

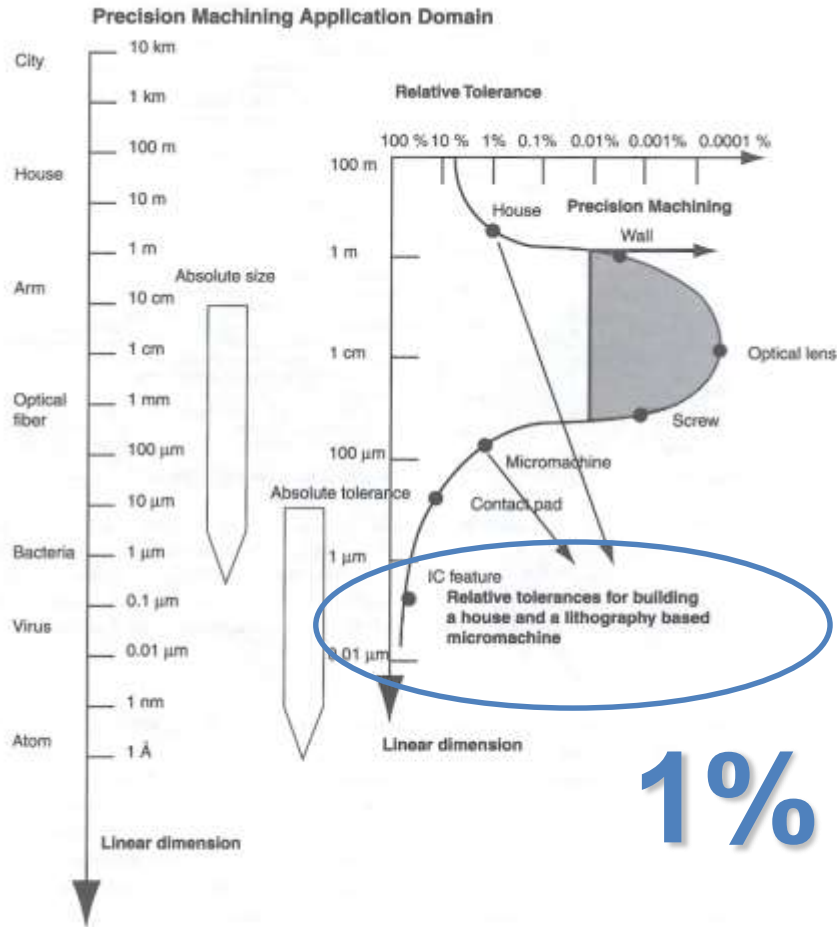
# Nanofabrication technologies for nanophotonics

**Igor Ozerov**

Aix-Marseille Univ, CNRS, CINaM 13288 Marseille France



# Relative precision of nanofabrication

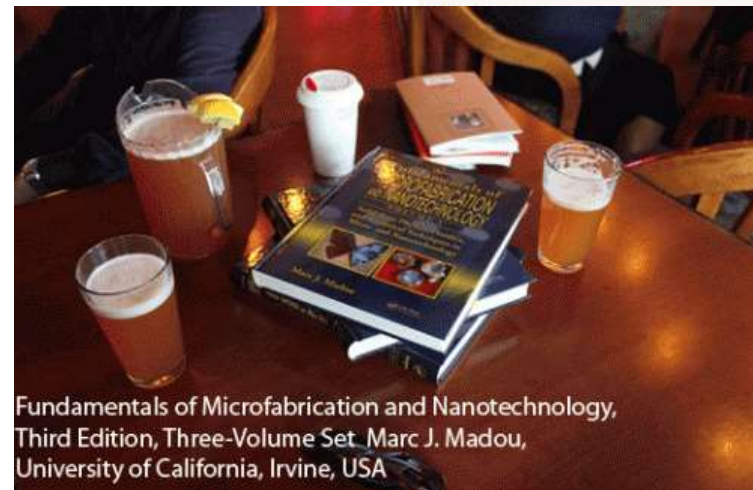


Application field for precision machining in terms of absolute sizes and absolute and relative tolerances.

1%

Fundamentals of Microfabrication

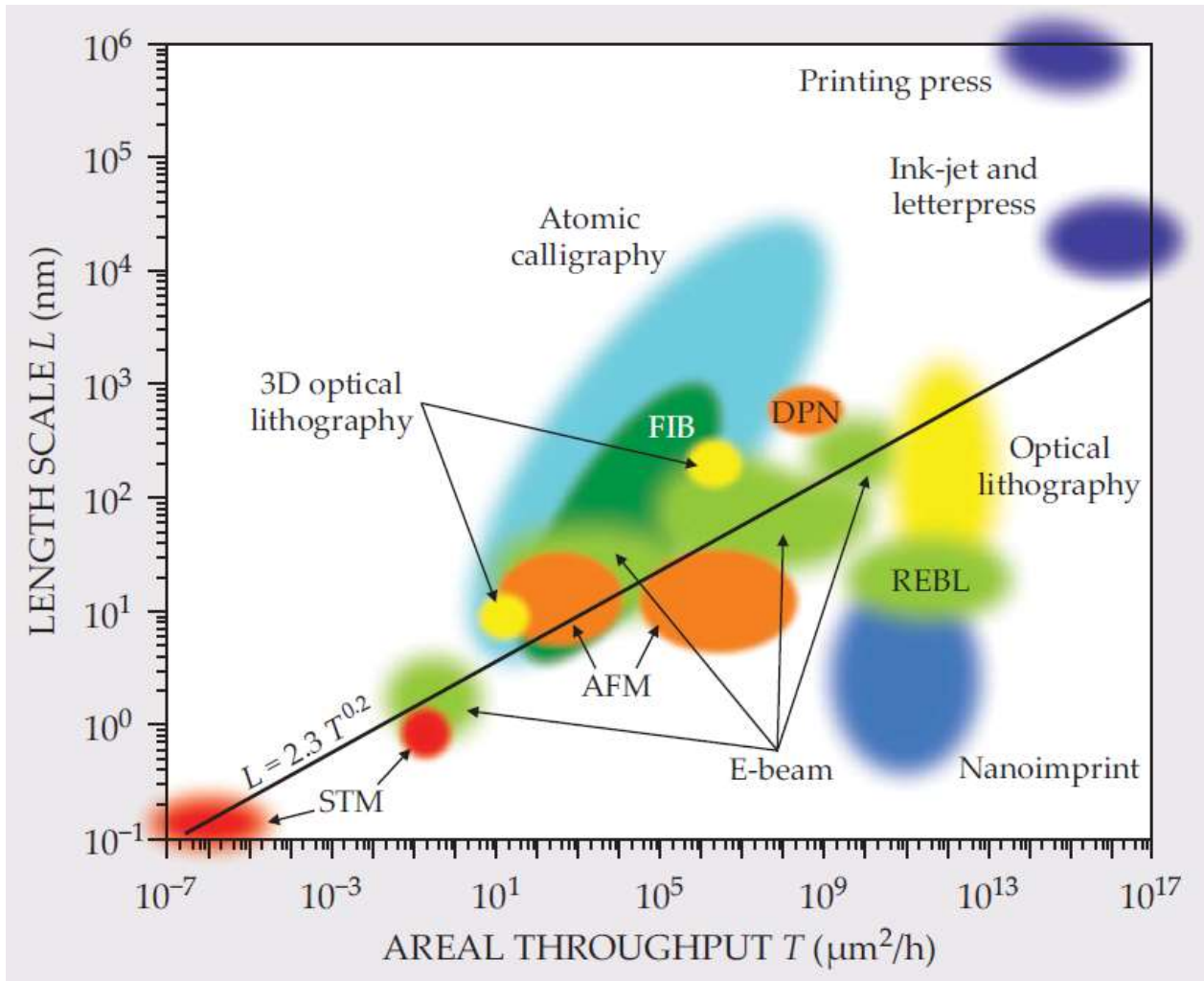
Marc Madou's BLOG



Fundamentals of Microfabrication and Nanotechnology, Third Edition, Three-Volume Set, Marc J. Madou, University of California, Irvine, USA

Image: M. Madou, 'Fundamentals of microfabrication'

# Nanomanufacturing

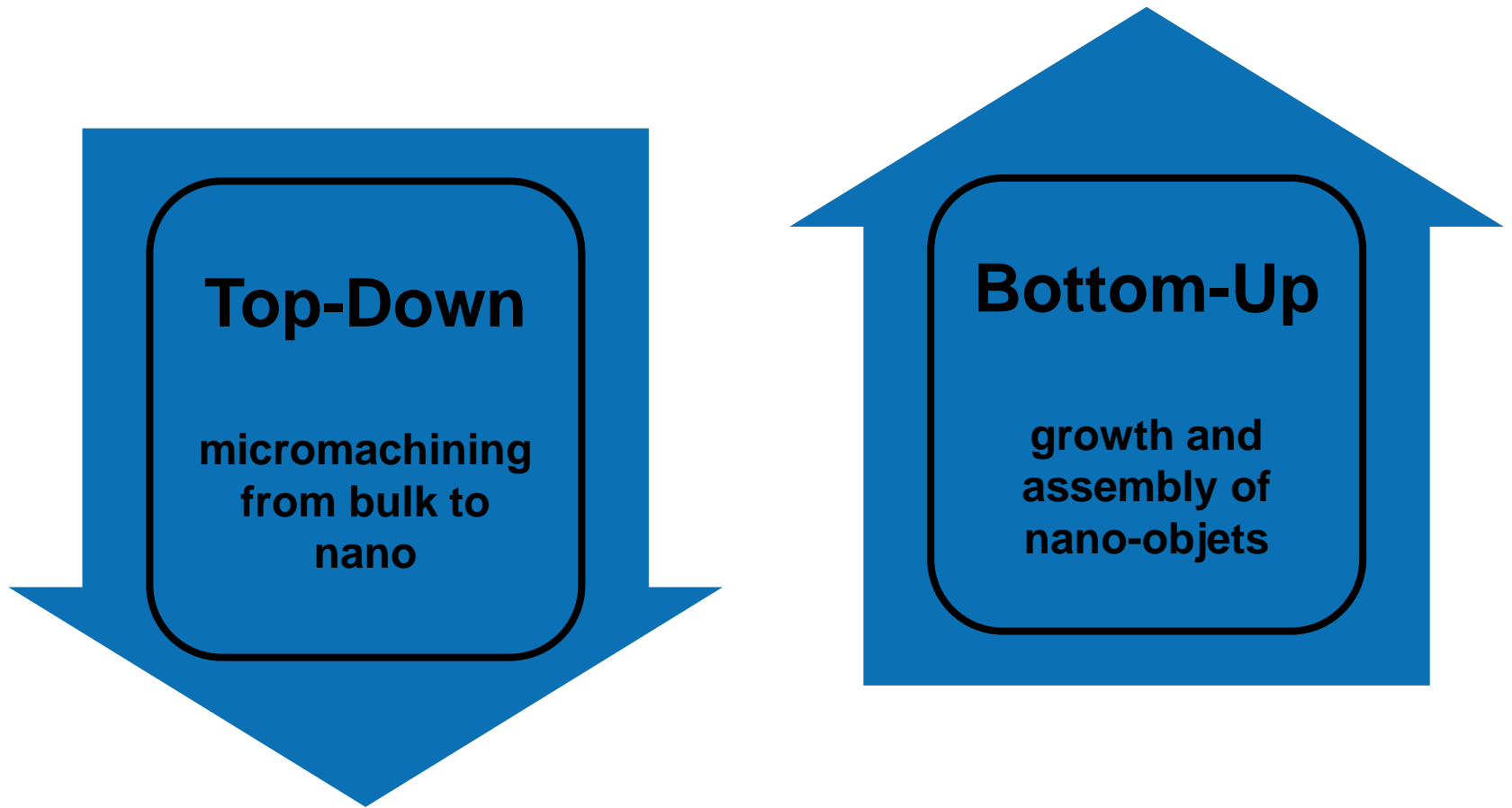


Imboden and Bishop, **Top-down nanomanufacturing**, Physics Today **67**, 45 (2014)

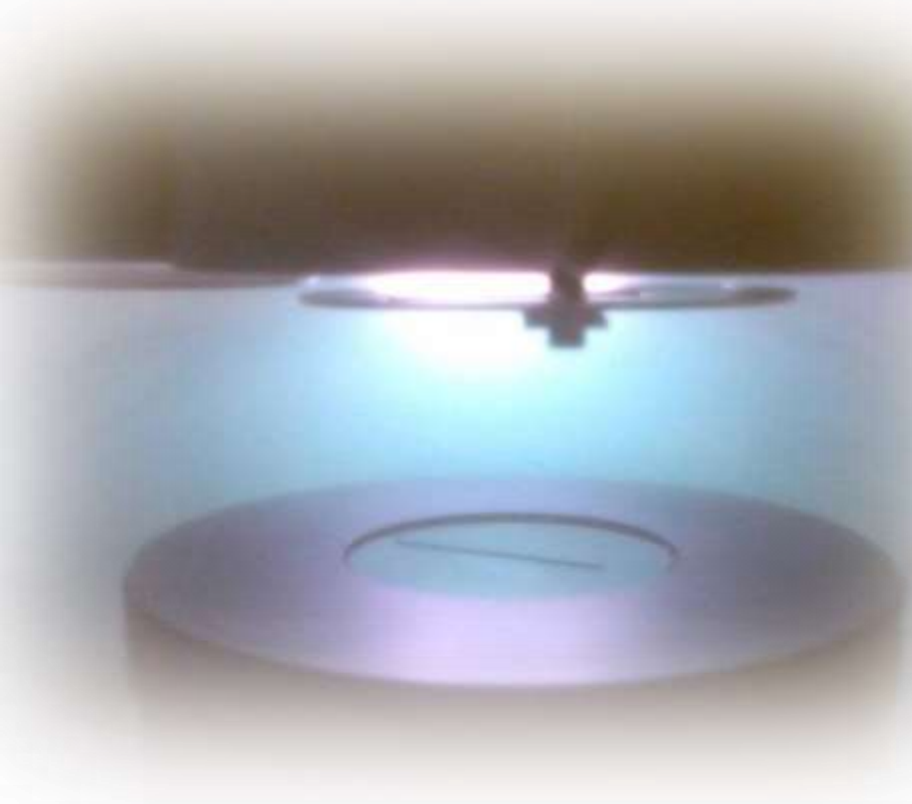
# Plan

- Introduction (top-down processes)
  - Deposition
  - Etching
  - Lithography
  - Focused electron and ion beam techniques
- Exemples plasmonic
- Exemples chiral structures
- Dielectric photonics, silicon
- Exemples, coloration
- Nanosphere lithography (bottom-up)
- Laser-driven methods
- Nanofabrication using vortex beams

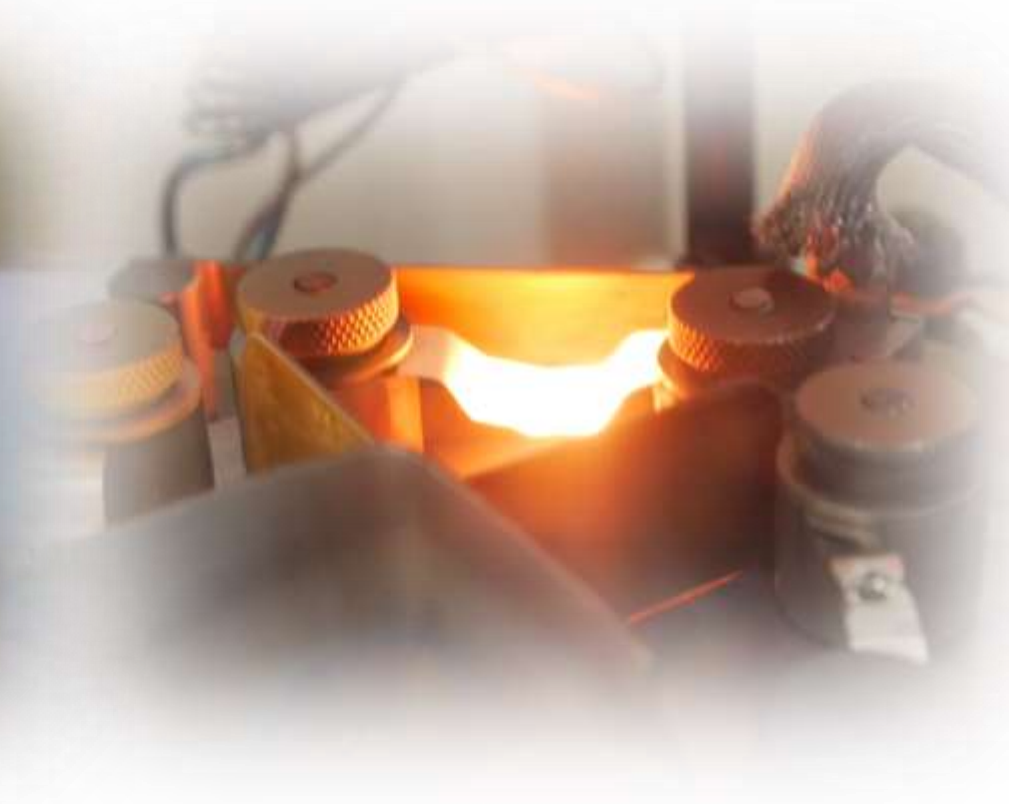
# Nano- et micro- fabrication approaches



