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Manufacturing of metamaterials

SEVENTH FRAMEWORK PROGRAMME

cost

UNIA EUROPEJSKA
EUROPEJSKI FUNDUSZ
ROZWOJU REGIONALNEGO

meta morphose

FNP
Fundacja na rzecz Nauki Polskiej

INNOWACYJNA
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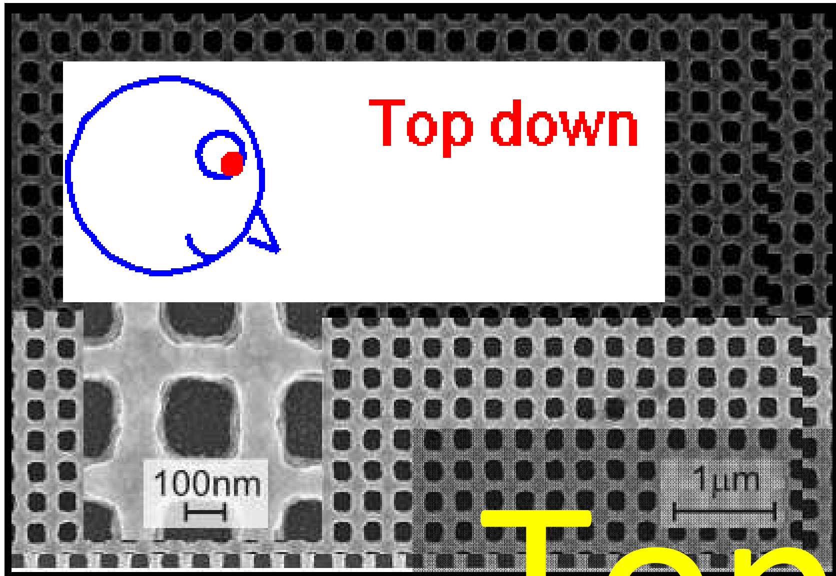
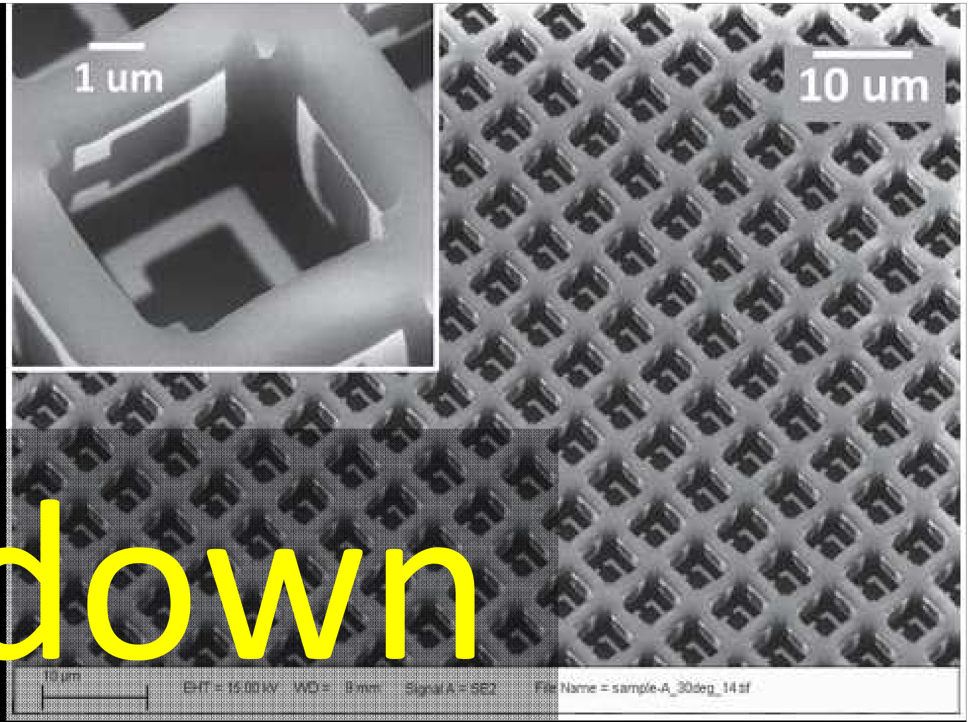
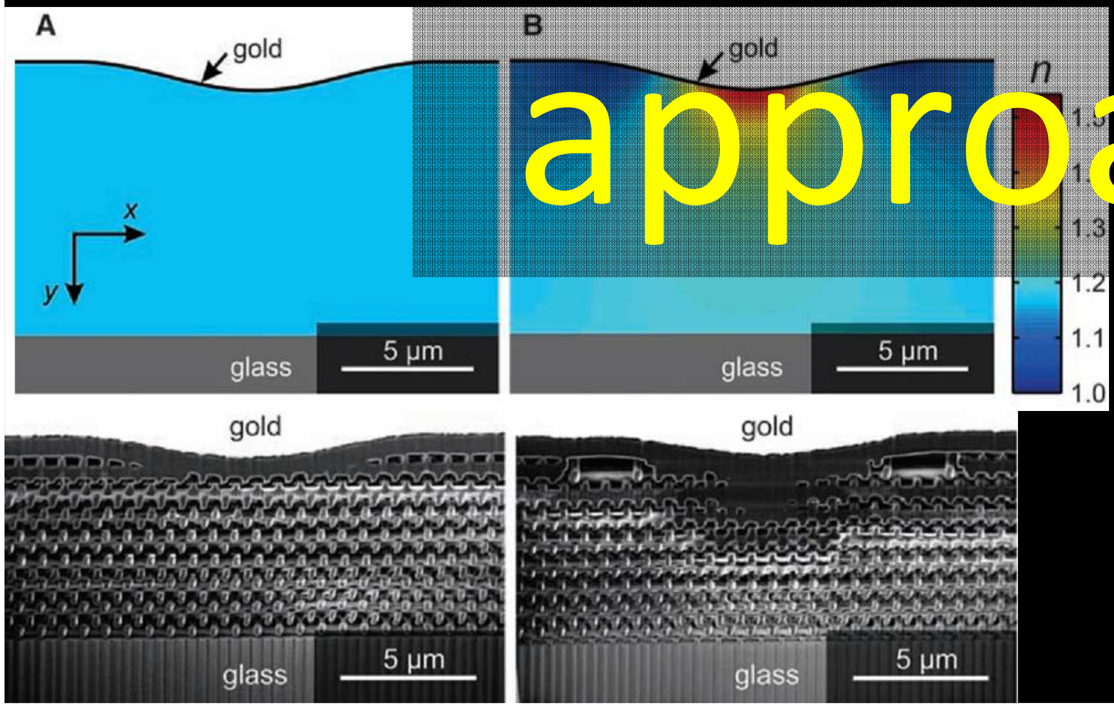
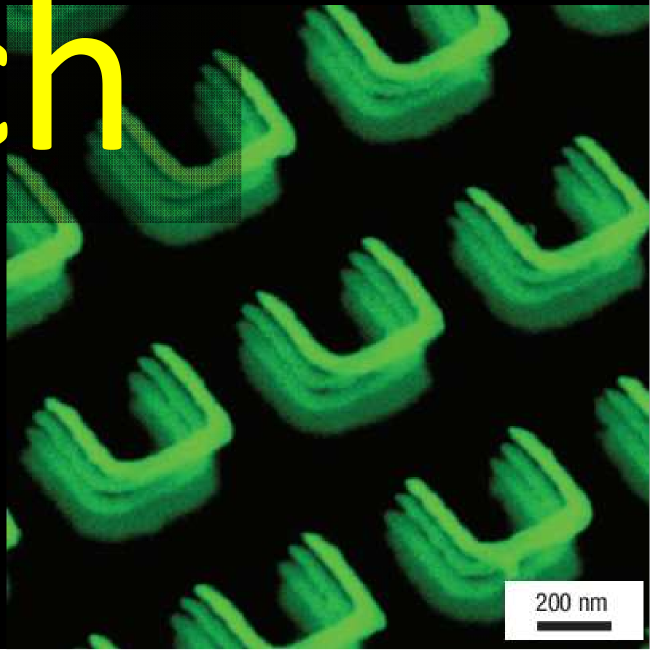
Top-down approach





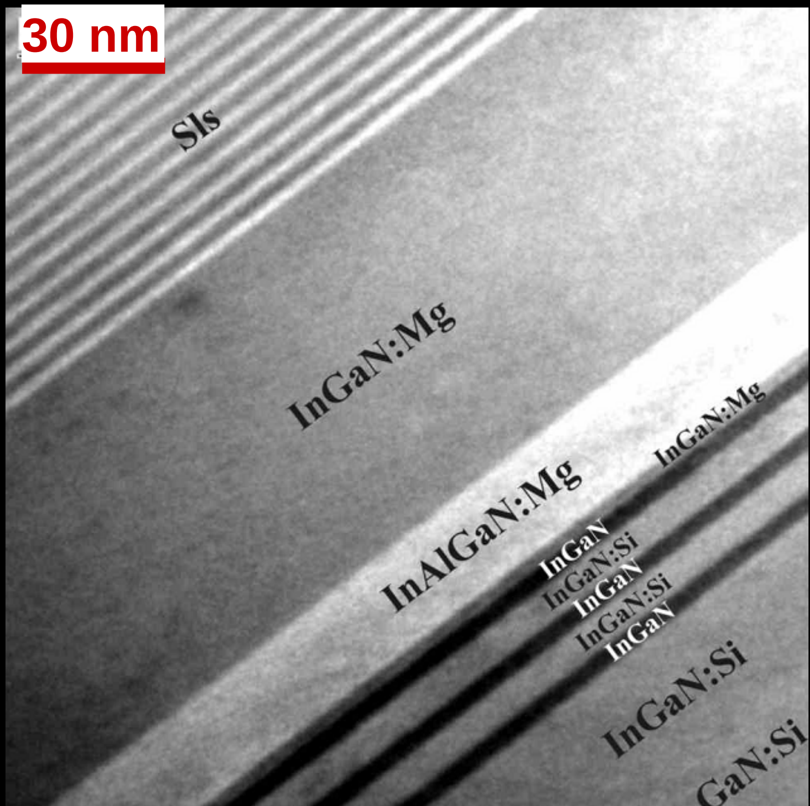




Why can’t we use common nanofabrication techniques for metals?

MOCVD – substrate is exposed to one or more volatile metalloorganic precursors, which react and/or decompose on the substrate surface to produce thin film

MOCVD (Metal-Organic Chemical Vapour Deposition)



TEM image of GaN/InGaN blue laser diode fabricated by MOCVD

Photolithography

INTEL Ivy Bridge Central Processing Unit (chip fabricated by photolithography - 22 nm technology; 1,4 billion of transistors)
http://www.infocast.pl/nowe-procesory-serii-ivy-bridge-3586

Why can't we use common nanofabrication techniques for metals?

✓ Gold and silver are mostly used materials in plasmonics/metamaterial nanofabrication

Problems with metals in MOCVD/evaporation/sputtering

-MOCVD films - degraded optical properties due to inherent contaminants from the precursor materials

-evaporated or sputtered metal films - polycrystalline

$\rightarrow$ surface roughness and grain-boundary SPP scattering

-silver films under 30 nm - discontinuous

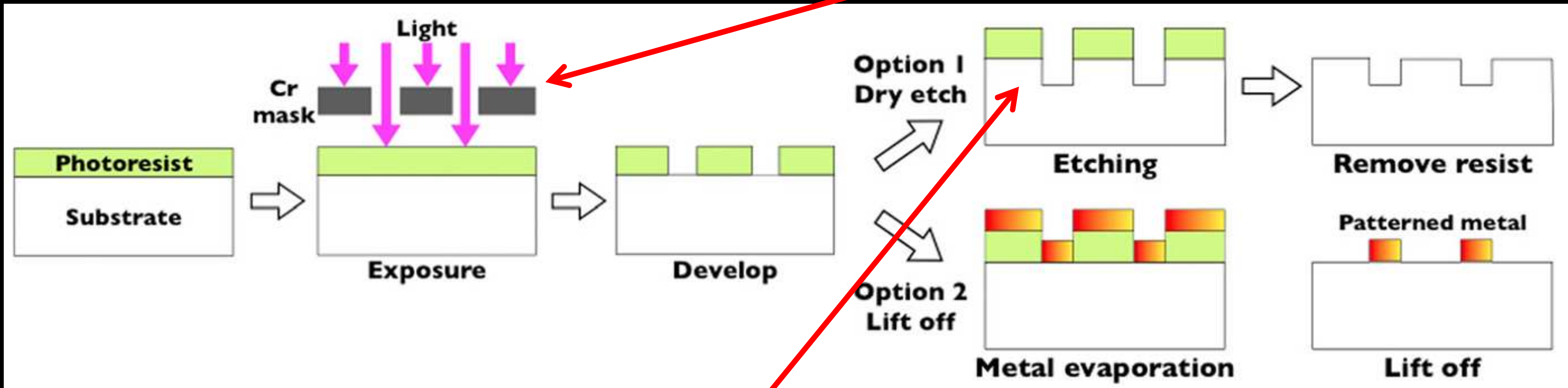
N C Lindquist et al. Rep. Prog. Phys. 75, 036501 (2012)

Why can't we use common nanofabrication techniques for metals?

✓ Gold and silver are mostly used materials in plasmonics/metamaterial nanofabrication

$$$ expensive photomask (good only for mass-scale fabrication)
very expensive state-of-the-art lithography equipment

In case of classic photolithography

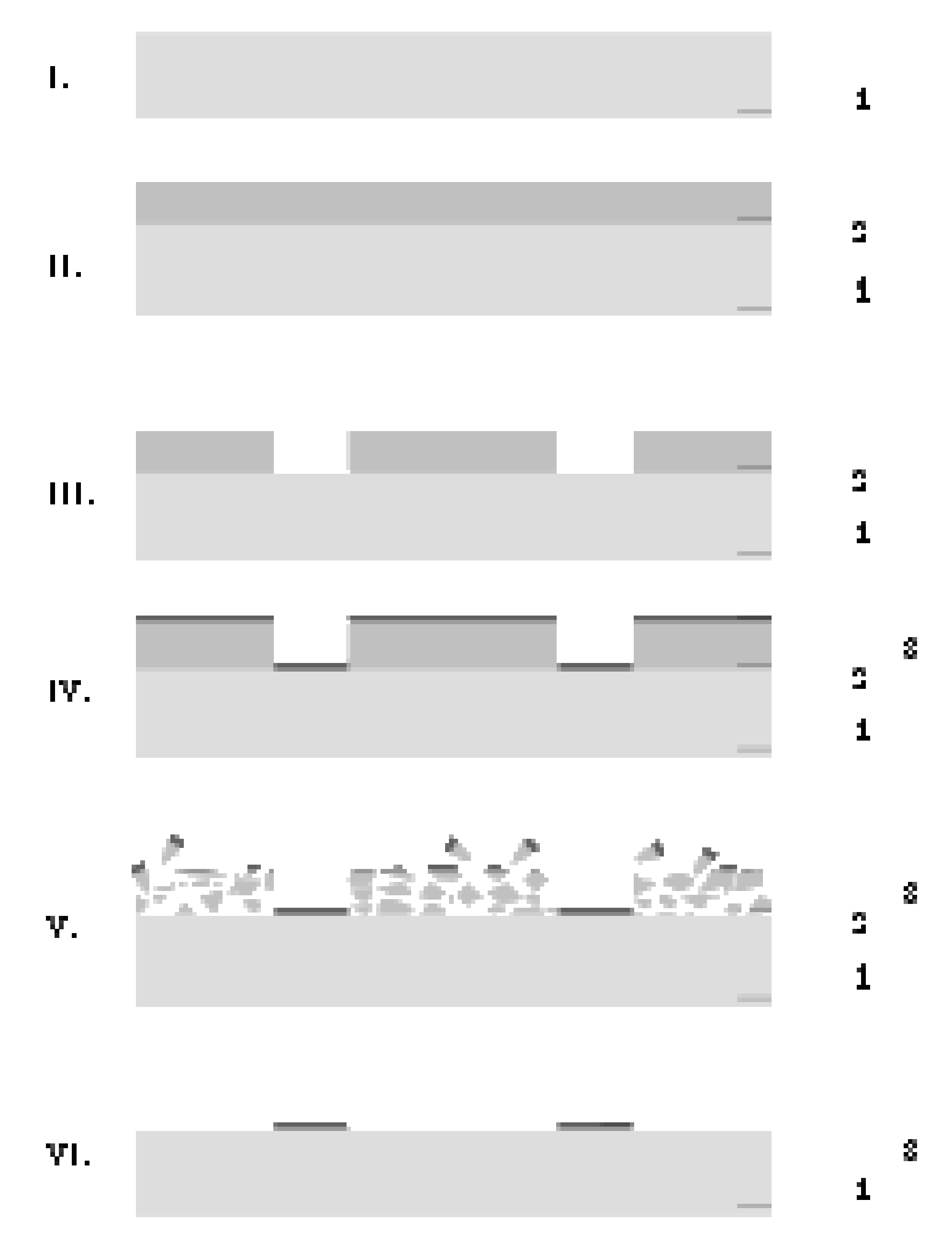


gold and silver cannot be easily plasma etched
because their etch by-products are non-volatile thus
ion beam milling is required

+ strongly limited spatial resolution => UV light

N C Lindquist et al. Rep. Prog. Phys. 75, 036501 (2012)

To avoid etching: lift off



I. Preparation of the substrate

II. Deposition of the resist

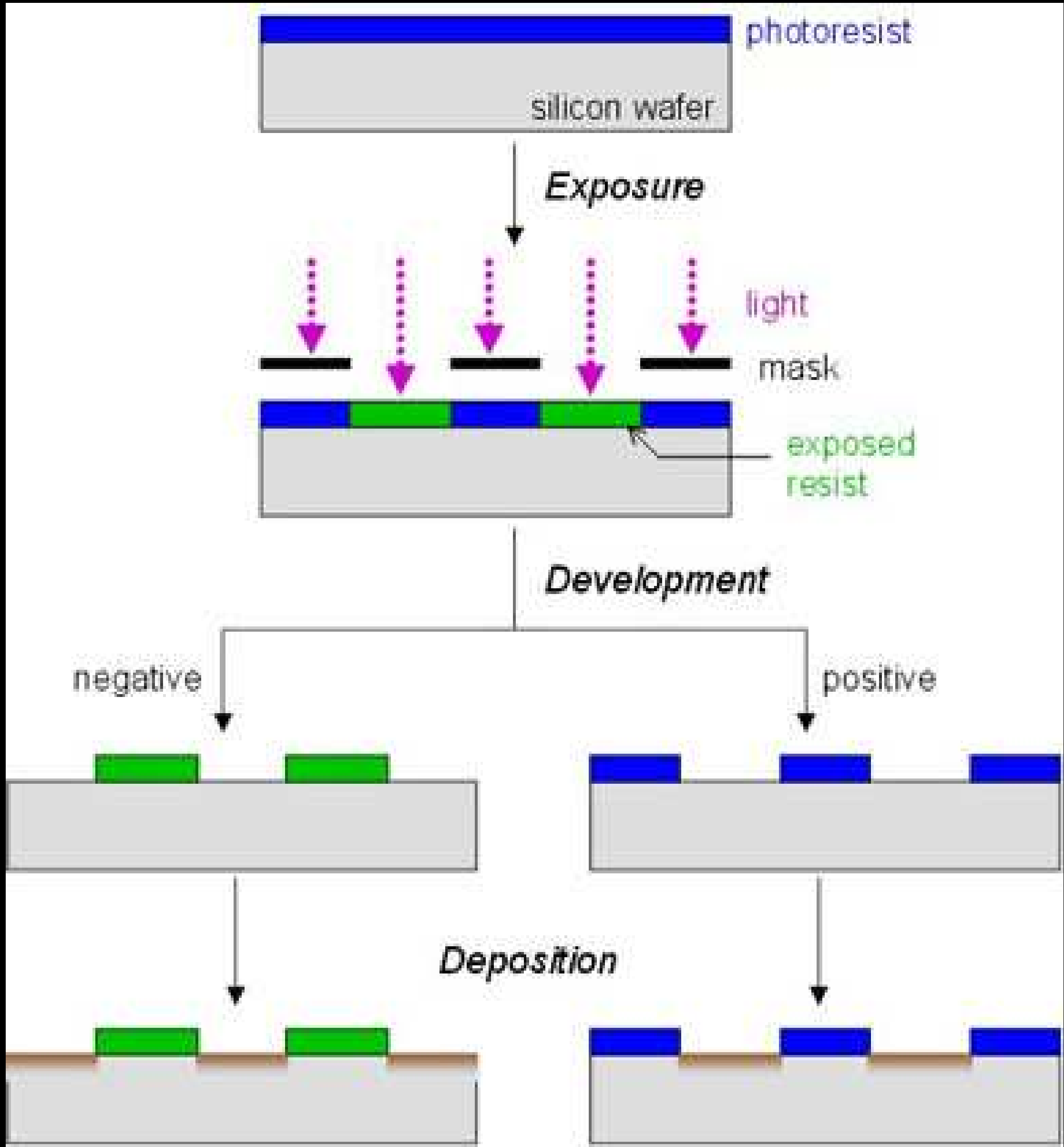
III. Resist patterning

IV. Deposition of the target material

V. Washing out the resist together with the target material on its surface

VI. Final pattern

Lithography - negative and positive resist



http://pluggedin.kodak.com/pluggedin/post/?id=655003

Metal film deposition

Electron beam evaporation
(electron beam physical vapor deposition)

✓uses electron beam to evaporate target material onto the substrate

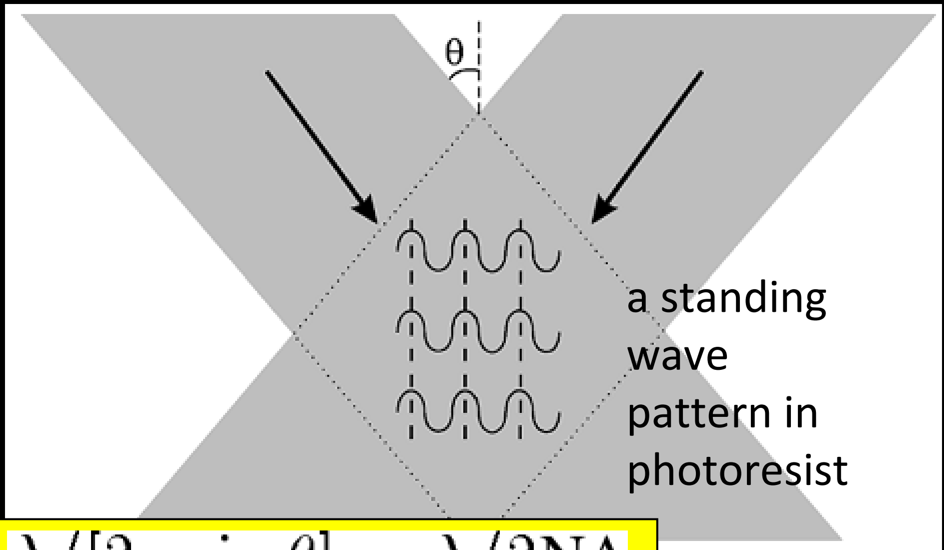
✓layers produced from 1 nm/minute to few micrometers/minute with precise thickness control

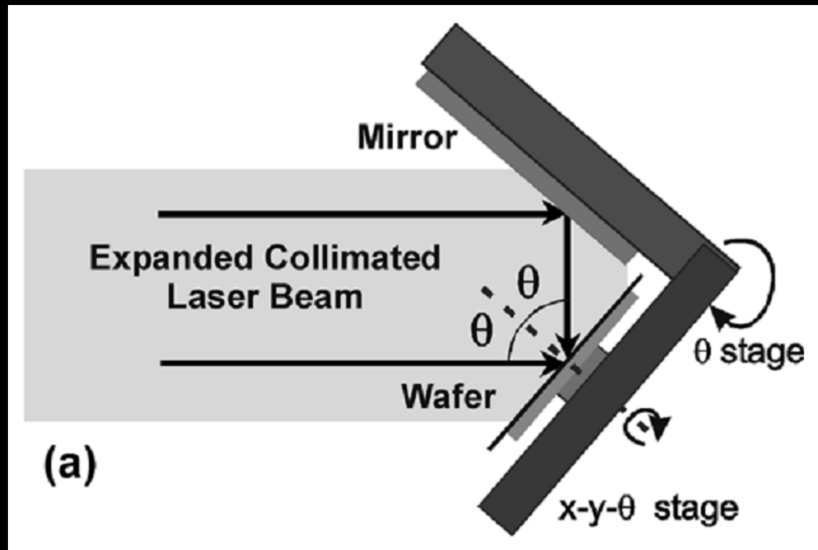
✓commonly used in lithography techniques

Interferometric photolithography (IL)
for maskless and large area patterning

$$$ expensive photomask (good only for mass-scale fabrication)

Two (or more) laser beams





$$\lambda/[2n \sin \theta] = \lambda/2\mathrm{NA}$$

Period of the interference pattern

Advantages:

•large-area of <u>periodic</u> nanostructures patterning

•maskless

Disadvantages:

