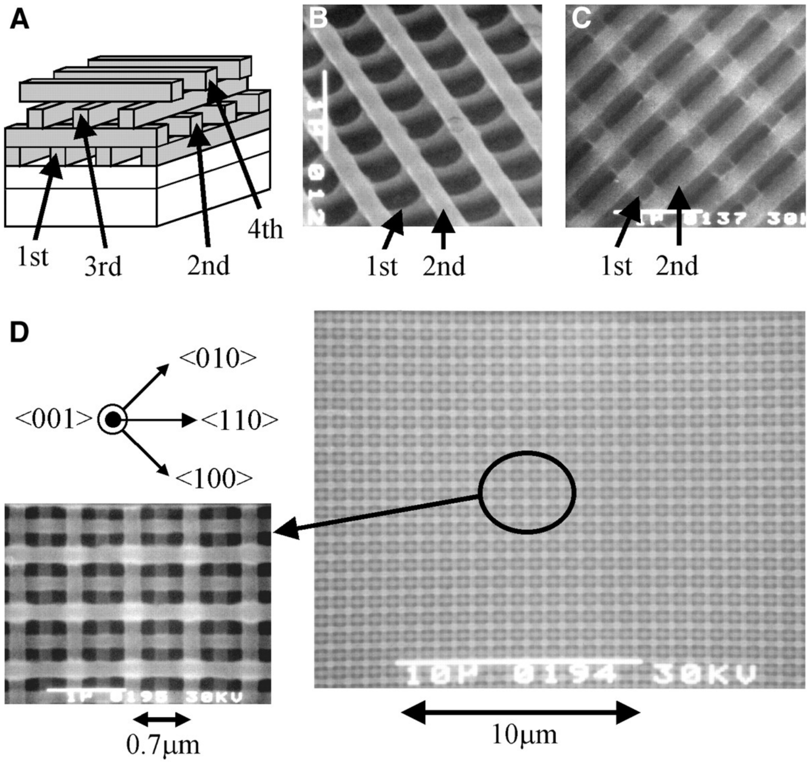
Woodpile by Wafer Fusion

double, double, toil and trouble…



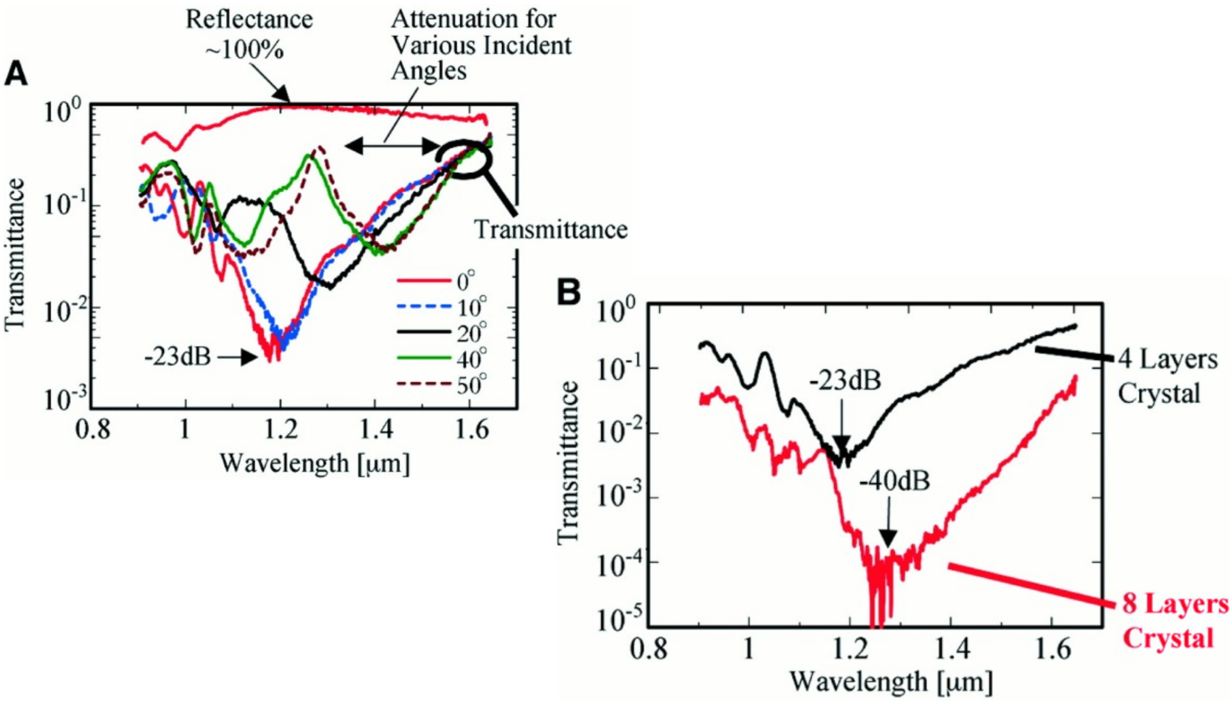
[S. Noda *et al.*, *Science* **289**, 604 (2000)]

“It’s only wafer-thin.” [M. Python]



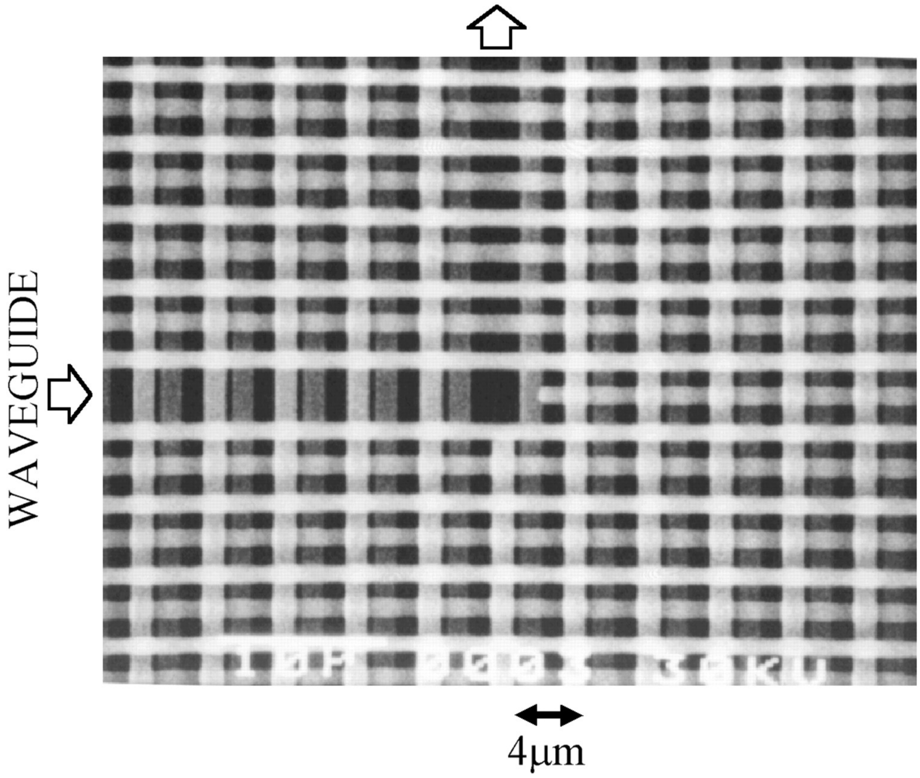
[S. Noda *et al*., *Science* **289**, 604 (2000)]

Woodpile Gap from 1.3–1.55μm



[S. Noda *et al*., *Science* **289**, 604 (2000)]

Finally, a Defect!