# Deposition (additive technics)

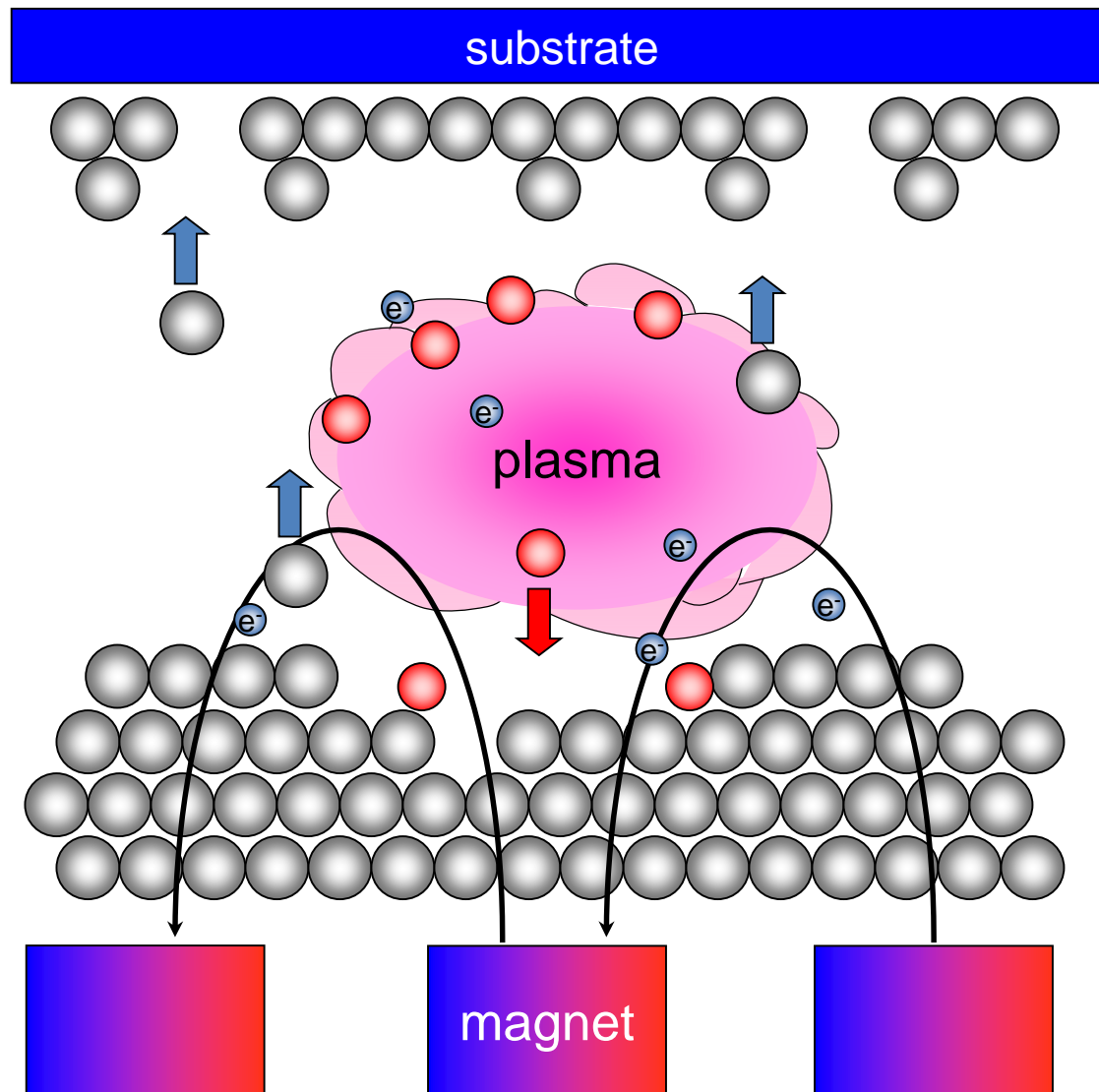


**Magnetron sputtering** (Al, Cr, Ti & W)  
**Reactive sputtering** (nitrides and oxides)  
in gas environment



**Evaporation** (Ag, Al, Au, Cr, Cu & Ni)  
in vacuum

# Magnetron Sputtering



# Step coverage in sputtering and evaporation deposition



**Figure 7.17** (a) Gap filling with conformal step coverage. (b) Conformal deposition of a larger gap with the same process does not lead to gap filling but the original step height remains. (c) Void and (d) cusp are formed when step coverage is maximum at the step corner

S. Franssila, Introduction to Micro Fabrication. Wiley, 2004.



# Nanocones by Directional Evaporation

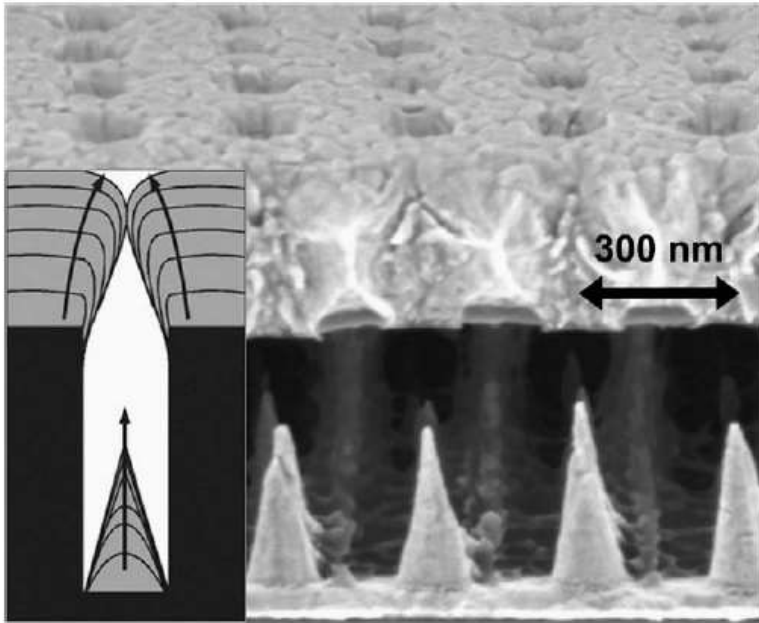
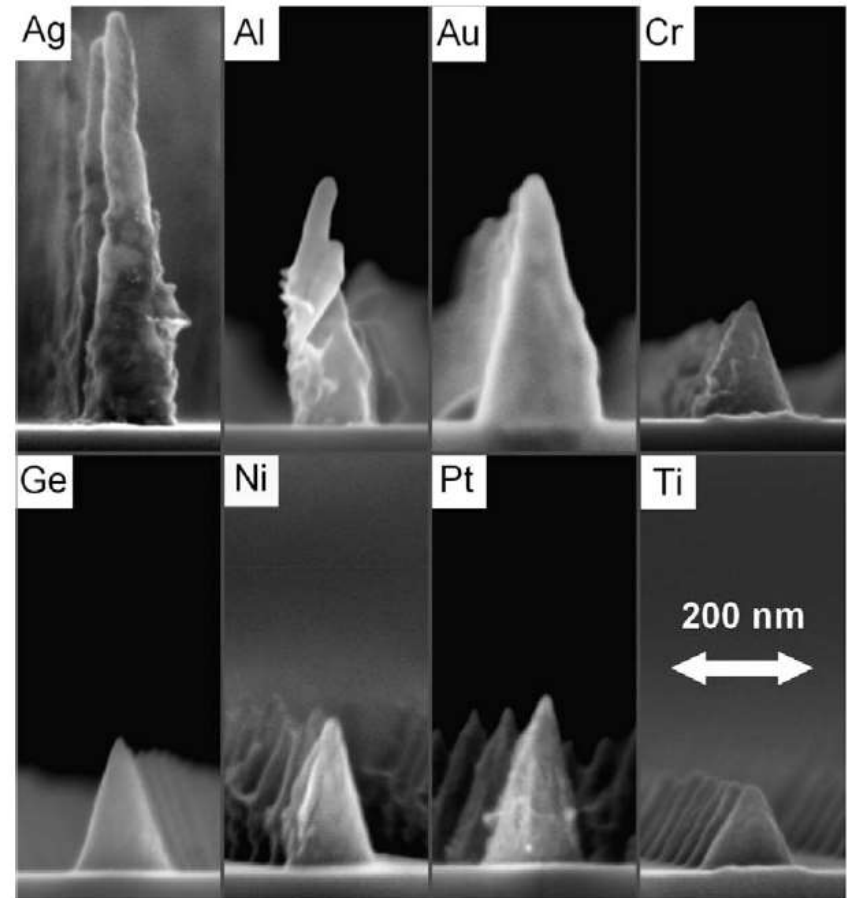


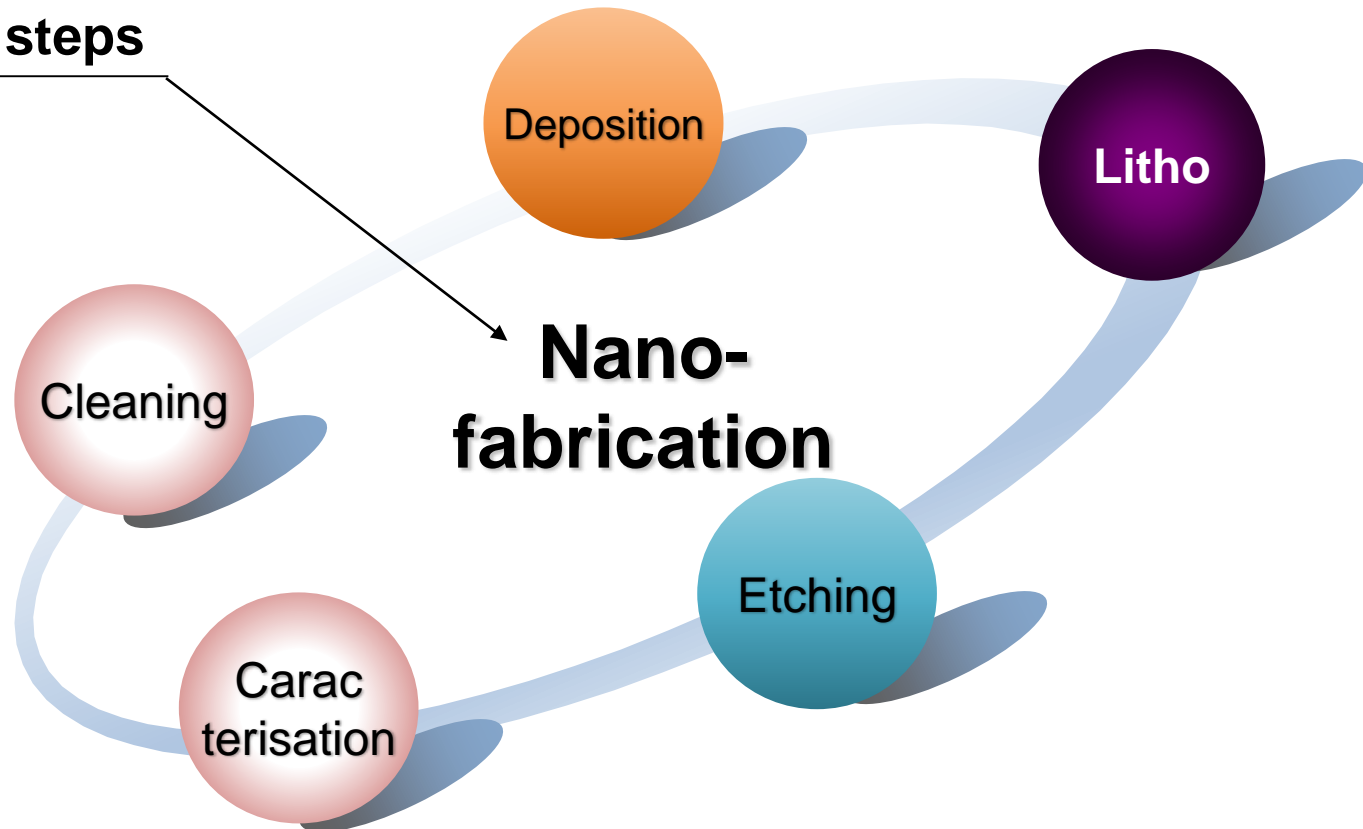
Fig. 3. An SEM image of a sectional view of the structure upon gold evaporation before lift-off. The conical shape is formed spontaneously when the holes in the mask shrink during evaporation (inset). The arrows mark the growth direction of the Au layer.



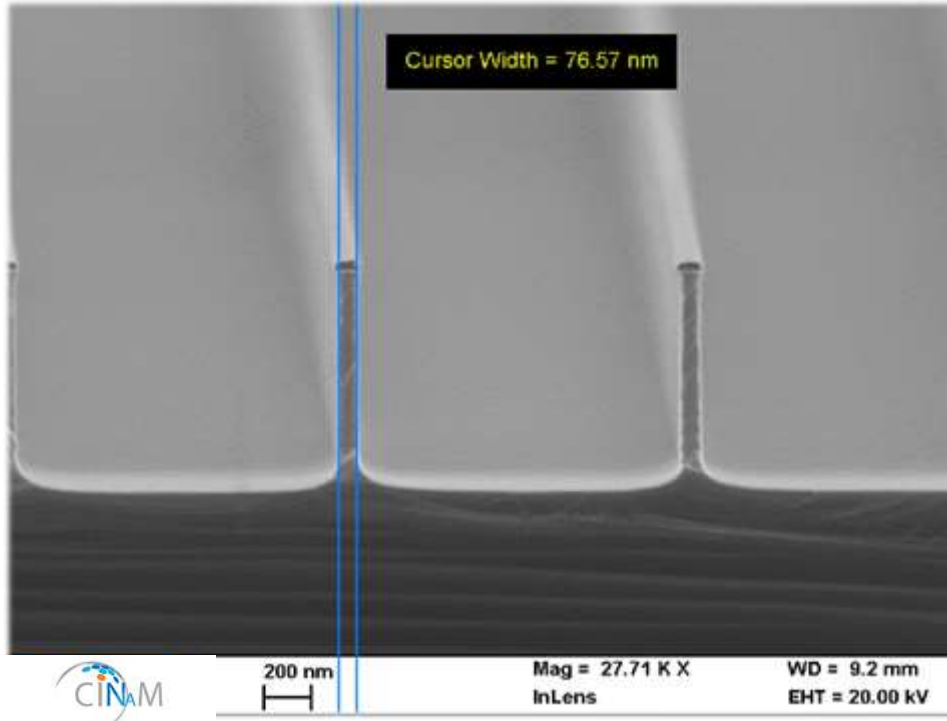
J.M. Kontio et al. / Microelectronic Engineering 87 (2010) 1711–1715