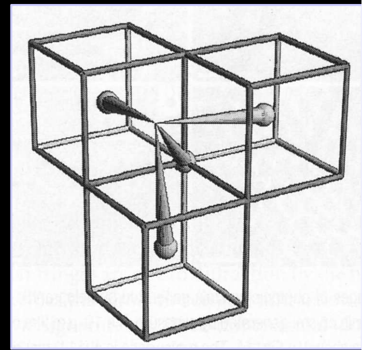
•limited spatial resolution

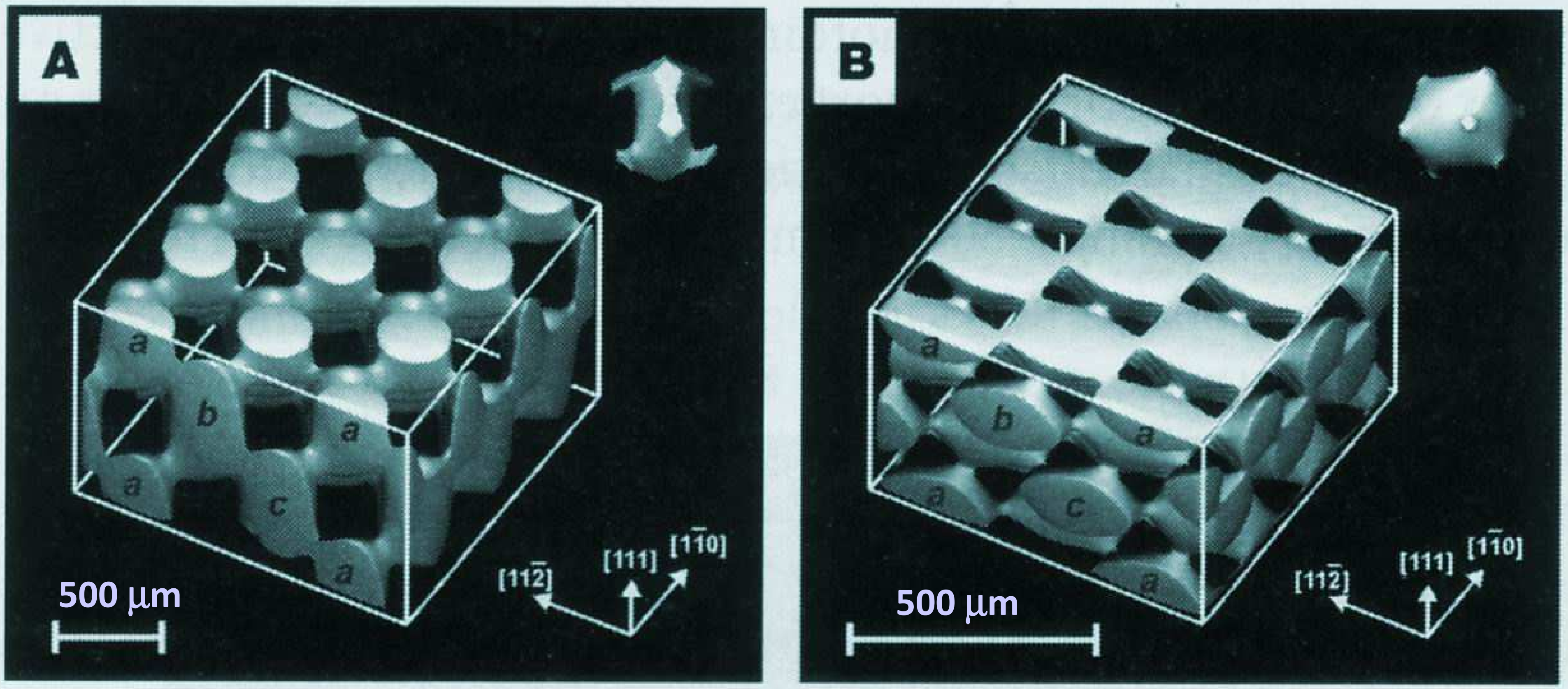
(e.g 34 nm for 193 nm ArF excimer laser)

S. R. J. Brueck PROCEEDINGS OF THE IEEE 93 (2005)

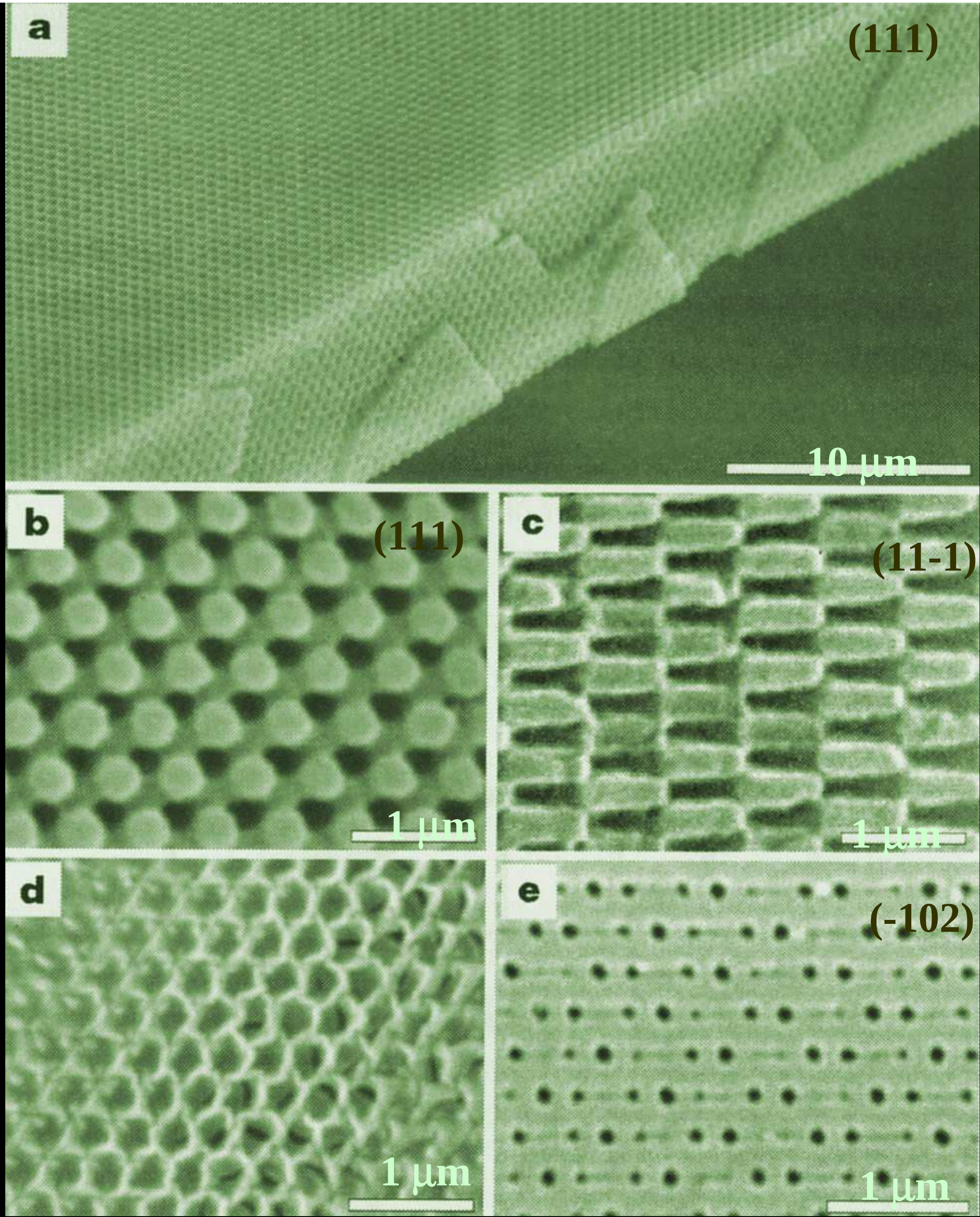
HOLOGRAPHIC LITHOGRAPHY–

by interference of four non-coplanar laser beams in a film of photoresist



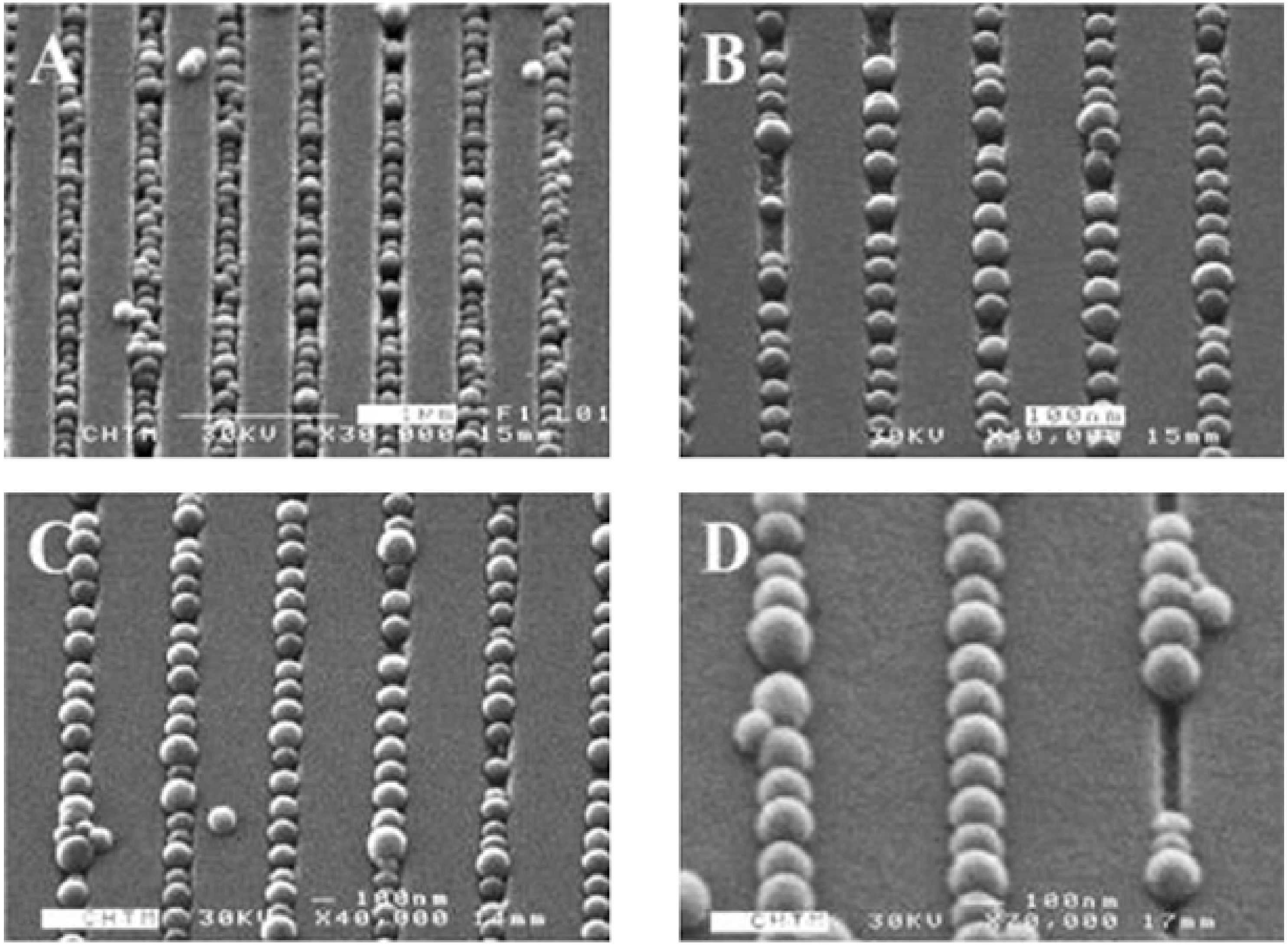


M. Campbell et al., Nature 404 (2000) 53.



M. Campbell et al., Nature 404 (2000) 53.

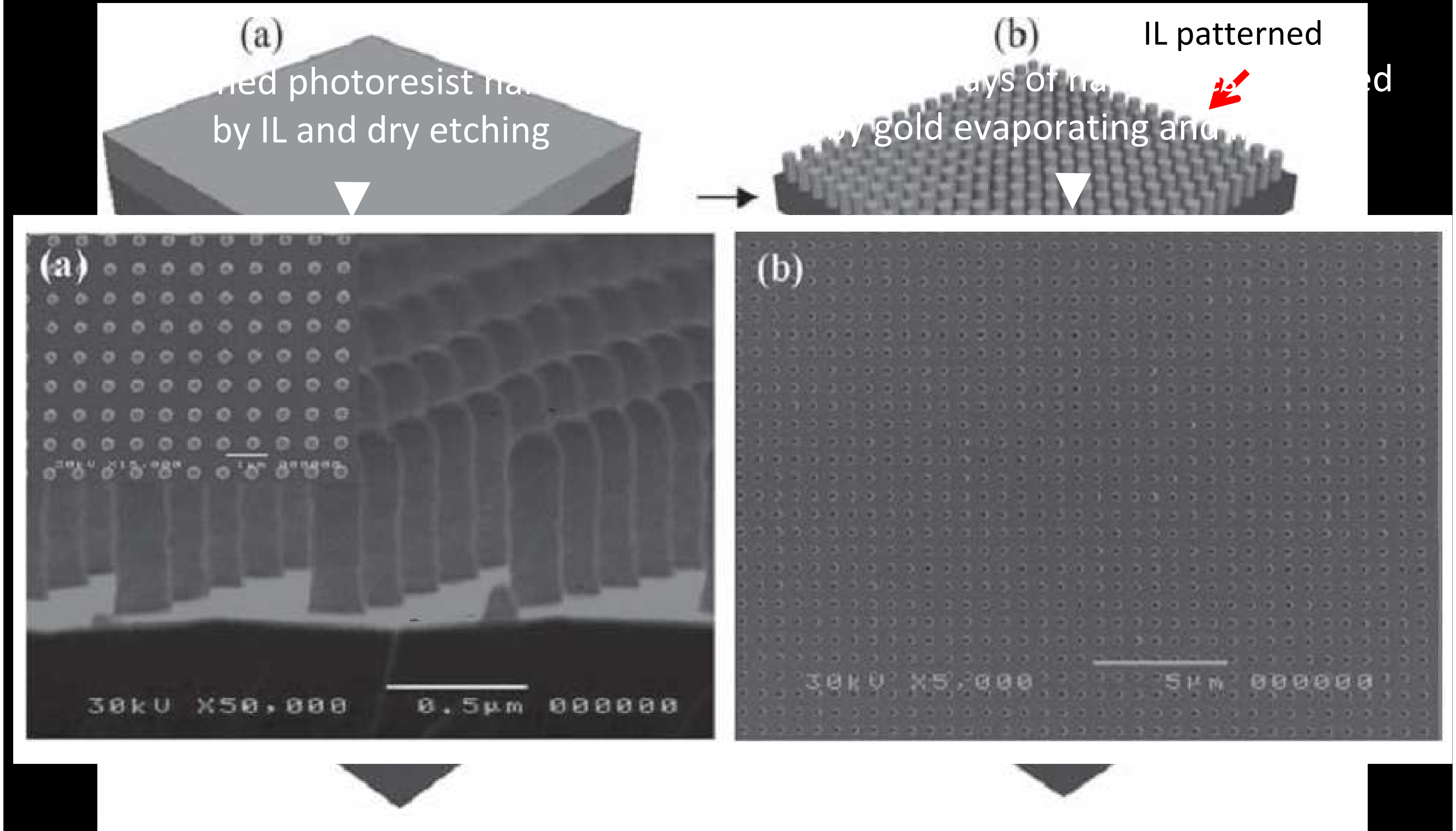
Interferometric photolithography (IL)
combined with other techniques



Self-assembled arrays of SiO_2 nanoparticles spin-coated on IL patterned SiO_2 surface

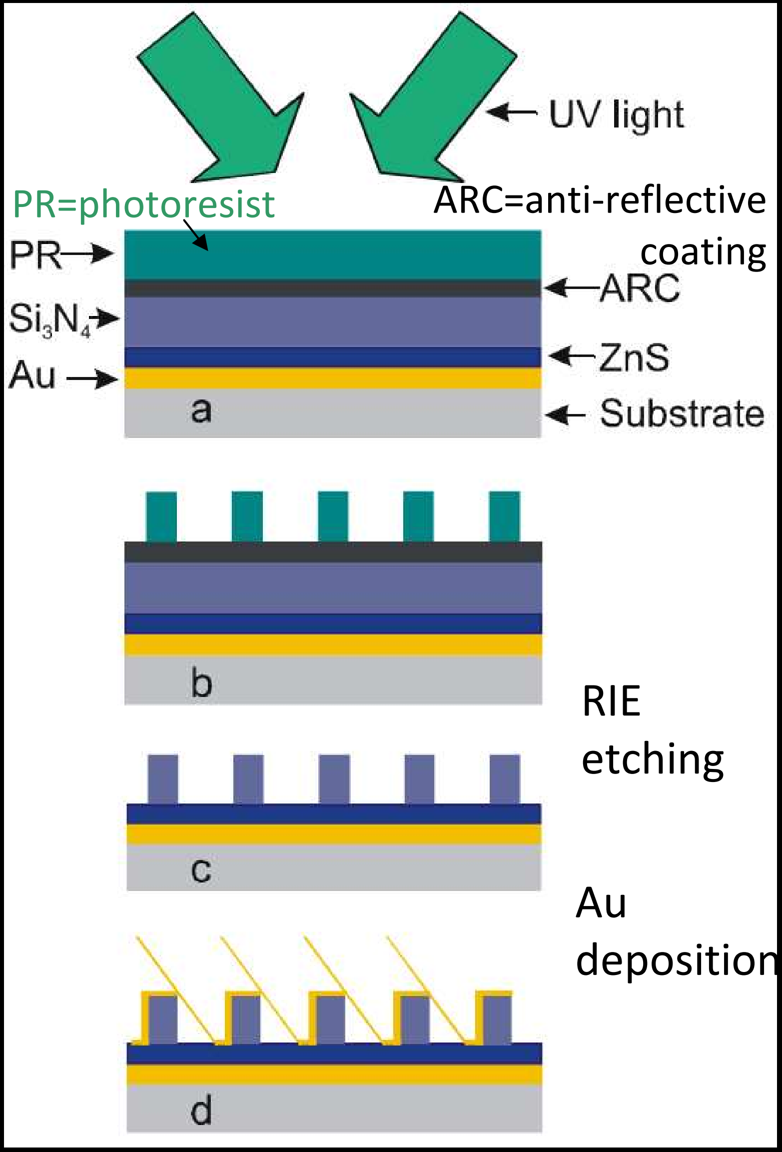
S. R. J. Brueck PROCEEDINGS OF THE IEEE 93 (2005)

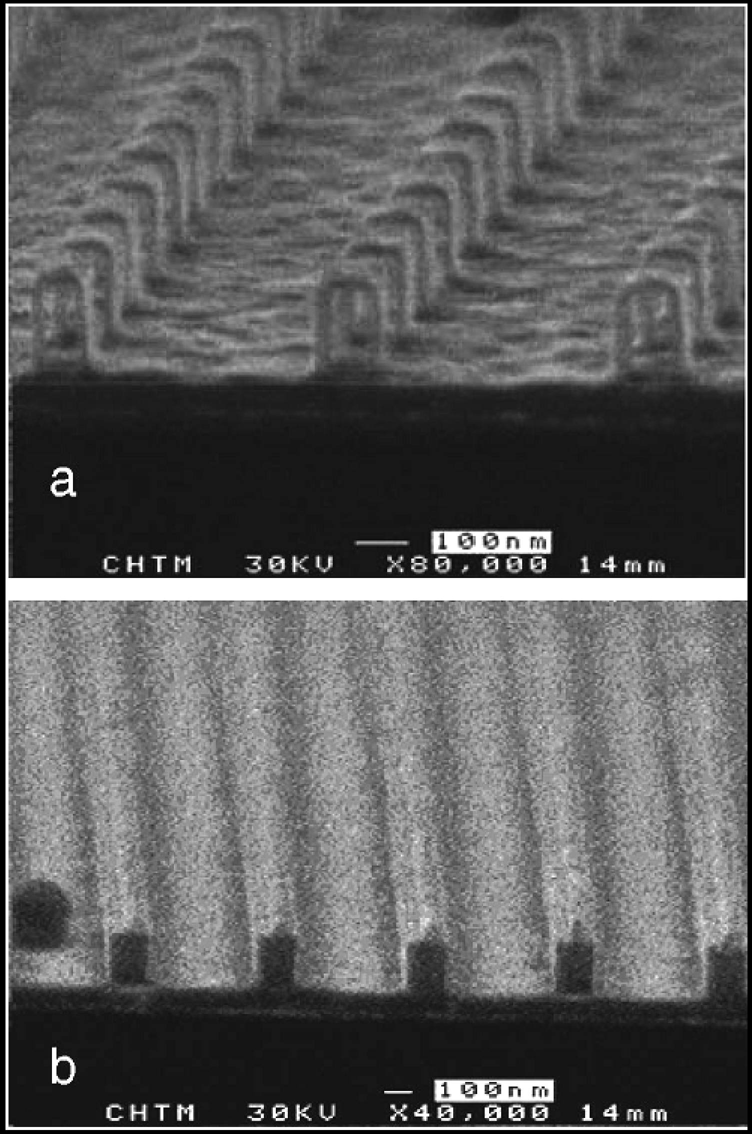
Interferometric photolithography (IL)



J. W. Menezes et al. Adv. Funct. Mater. 2010, 20, 3918–3924

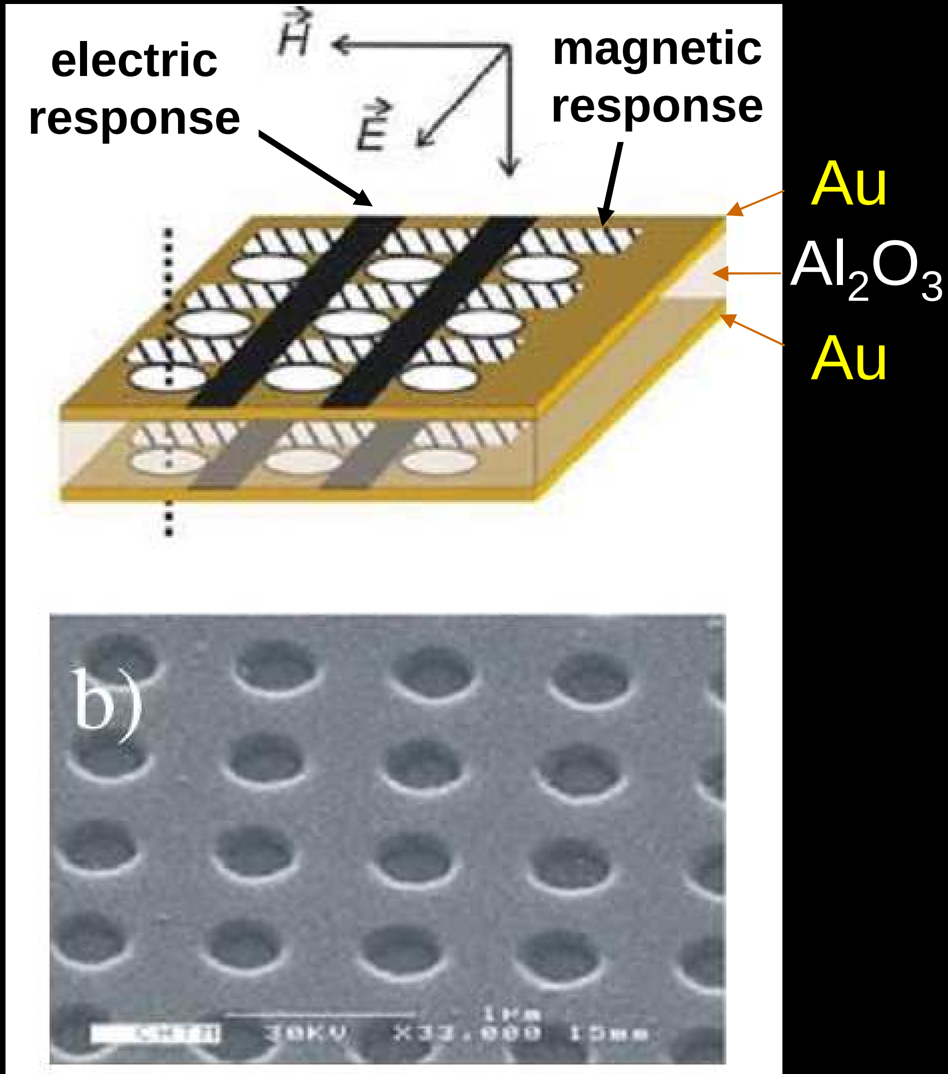
Interferometric photolithography (IL) meets negative permeability …