[S. Noda *et al.*, *Science* **289**, 604 (2000)]

Stacking by Micromanipulation

[K. Aoki *et al.*, Appl. Phys. Lett. 81 (17), 3122 (2002)]

microsphere into hole

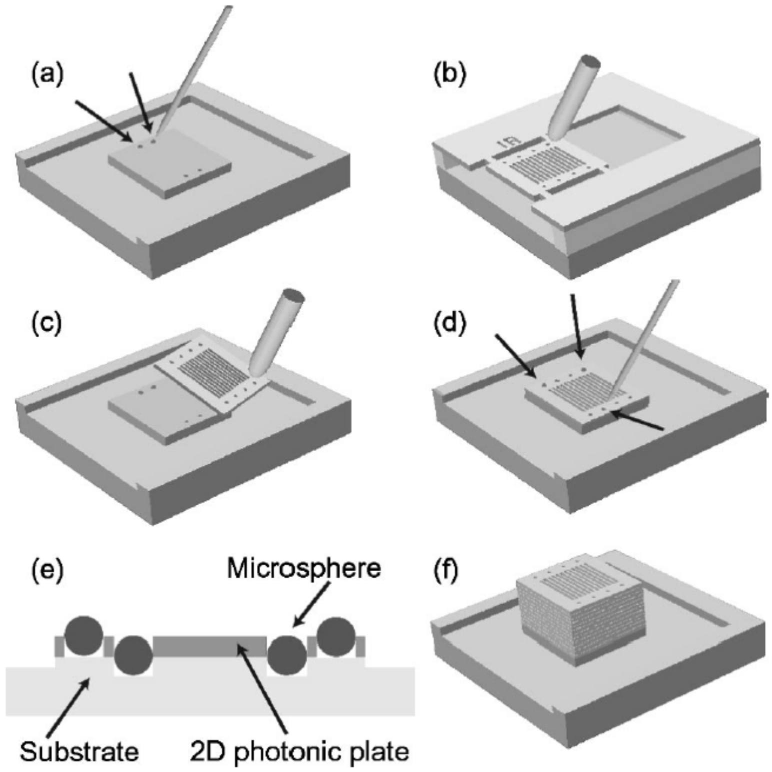
break off suspended layer

lift up and move to substrate

tap down holes onto spheres

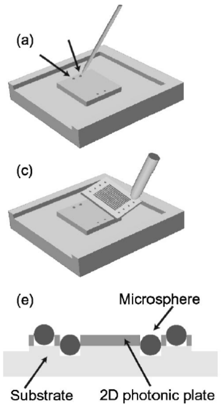
spheres enforce alignment

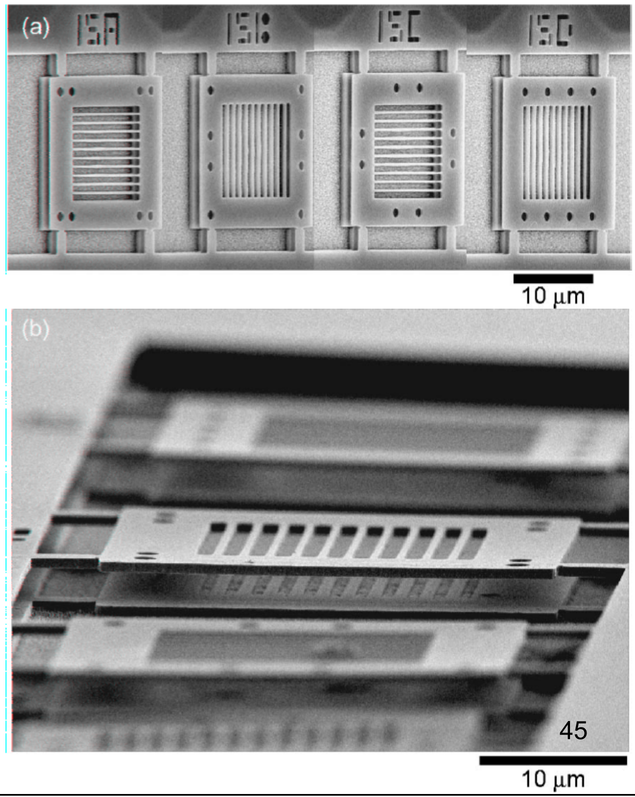
`goto a;`



Stacking by Micromanipulation

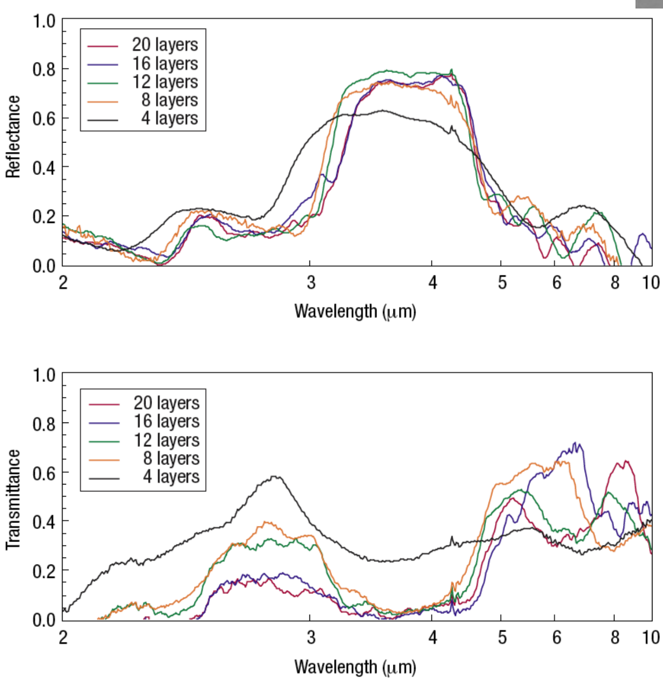
[K. Aoki *et al.*, Appl. Phys. Lett. 81 (17), 3122 (2002)]