# Top-Down Approach

Typical steps

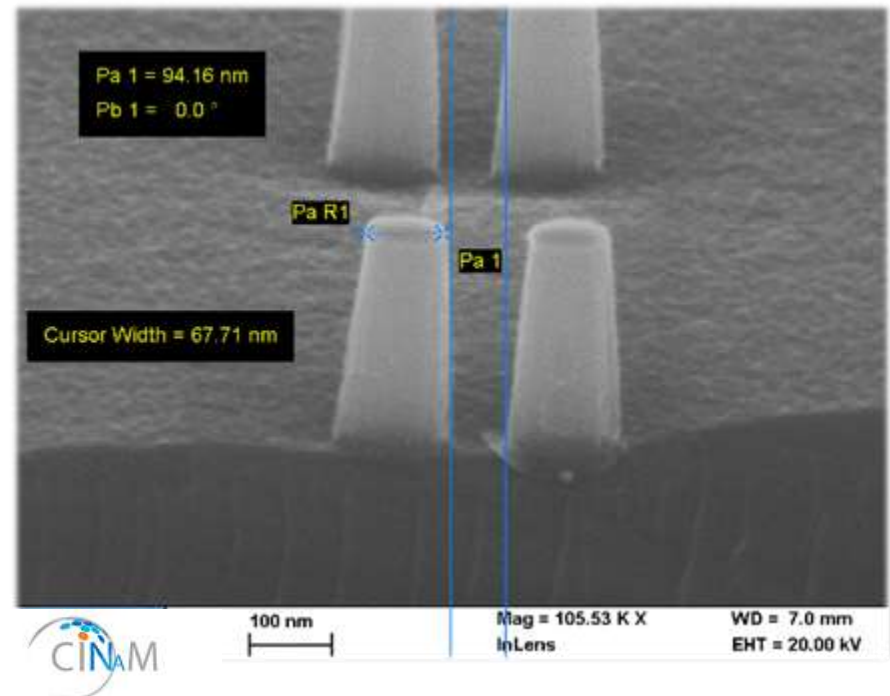


# Dry Plasma and Wet Etching

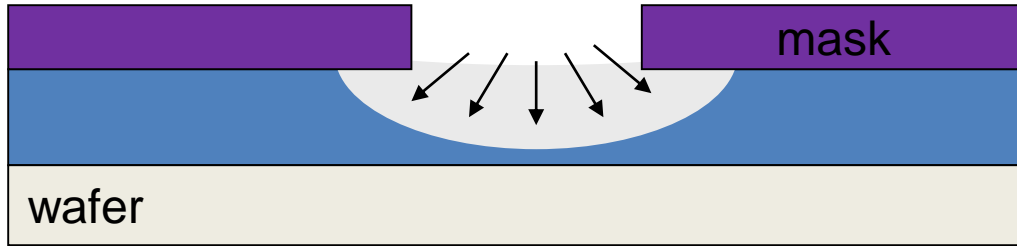


High aspect ratio reactive ion etching of silicon

**Wet Chemical Etching**  
Reactive Ion Etching (RIE) by **Plasma**  
gases:  $\text{CHF}_3$   $\text{SF}_6$   $\text{O}_2$   
materials :  $\text{Si}$   $\text{SiO}_2$   $\text{Si}_3\text{N}_4$   $\text{TiO}_2$   $\text{WO}_3$   
Capacitively (CCP) and  
Inductively coupled plasma (ICP)  
Argon **ion milling**

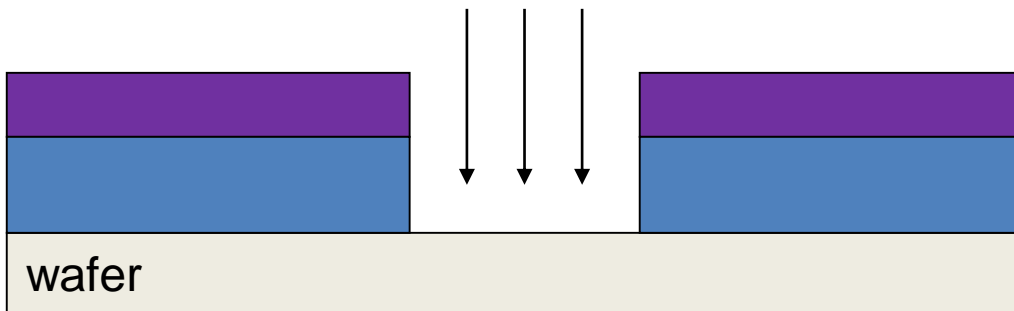


# Dry Plasma and Wet Etching



Isotropic

(Example wet : Au in  $KI_3$ )



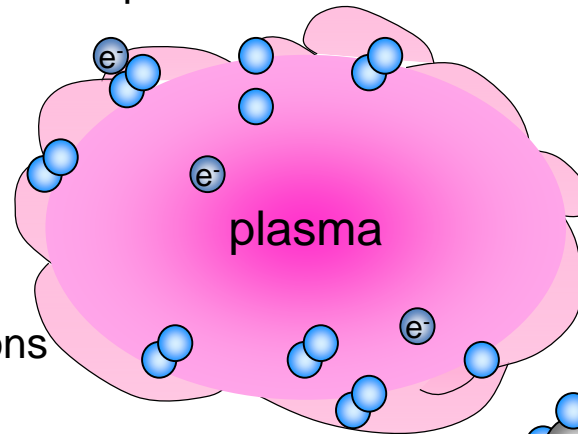
Anisotropic

Example wet : Si in KOH

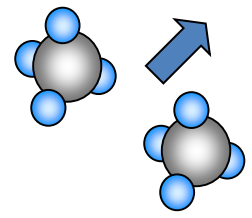
Example dry : Si by  $SF_6:O_2$

# Reactive Ion Etching

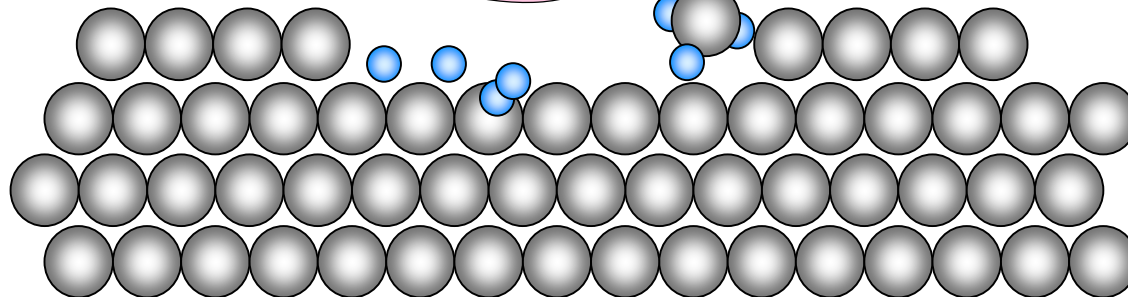
Formation of active species in plasma



Elimination of volatile products

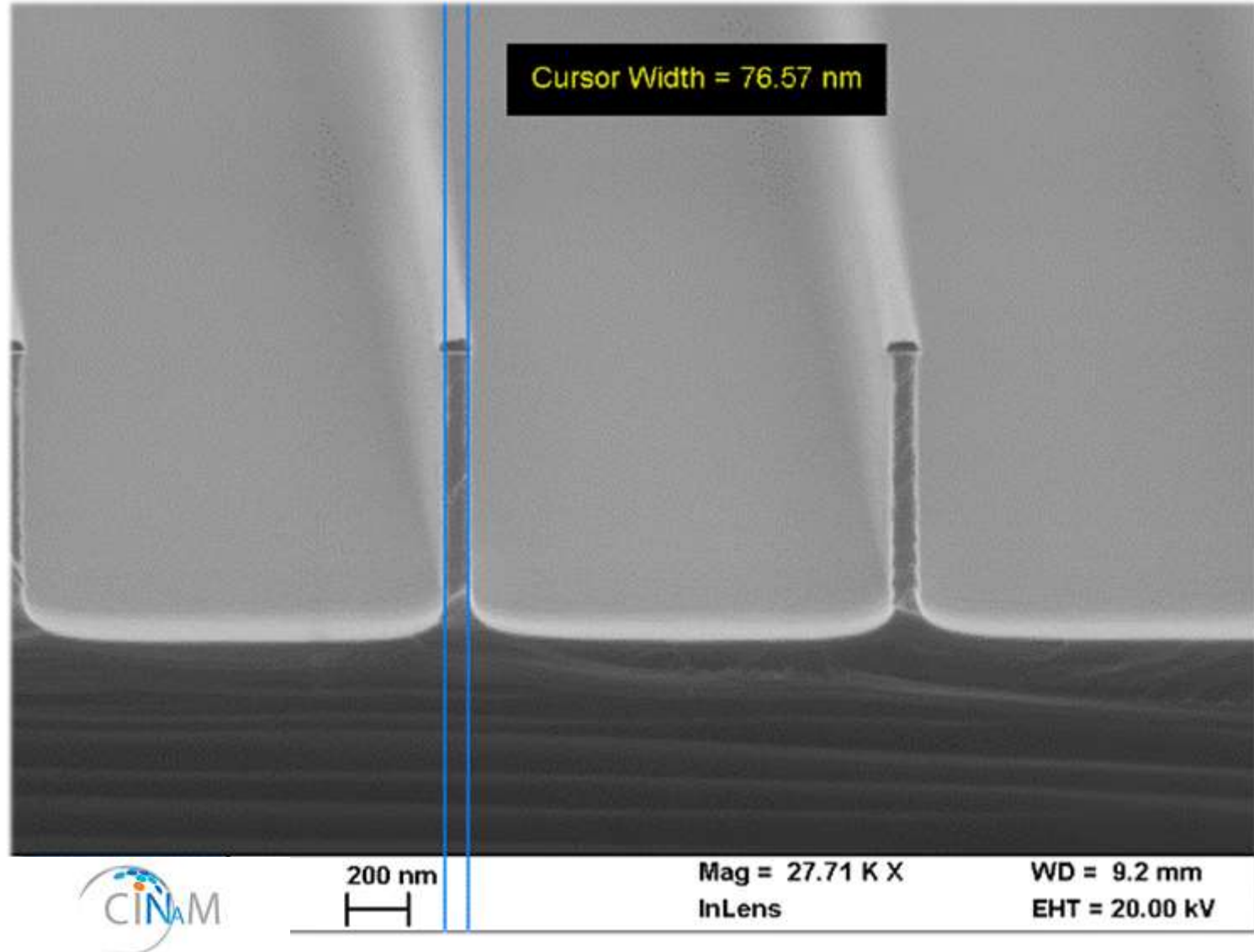


Surface chemical reactions

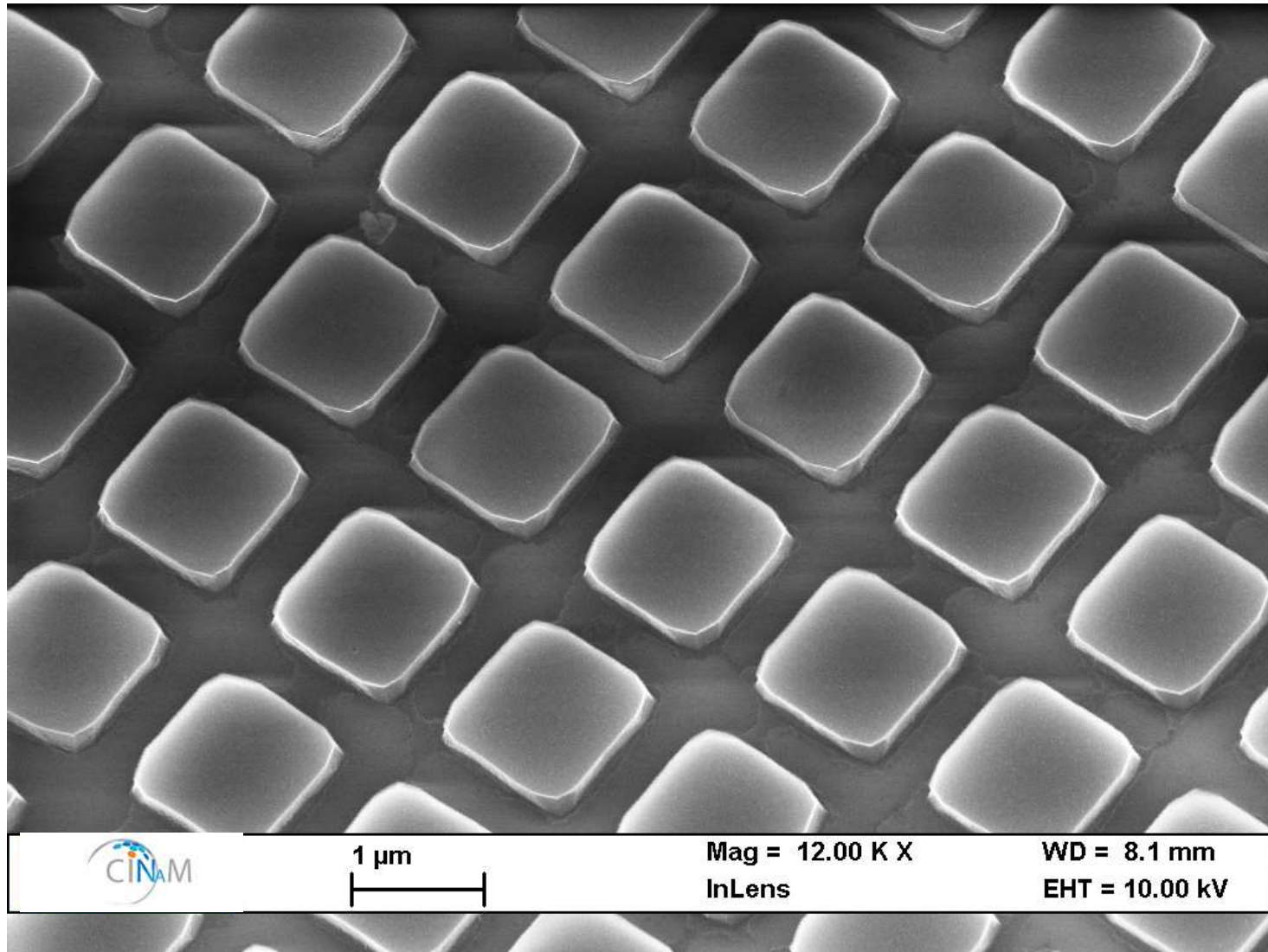


Surface Desorption

# Reactive Ion Etching of Si



# Alcaline Wet Etching of Silicon

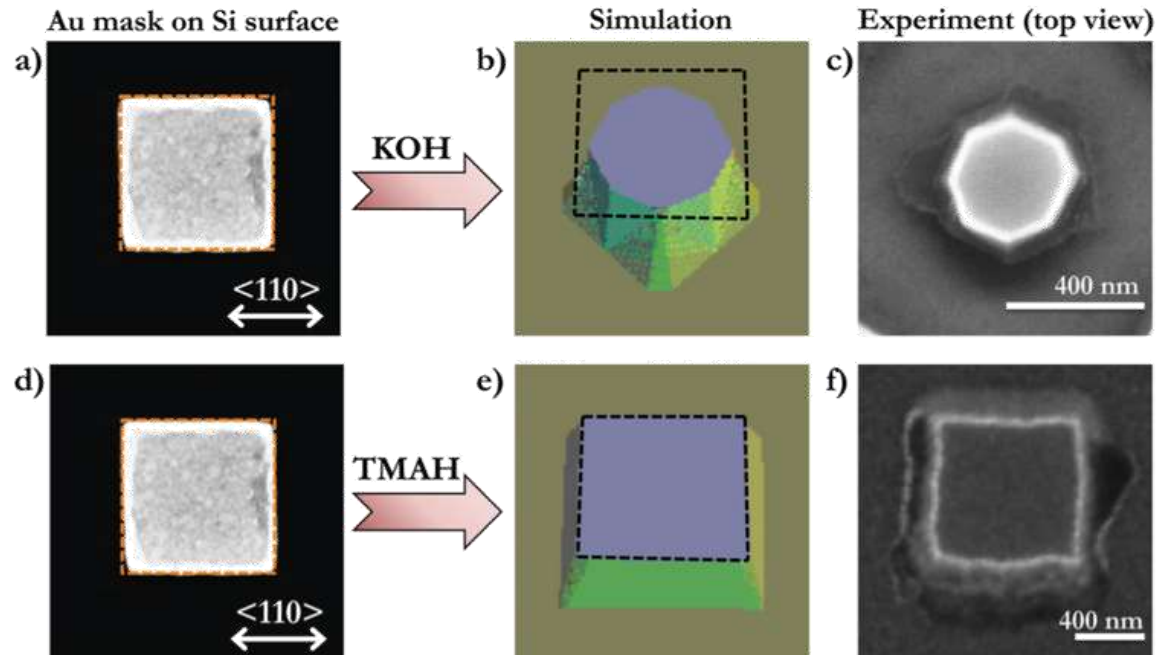


# Crystalline silicon nanostructures

KOH or TMAH ?