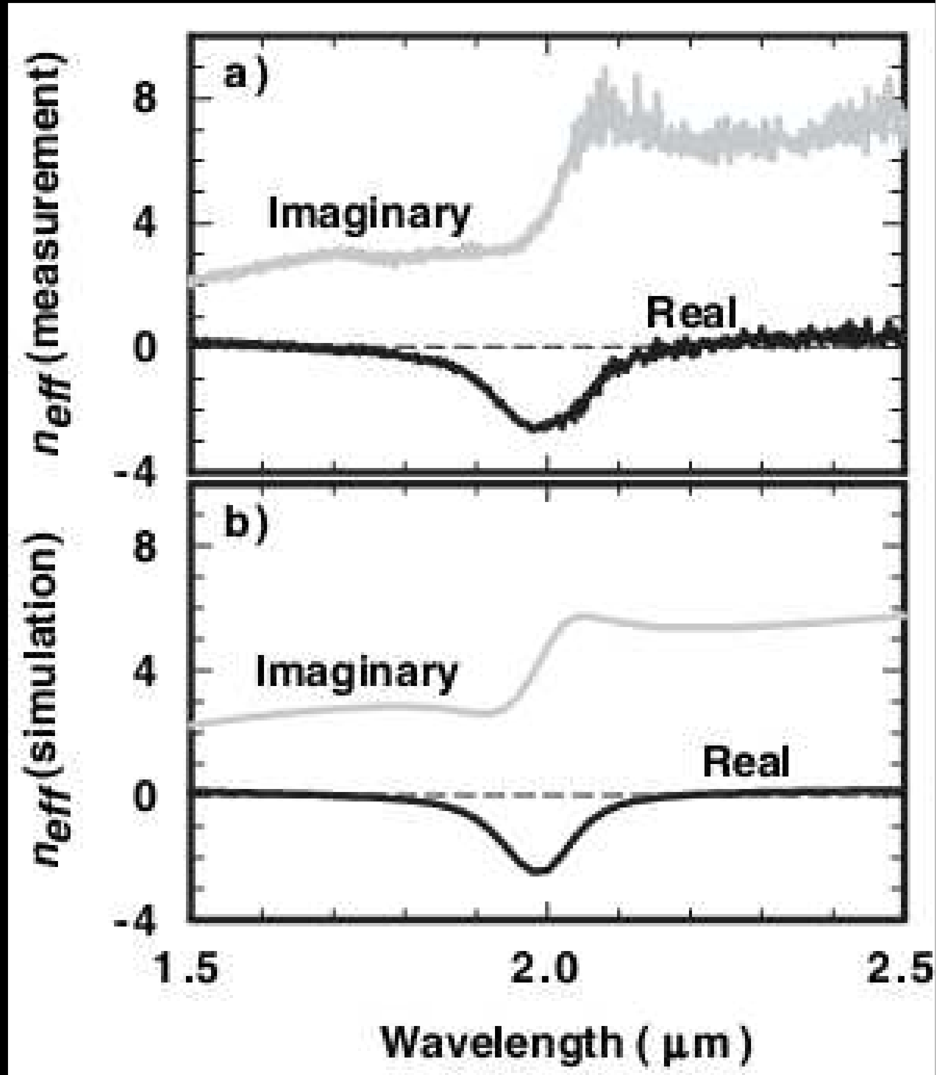


S. Zhang … S.R.J. Brueck et al. PRL 94, 037402 (2005)

and negative refractive index…



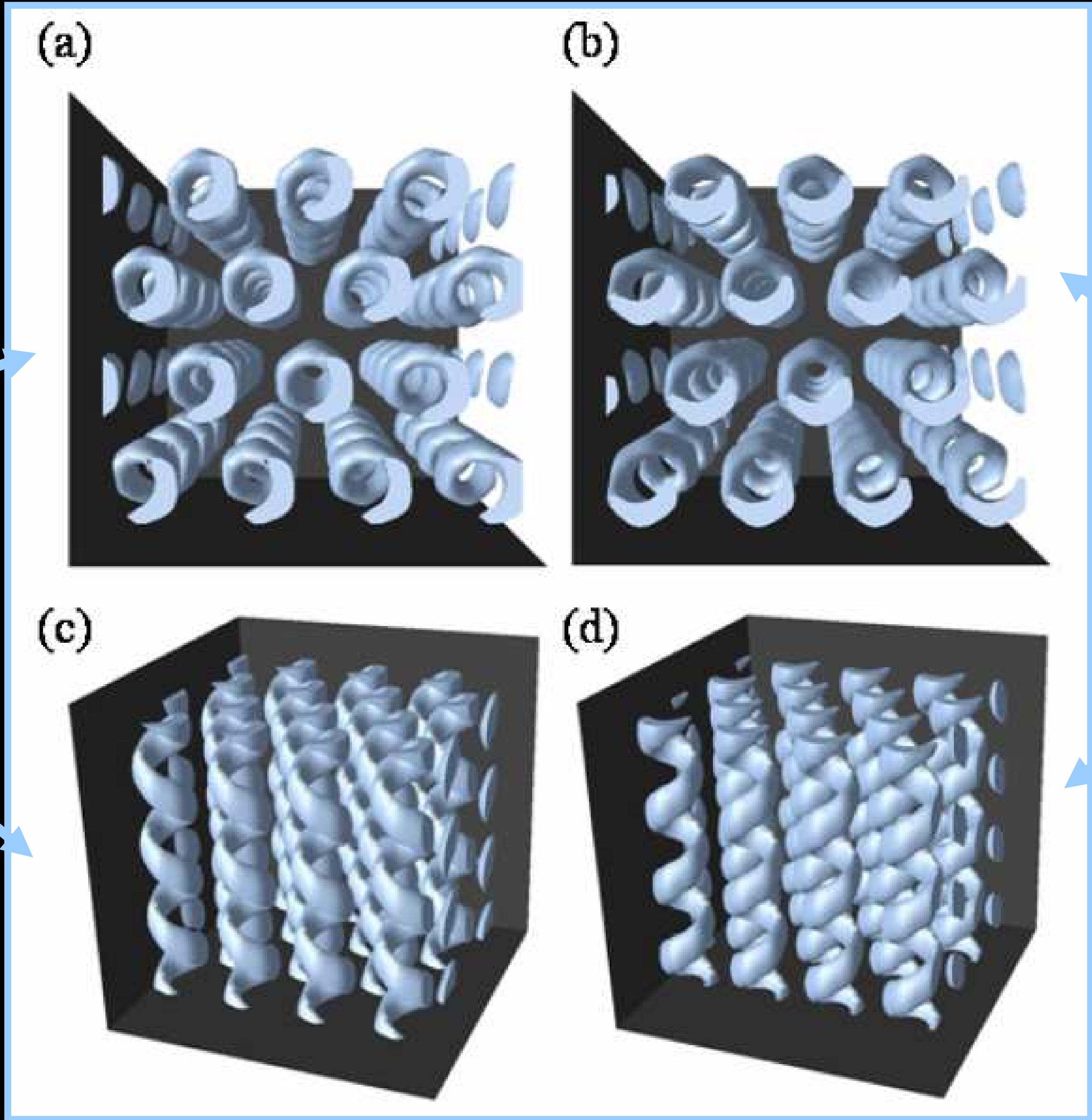
Fishnet-like structure



S. Zhang et al. PRL 95, 137404 (2005)

The overall sample size was **1cm²**

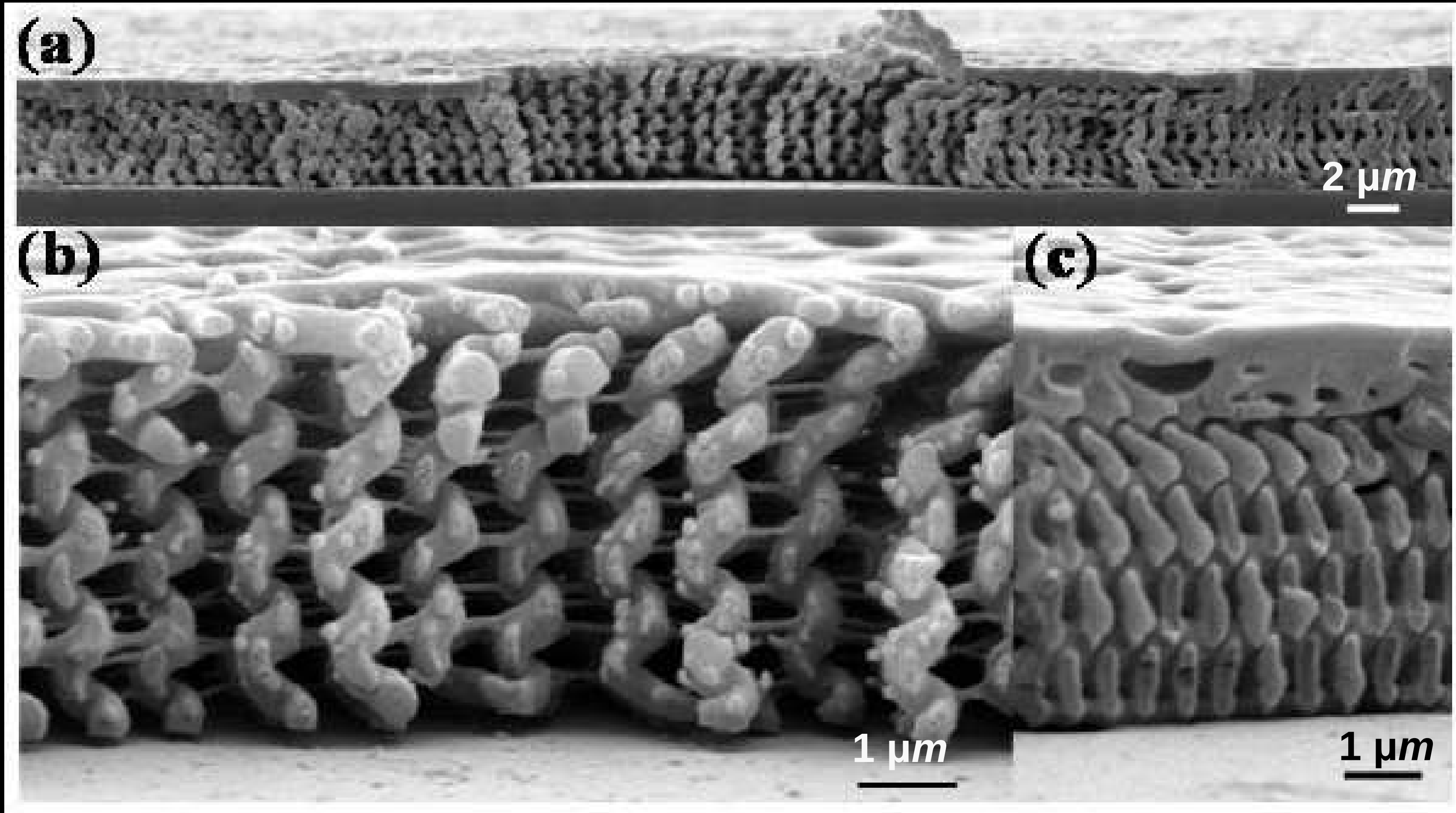
Intensity contour surfaces



left handed spirals

right handed spirals

overall



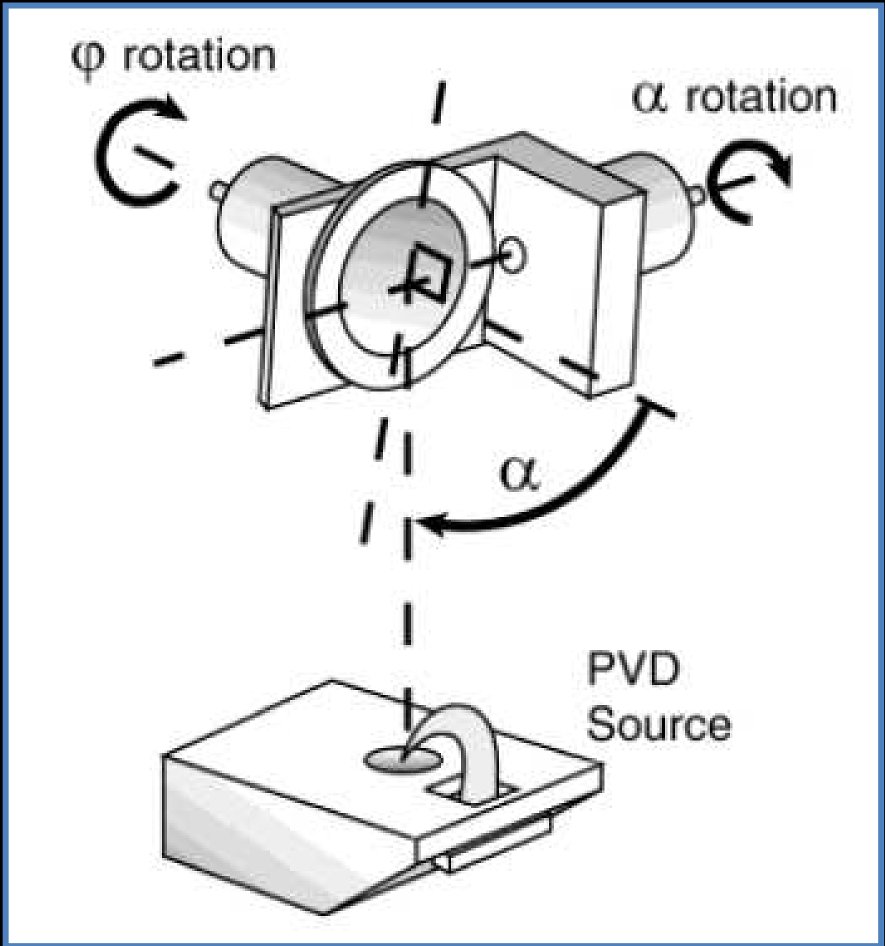
close up view

structure with out of
phase interference

Y. K. Pang, J. Ch. W. Lee, W. Y. Tam, C. T. Chan, P. Sheng

GLAD - Glancing Angle Deposition method

PRINCIPLE → **deposition of highly porous films at extreme incidence angles**

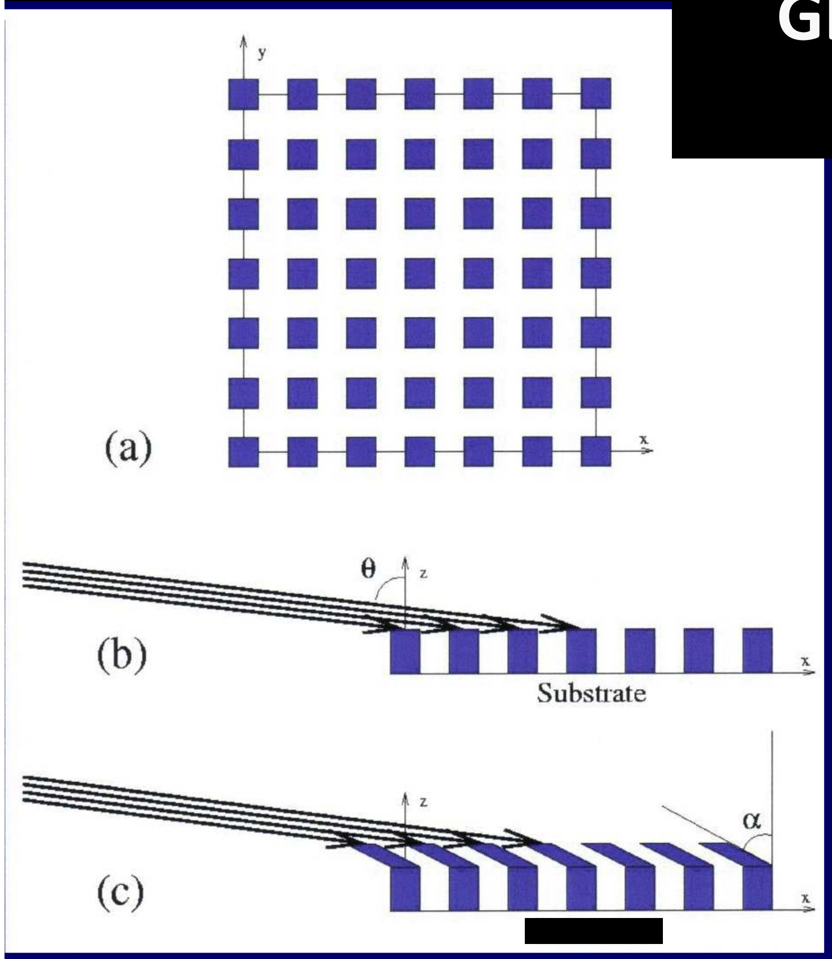


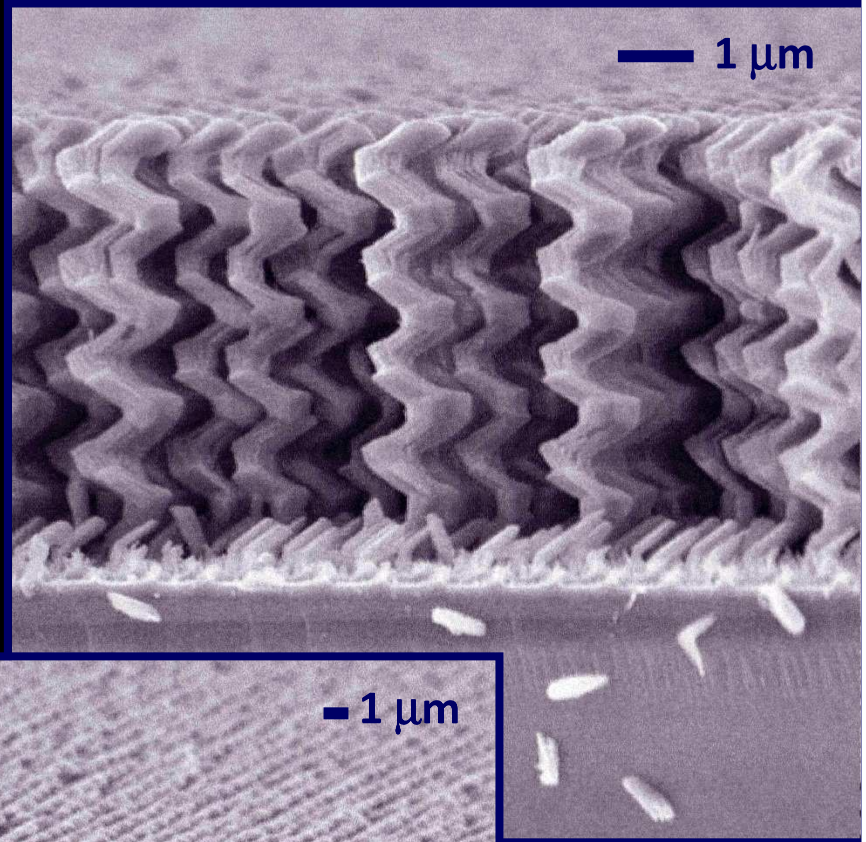
- physical vapor deposition is used in a high vacuum chamber with an electron beam source

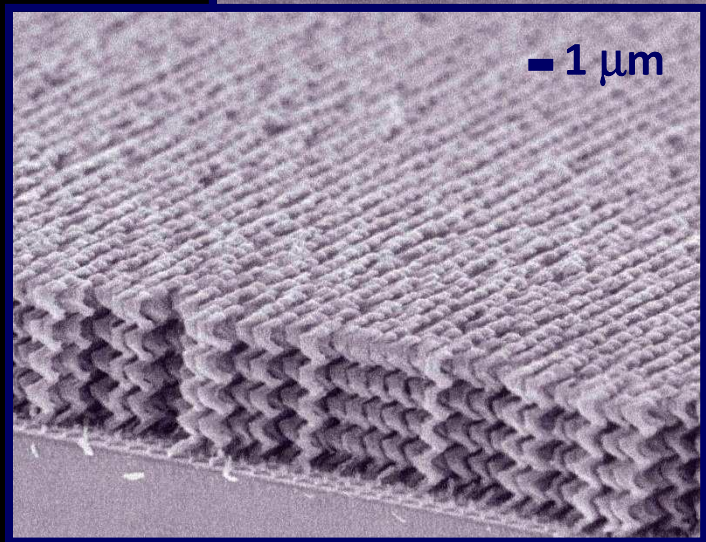
- throw distance between the source and substrate is greater than 30 cm so that flux reaching the substrate is collimated

- the substrate is held at a constant angle of incidence of 80-90° from the normal

GLAD - Glancing Angle Deposition method







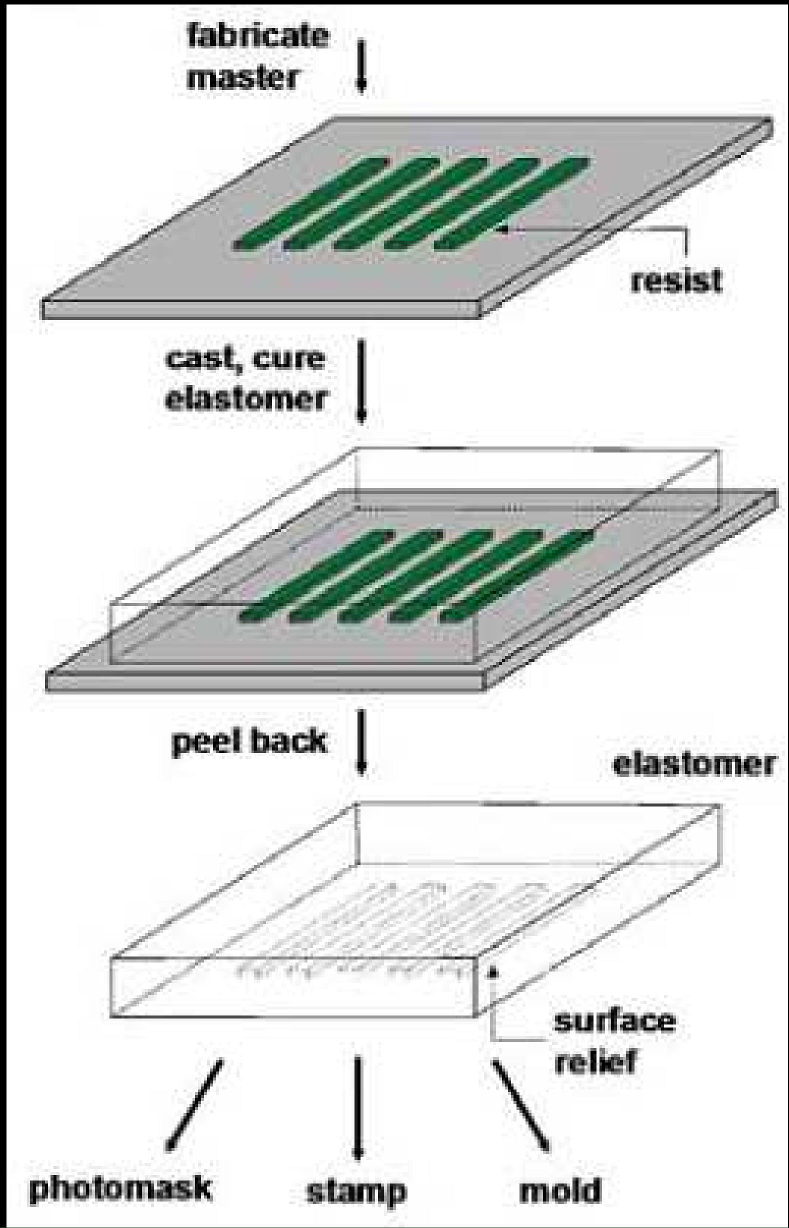
S. Kennedy, M. Brett, O. Toader, S. John, Nano Letters (2002)

Soft lithography – technology for fast and large-area MTMs fabrication

MASTER (*stamp*) **$$$**
patterning
(e.g. by IL, EBL FIB etc.)
made from e.g. silicon

Transparent elastomer
(e.g. PDMS)
casting & curing

PDMS after
removing
master



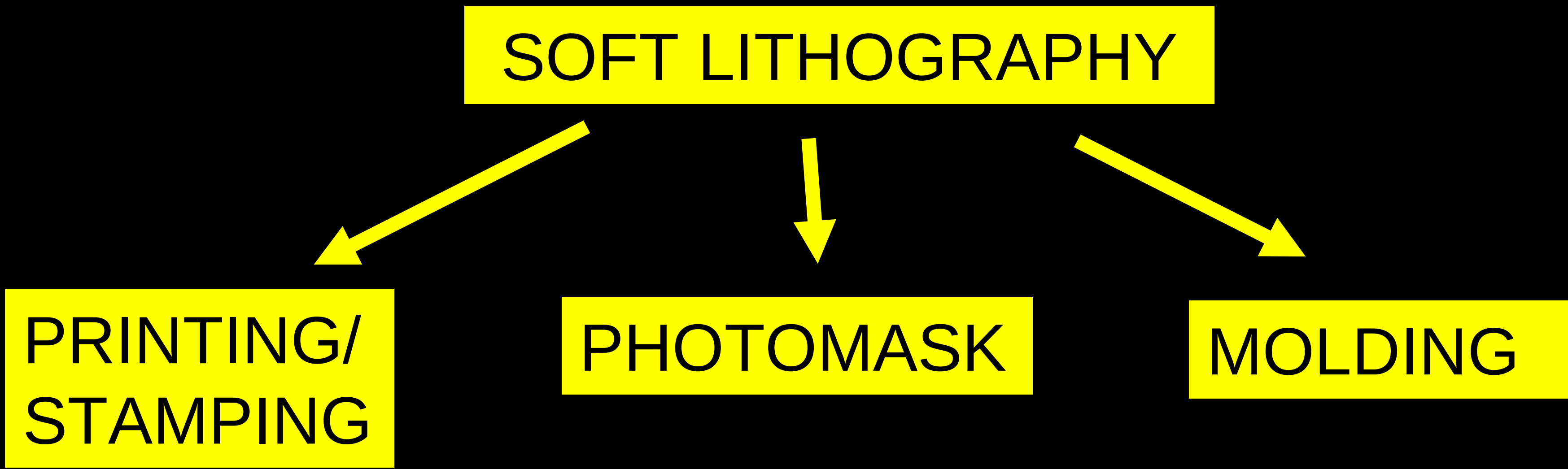
PDMS photomask/stamp/mold fabrication scheme

John A. Rogers and Ralph G. Nuzz
Materials Today (2005)

PDMS
(polydimethylsiloxane)
- transparent
elastomer

Soft lithography

– technology for fast and large-area MTMs fabrication

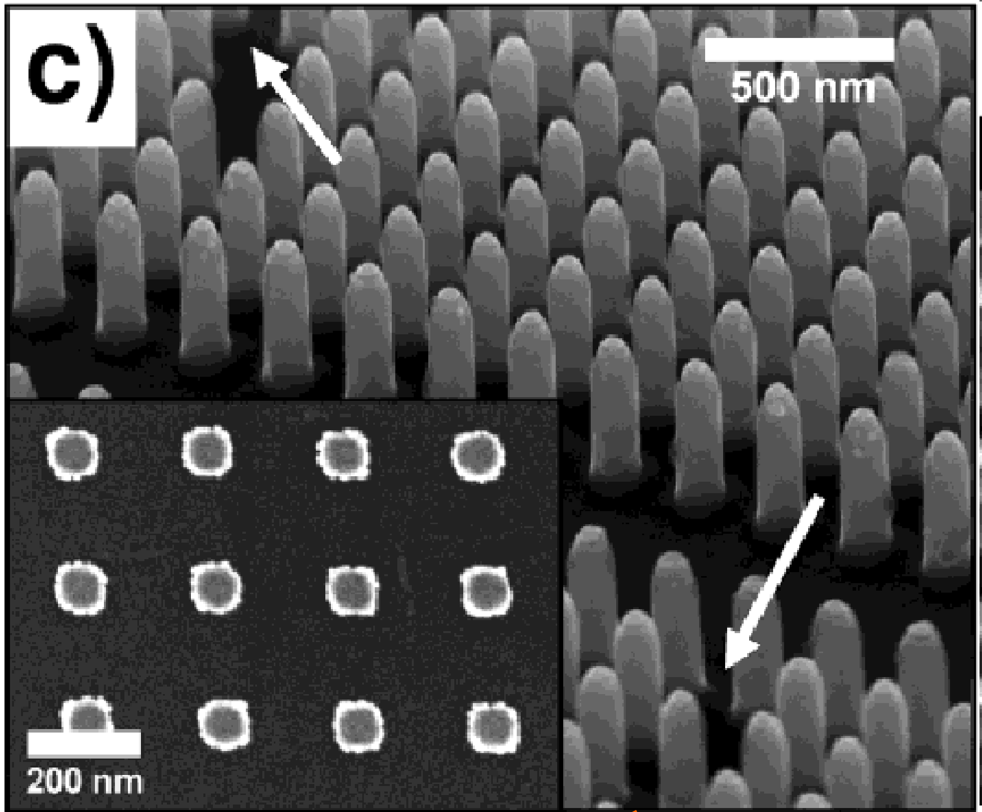


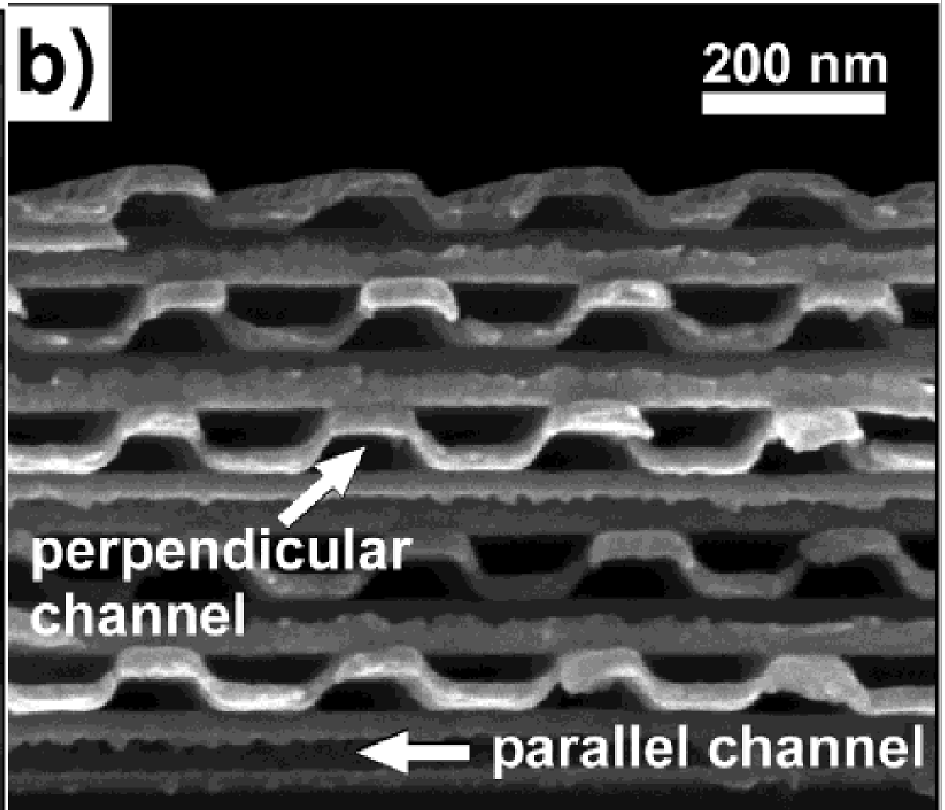
N C Lindquist et al. Rep. Prog. Phys. 75, 036501 (2012)