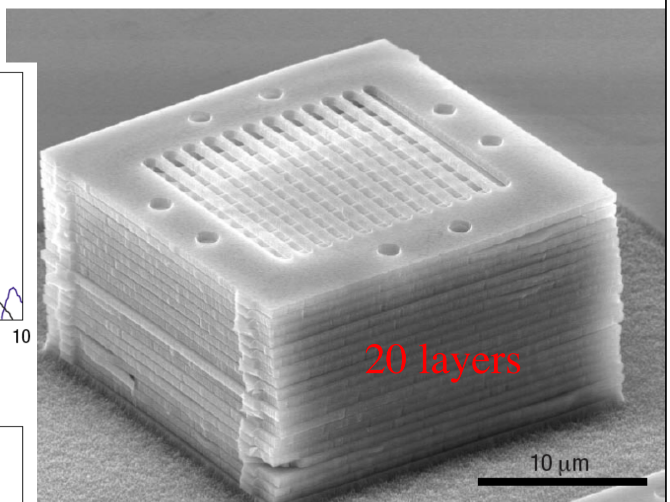




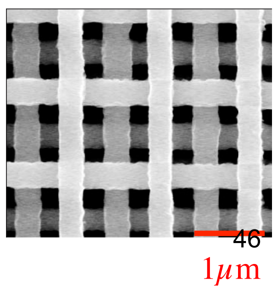
Yes, it works: Gap at ~4μm

[K. Aoki *et al.*, *Nature Materials* **2** (2), 117 (2003)]





50nm accuracy:

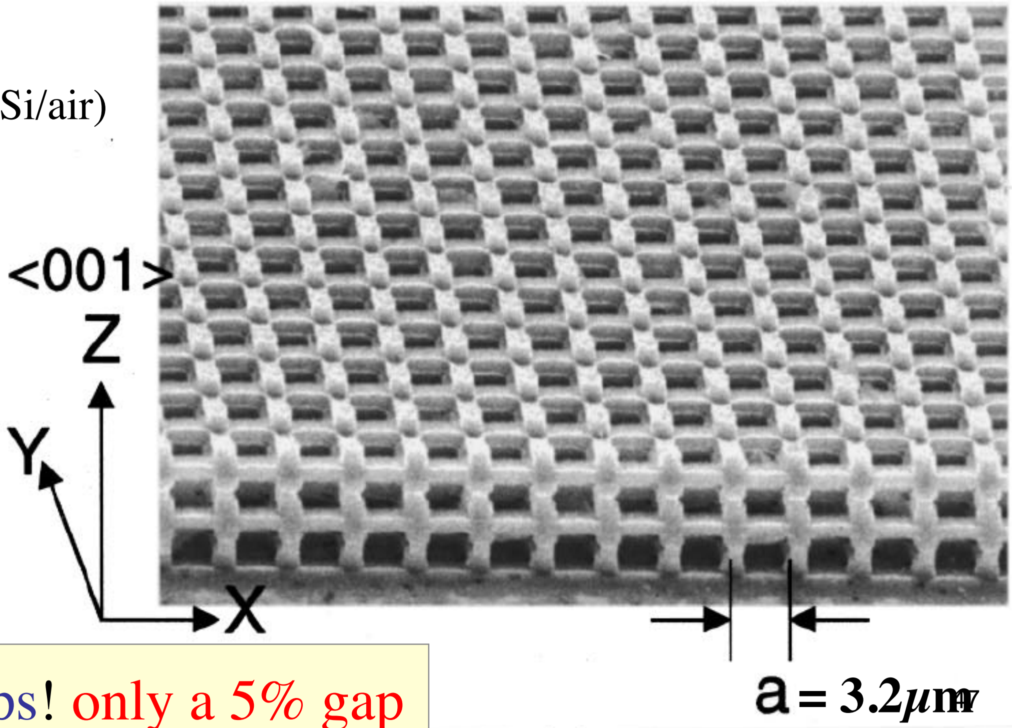


(gap effects are limited by finite lateral size)

Hey, forget these FCC crystals!

simple-cubic lattice [S.-Y. Lin *et al.*, *JOSA B* **18**, 32 (2001).]

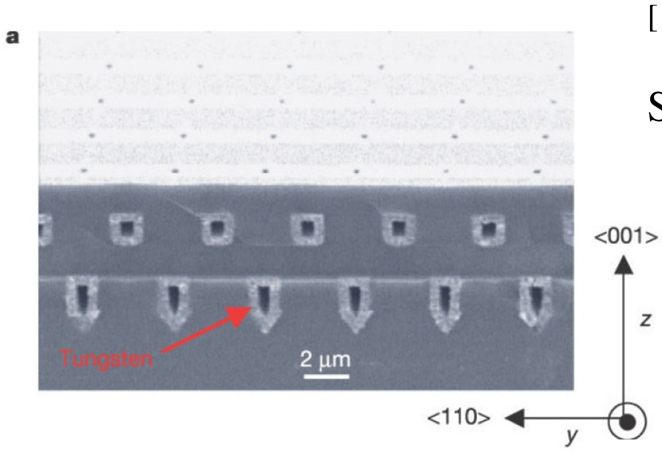
(UV stepper, Si/air)



Whoops! only a 5% gap

A *Metal* Photonic Crystal

[J. G. Fleming *et al.*, *Nature* **417**, 52 (2002)]