KOH  $\{110\} > \{100\} > \{111\}$

TMAH  $\{100\} > \{110\} > \{111\}$



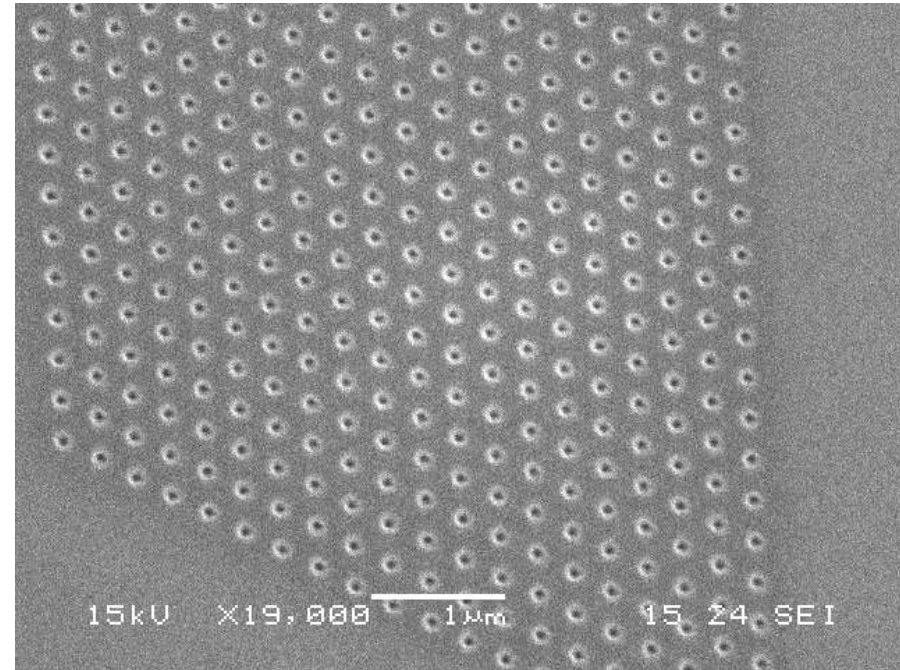
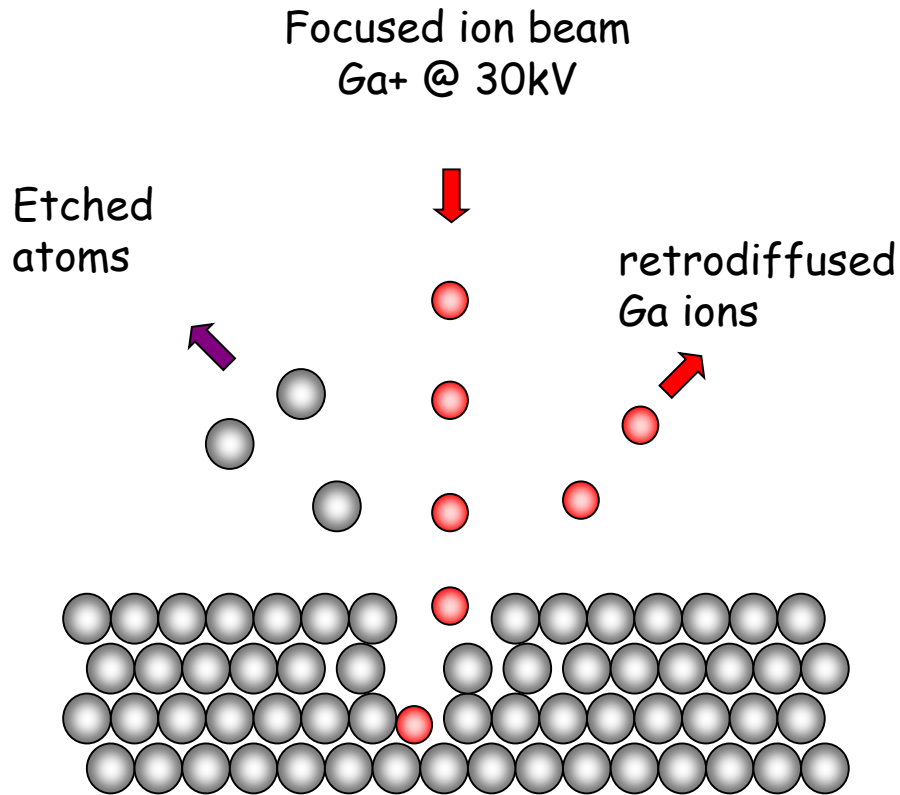
Selective chemical etching, Cr/Au mask

**ADVANCED  
OPTICAL  
MATERIALS**

J. Proust, F. Bedu, S. Chenot, I. Soumahoro, I. Ozerov, B. Gallas, R. Abdeddaim, and N. Bonod, *Advanced Optical Materials*, vol. 3, pp. 1280-1286, 2015.



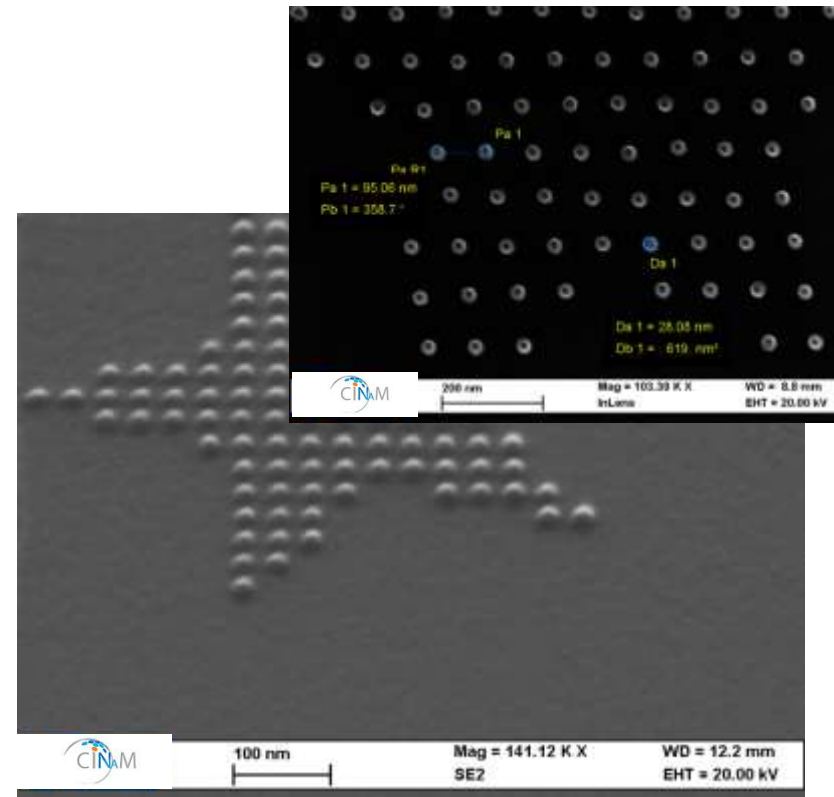
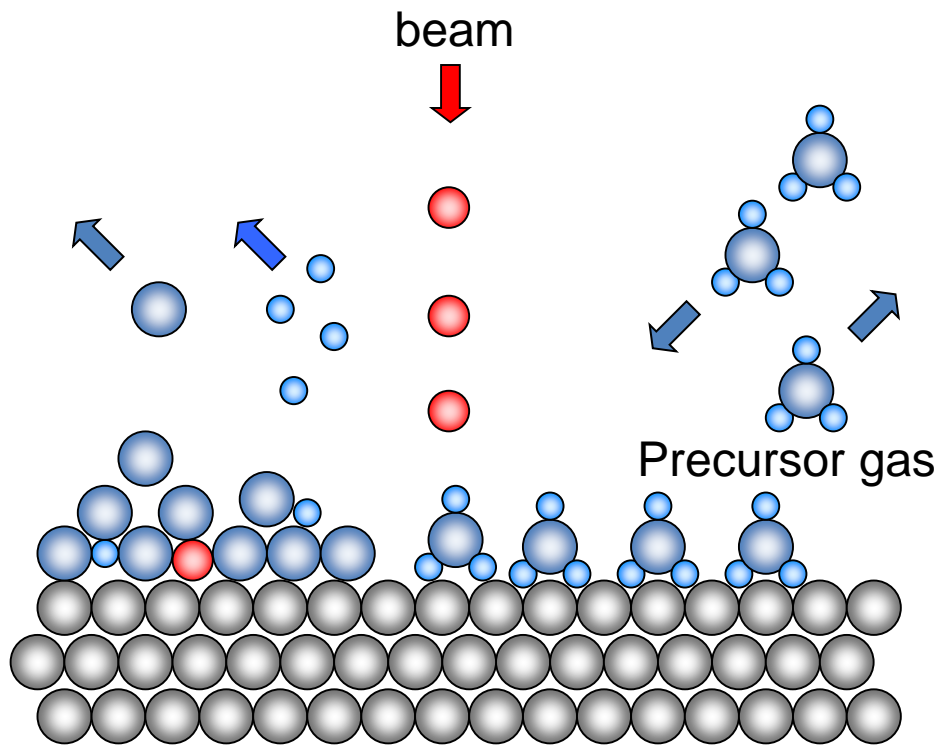
# Focused Ion Beam Milling



Nanohole array in a SiC crystal

Images: Frédéric BEDU

# Local Focused Ion Beam (FIBID) and Electron Beam Induced Deposition (EBID)

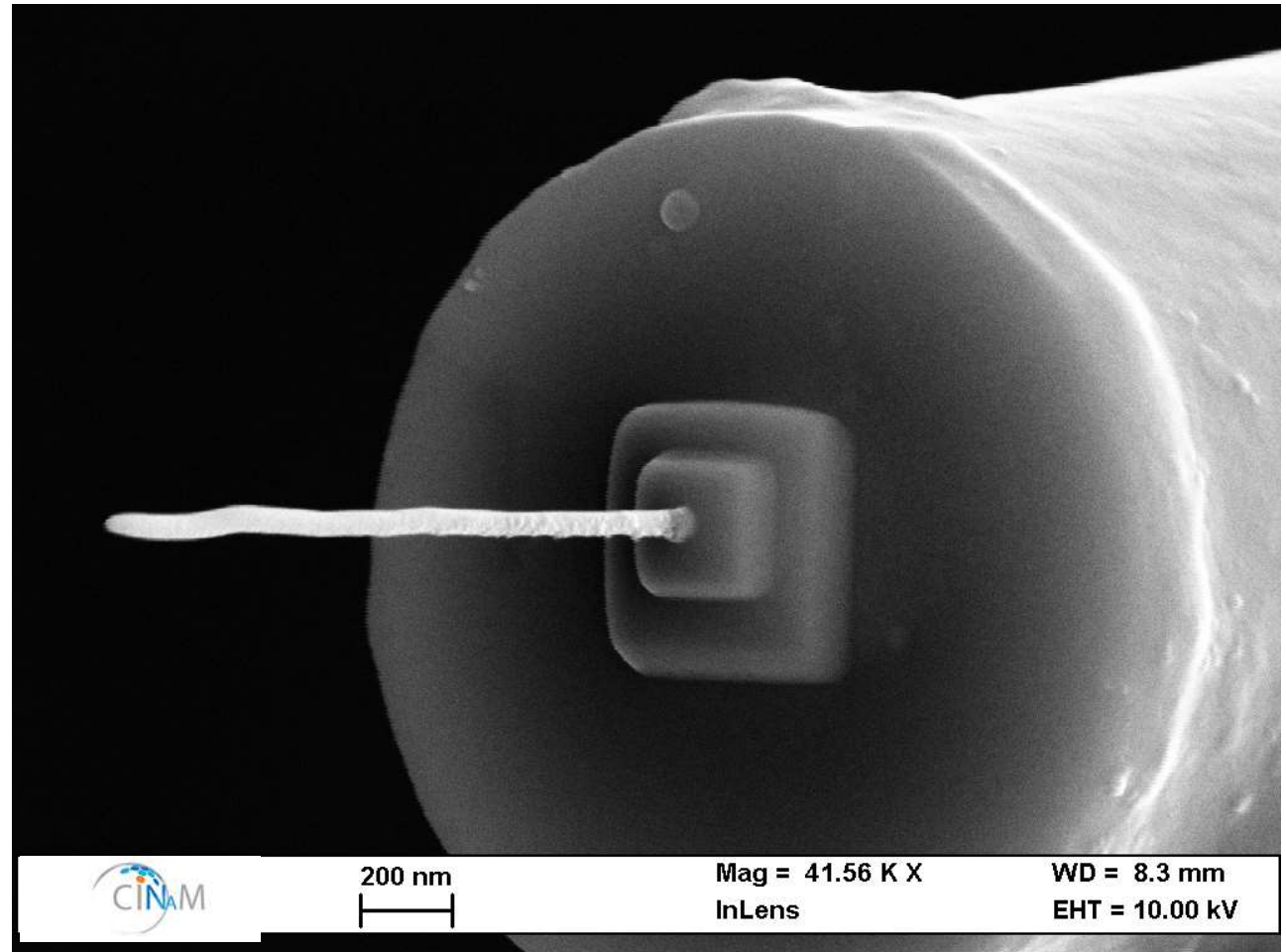


Tungsten nanodots deposition (EBID)