Nano-transfer printing (nTP)

PRINTING

Soft lithography





film can be attach to the substrate

Free-standing GaAs nanorods (with gold cover)

Gold nanochannels (woodpile-like structure)

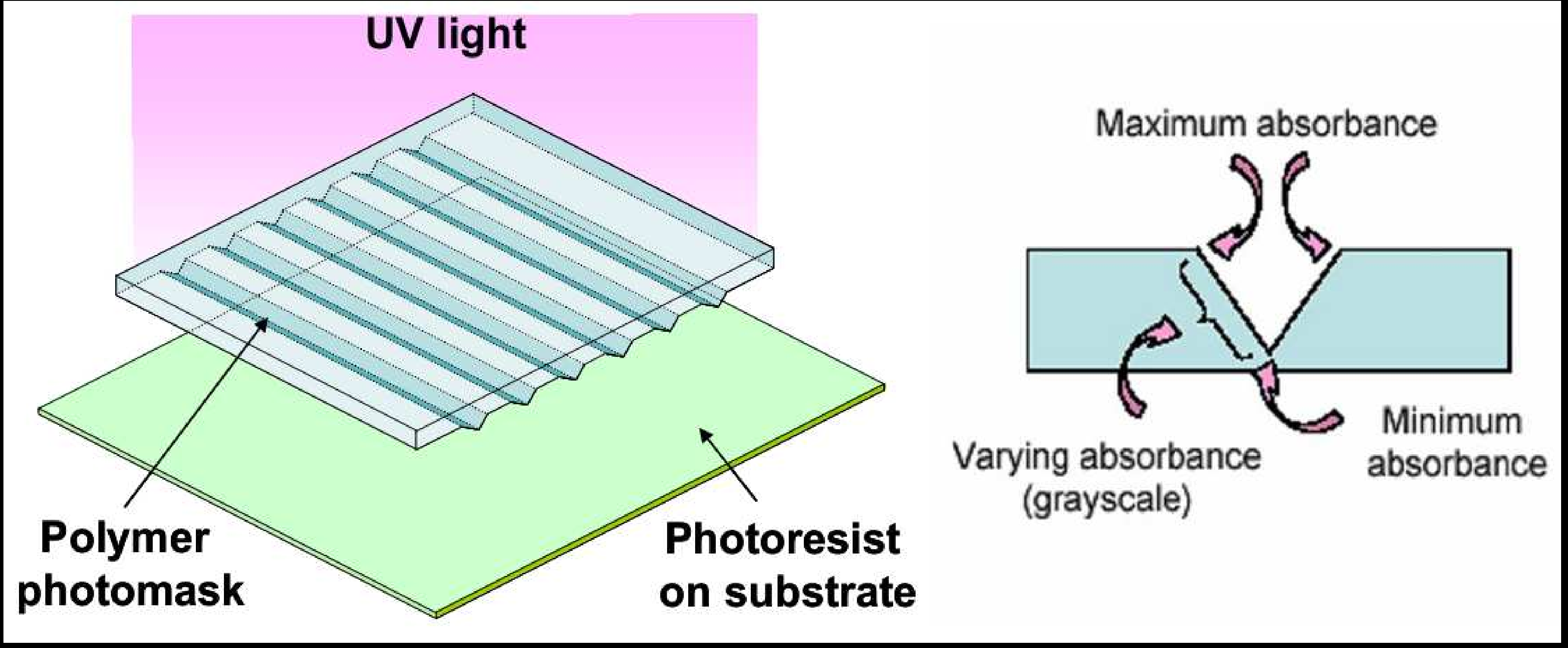
SAM (self-assembled monolayer) which reacts and bounds to metal

J. Zaumsei et al. Nano Lett. 3, 1224 (2003)

Soft interference lithography (SIL)

- ✓ SIL uses nanoscale patterns generated by interference lithography (IL) as high-quality masters for soft lithography
- ✓ PDMS photomask - by fabricated by casting onto IL fabricated master
- ✓ Cheaper masks – larger areas can be covered

J. Henzie et al., Nat. Nanotech. 2, 549 (2007)



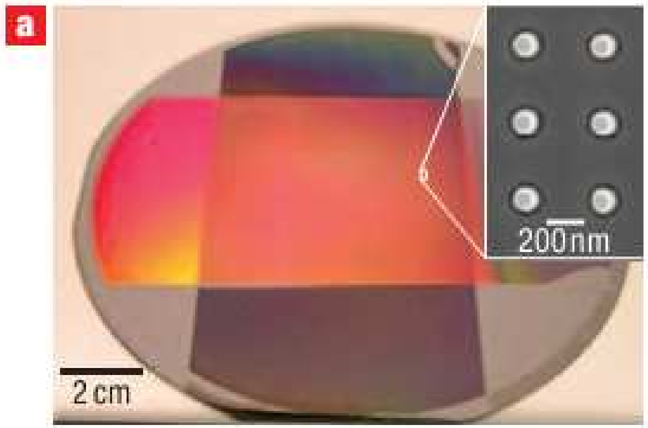
L. Jiang et al. Proc. of SPIE Vol. 7274 72742L-1

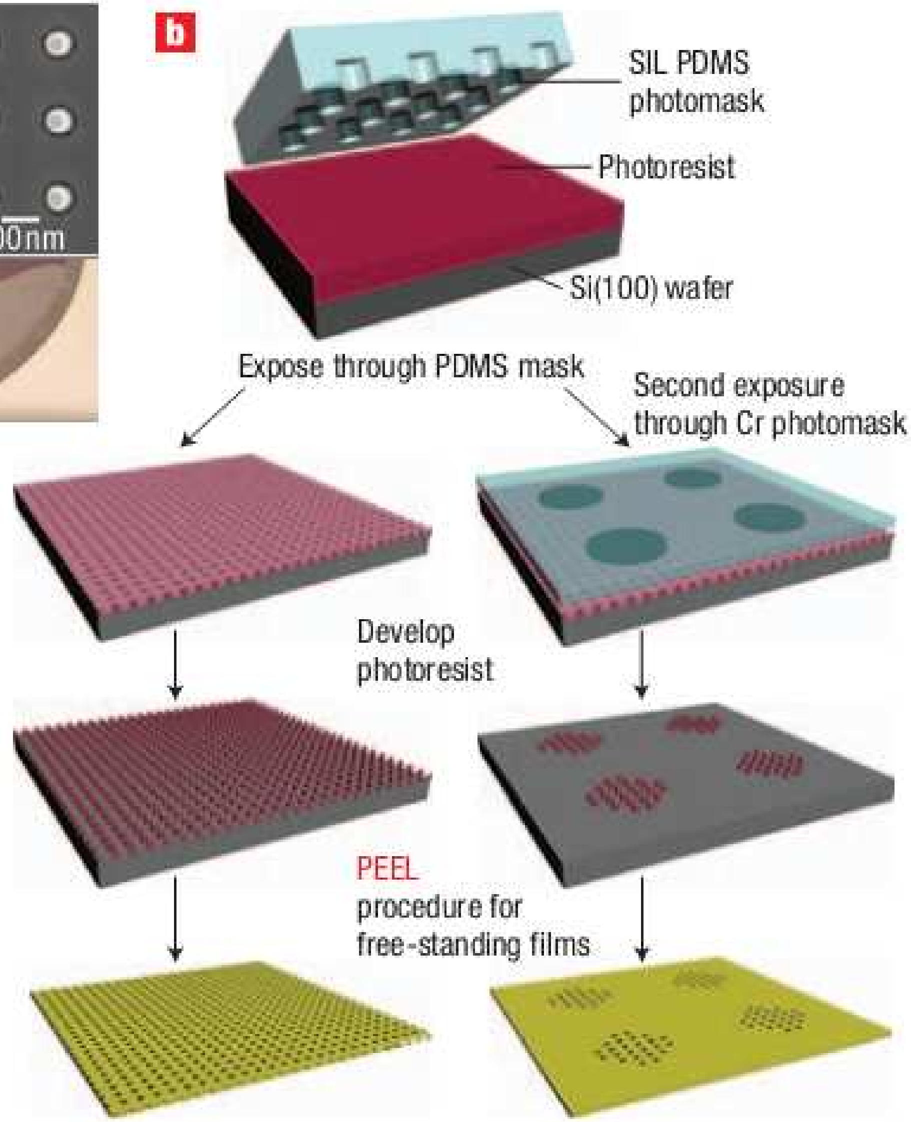
Soft interference lithography (SIL)

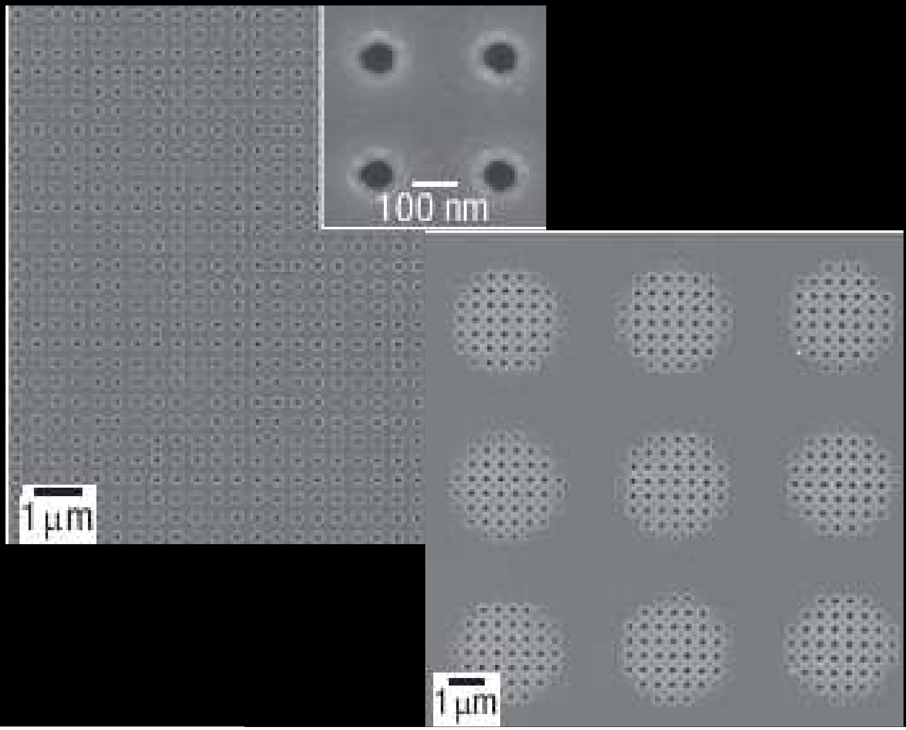
PHOTOMASK

Soft lithography

J. Henzie et al., Nat. Nanotech. 2, 549 (2007)







nanohole arrays in gold film

Nanoimprint lithography (NIL)

MOLDING

Soft lithography

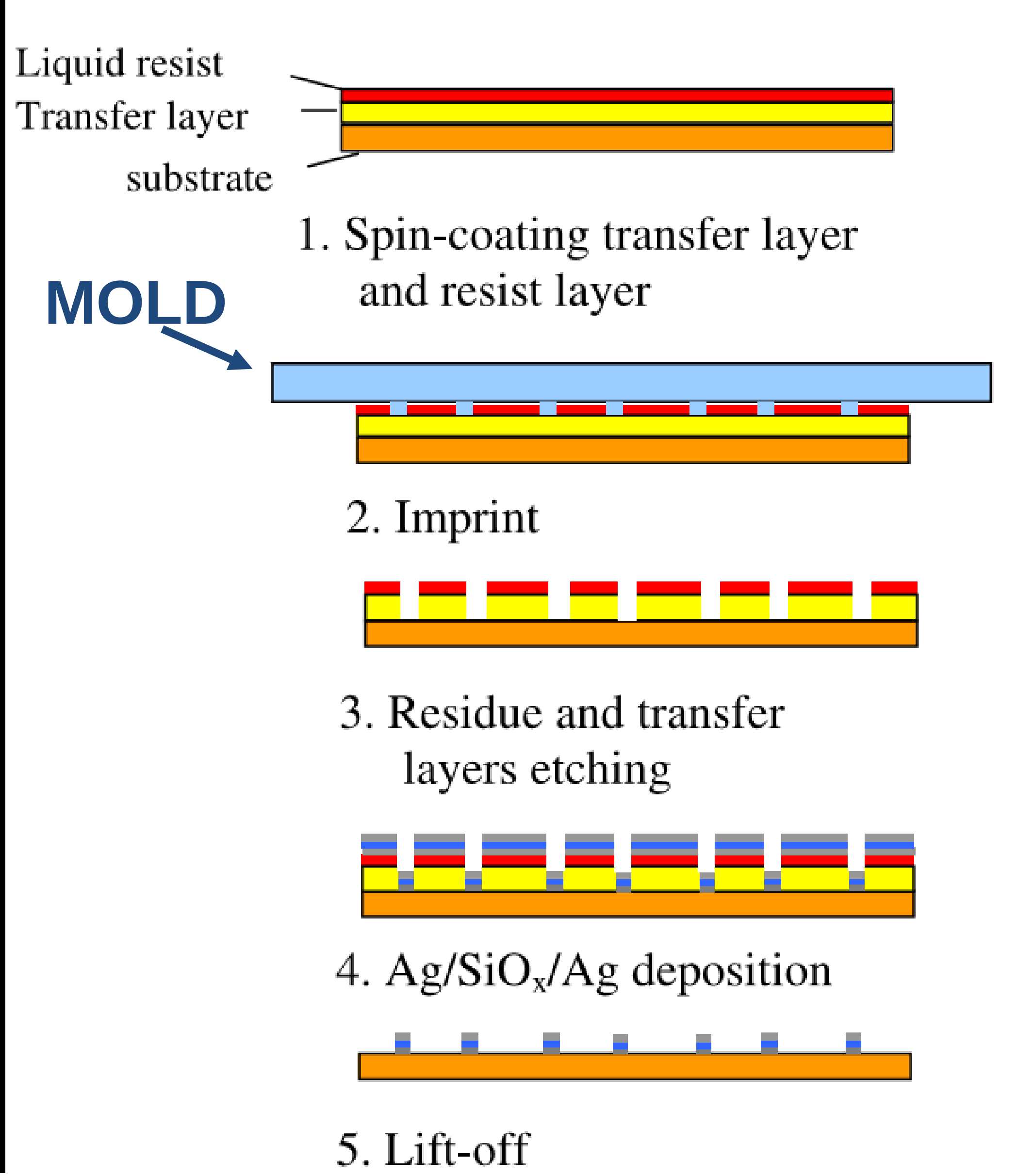
Thermoplastic NIL (t-NIL)

Thermoplastic resist -
the resist is pressed with hot mold the polimer gets softened and the pattern is created

Photo NIL (p-NIL)

Photocurable resist -
the mold is inserted into liquid polymer and than the resist is cured with light

W. Wu et al. Appl. Phys. A 87, 143–150 (2007)

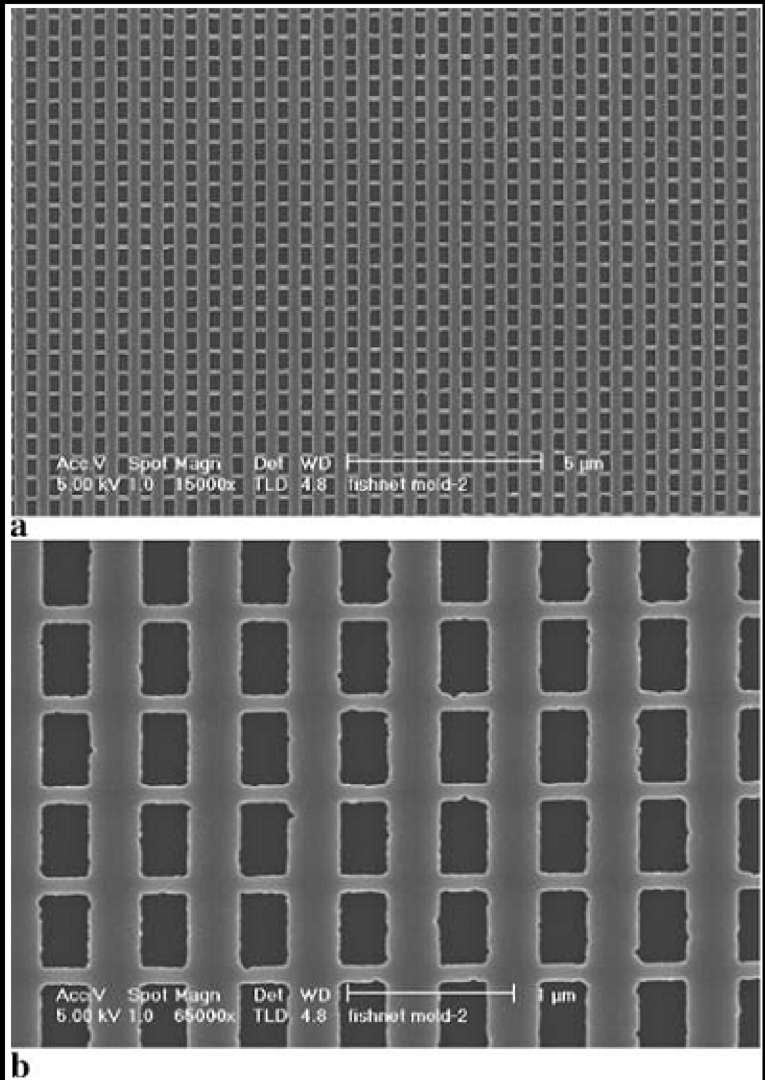


Nanoimprint lithography (NIL) and NIM…

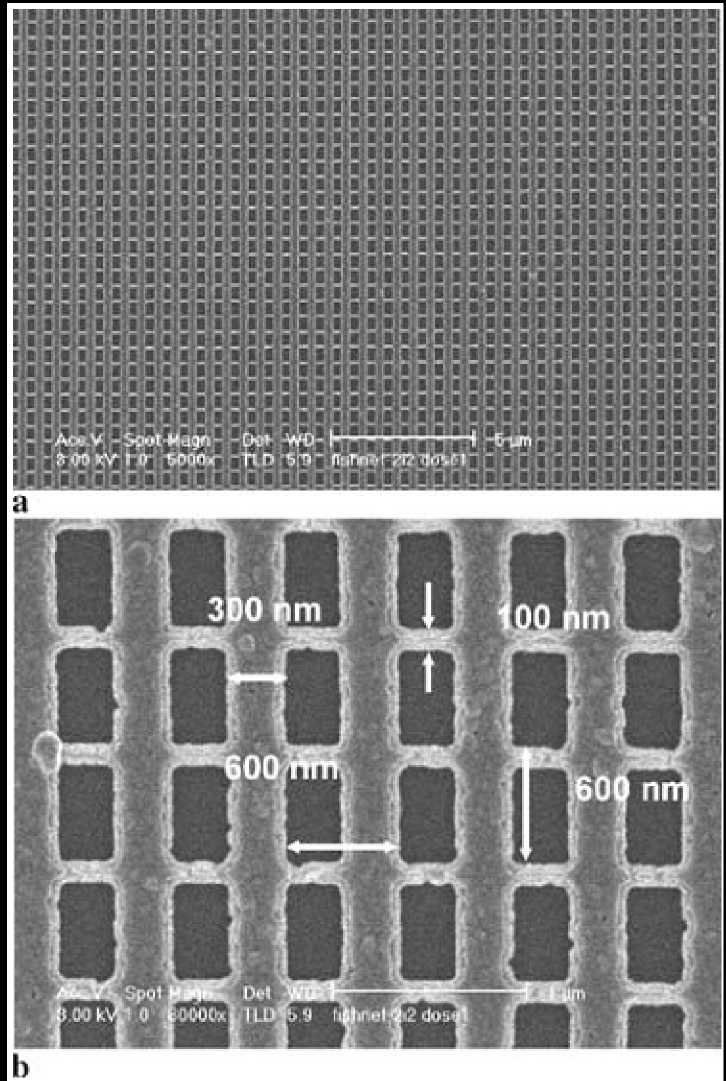
MOLDING

Soft lithography

MOLD (PMMA)



Ag/SiO2/Ag fishnet NIM



PMMA - Poly(methyl methacrylate)

W. Wu et al. Appl. Phys. A 87, 143–150 (2007)

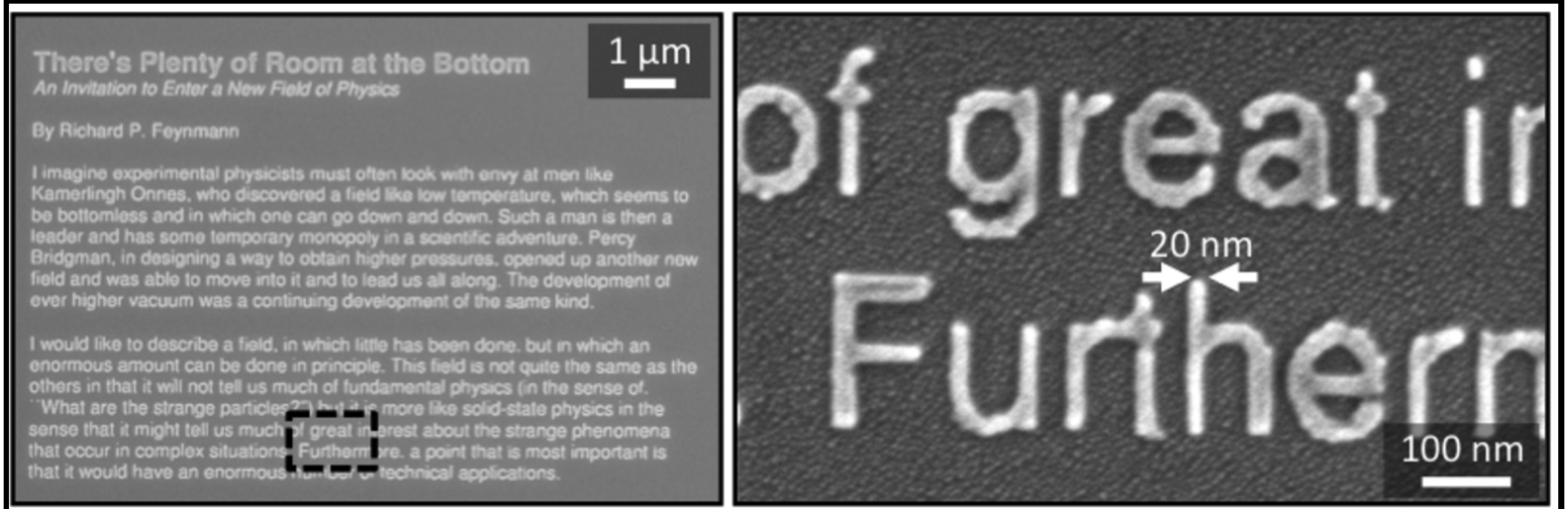
Samples of 0,5x0,5 mm area

Negative index –1 .55 @1,7 µm

When we need arbitrary shapes…
DIRECT WRITING

Electron beam causes local polimerization of the resist

Electron Beam Lithography (e-beam)



SEM image of EBL fabricated nanopattern

(Adopted from Bryan Cord at the University of Minnesota Nanofabrication Center)

„SCANNING”

H. Duan et al., ACS Nano 5, 7593 (2011)

Electron Beam Lithography (e-beam)