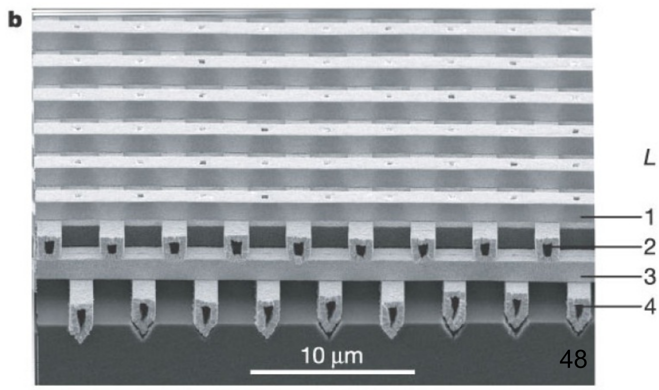


Start with Si woodpile in SiO_2…

dissolve Si with KOH…

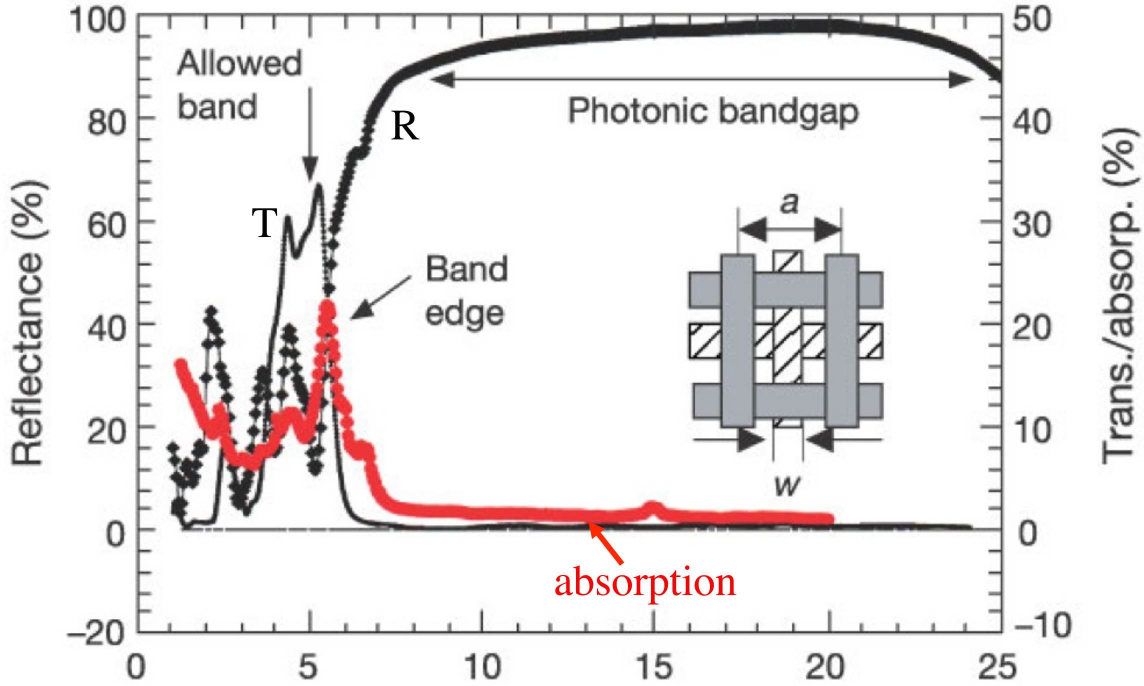
fill with Tungsten
via chemical vapor deposition (CVD)
(on thin TiN layer)

dissolve SiO_2 with HF…



Thermal properties of metal crystal

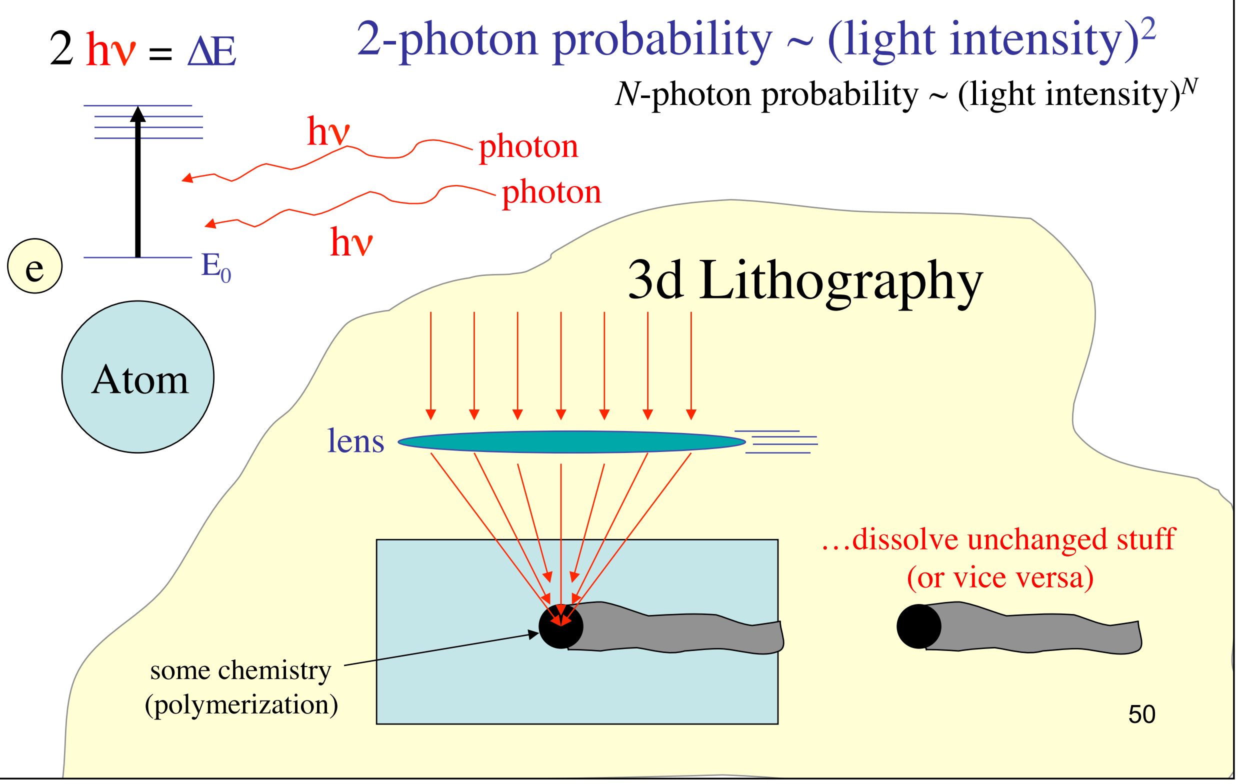
[J. G. Fleming *et al*., *Nature* **417**, 52 (2002)]



Kirchoff's Law: a good absorber is a good emitter …modify thermal emission!

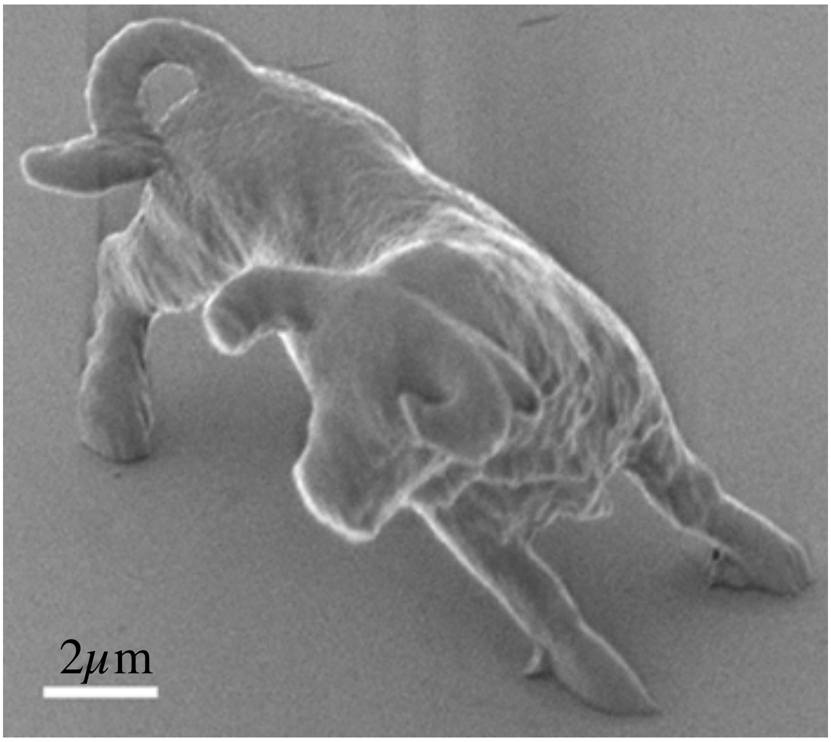
solar cells… light bulbs…

Two-Photon Lithography



Lithography is a Beast

[S. Kawata *et al.*, *Nature* **412**, 697 (2001)]