# Local Electron Beam Induced Deposition (EBID)



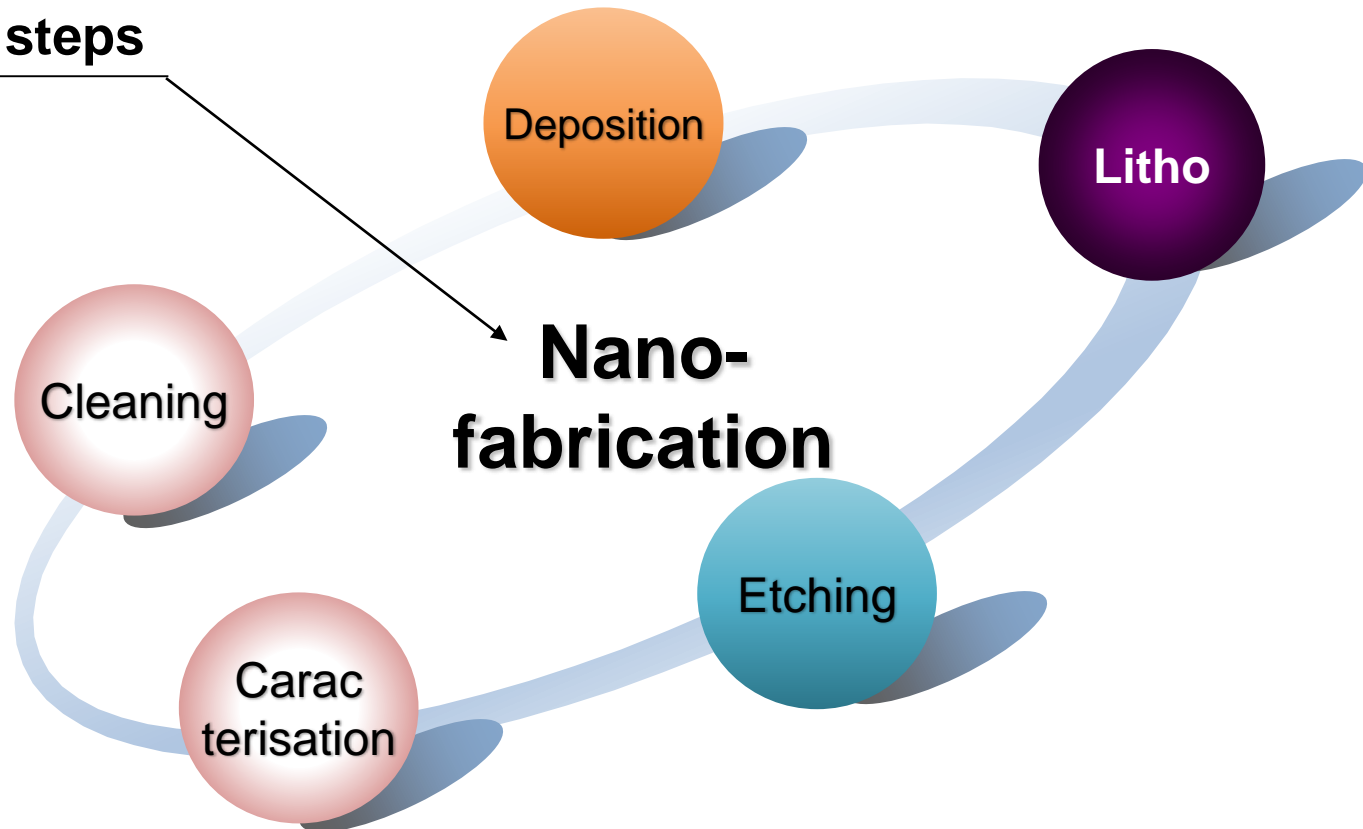
W nanowire



Courtesy Frédéric Bedu and Marion Descoins

# Top-Down Approach

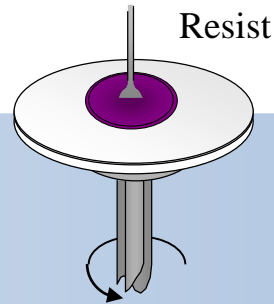
Typical steps



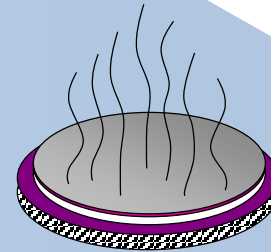
# UV and e-beam lithography



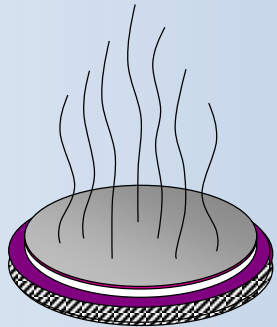
1) Plasma cleaning



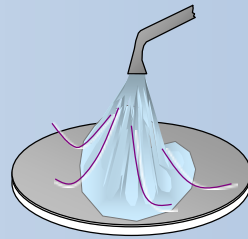
2) Spin-coating



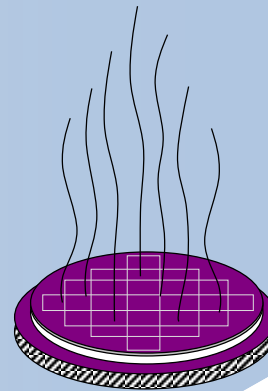
3) « SOFT » bake



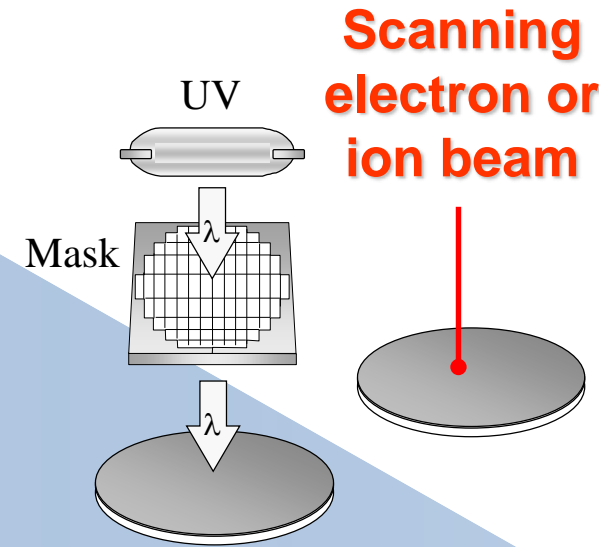
5) Post-exposure bake



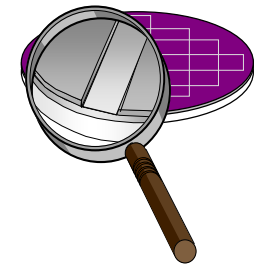
6) Development



7) « HARD » bake



4) Alignment and exposure



8) Inspection

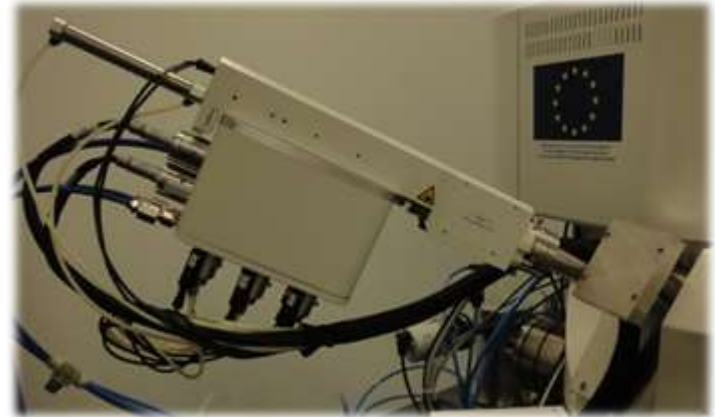
# Electron beam lithography

System Pioneer

**Raith**

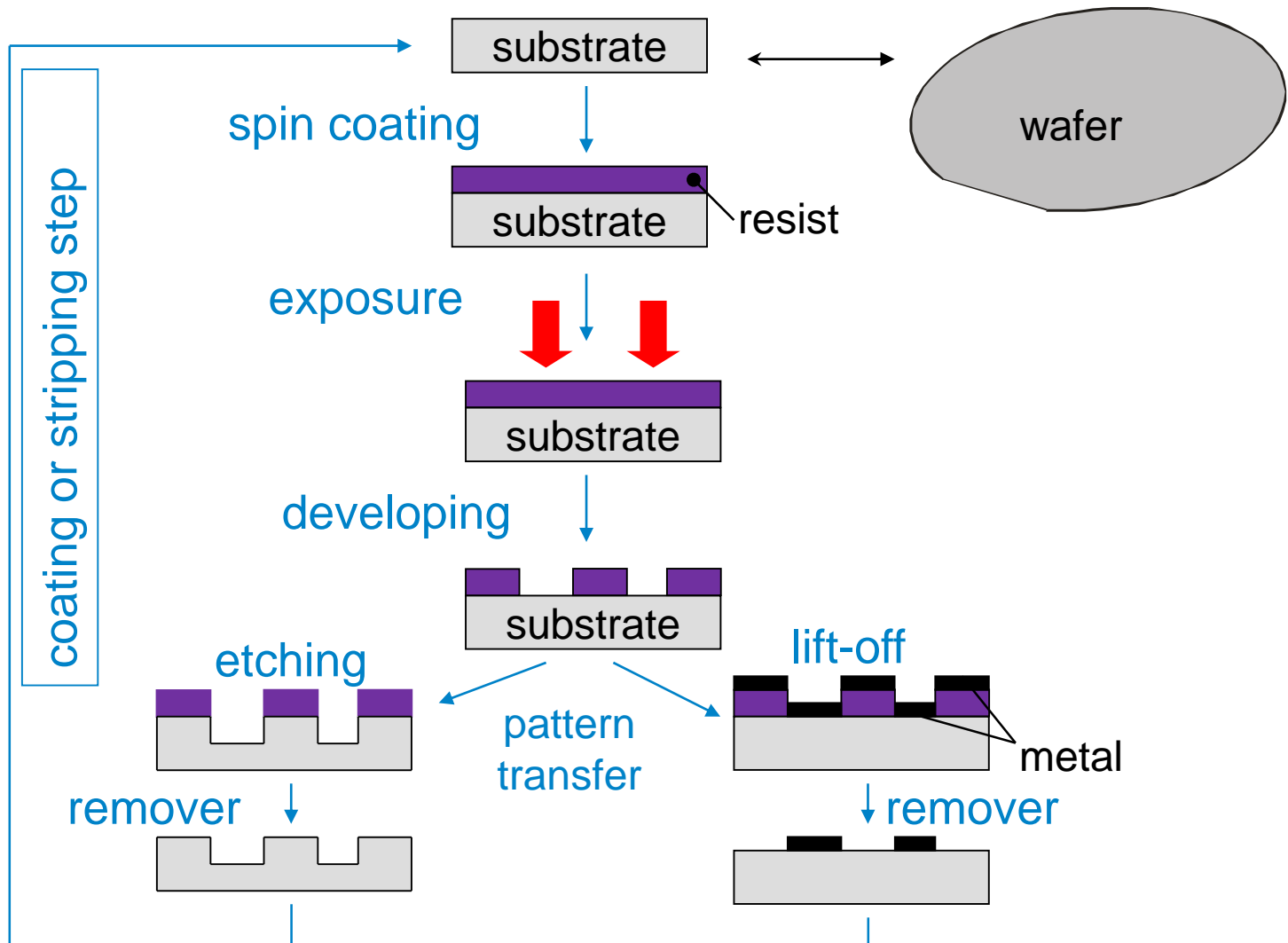


- Field Emission Gun (FEG) 2nm
- Laser interferometer Stage
- Stitching and Alignment <50nm
- Autofocus system
- Gas injection system

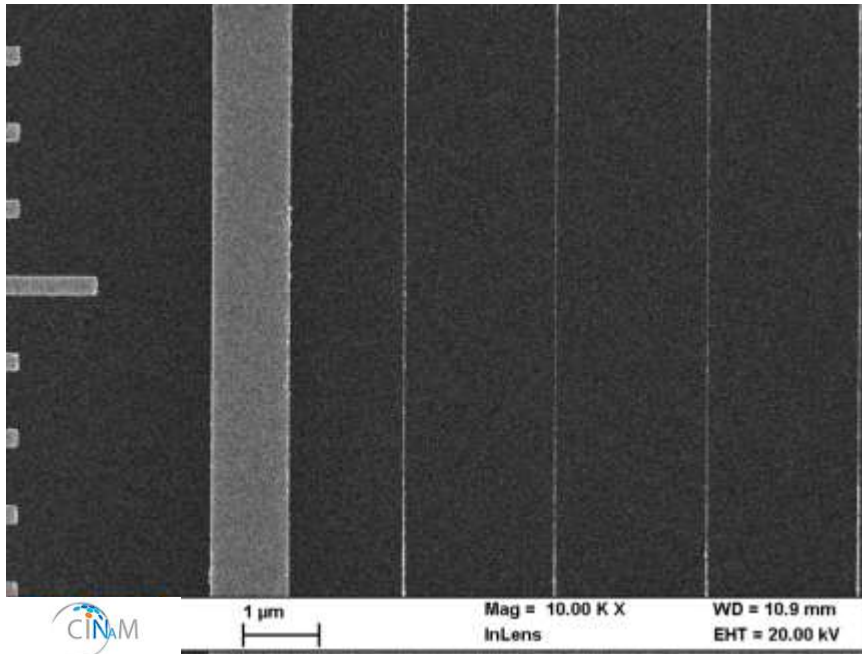


Gas Injection System (Orsay physics)

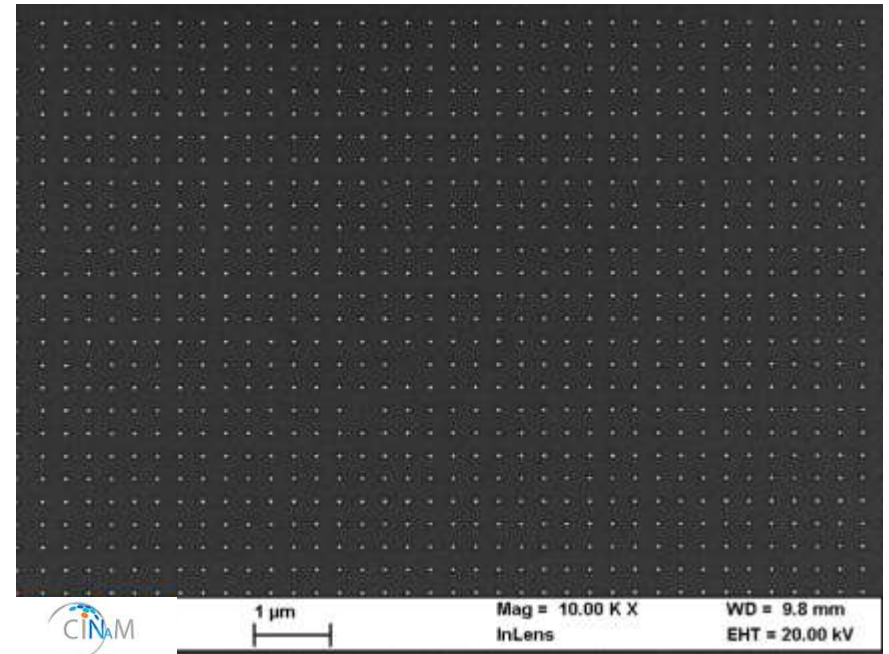
# Process technology



# Electron beam lithography



Metal lines  
(width < 20 nm)



Metal nanodots Cr/Au  
(diameter < 50 nm)

High resolution e-beam lithography + lift off process

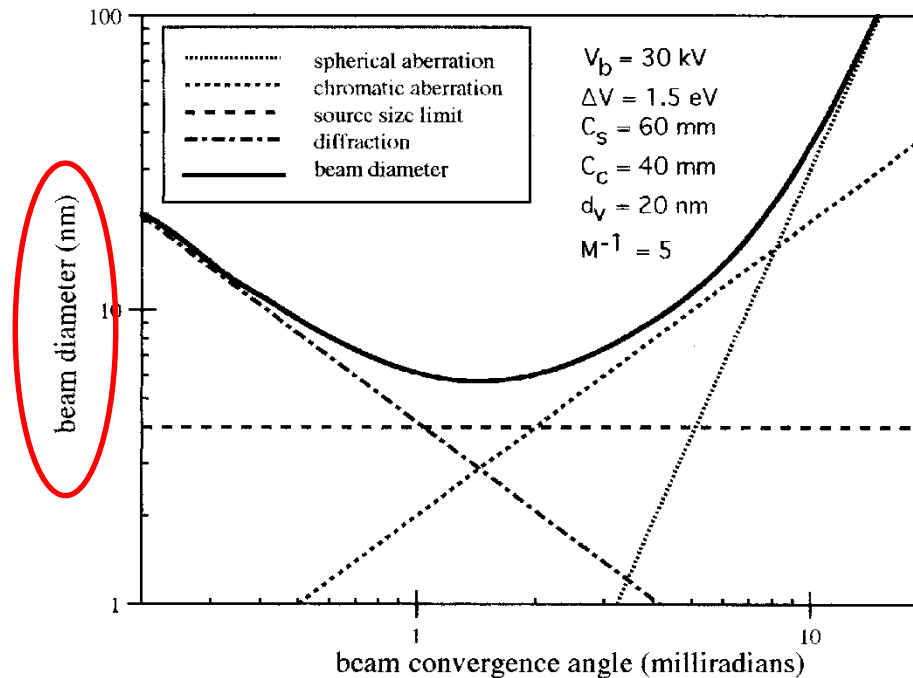
Images: Frédéric BEDU



# Resolution

⇒ De Broglie wavelength at 1 kV: 0.0387 nm

⇒ current resolution limit of electron optics is in the range 1 – 2 nm



SPIE Handbook of Microlithography

# Extreme resolution of EBL

NANO LETTERS

Letter

pubs.acs.org/NanoLett

## Aberration-Corrected Electron Beam Lithography at the One Nanometer Length Scale

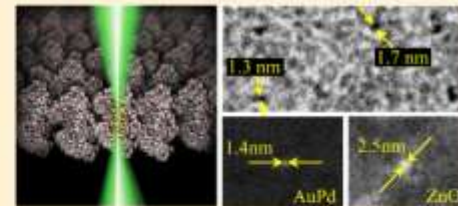
Vitor R. Manfrinato,<sup>†</sup> Aaron Stein,<sup>†</sup> Lihua Zhang,<sup>†</sup> Chang-Yong Nam,<sup>†</sup> Kevin G. Yager,<sup>†</sup> Eric A. Stach,<sup>\*,†</sup> and Charles T. Black<sup>\*,†</sup>

<sup>†</sup>Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York 11973-5000, United States

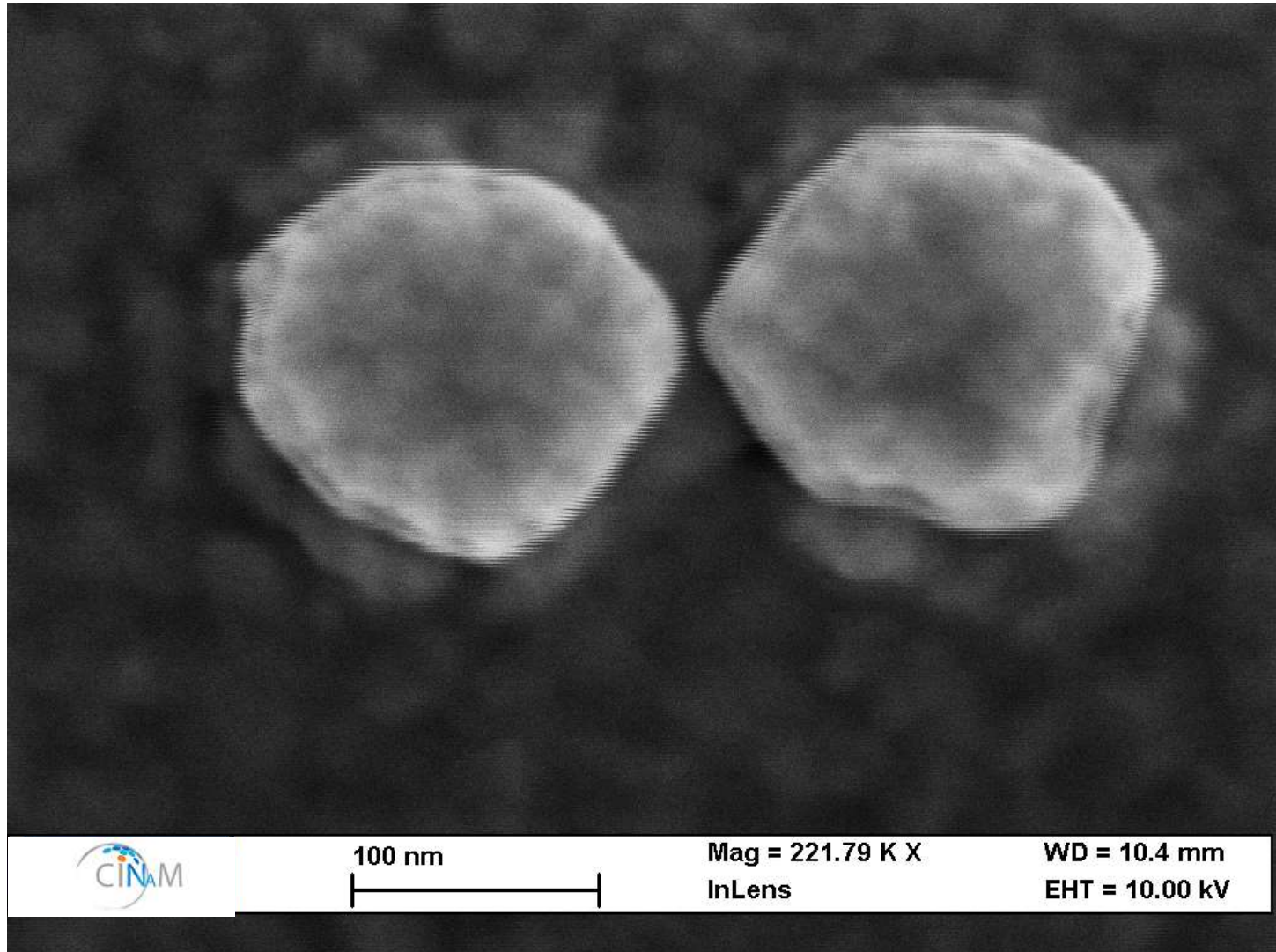
**S** Supporting Information

**ABSTRACT:** Patterning materials efficiently at the smallest length scales is a longstanding challenge in nanotechnology. Electron-beam lithography (EBL) is the primary method for patterning arbitrary features, but EBL has not reliably provided sub-4 nm patterns. The few competing techniques that have achieved this resolution are orders of magnitude slower than EBL. In this work, we employed an aberration-corrected scanning transmission electron microscope for lithography to achieve unprecedented resolution. Here we show aberration-corrected EBL at the one nanometer length scale using poly(methyl methacrylate) (PMMA) and have produced both the smallest isolated feature in any conventional resist ( $1.7 \pm 0.5$  nm) and the highest density patterns in PMMA (10.7 nm pitch for negative-tone and 17.5 nm pitch for positive-tone PMMA). We also demonstrate pattern transfer from the resist to semiconductor and metallic materials at the sub-5 nm scale. These results indicate that polymer-based nanofabrication can achieve feature sizes comparable to the Kuhn length of PMMA and ten times smaller than its radius of gyration. Use of aberration-corrected EBL will increase the resolution, speed, and complexity in nanomaterial fabrication.