EBL

DIRECT WRITING

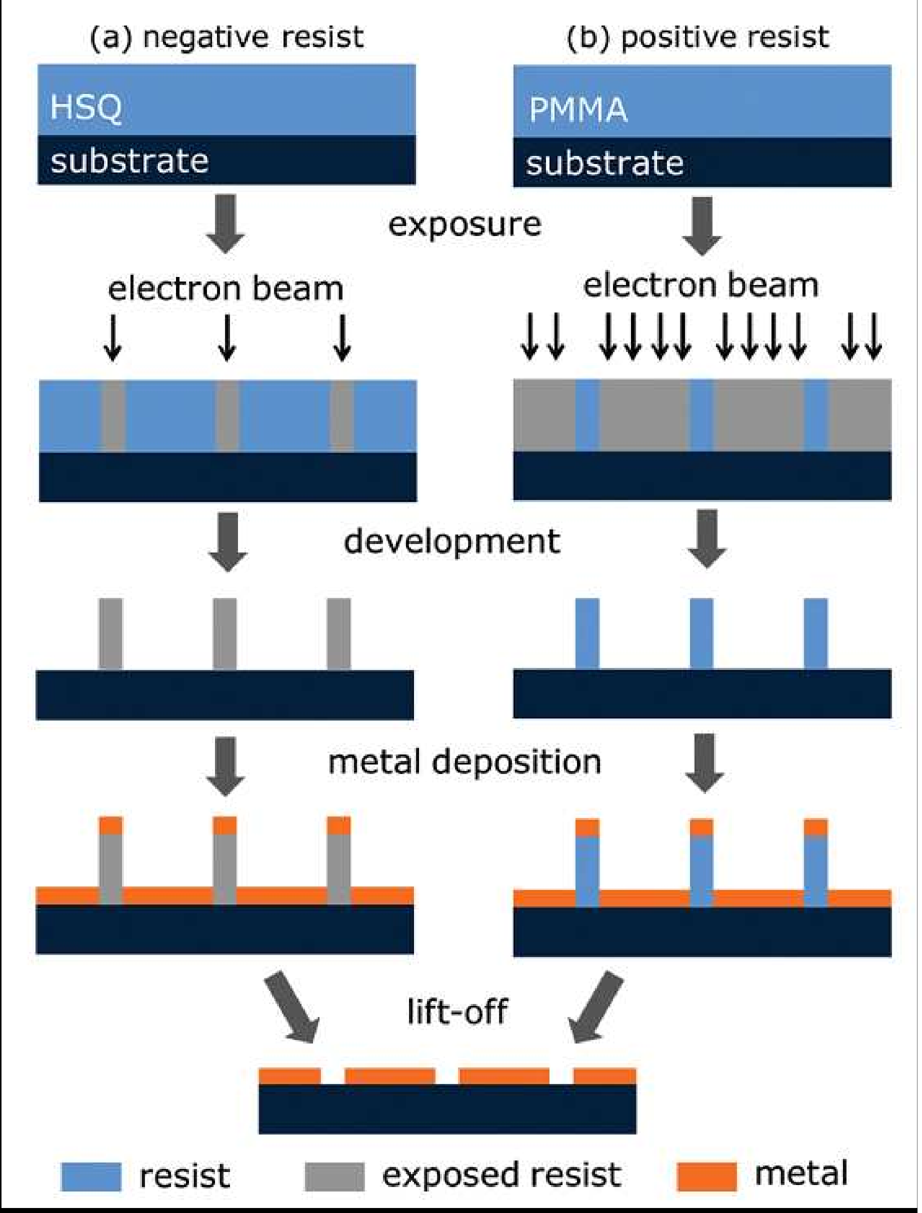
- ✓ in principle the same as photolithography but with use of electrons and maskless
- ✓ electron wavelength (= patterning resolution) depends on electrons energy
- ✓ shape of the beam (cross section) can be precisely controlled and rapidly change

Advantages:

•very good resolution (down to 10 nm)
•maskless = direct writing
•arbitrary shapes possible
•good for proof-of-concept demonstrations

Disadvantages:

•expensive equipment
•very slow patterning process
•small-area
•multi-stage fabrication procedure
•only 2D patterning

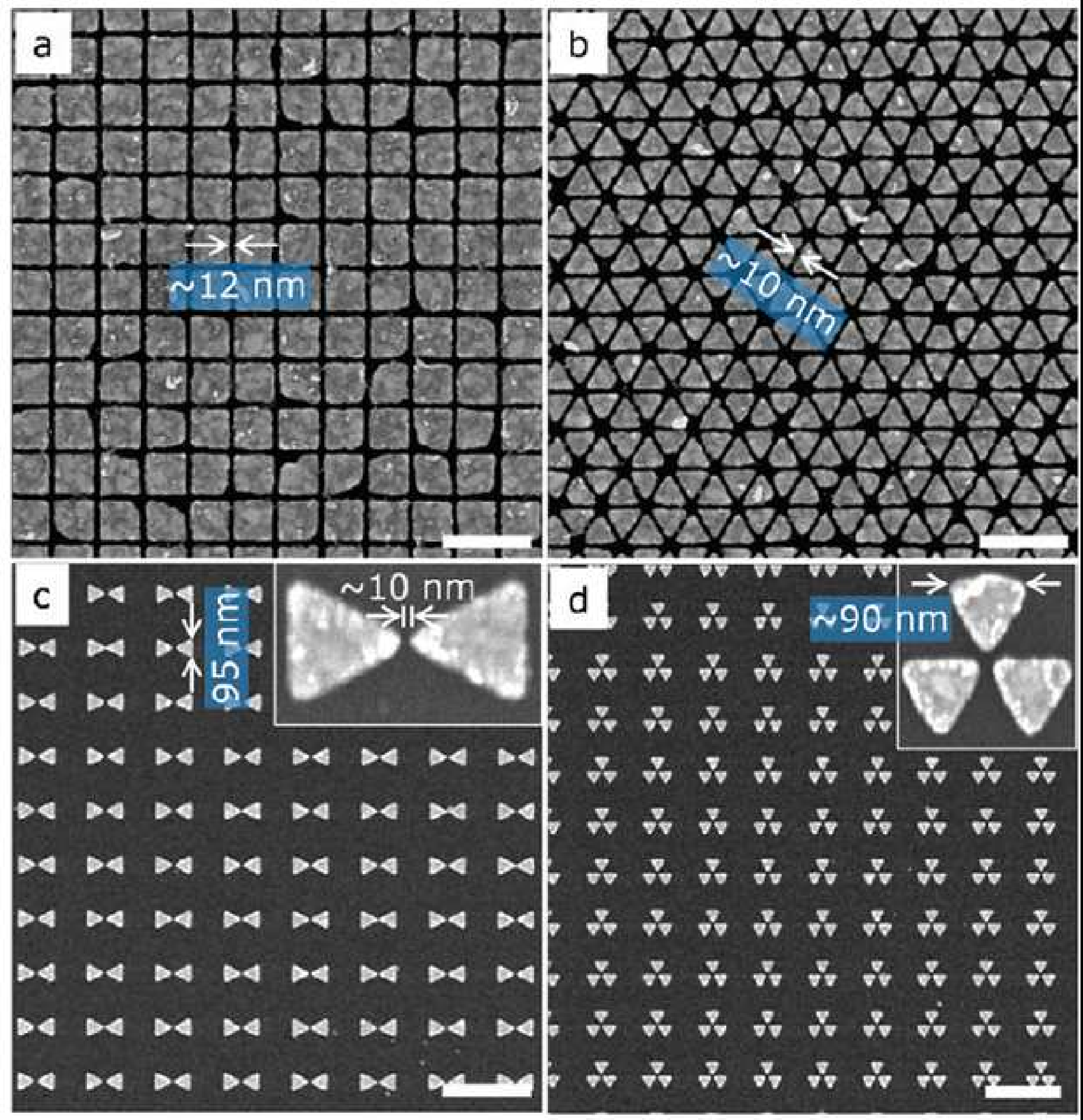


H. Duan et al., ACS Nano 5, 7593 (2011)

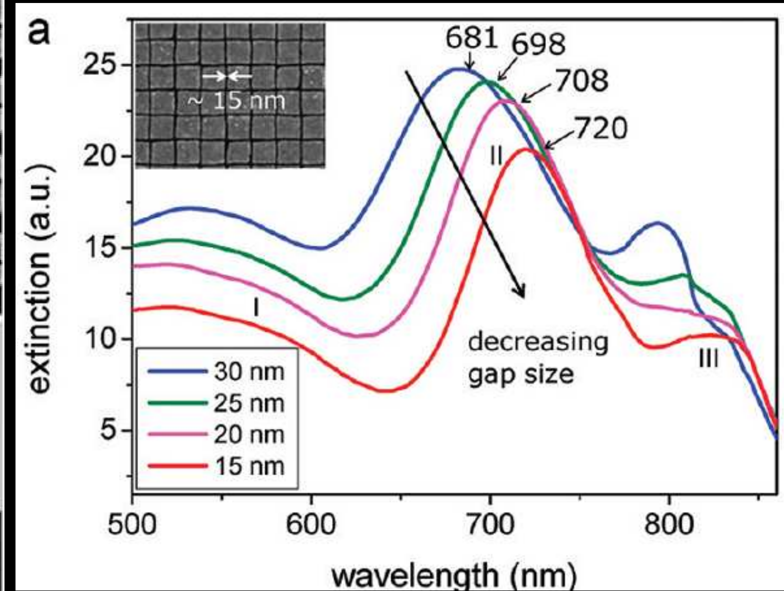
Electron Beam Lithography (e-beam)

EBL

DIRECT WRITING



Close-packed gold nanostructures obtained by EBL and lift-off



With the decrease in size of the gap the plasmon resonance is red-shifted

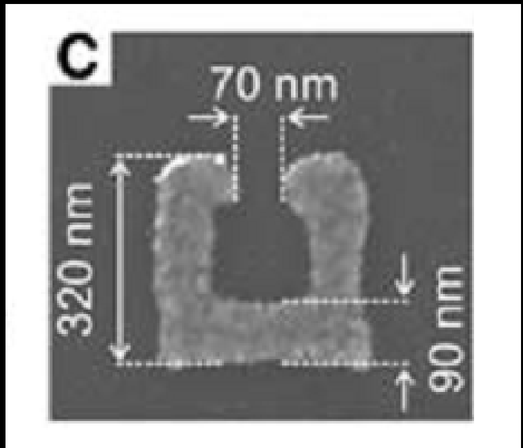
H. Duan et al., ACS Nano 5, 7593 (2011)

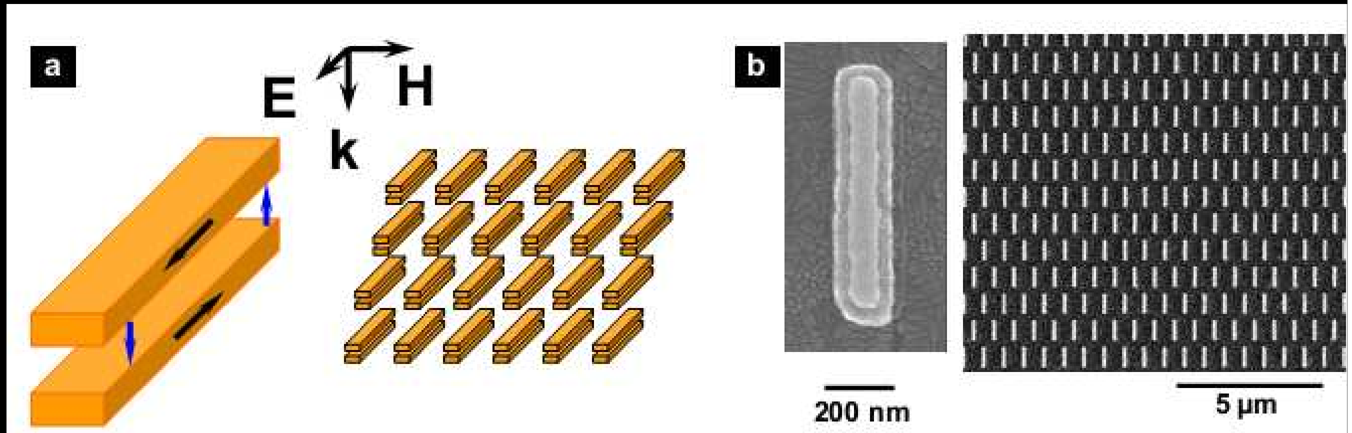
Electron Beam Lithography (e-beam)

EBL

DIRECT WRITING

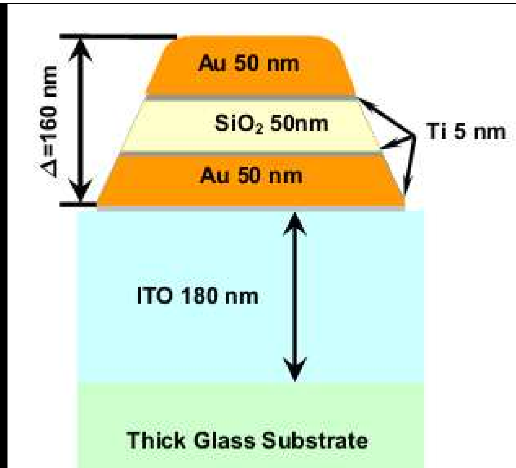
The way to obtain negative index metamaterials (NIM) at optical wavelength…





Metamaterial made of gold split-ring resonators with magnetic response at 100 THz obtained by EBL and lift off procedure

S. Linden … C. Soukoulis, et al. Science 306, 1351 (2004)



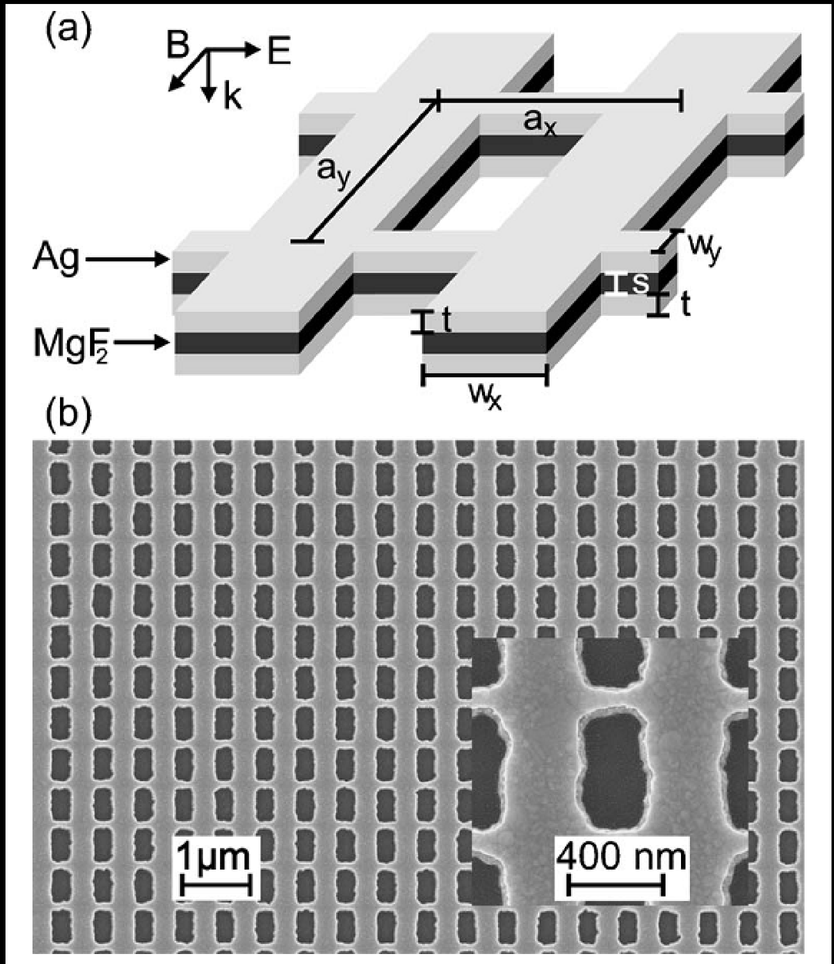
Metamaterial with negative refractive index at $\lambda \approx 1\mu m$ obtained by EBL and lift off

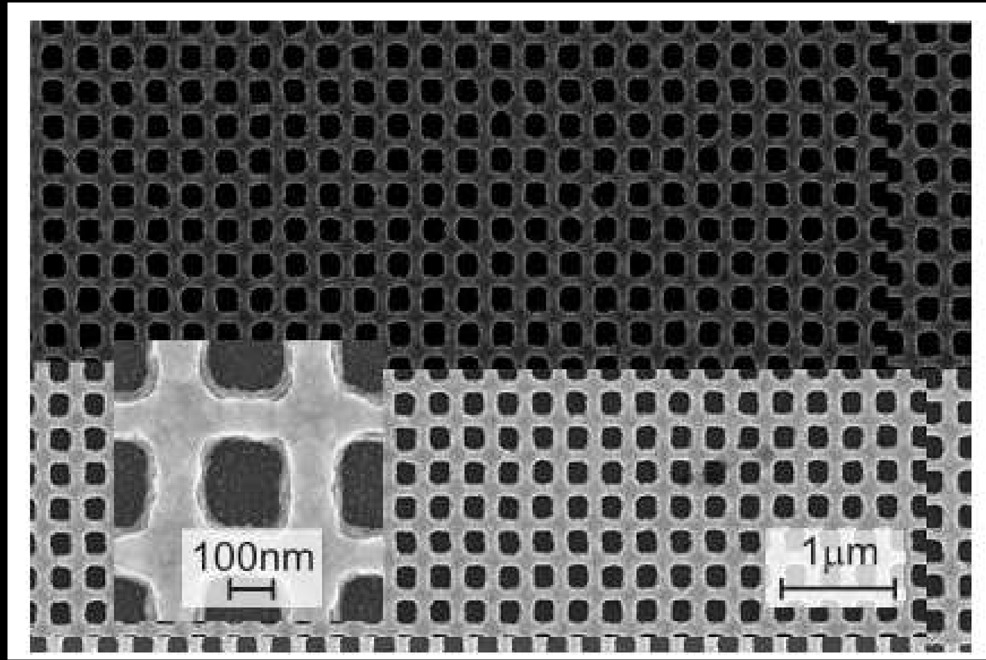
V. M. Shalaev et al. Optics Letters, 30, 3356-3358 (2005)

Electron Beam Lithography (e-beam)

DIRECT WRITING

the way to obtain negative index metamaterials (NIM) at optical wavelength…





G. Dolling …M. Wegener… C. Soukoulis, et al., Opt. Lett. 32, 53 (2007)

G. Dolling…M. Wegener… C. Soukoulis, et al., Opt. Lett. 31, 1800 (2006)

FISHNET made from silver/MgF2 layers fabricated by EBL and lift-off with negative refractive index at 1,5 µm (left) and 780 nm wavelength (right)

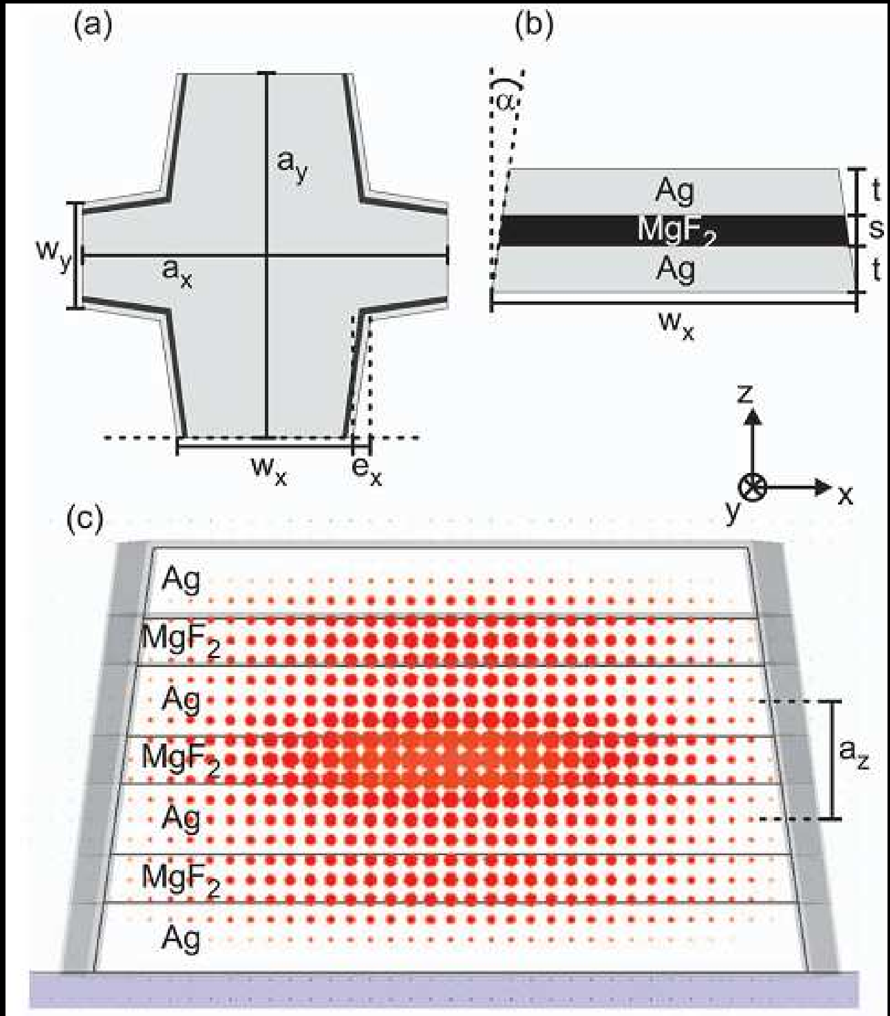
Stacked (layer-by-layer) Electron Beam Lithography

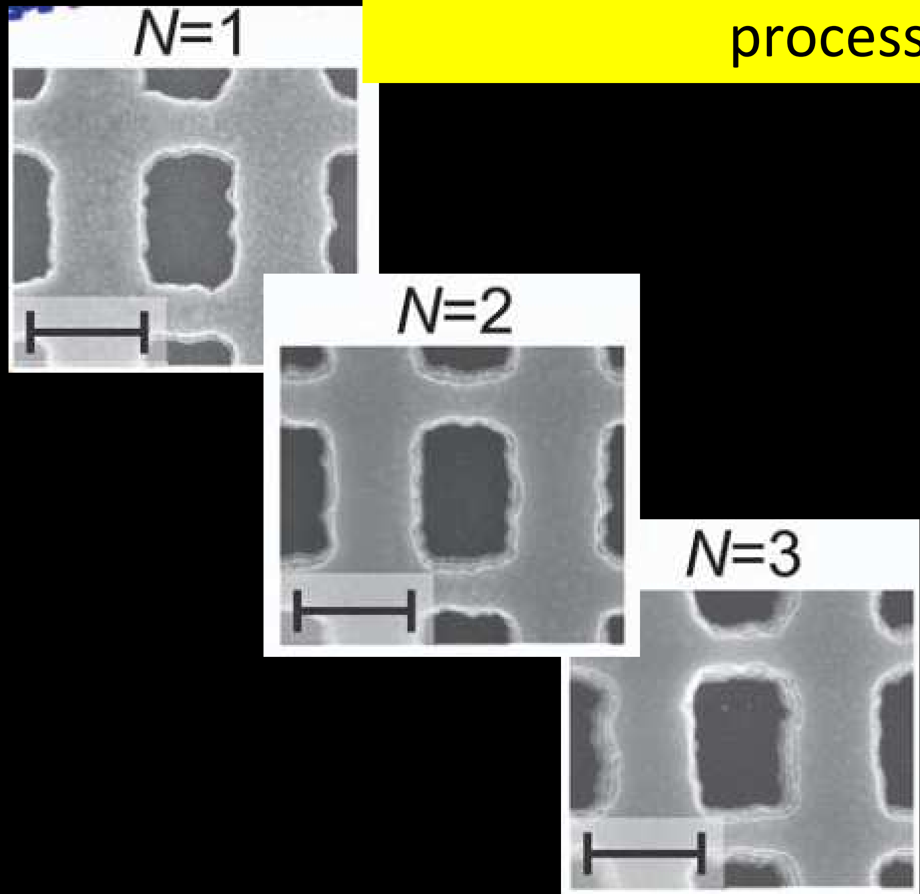
EBL

DIRECT WRITING

- from 2D to 3D…

For planar surfaces – serial layer-by-layer process





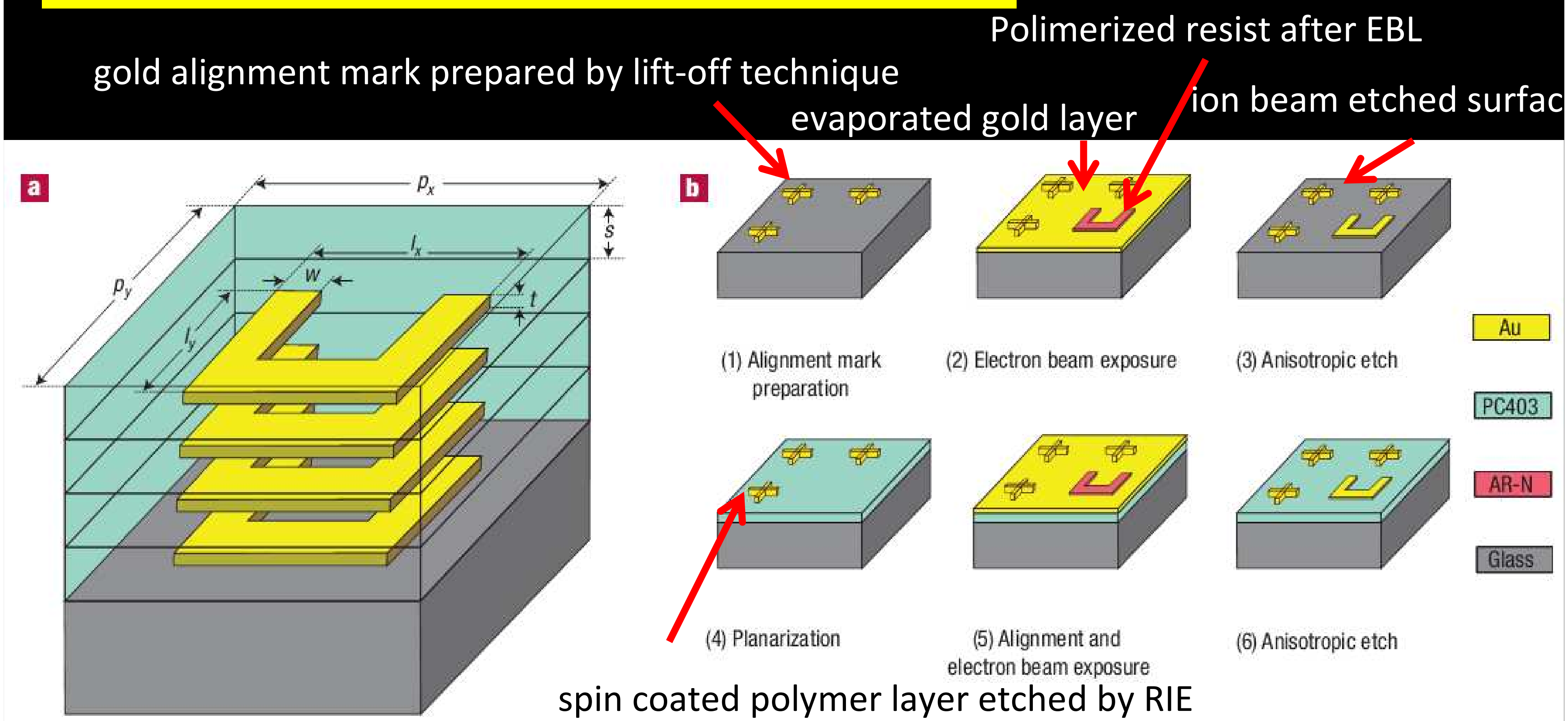
Metamaterial made from stacked silver/MgF2 multi-layers fabricated by EBL and lift-off with negative refractive index at 1,41 µm