λ = 780nm

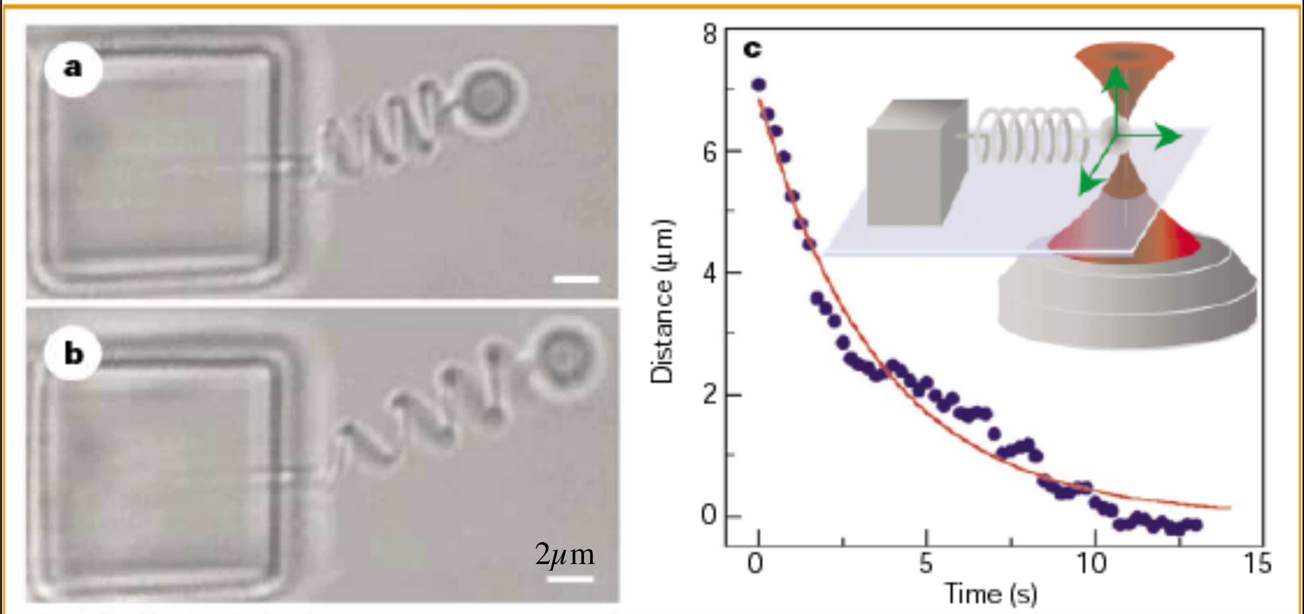
resolution = 150nm

7μm

(3 hours to make)

For a physicist, this is cooler…

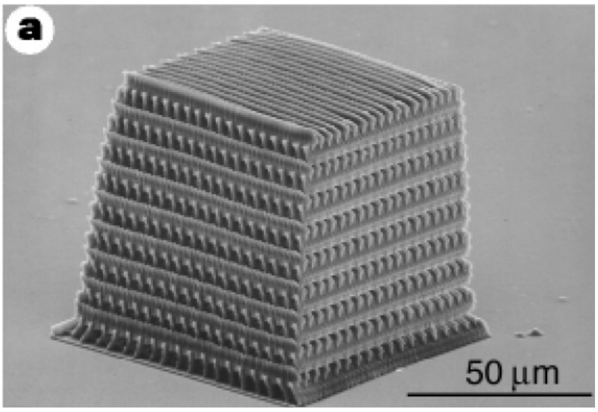
[S. Kawata *et al.*, *Nature* **412**, 697 (2001)]



(300nm diameter coils, suspended in ethanol, viscosity-damped)

A Two-Photon Woodpile Crystal

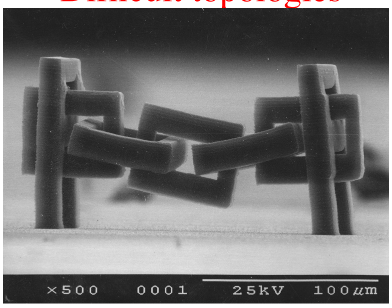
[B. H. Cumpston *et al*., *Nature* **398**, 51 (1999)]



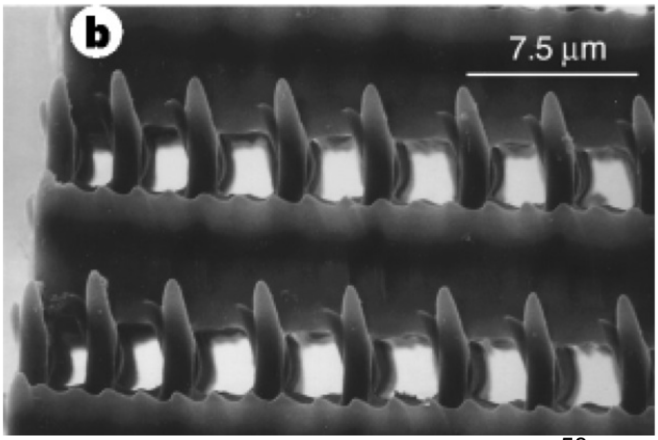
(much work on materials
with lower power 2-photon process)

• Arbitrary lattice
• No "mask"
• Fast/cheap prototyping

Difficult topologies



[fig. courtesy J. W. Perry, U. Arizona]

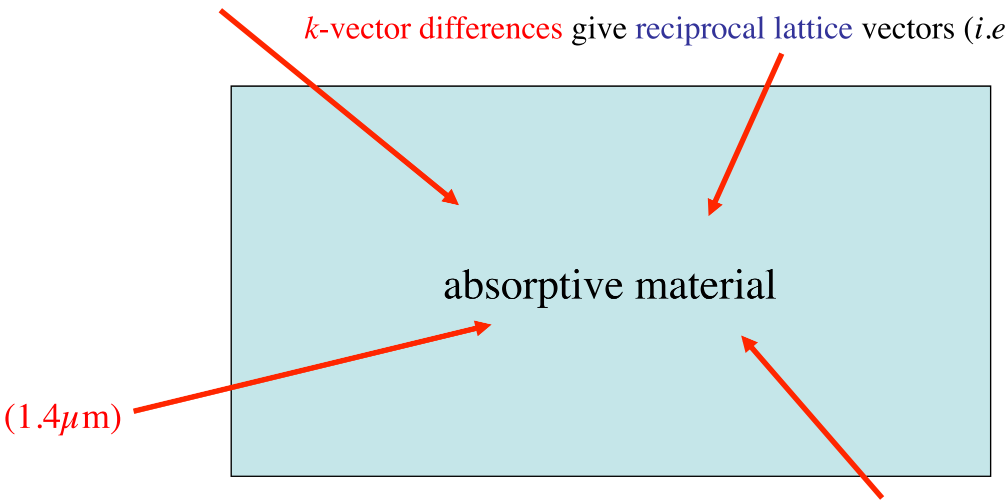


One-Photon
Holographic Lithography

[D. N. Sharp *et al*., *Opt. Quant. Elec.* **34**, 3 (2002)]