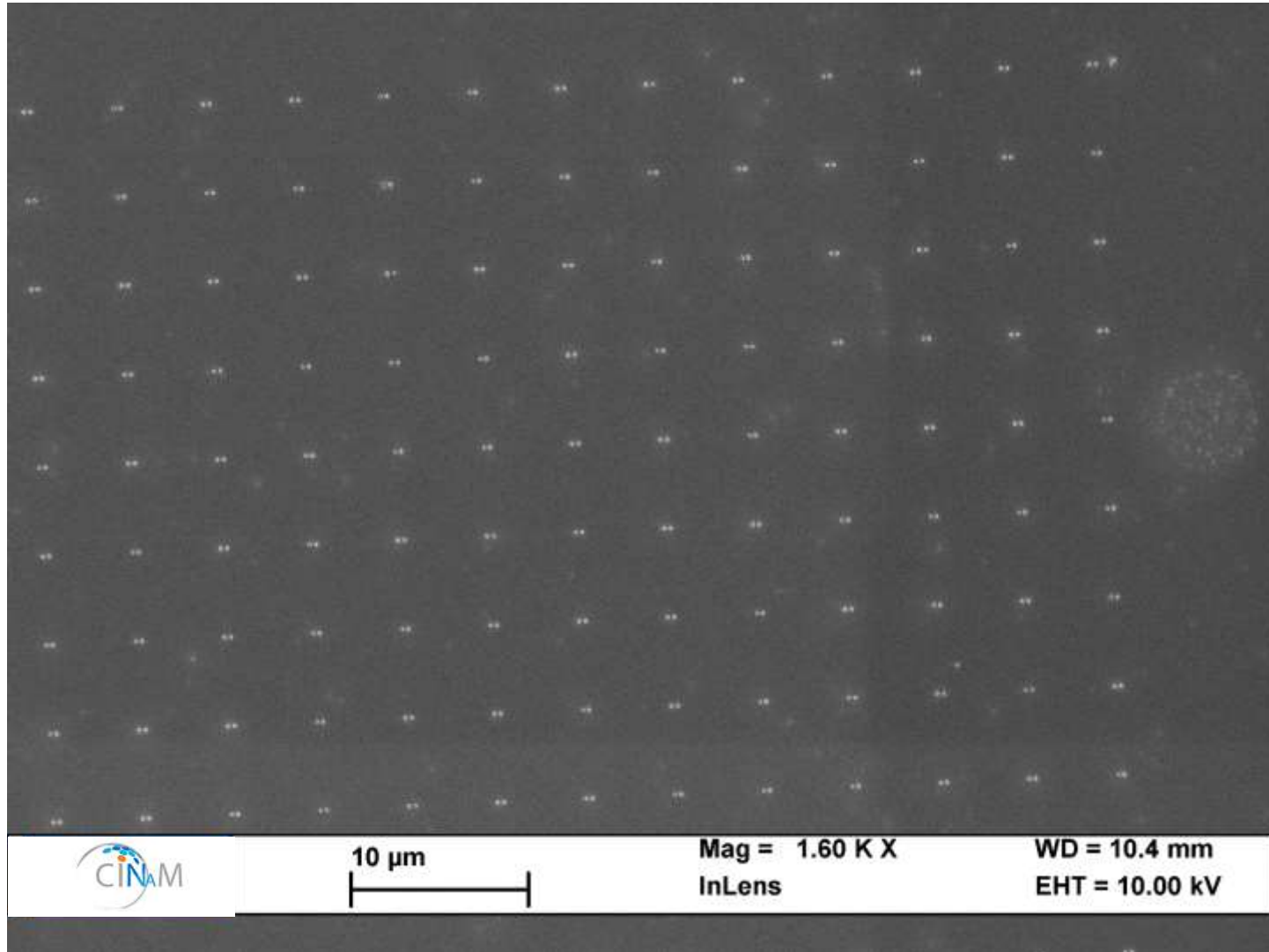
**KEYWORDS:** Nanofabrication, electron-beam lithography, aberration correction, electron microscopy, nanomaterials, pattern transfer, poly(methyl methacrylate)



# Resolution of EBL

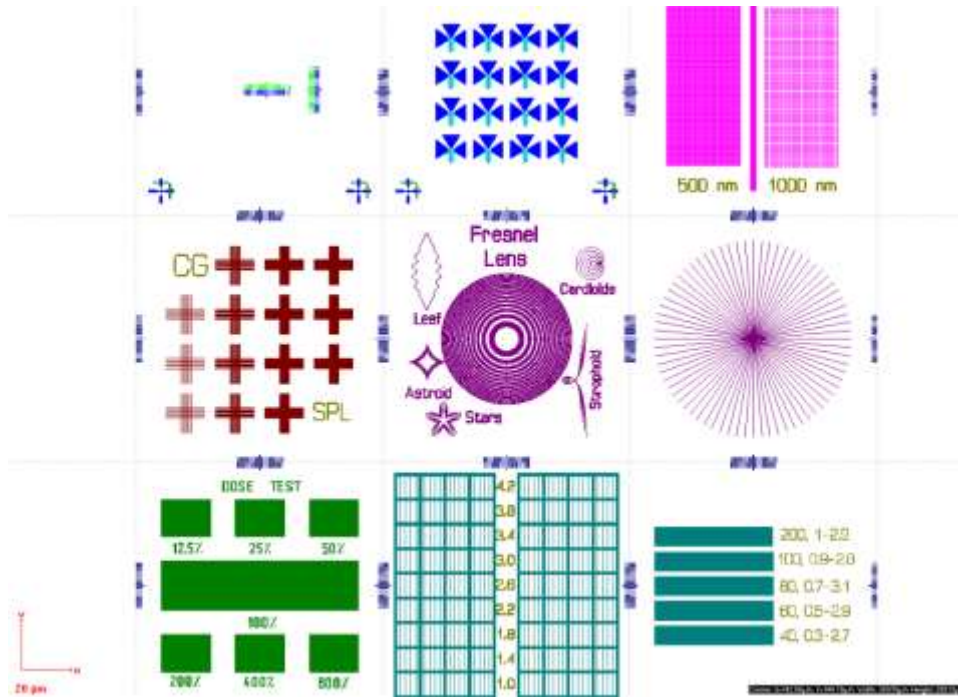


# Resolution of EBL

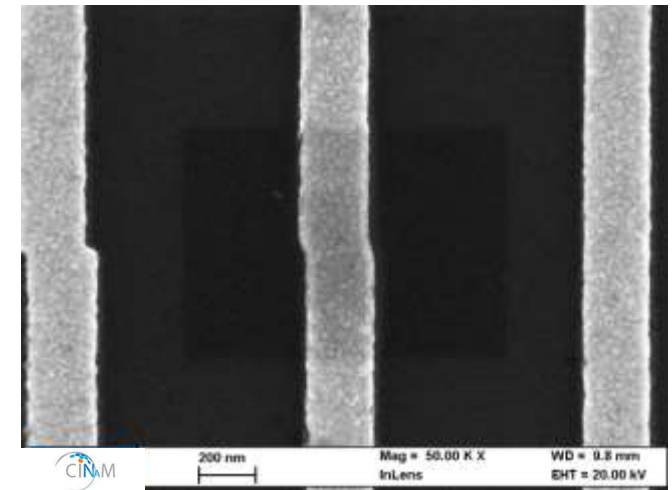
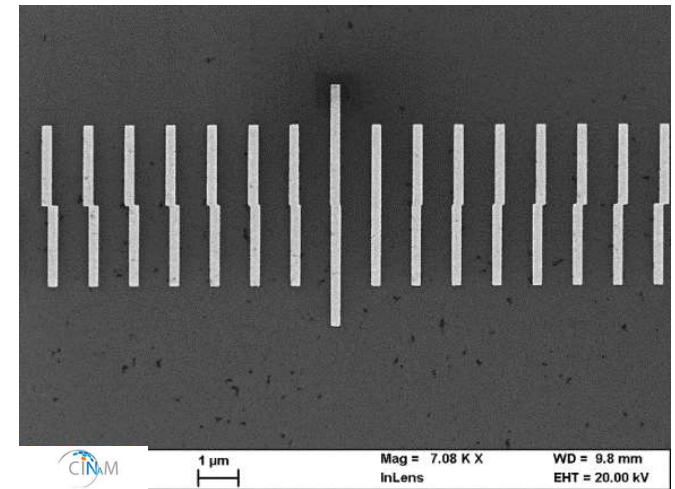


# Large area e-beam lithography?

## Stitching



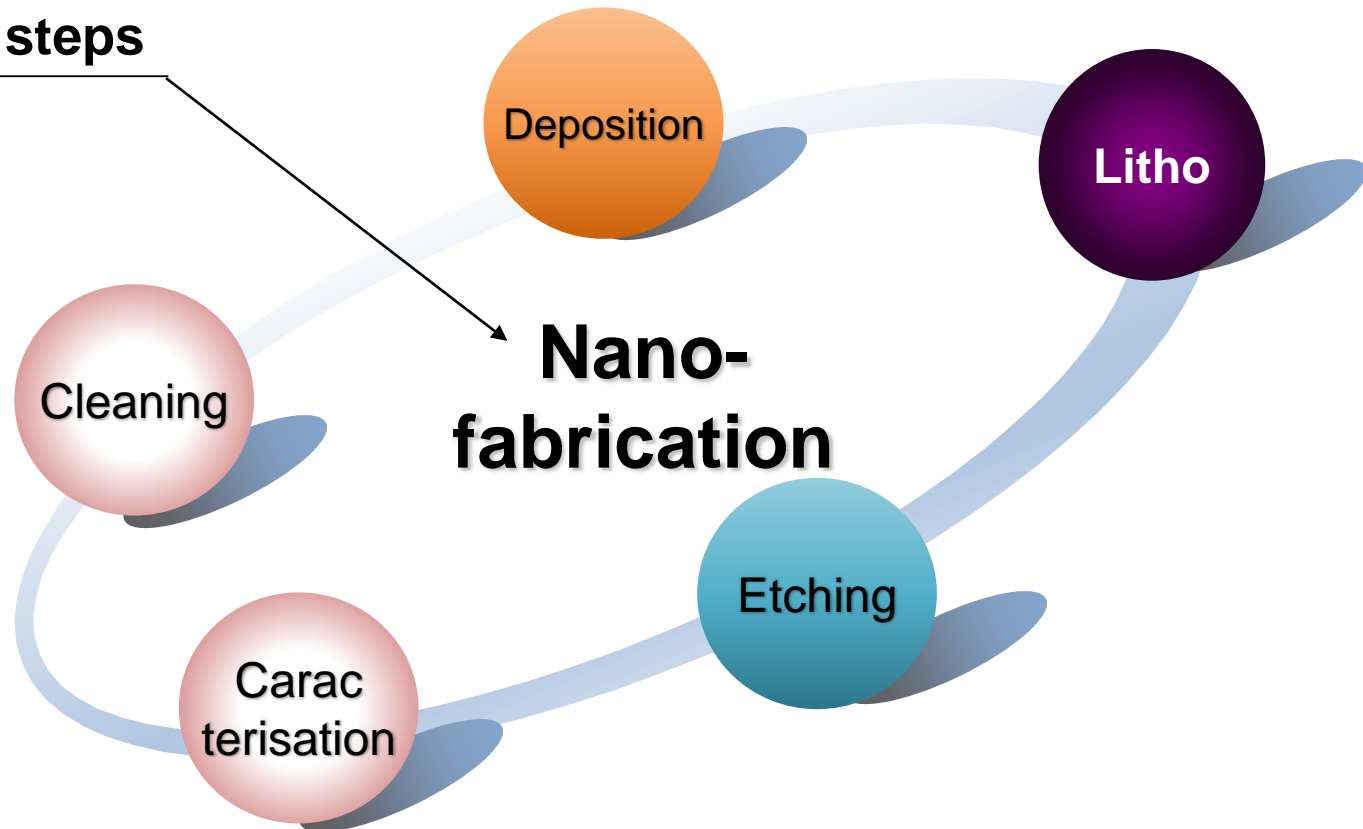
Working Area 300x300 $\mu$ m  
Write field 100 $\mu$ m



Displacement precision 20 nm  
(Working Area 900 $\mu$ m)