G. Dolling … M. Wegener, et al., Opt. Lett. 32, 551 (2007)

Stacked (layer-by-layer) Electron Beam Lithography - from 2D to 3D…

EBL

For non-planar surfaces – PLANARIZATION



Stacked non-planar EBL fabrication steps :

- ✓alignment mark preparation
- ✓first layer of nanostructures prepared by EBL
- ✓planarization (spin coating of dielectric layer) + RIE thinning
- ✓alignment of second layer with alignment marks
- ✓etc

N. Liu … H. Giessen, et al. Nat. Mater. 7 (2008)

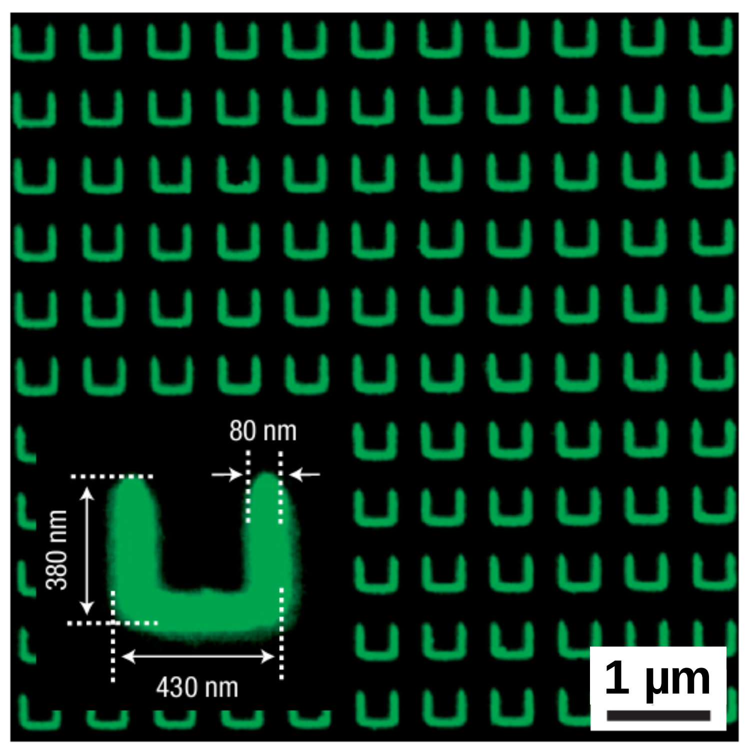
Stacked (layer-by-layer) Electron Beam Lithography

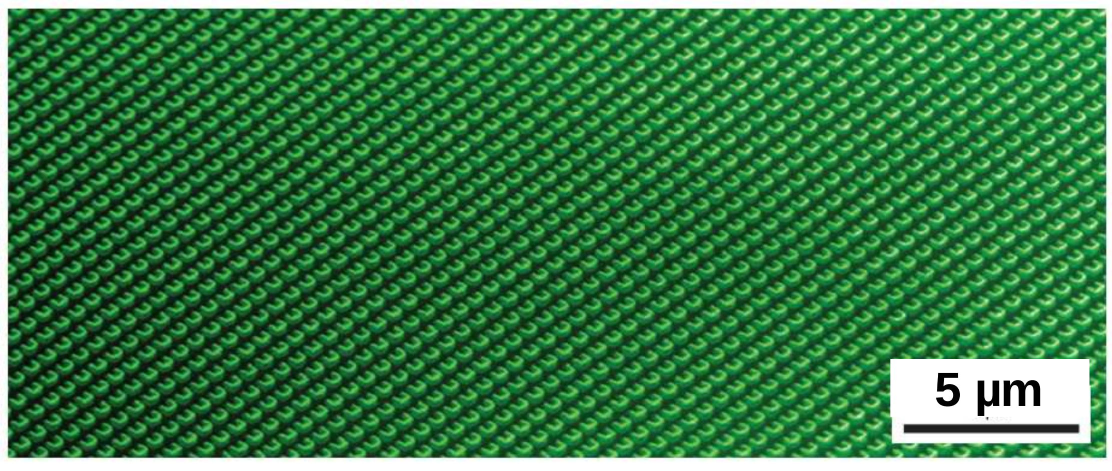
EBL

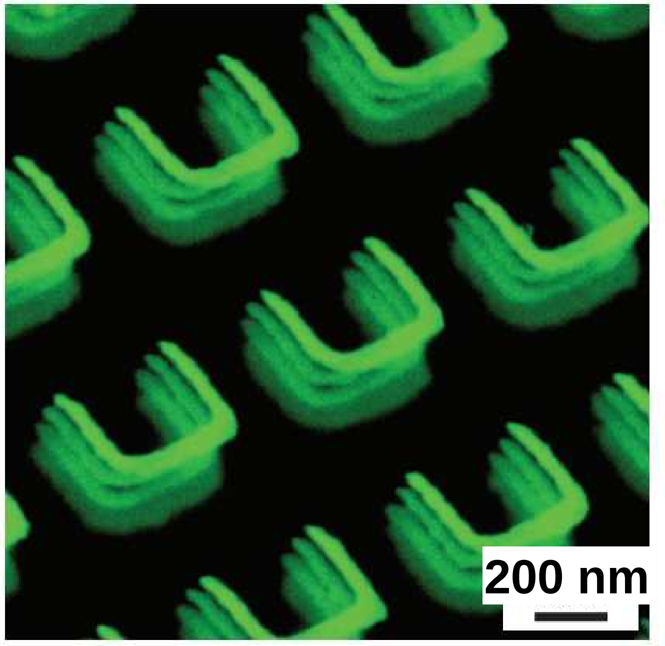
- from 2D to 3D...

DIRECT WRITING

For non-planar surfaces – PLANARIZATION





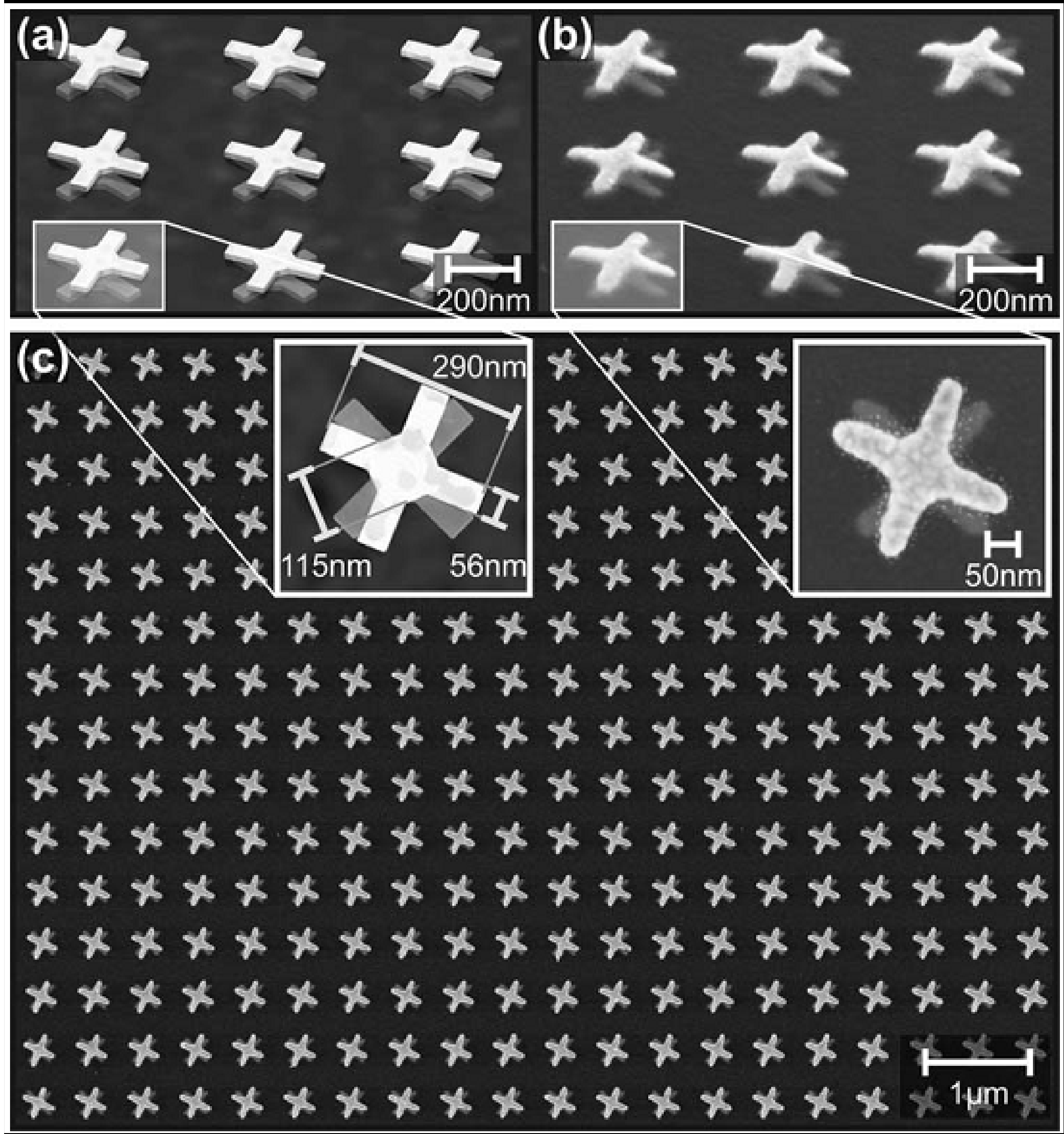


Na Liu … H. Giessen, et al. Nat. Mater. 7 (2008)

Stacked Electron Beam Lithography - from 2D to 3D…

EBL

DIRECT WRITING

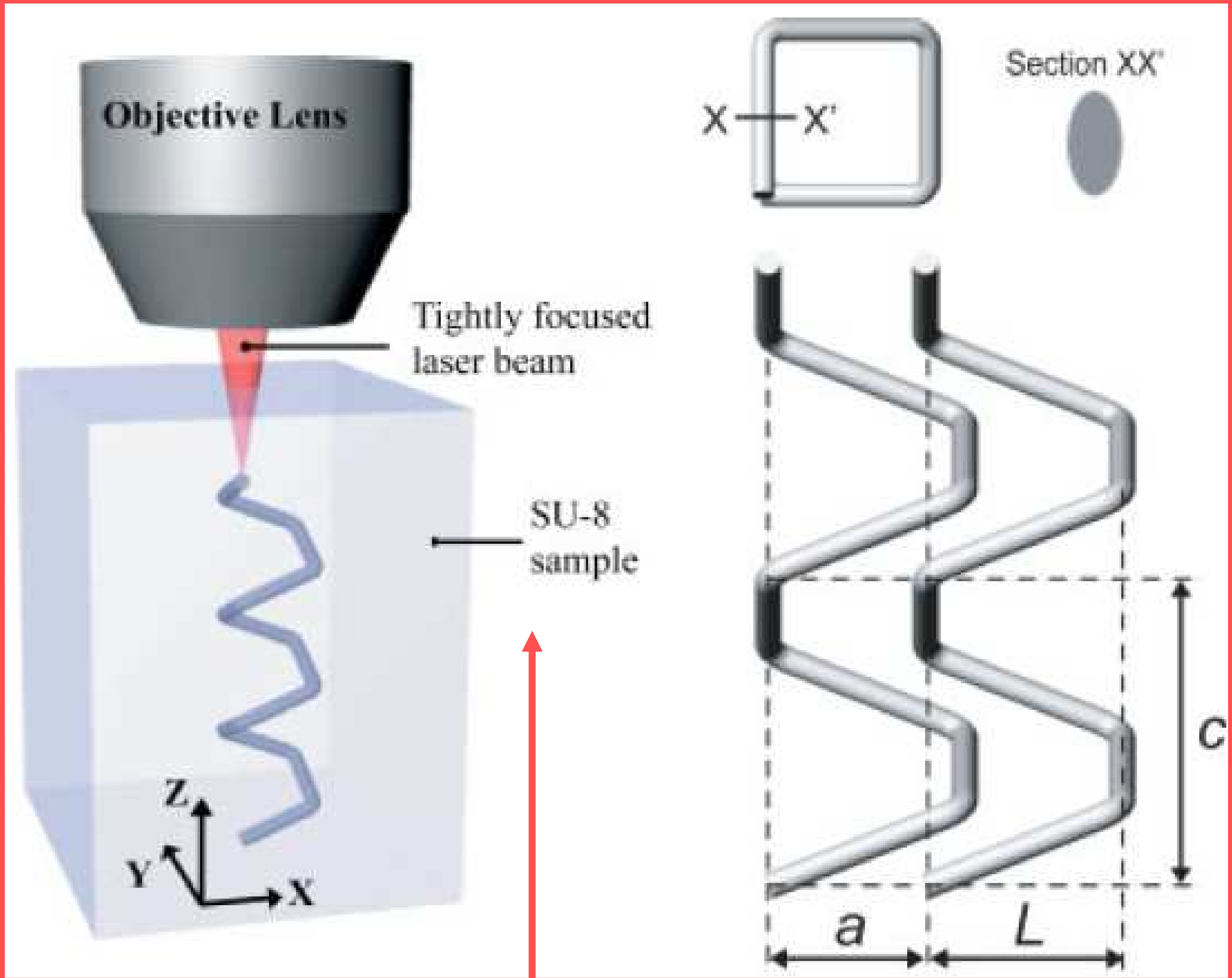


For non-planar surfaces – PLANARIZATION

Twisted gold crosses metamaterial exhibiting circular dichroism @1,36µm

M. Decker …C. Soukoulis…. M. Wegener, et al. Optics Letters 35, 1593-1595 (2010)

Direct Laser Writing



SU-8 is solid before and after optical exposure

DIRECT WRITING

A permanent photomodification, seeded by multiphoton absorption, is induced in the optically transparent dielectric material at the focal region of a tightly focused laser beam. The photomodification is localized within the spatial domain defined by the multiphoton absorption point-spread function. By translating the sample, arbitrarily shaped patterns can be drawn.

Adv. Mater. 17 (2005) 541, K. K. Seet et al.

In DLW multiphoton polymerization,

a photoresist is illuminated by laser light at a frequency below the single photon polymerization threshold of the resist. When this laser light is tightly focused inside the photoresist, the light intensity inside a small volume (the focus) may exceed the threshold for initiating multiphoton polymerization. The size and shape of these so-called VOXELS depend on the iso-intensity surfaces of the microscope objective, and the exposure threshold for multiphoton processes of the photosensitive medium.

SU-8

SU-8(MicroChem)

consists of an octafunctional epoxy **RESIN** (PON SU-8),
a **PHOTOINITIATOR** (mixed triarylsulphonium/hexafluoroantimonate salt in propylee carbonate solvent), both dissolved in gamma-butyrolactone (GBL)

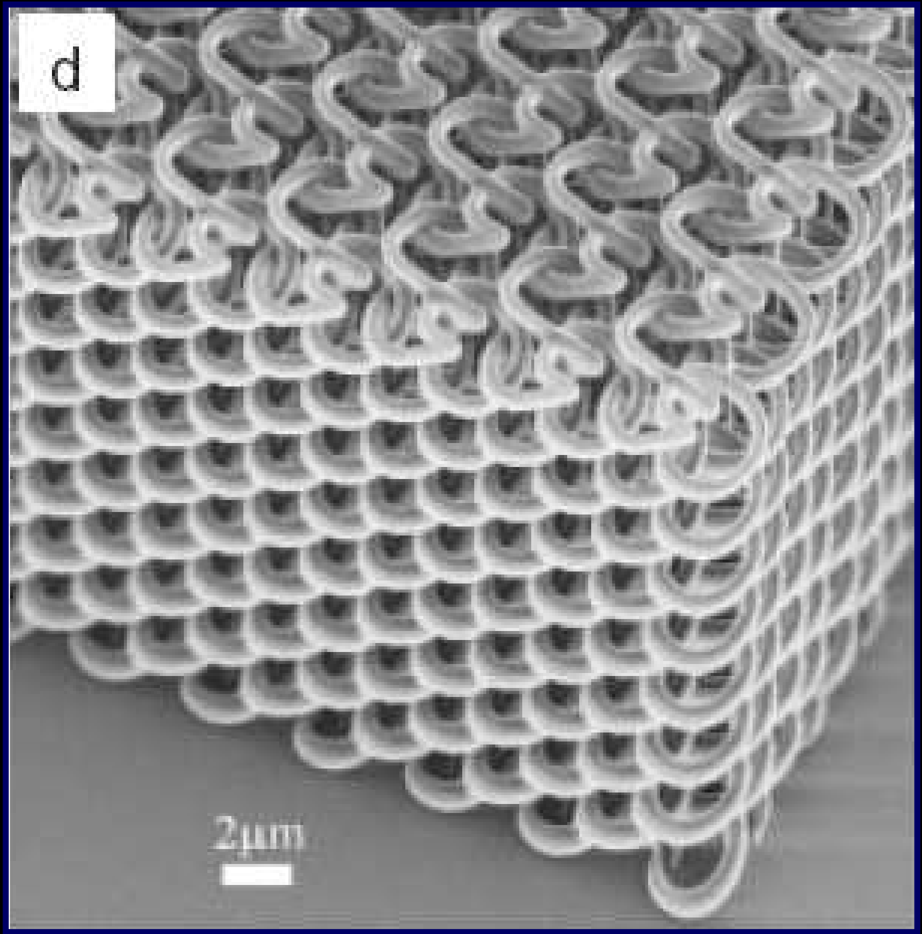
EXPOSURE → On irradiation by near-ultraviolet light, the photoinitiator generates an acid

POSTEXPOSURE BAKE → In a postexposure bake, this acid catalyzes the cross linking reaction of the monomers to the polymer

DEVELOPMENT → Sufficiently illuminated resin remains whereas underexposed resin is washed out by a solvent in a development step

- SU-8 is solid before and after optical exposure
- Chemical development is required in order to reveal the photomodified regions
- Absence of a liquid-to-solid transition during the DLW creates stable recording conditions
- It permits the fabrication of areas behind the already fabricated features

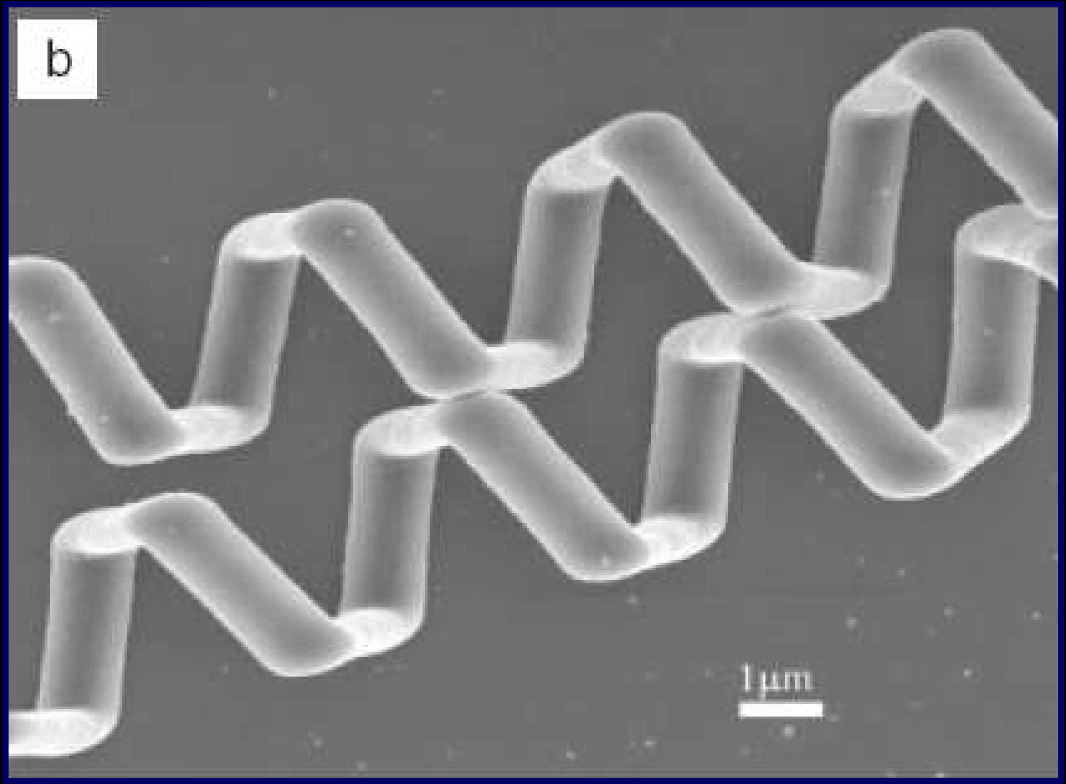
DLW



The circular-spiral sample with 180deg phase shift between adjacent spirals

Although the simplest square-spiral structures were successfully fabricated from silicon by the GLAD technique, their more-complex variants (e.g. containing phase shifted spirals) can only be realized by DLW

Adv. Mater. 17 (2005) 541, K. K. Seet et al.

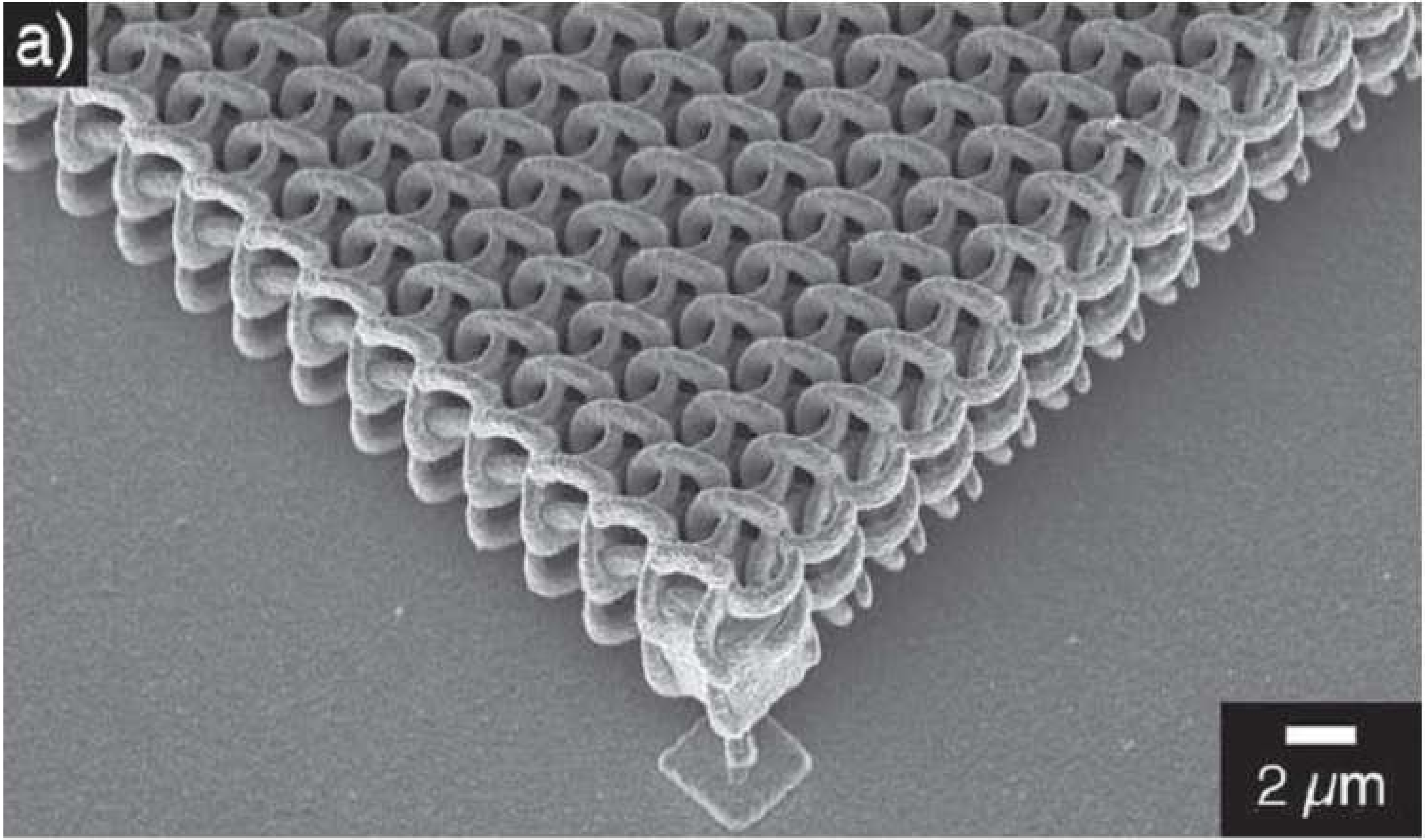


Advantage

The spiral structures are self-supporting and are almost shrinkage free

Adv. Mater. 17 (2005) 541, K. K. Seet et al.