Four beams make 3d-periodic interference pattern

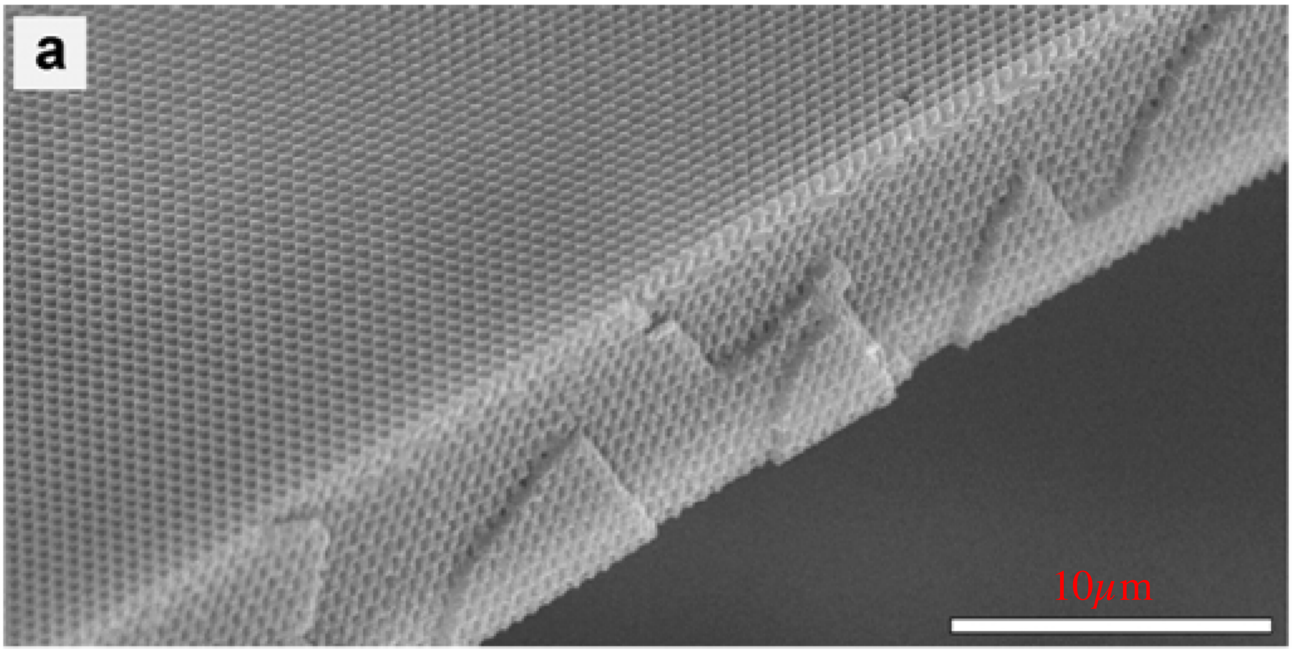
k-vector differences give reciprocal lattice vectors (*i.e.* periodicity)



beam polarizations + amplitudes (8 parameters) give unit cell

One-Photon
Holographic Lithography

[D. N. Sharp *et al*., *Opt*. *Quant*. *Elec*. **34**, 3 (2002)]

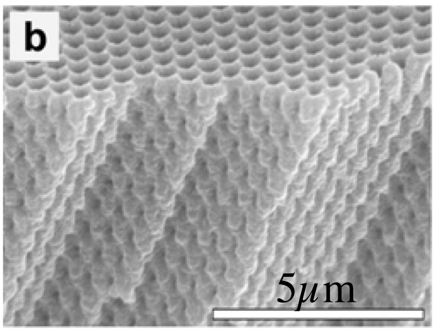


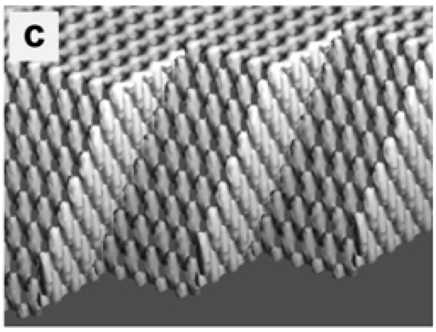
huge volumes, long-range periodic, fcc lattice…backfill for high contrast

One-Photon
Holographic Lithography

[D. N. Sharp *et al*., *Opt*. *Quant*. *Elec*. **34**, 3 (2002)]