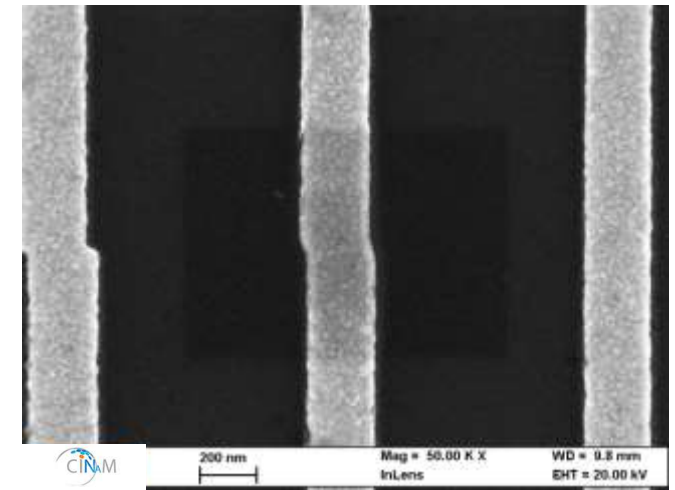
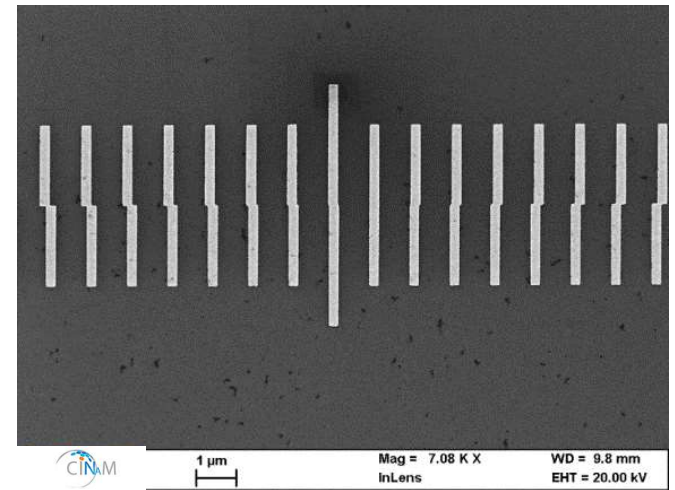
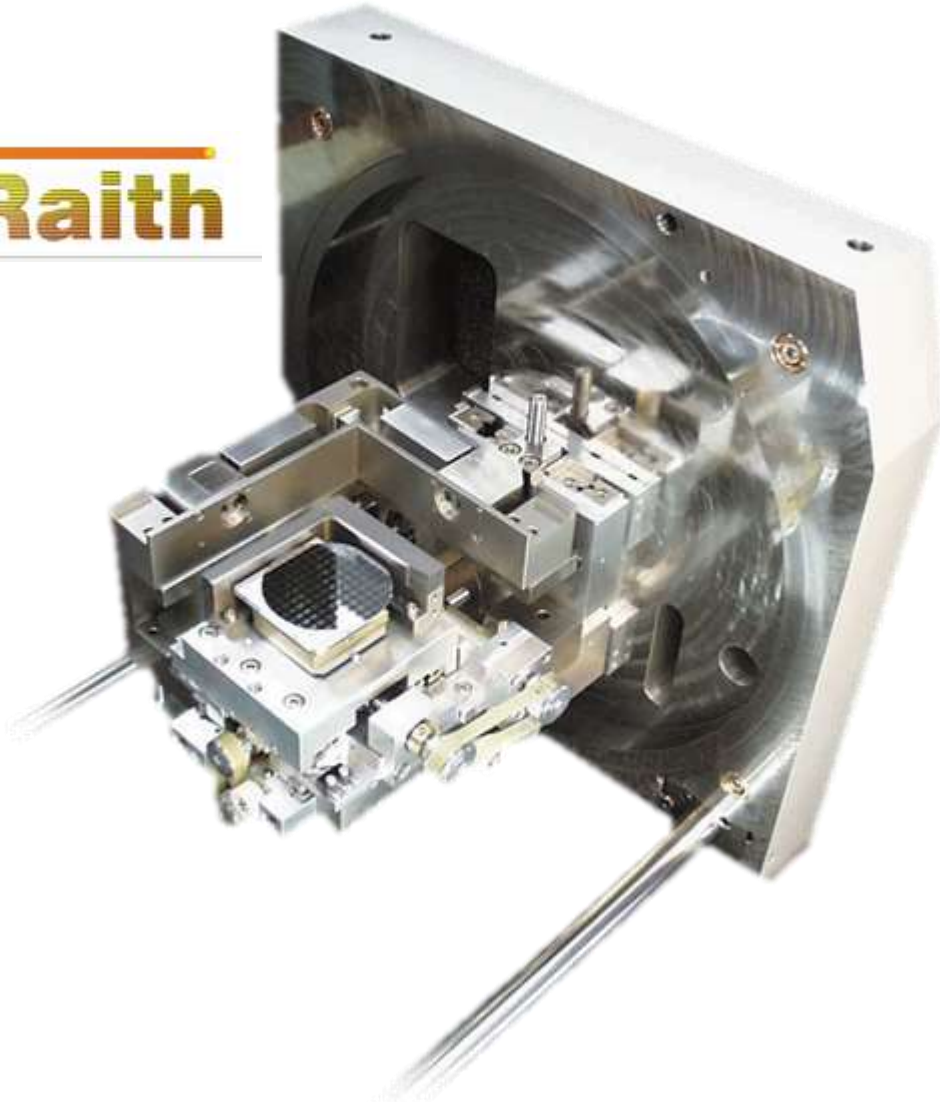
# Top-Down Approach

Typical steps



# Alignment of two layers using e-beam lithography

**Raith**

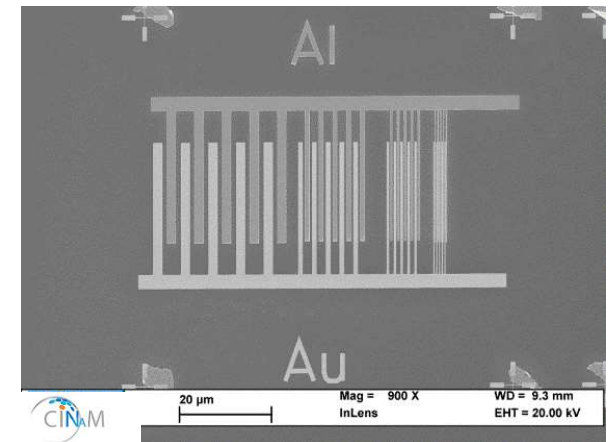
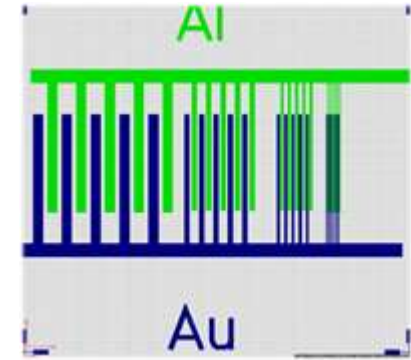


Interferometric movement control (better than 20 nm)

# Alignment of two layers using e-beam lithography

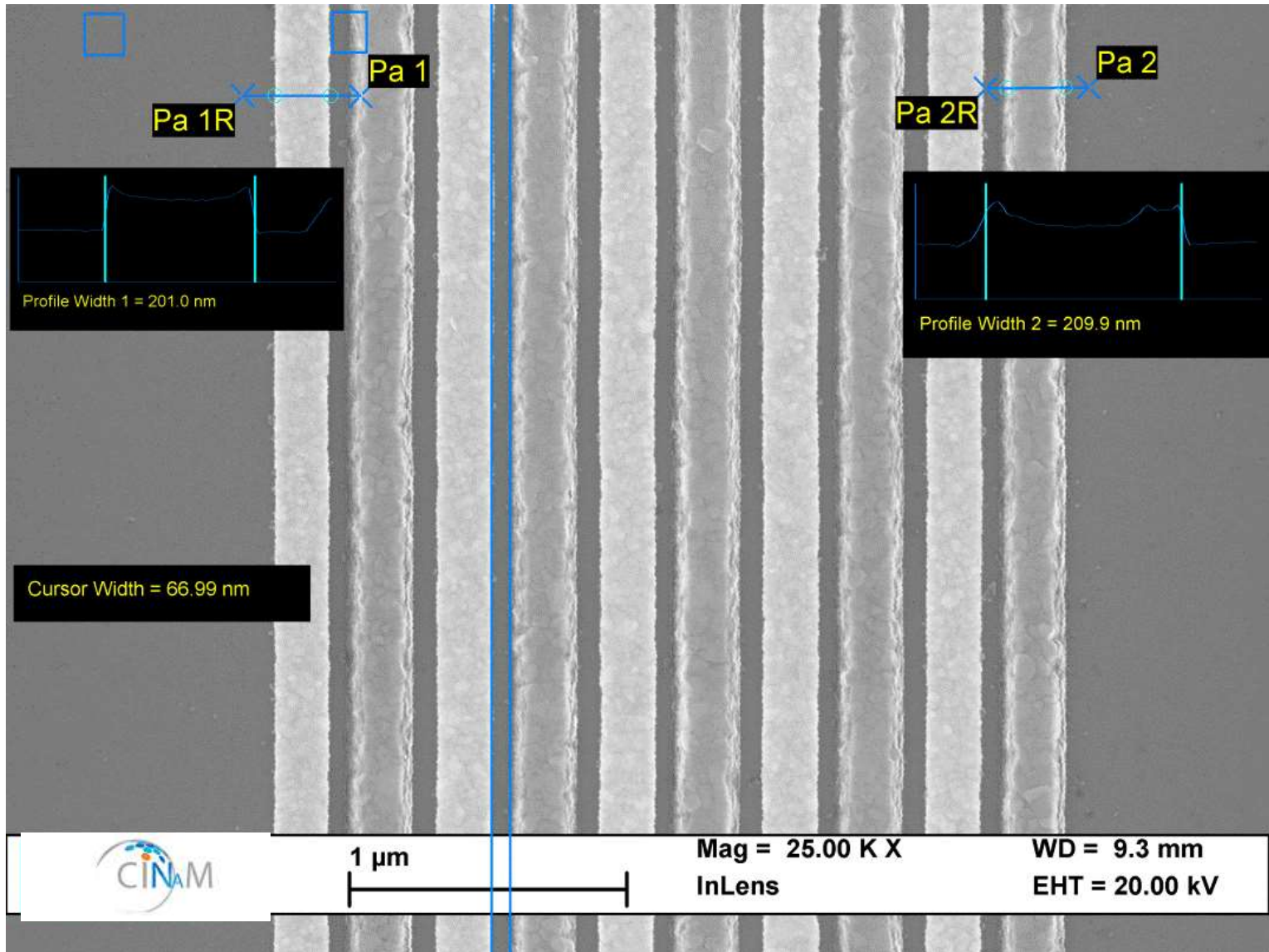
## Process steps:

- Feature design
- 1st Resist Spin-coating
- E-beam exposure
- Development
- Gold deposition
- Lift-off
- 2<sup>nd</sup> Resist Spin-coating
- Alignment
- E-beam exposure
- Development
- Aluminum deposition
- Lift-off

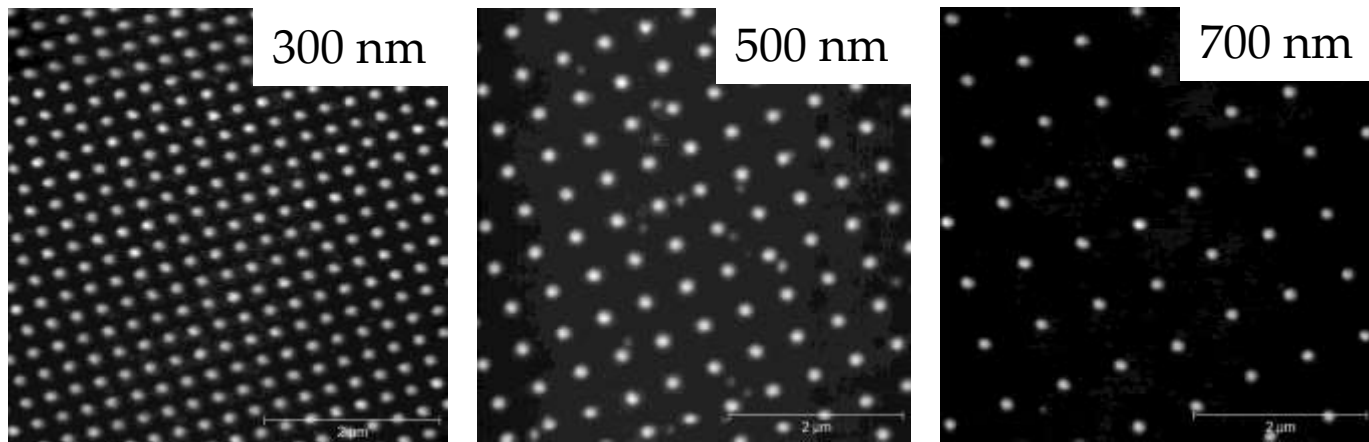




# Alignment of two layers using e-beam lithography

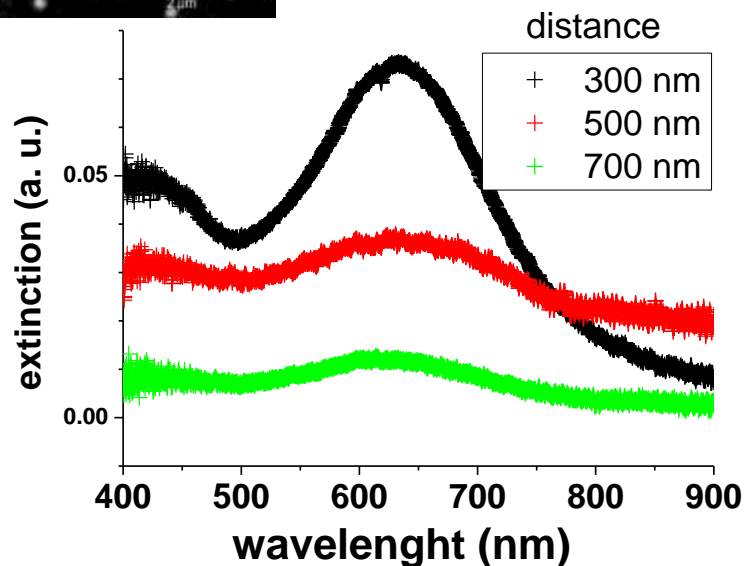


# Example: Indirect Humidity Sensor

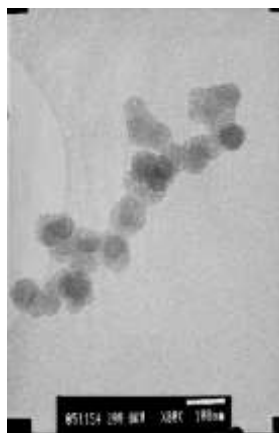


tapping mode topographical AFM images of gold nanodisks respectively with  $d = 300$  nm,  $d = 500$  nm,  $d = 700$  nm.

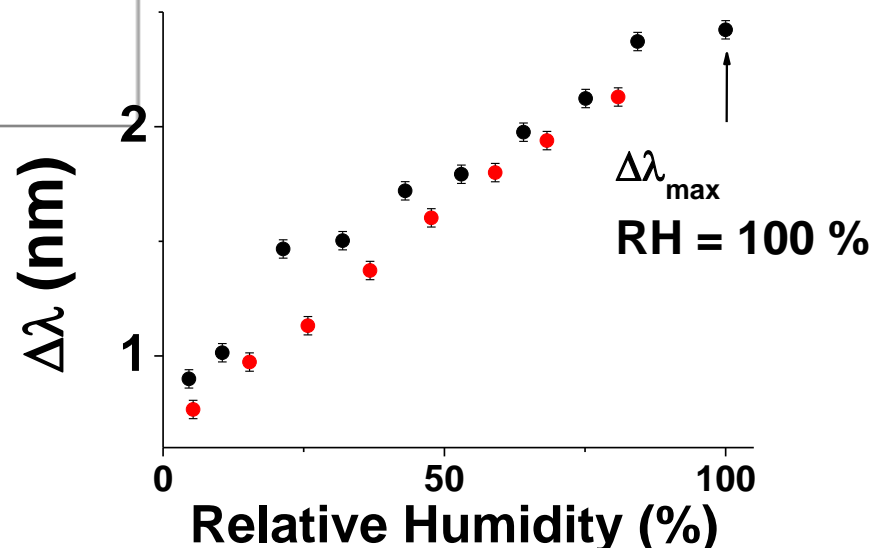
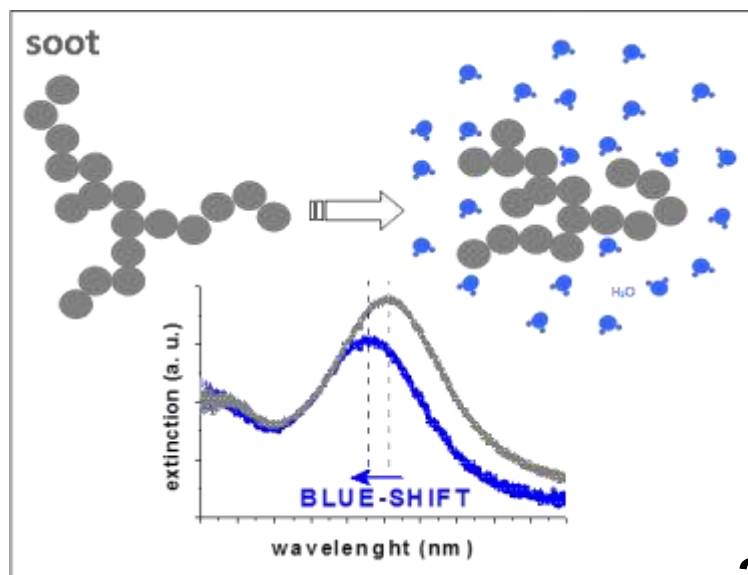
On the right: LSPR signals corresponding to these different samples.