Bichiral metamaterial obtained by DLW and electroless silver plating



A. Radke et al. Adv. Mat. 23, 3018 (2011)

DLW

Possibilities for practical infiltration of 3D SU-8 templates

Single infiltration and template removal will produce an inverse structure

1. Sol-gel infiltration

eg. with TiO_2 (n=2.2, 2.6) or other nanoparticles into the air voids followed by the removal of the template

2. Low-temperature chemical vapor deposition (CVD)

SU-8 retains its thermal and chemical robustness for temperatures up to 380degC

3. Electrodeposition

For infiltration of semiconductors

Possibilities for practical infiltration of 3D SU-8 templates

DOUBLE-TEMPLATING APPROACH

↓

CVD – infiltration of silica into the template

↓

Removal of SU-8 template - thermally

↓

Infiltration by other material as semiconductor/metal

into remaining secondary silica template

↓

chemical etching - removal of silica template

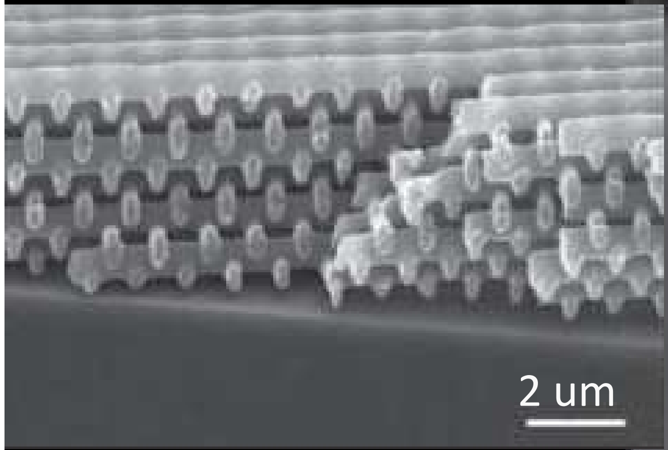
↓

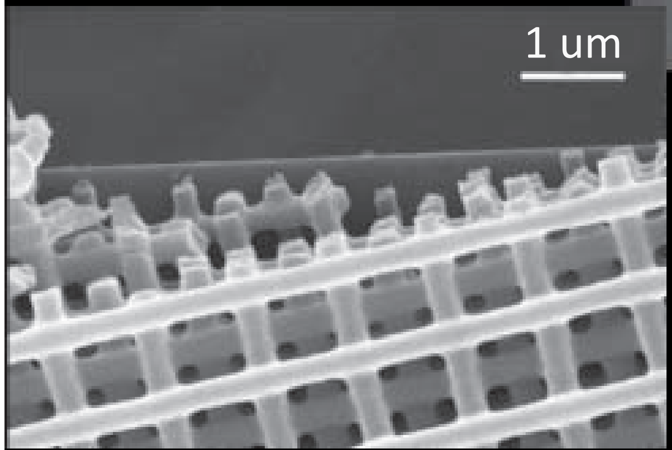
direct structure is obtained

Direct laser writing (DLW) of 3 D PC templates for telecommunication

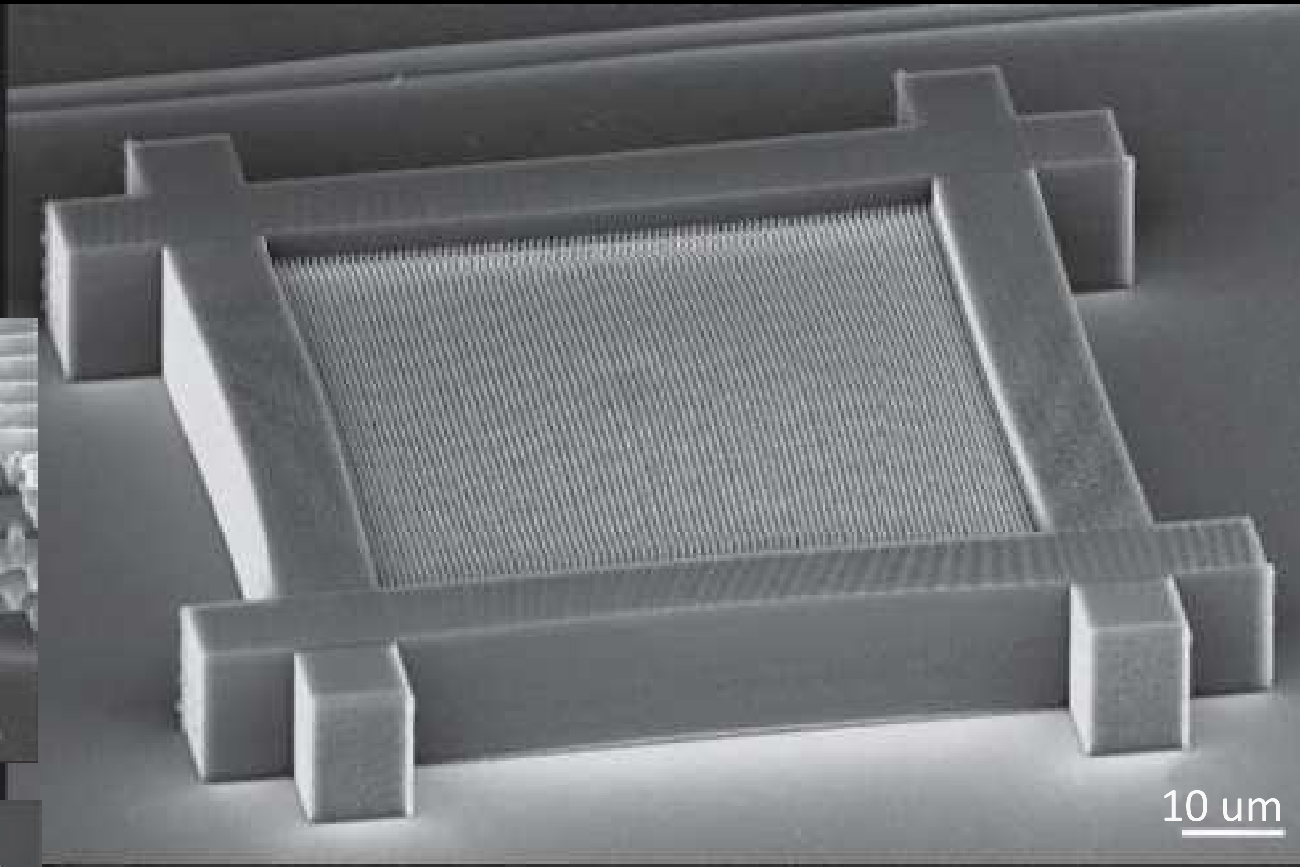
DLW

Side view





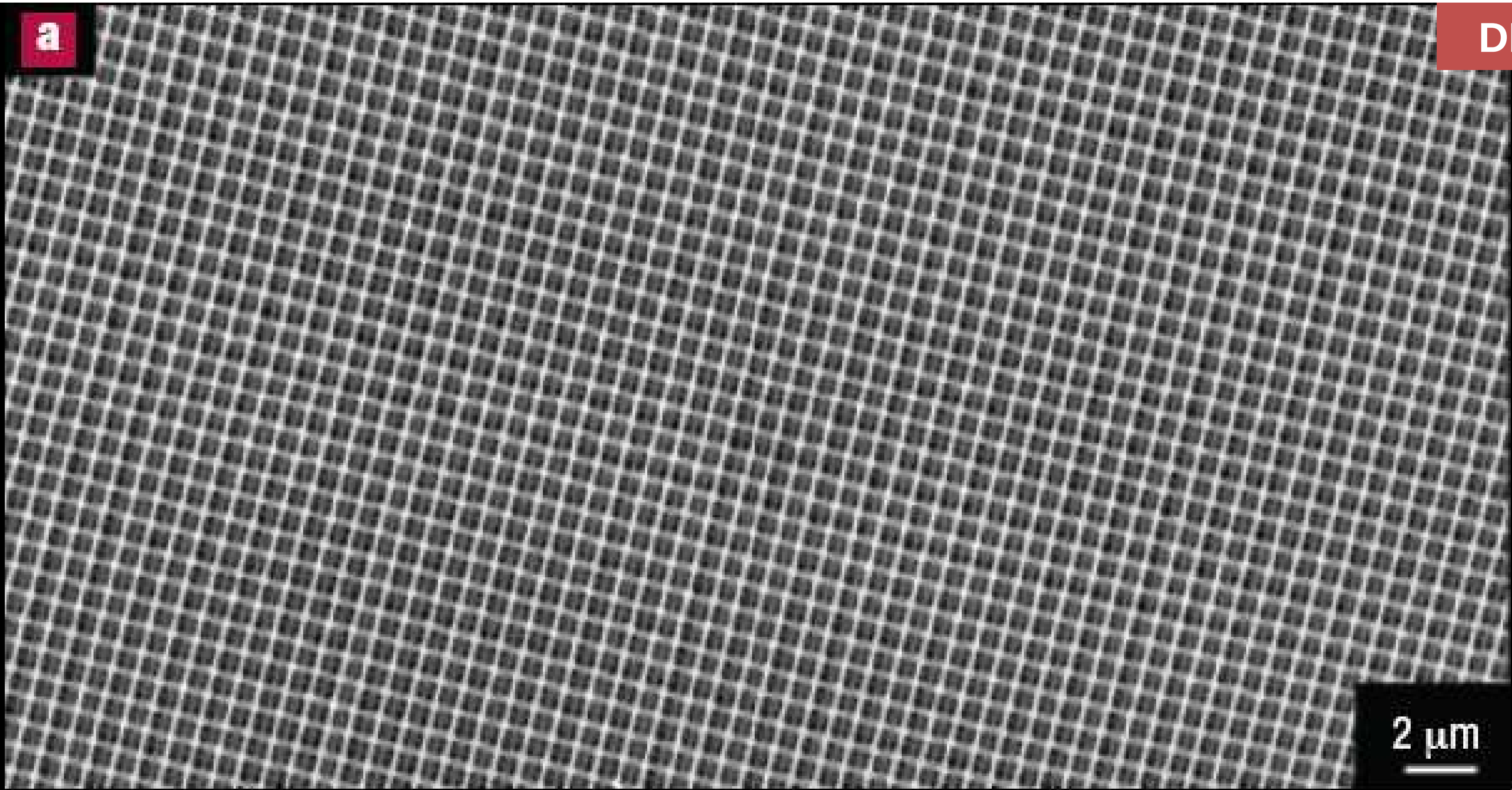
Top view



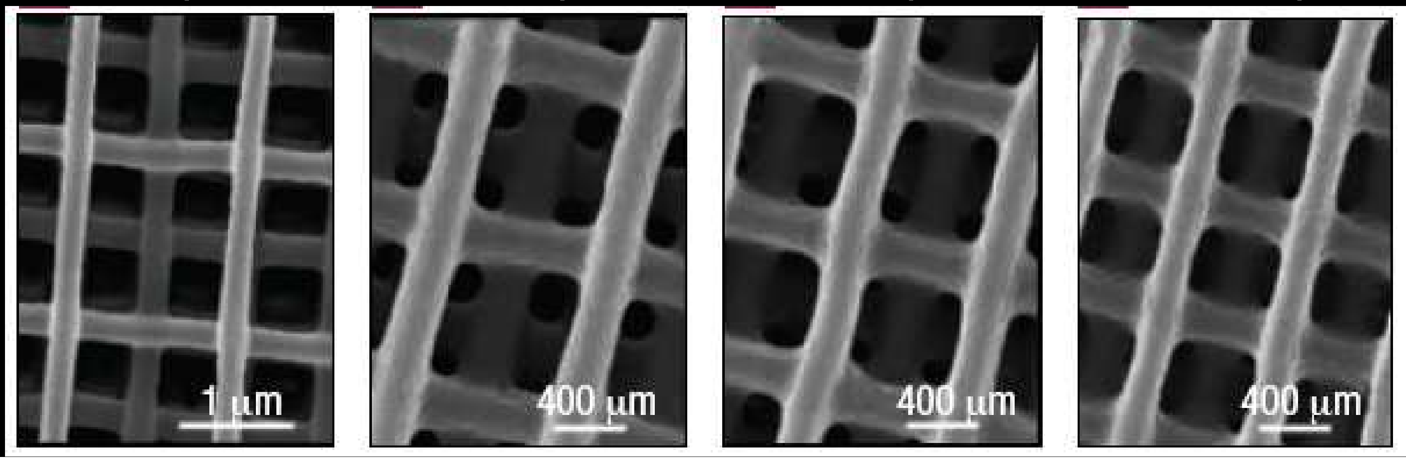
Layer-by-layer structure with 40 layers and a massive wall that prevents bending and reduces distortions due to polymer shrinkage during polymerization

Nature Materials 3 (2004) 444, Deubel M.

DLW



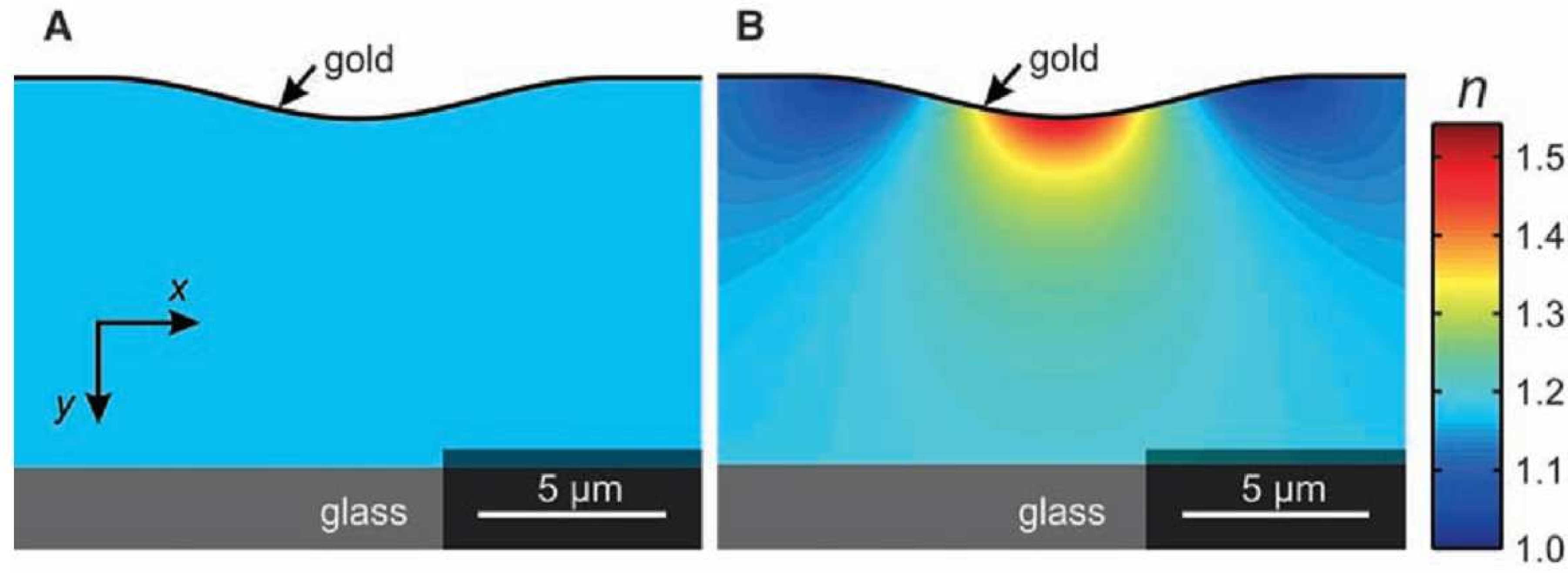
a = 1.5 µm   *a* = 1.0 µm   *a* = 0.8 µm   *a* = 0.65 µm



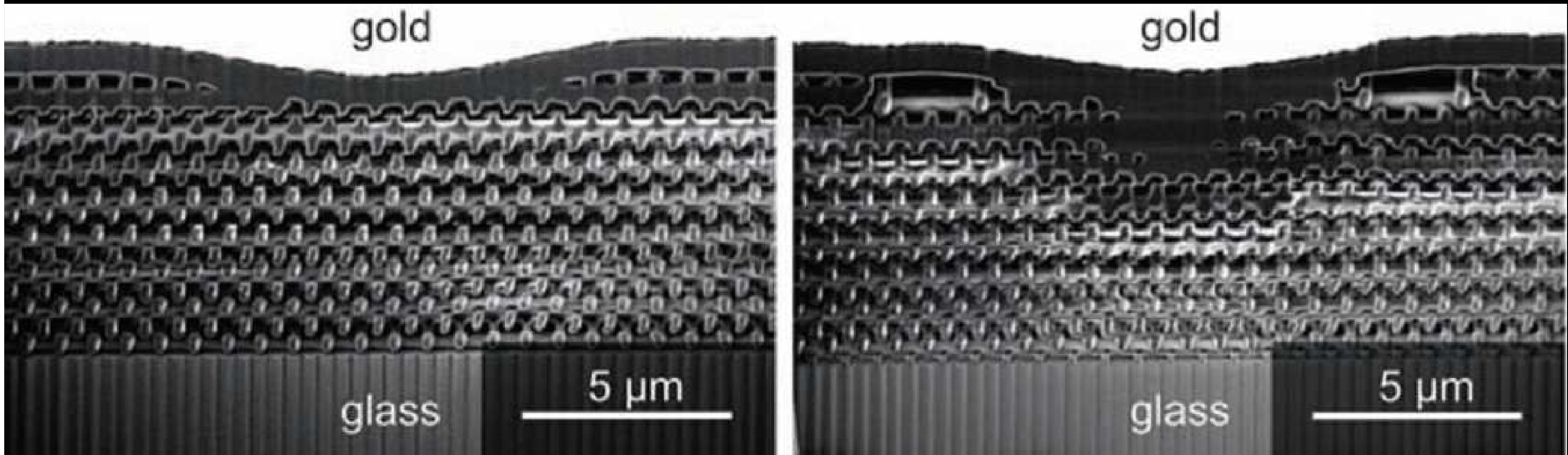
Nature Materials 3 (2004) 444, Deubel M.

Direct Laser Writing and Transformation Optics (TO)

DLW



Refractive index distribution in woodpile structure without cloak (left) with cloak (right)



T. Ergin …
J.B. Pendry,
M. Wegener,
et al. Science
328 337
(2010)

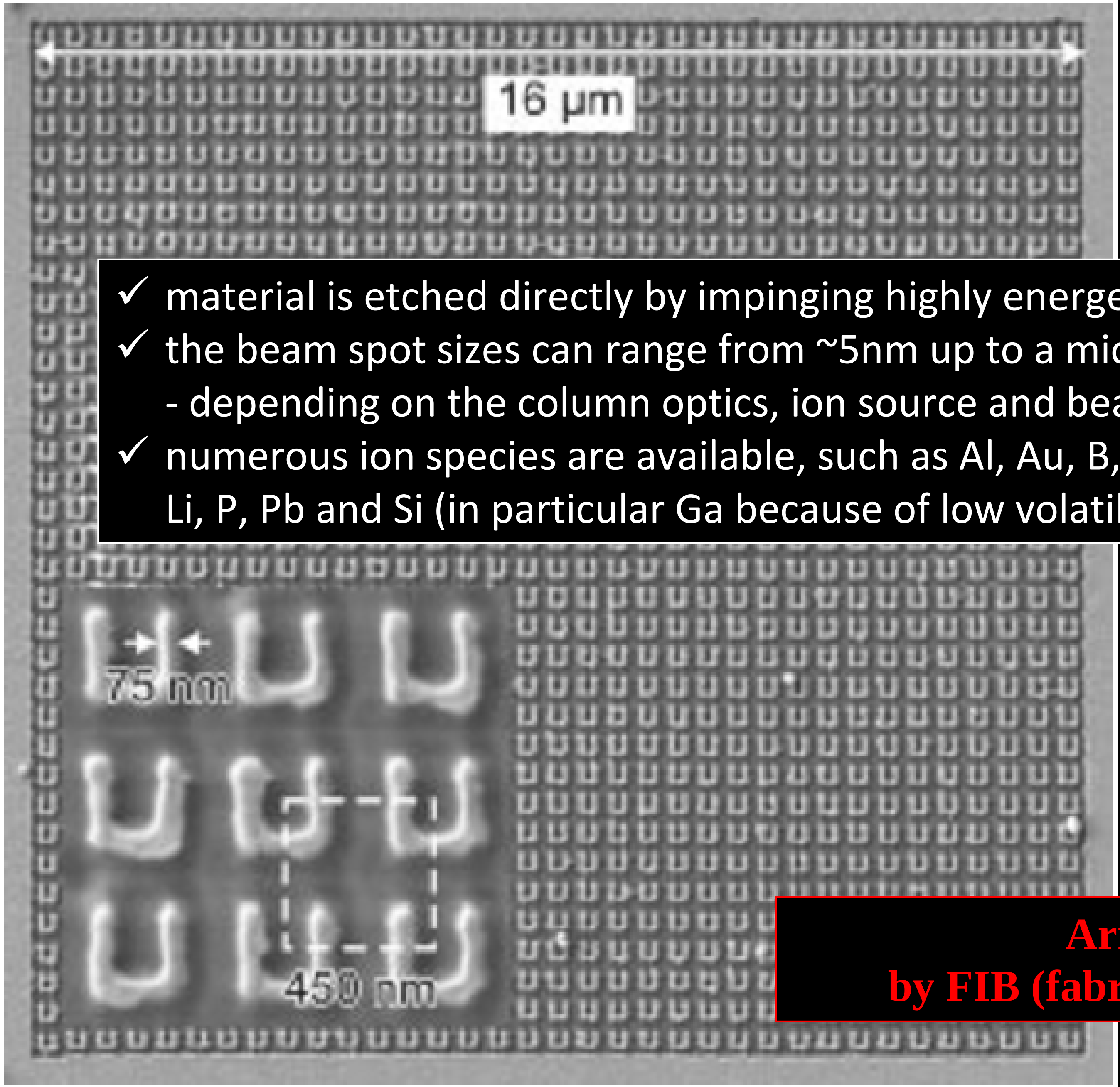
3D broadband optical (1.4 to 2.7 µm) carpet-cloak

Ion Beam Lithography (Focus Ion Beam – FIB, ion milling)

FIB

DIRECT WRITING

S. Enkrich et al.
Adv. Mater. 17 ,
2547–2549
(2005)



- ✓ material is etched directly by impinging highly energetic ions
- ✓ the beam spot sizes can range from ~5nm up to a micrometer
  - depending on the column optics, ion source and beam current
- ✓ numerous ion species are available, such as Al, Au, B, Be, Cu, Ga, Ge, Fe, In, Li, P, Pb and Si (in particular Ga because of low volatility and melting temp.)

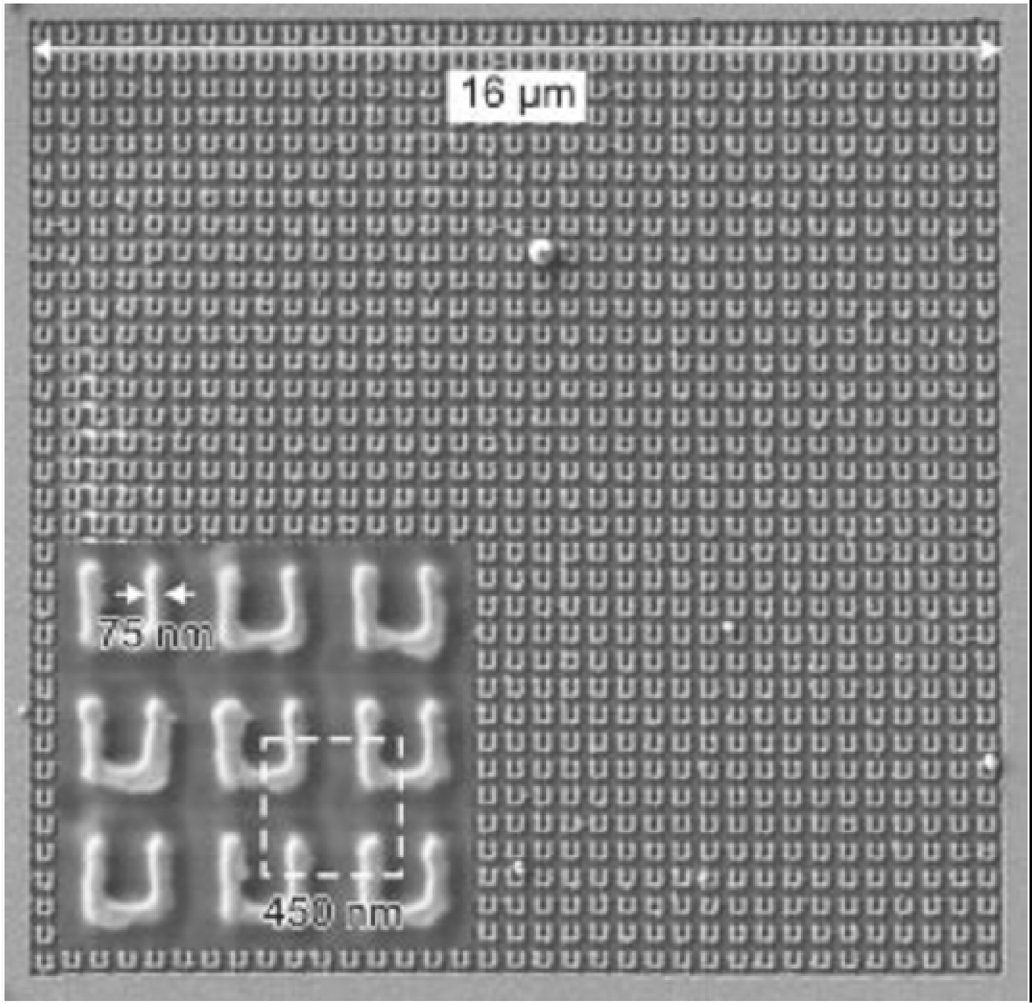
Arrays of SRRs obtained by FIB (fabrication time ≈ 20 min)

Ion Beam Lithography (Focus Ion Beam – FIB, ion milling)

FIB

DIRECT WRITING

S. Enkrich et al. Adv. Mater. 17 , 2547–2549 (2005)



Advantages:

- very good resolution
- maskless = direct writing
- arbitrary shapes possible
- good for proof-of-concept demonstrations and rapid prototyping
- fully anisotropic etching
- can be adopted as a SEM accessory