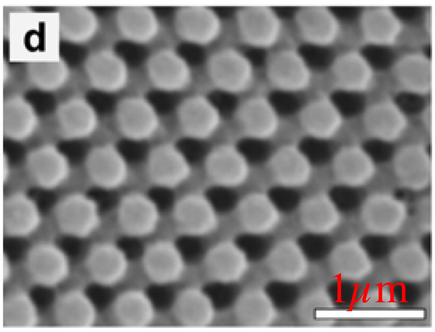
[111] cleavages

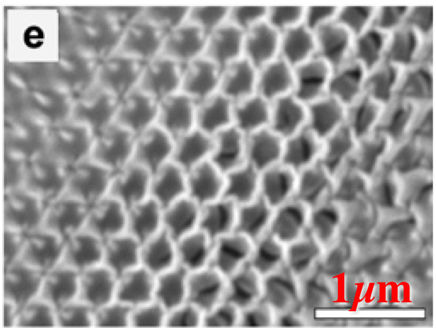




simulated structure

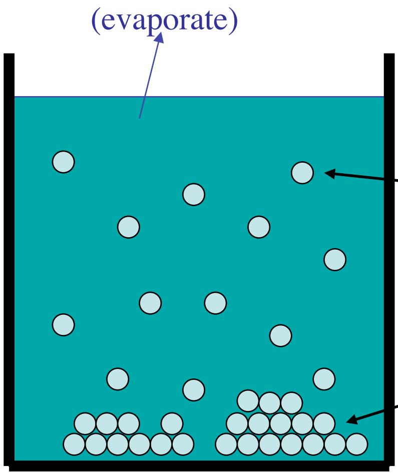
[111] closeup





titania inverse structure

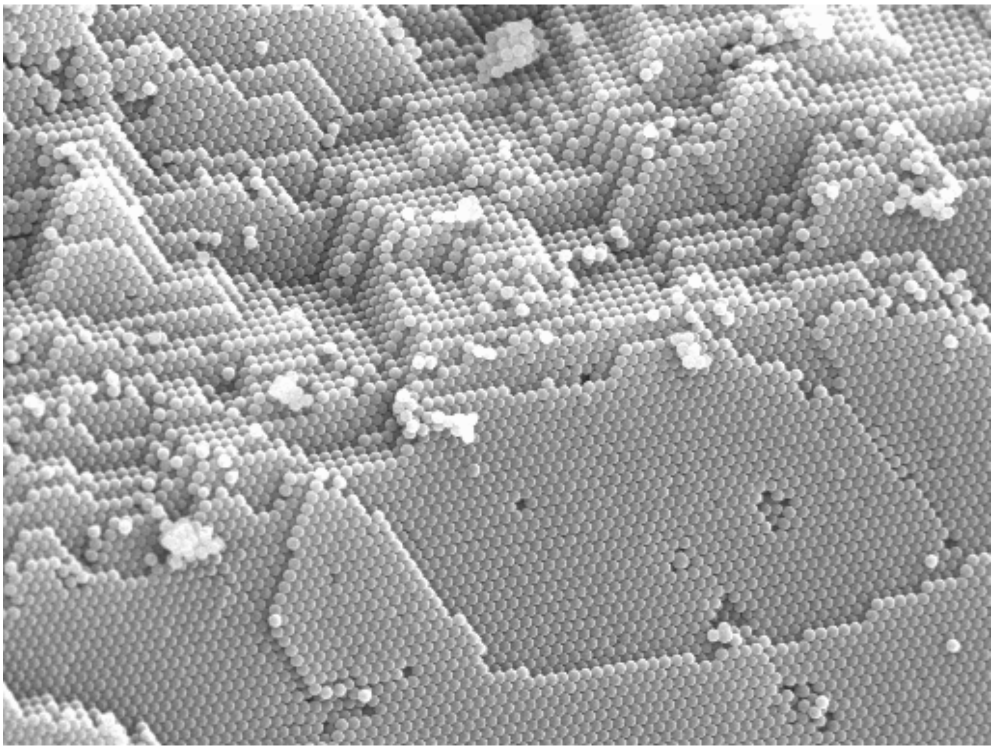
Mass-production II: Colloids



silica (SiO_2)
microspheres (diameter < 1μm)

sediment by gravity into
close-packed fcc lattice!

Mass-production II: Colloids



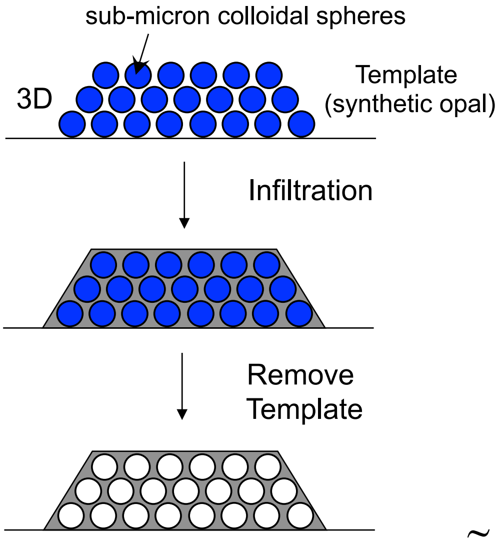
http://www.icmm.csic.es/cefe/

Inverse Opals

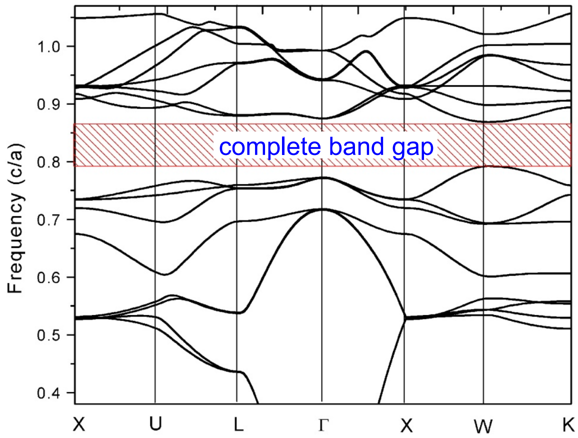
[figs courtesy
D. Norris, UMN]

fcc solid spheres do not have a gap…

…but fcc spherical holes in Si *do* have a gap



"Inverted Opal"

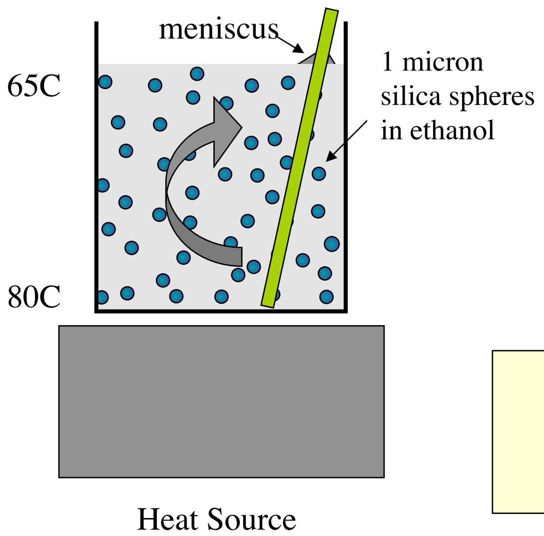


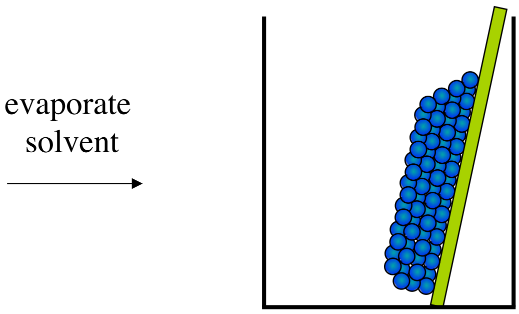
~ 10% gap between 8th & 9th bands

small gap, upper bands: sensitive to disorder

In Order To Form a More Perfect Crystal…

[figs courtesy
D. Norris, UMN]