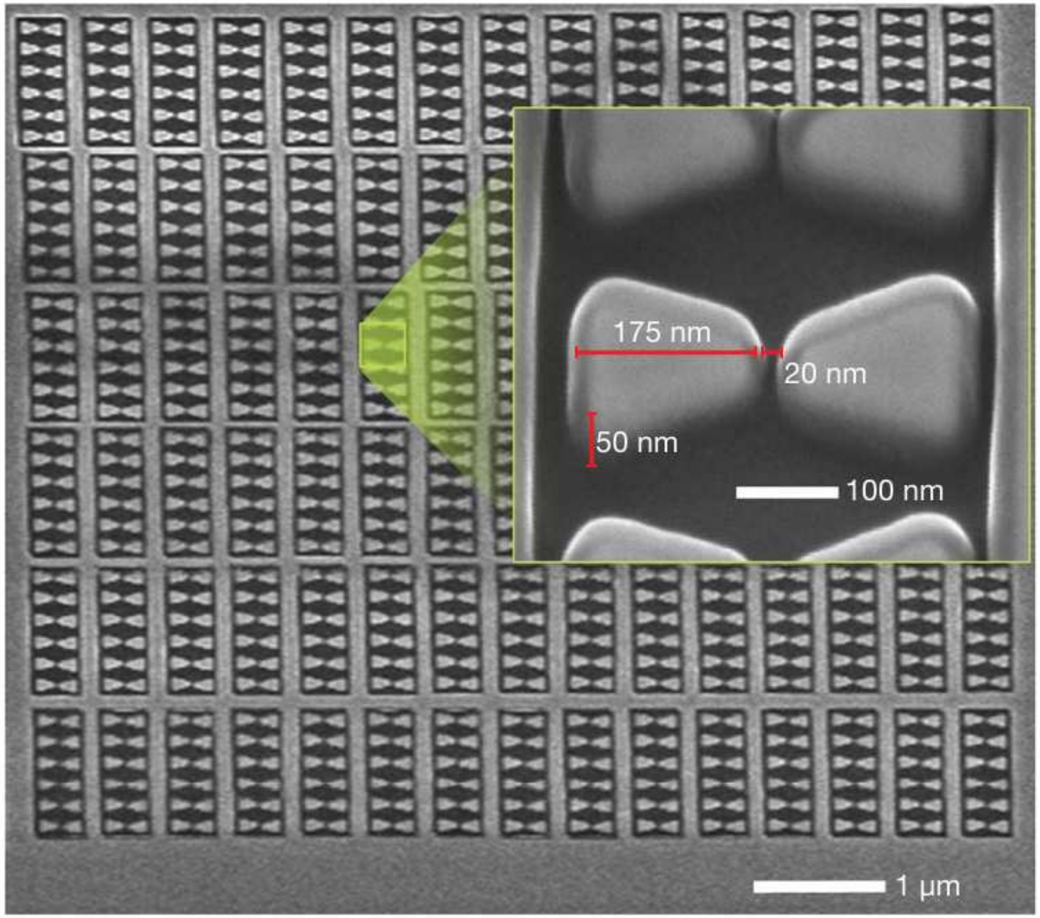
Disadvantages:

- small-area fabrication
- difficult three-dimensional nanostructure patterning
- unintentional doping and structure damaging
- patterning structures below 100 nm starts to be very slow

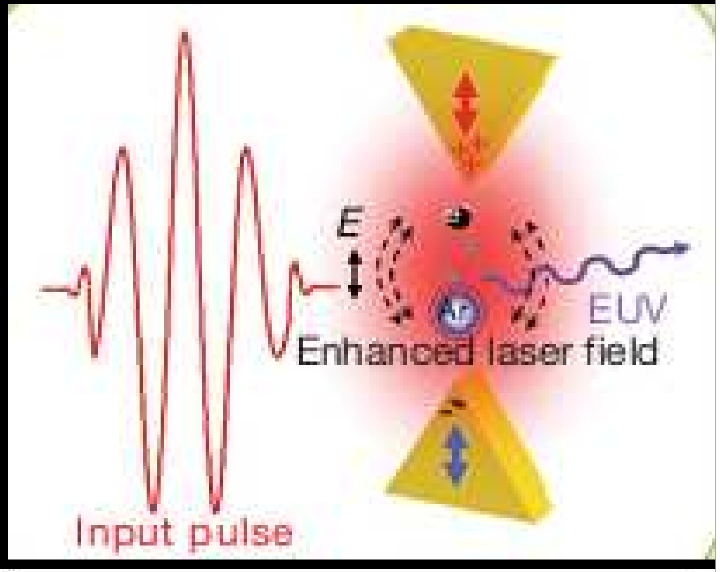
Ion Beam Lithography (Focus Ion Beam – FIB, ion milling)

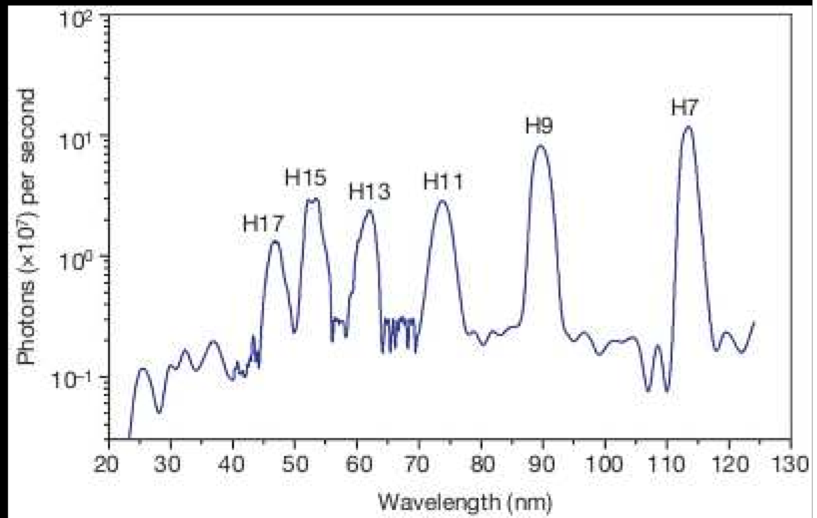
FIB

DIRECT WRITING



10-fs ,800 nm, 75 MHz Ti:sapphire laser





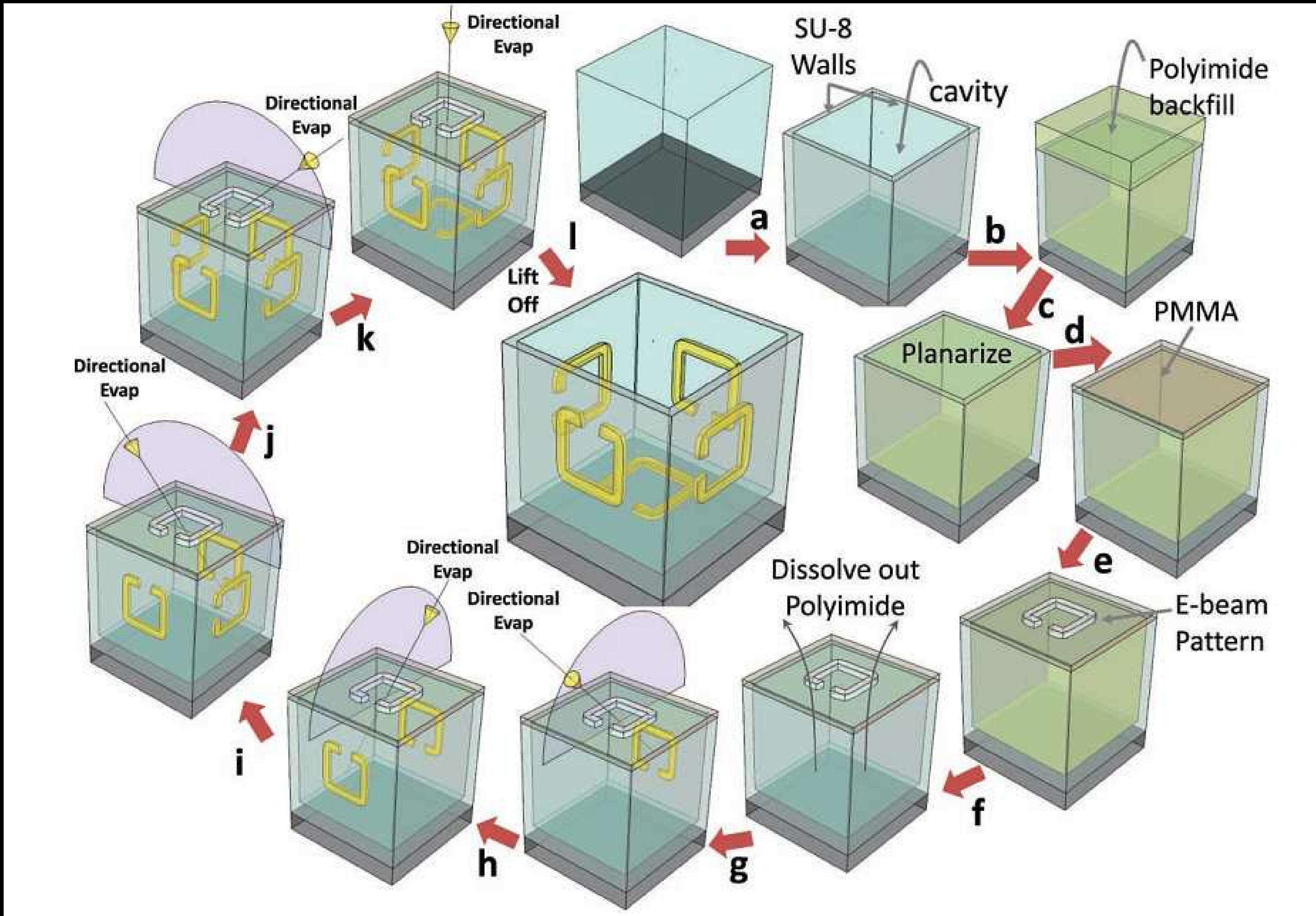
Gold bow-tie nanoantennas obtained by FIB

Generation of Extreme-UV light with pulse intensity 10^{11} Wcm^{-2} (normally required $>10^{13}$ Wcm^{-2})

S. Kim et al. Nature 453 (2008)

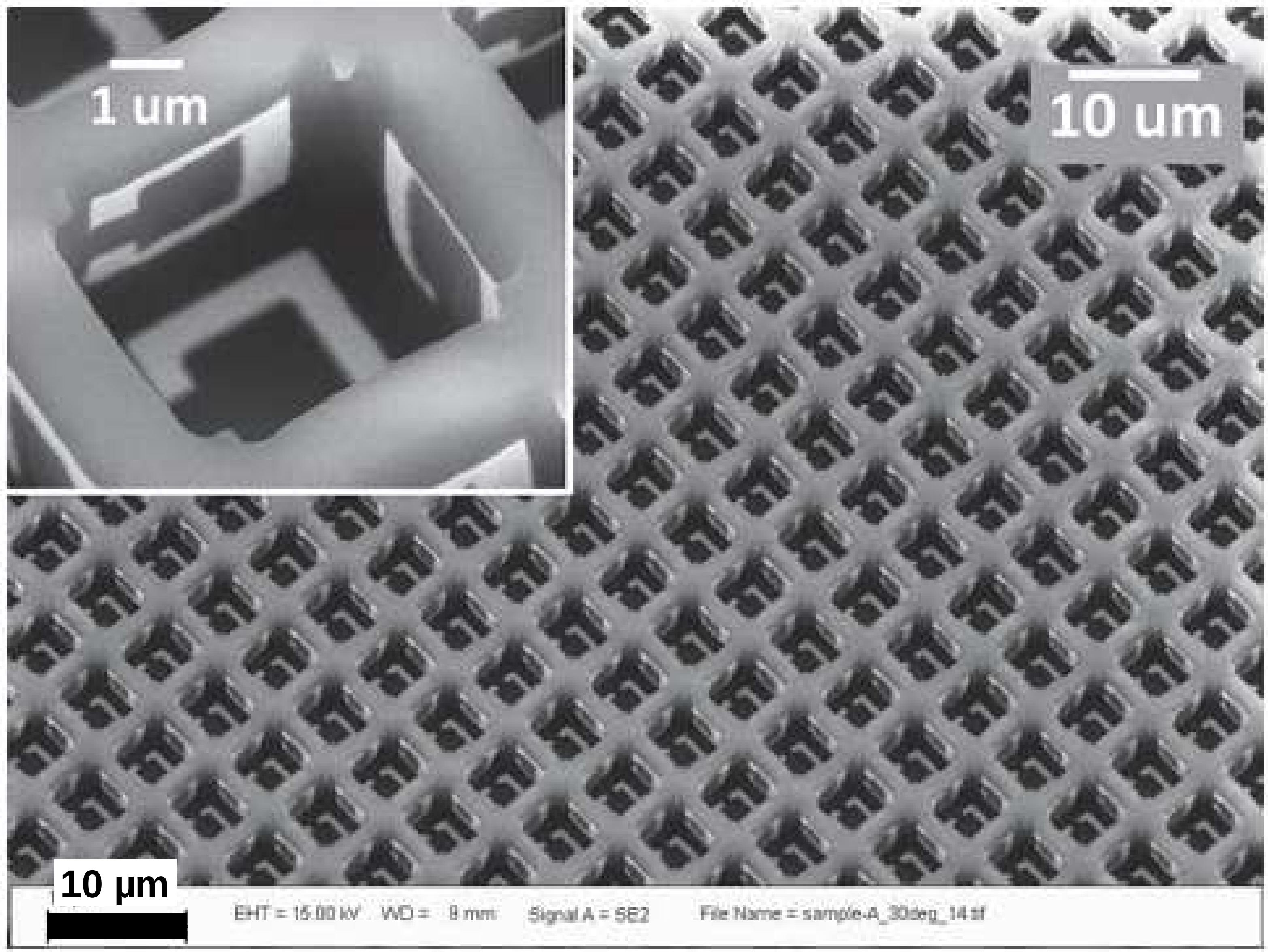
Measured spectrum of generated high harmonics

Self-Aligned Membrane Projection Lithography (SAMPL)



D. B. Burckel…M. B. Sinclair, AFM, **2010**, 22, 5053

Self-Aligned Membrane Projection Lithography (SAMPL)



Gold SRRs multi-3D-structure fabricated with SAMPL

D. B. Burckel…M. B. Sinclair, AFM, **2010**, 22, 5053

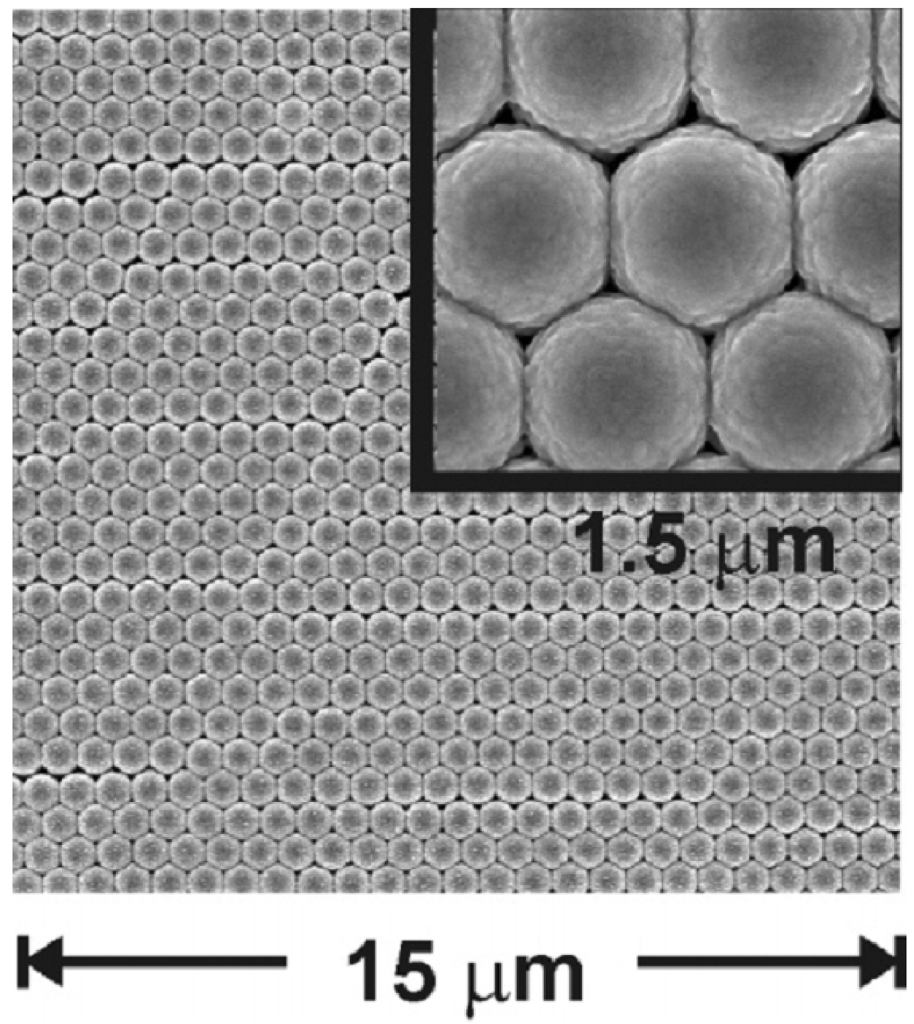
Atomic Layer Deposition (ALD) in MTMs and plasmonics

ALD

- ✓ ALD in principle is similar to chemical vapor deposition process
- ✓ in ALD two precursors of deposited material are deposited separately (in separate reactions) this allows to obtain layers controlled with atomic precision (due to the self-limiting surface reactions)
- ✓ ALD enables obtaining super-thin films (from 1 Å) which could be very useful for plasmonics and MTMs

X. Zhang et al. J. Am. Chem. Soc. 128, 10304 -10309 (2006)

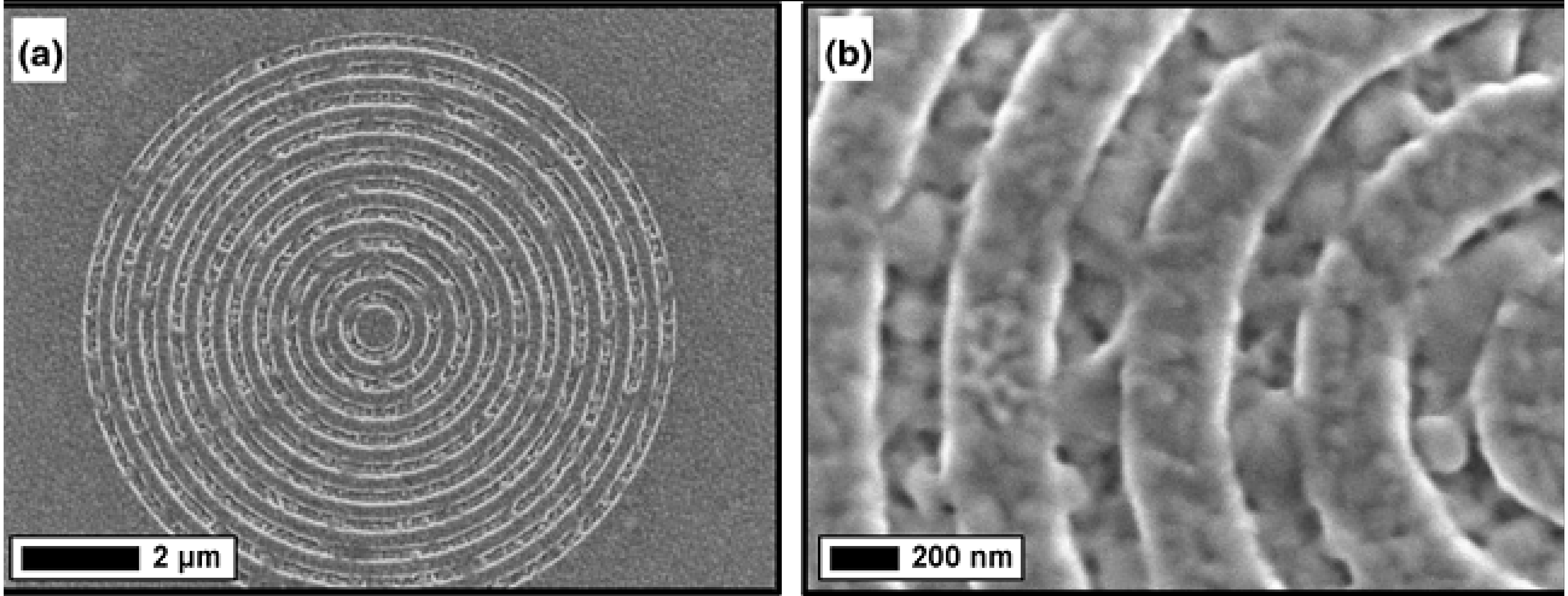
For SERS: (i) protection of Ag, (ii) proximity of molecules to plasmonic particles



Self-assembled silver film-over-nanosphere (AgFON) prepared by drop-coating polysterene spheres onto the substrate and covered with silver and coated with Al_2O_3 (ALD -2 Å)

Bull's eye pattern by Focused Ion Beam

Typical as-deposited silver ion beam milled polycrystalline films are inherently rough and posses implant impurities…



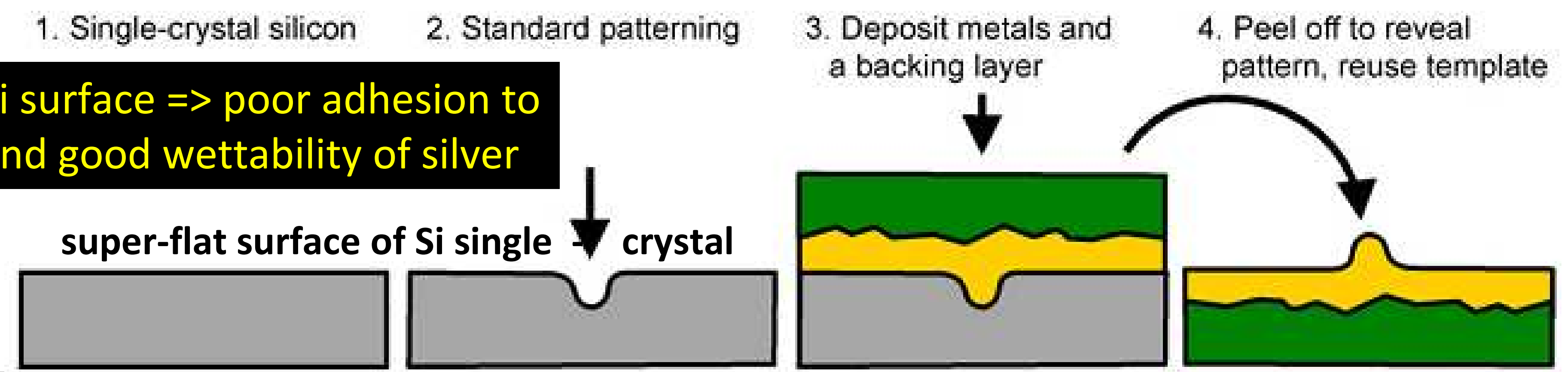
Bull's eye pattern milled into an as-deposited silver film via FIB

One of the newest idea to make the film (and pattern) smoother is template stripping

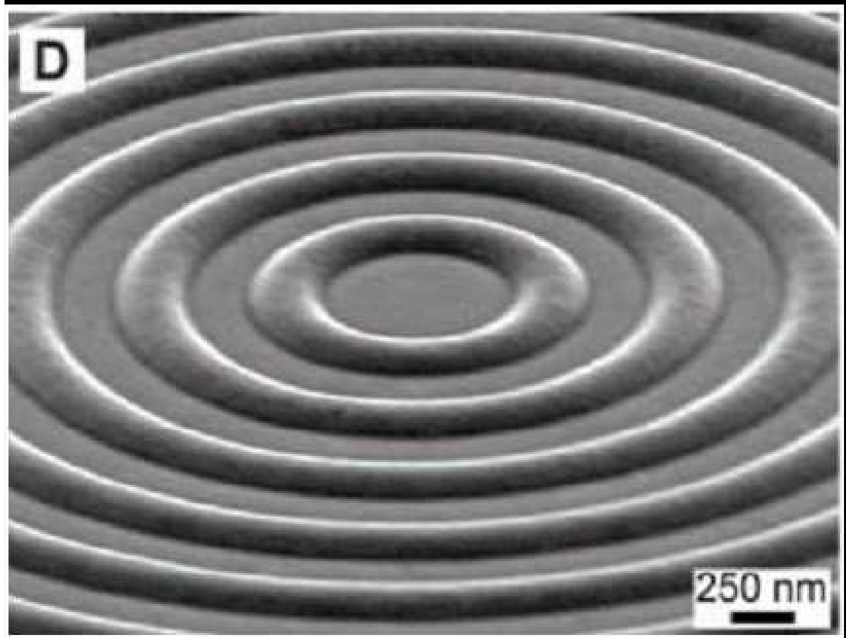
N C Lindquist et al. Rep. Prog. Phys. 75, 036501 (2012)

Template stripping for ultrasmooth patterned metals

Si surface => poor adhesion to and good wettability of silver

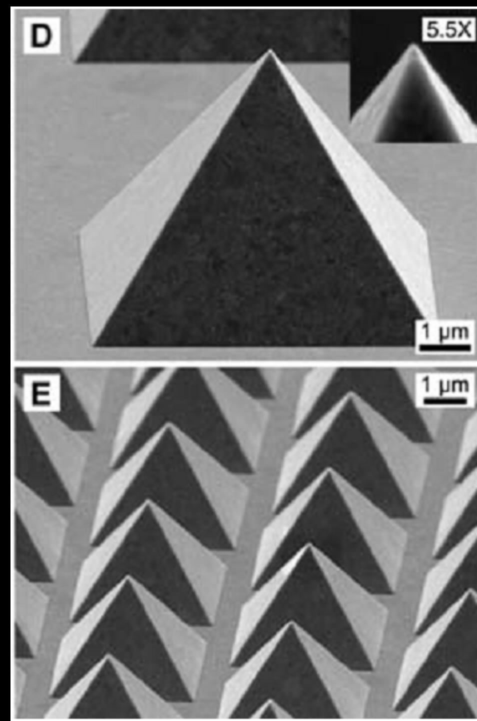


N C Lindquist et al. Rep. Prog. Phys. 75, 036501 (2012)



Silver bull's eye pattern

Gold pyramid array



P. Nagpal... D. J. Norris, et al. Science 325, 594 (2009)

Top-down methods

Means of patterning	PHOTONS • Photolithography + lift-off • Holographic Lithography • Direct Laser Writing	ELECTRONS • Electron Beam Evaporation • Electron Beam Lithography	IONS • Ion Beam Lithography
Way of exposure	ENTIRE AREA EXPOSURE • Photolithography + lift-off • Electron Beam Evaporation • Holographic lithography • Soft Lithography • Glancing Angle Deposition Method • Atomic Layer Deposition • Template Stripping	SCANNING Direct Writing: • Direct Laser Writing • Electron Beam Lithography • Ion Beam Lithography	
Other	FAST & LARGE AREA • Soft Lithography	ARBITRARY SHAPES • Direct writing	ULTRA SMOOTH • Template stripping

THANK YOU FOR YOUR ATTENTION!