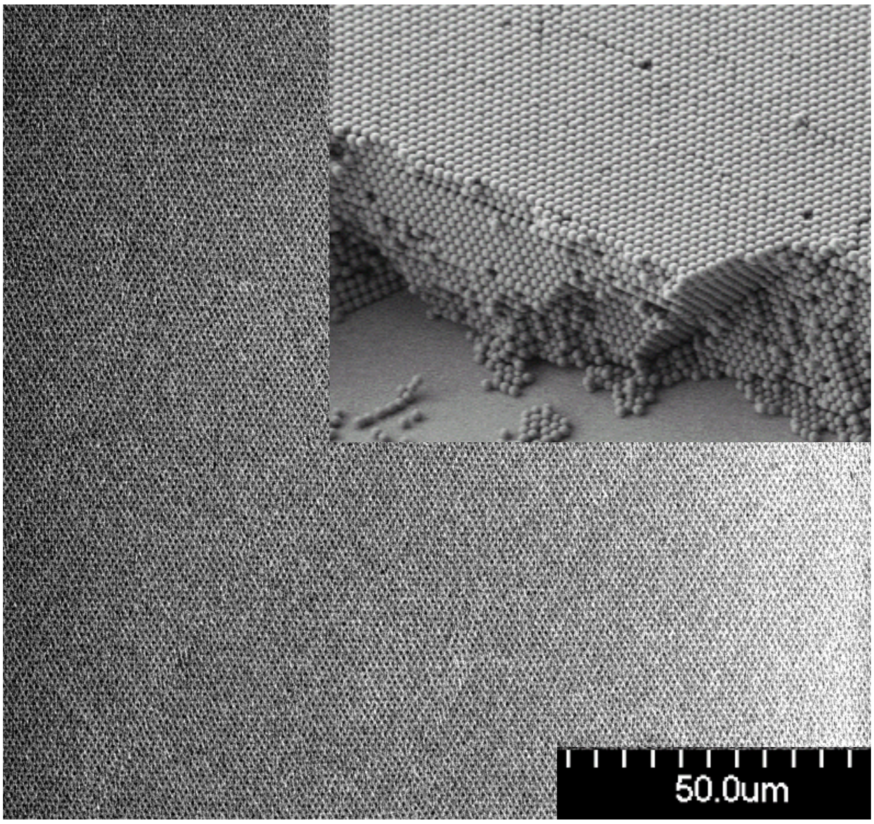
Convective Assembly

[Nagayama, Velev, *et al.*, *Nature* (1993)
Colvin *et al.*, *Chem. Mater.* (1999)]

- Capillary forces during drying cause assembly in the meniscus
- Extremely flat, large-area opals of controllable thickness

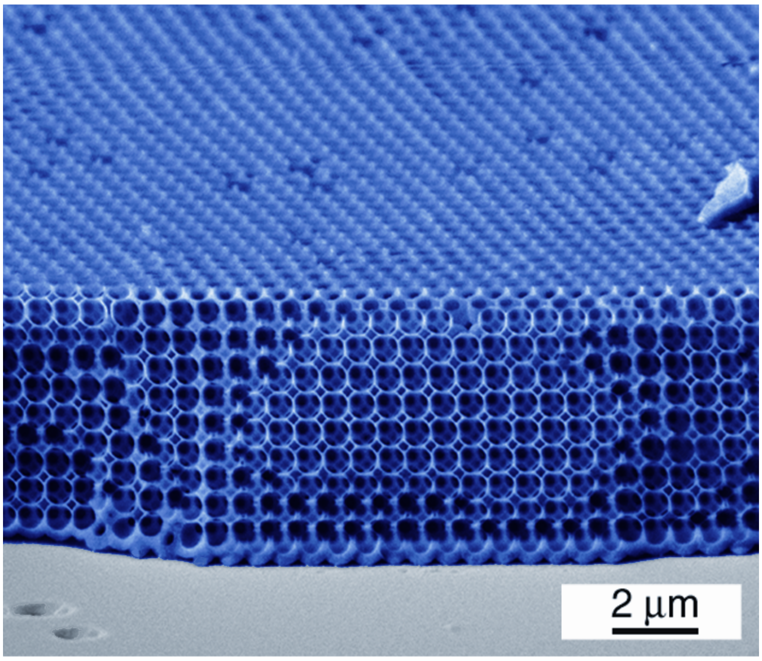
A Better Opal

[fig courtesy
D. Norris, UMN]



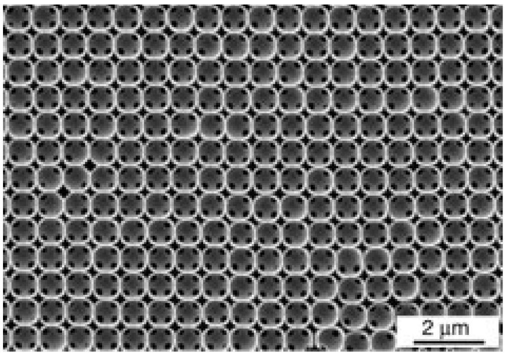
Inverse-Opal Photonic Crystal

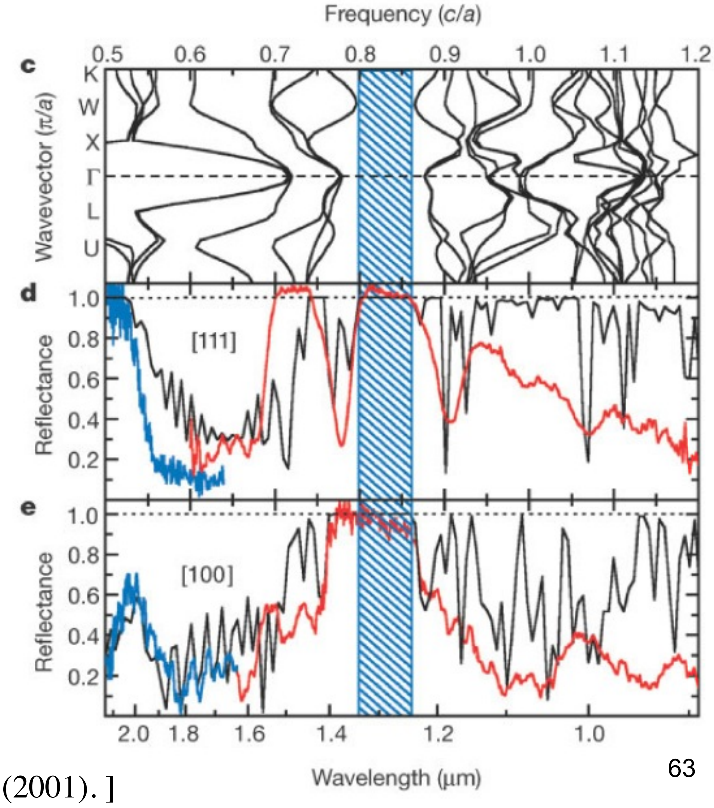
[fig courtesy
D. Norris, UMN]



[Y. A. Vlasov *et al*., *Nature* **414**, 289 (2001).]

Inverse-Opal Band Gap





good agreement
between **theory** (black)
& experiment (red/blue)

[Y. A. Vlasov *et al*., *Nature* **414**, 289 (2001).]

Engineering of Nanomaterials for Enhanced Functionality