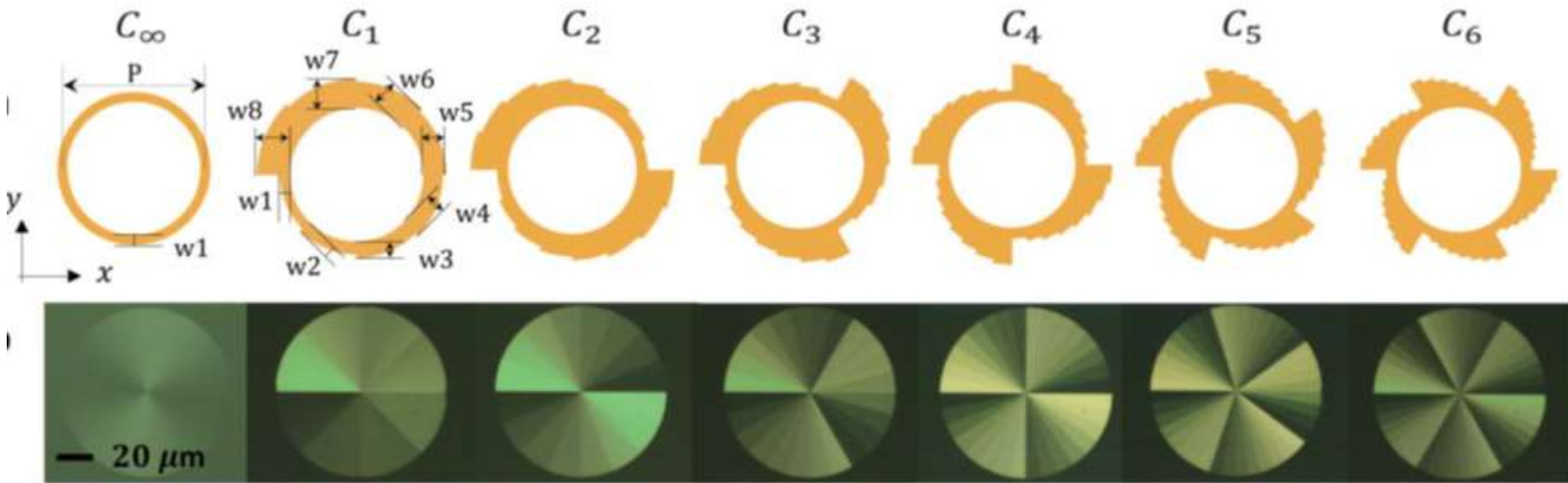
# Example: Indirect Humidity Sensor



TEM image of the soot particles



# Example: Cyclic Group Symmetric Metamaterial for Spin-Orbital Interaction of Light



Tapered arc antennas

*YU Lee, I Ozerov, F Bedu, JS Kim, F Fages and JW Wu*

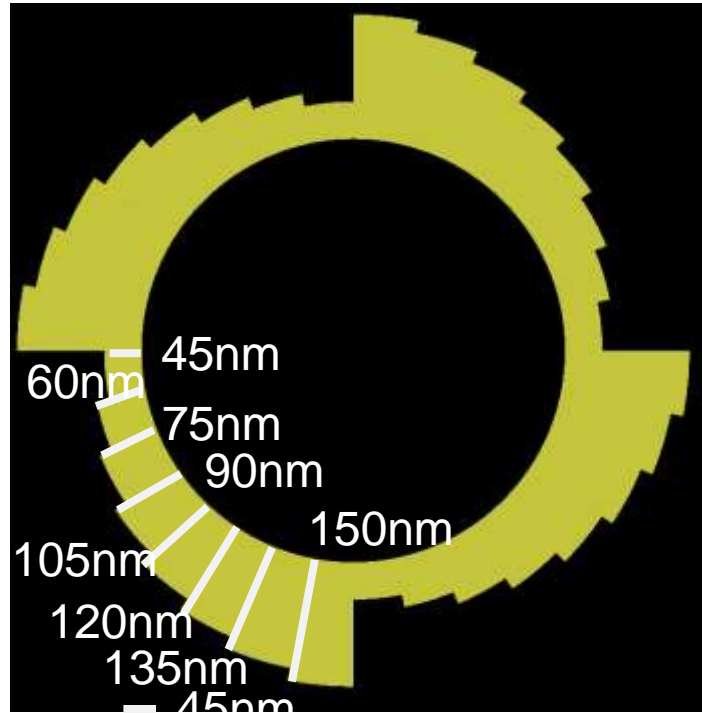
arXiv:1607.04806



# Example: Cyclic Group Symmetric Metamaterial for Spin-Orbital Interaction of Light



Width 45, 60, 75, 90, 105, 120, 135, 150nm for every  $1/8$  of  $2\pi/4$



*YU Lee, I Ozerov, F Bedu, JS Kim, F Fages and JW Wu*

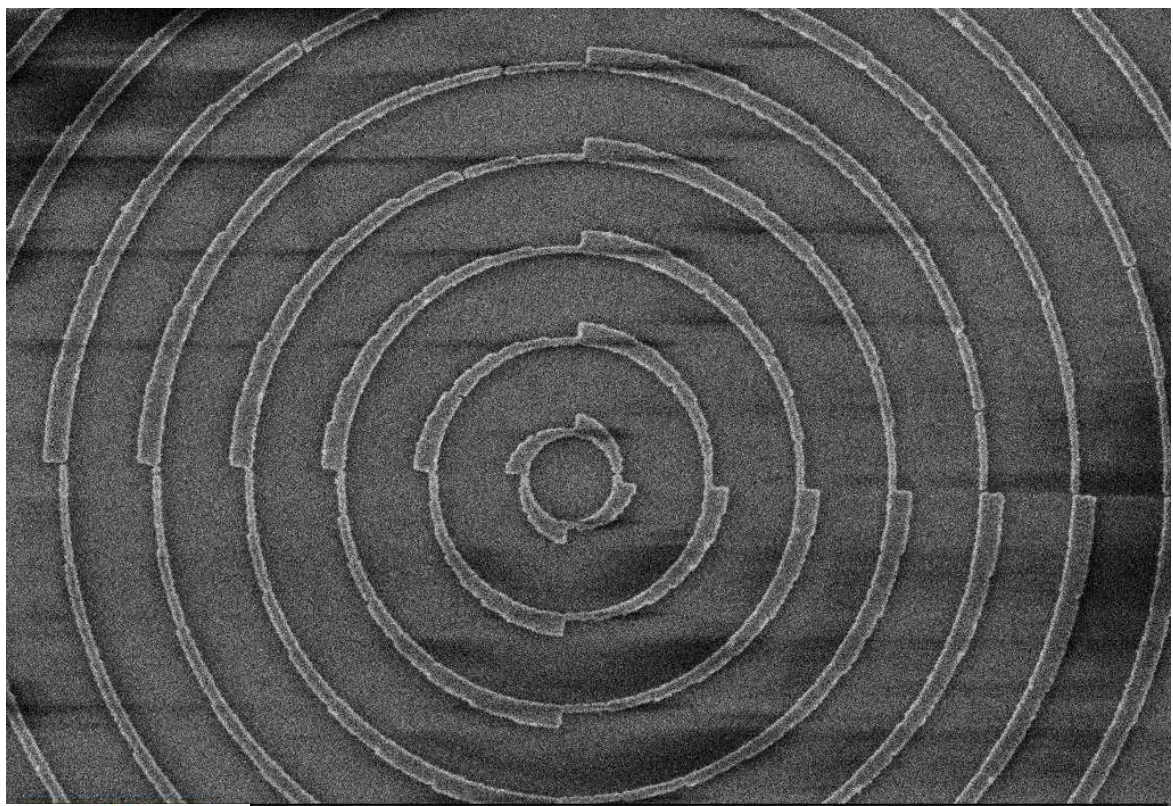
arXiv: [1607.04806](https://arxiv.org/abs/1607.04806)




# Example: Cyclic Group Symmetric Metamaterial for Spin-Orbital Interaction of Light



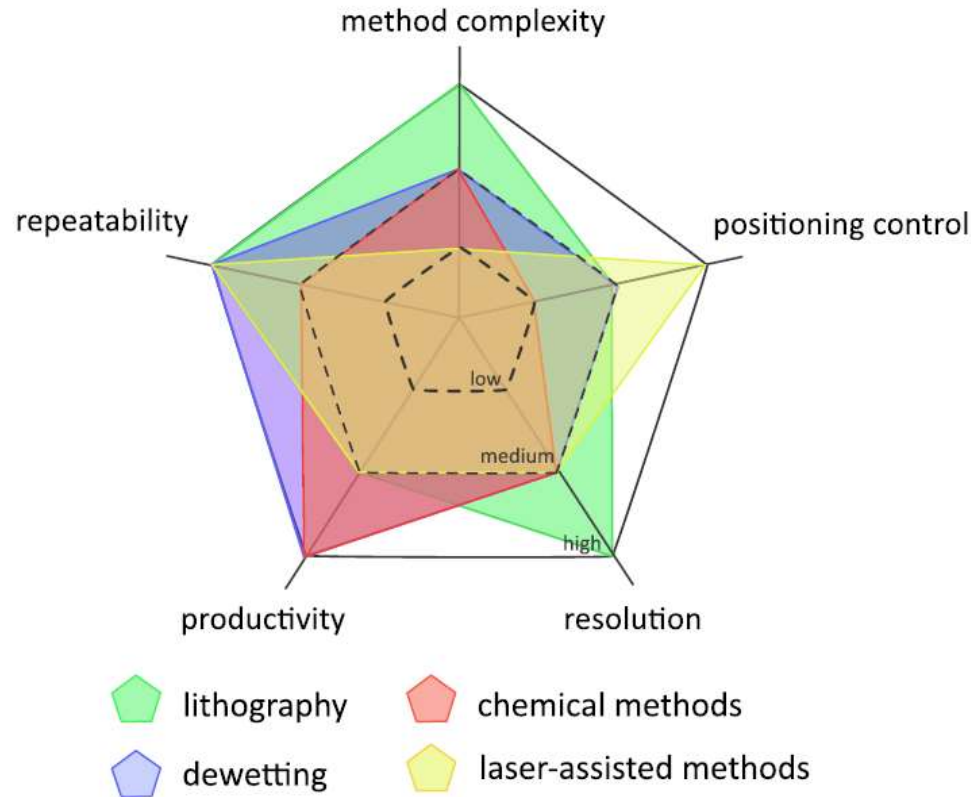
Width 45, 60, 75, 90, 105, 120, 135, 150nm for every  $1/8$  of  $2\pi/4$



 1  $\mu$ m Mag = 15.00 K X InLens WD = 5.1 mm EHT = 2.99 kV

*YU Lee, I Ozerov, F Bedu, JS Kim, F Fages and JW Wu* arXiv:[1607.04806](https://arxiv.org/abs/1607.04806)

# The quest for better materials and fabrication techniques



**Fig. 5.** Schematic comparison of fabrication techniques of high-index nanostructures.

2017 BARANOV, ZUEV, LEPESHOV, KOTOV, KRASNOK, EVLYUKHIN & CHICHKOV

# Soft UV Nanoimprint Lithography

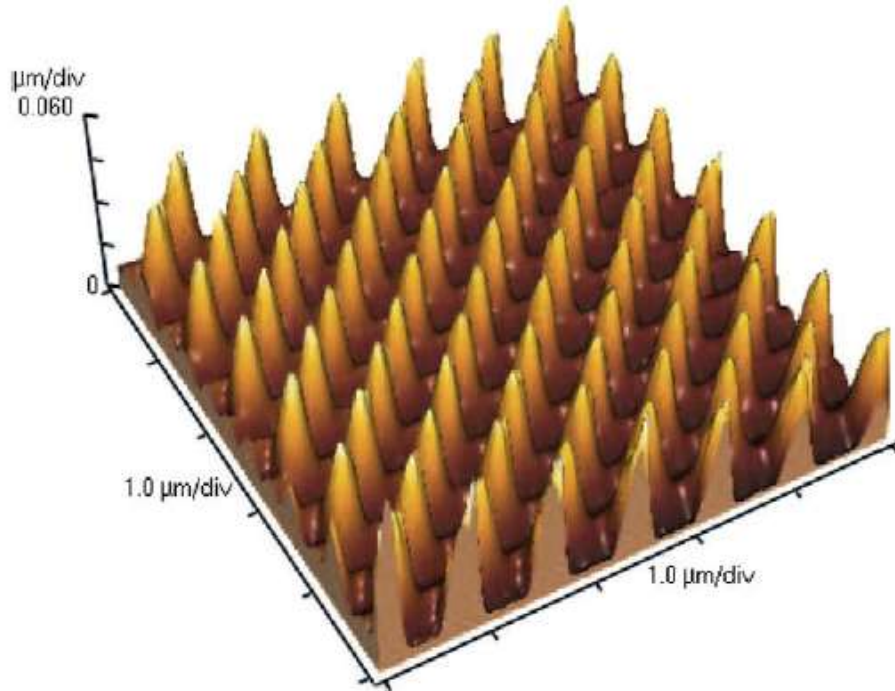


Fig. 2. AFM image of the dots in H-PDMS stamp (periodicity:  $\sim 500$  nm, height: 150 nm, diameter (FWHM): 160 nm).

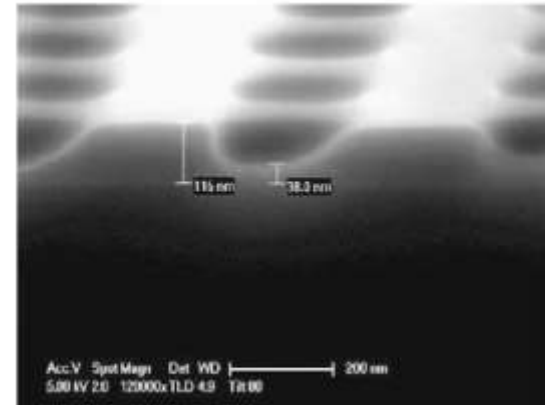


Fig. 3. SEM image of imprint in AMONIL with a PMMA underlayer.

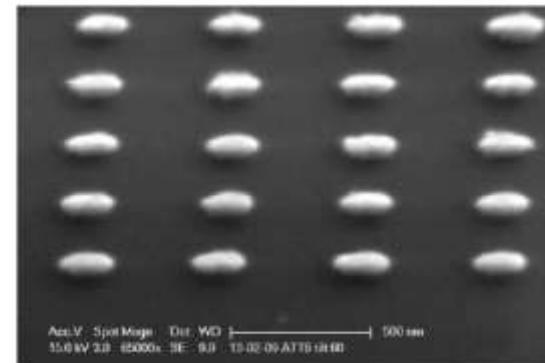


Fig. 4. SEM image of gold nanoparticles after annealing (diameter:  $\sim 165$  nm, periodicity: 500 nm).

G. Barbillon et al. / Microelectronic Engineering 87 (2010) 1001–1004



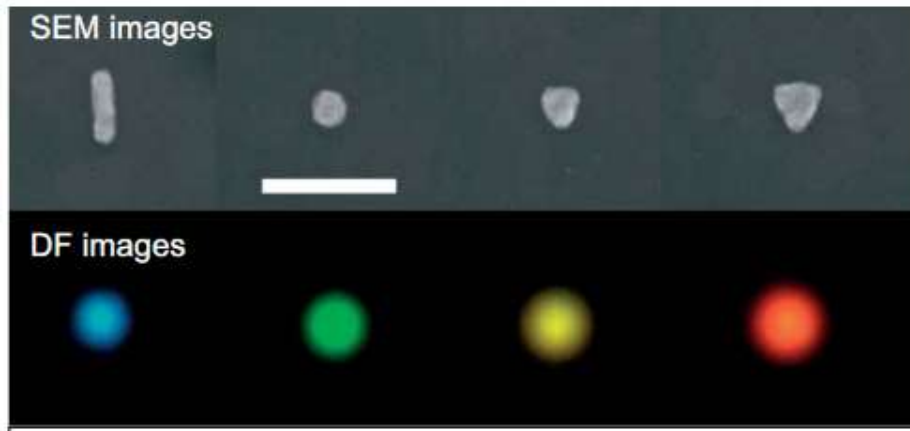
# Nanofabrication for high-resolution color printing

W. A. Murray, W. L. Barnes/Plasmonic Materials

**ADVANCED MATERIALS**

2007, 19, 3771–3782

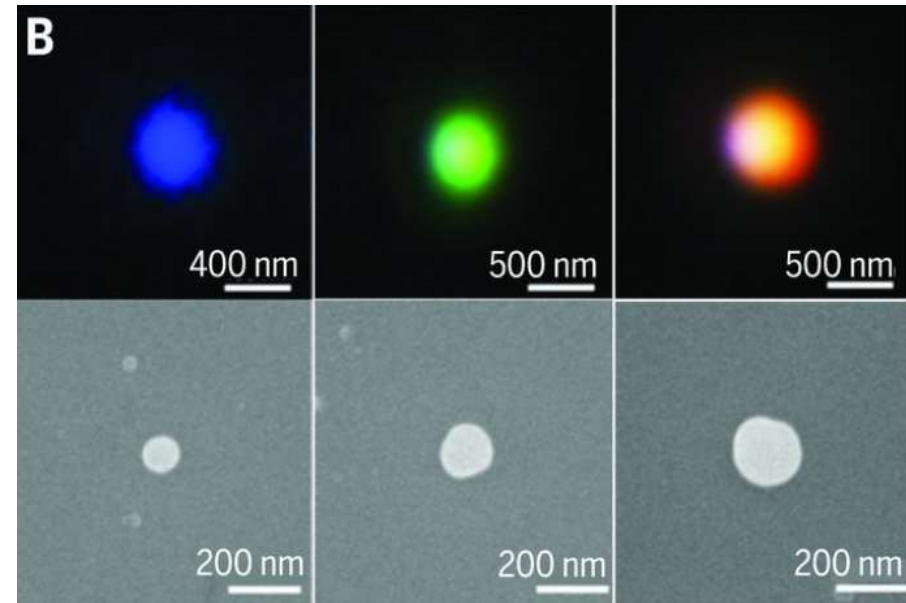
Scale bar = 300



Metallic plasmonic particles

## Resonant dielectric nanostructures

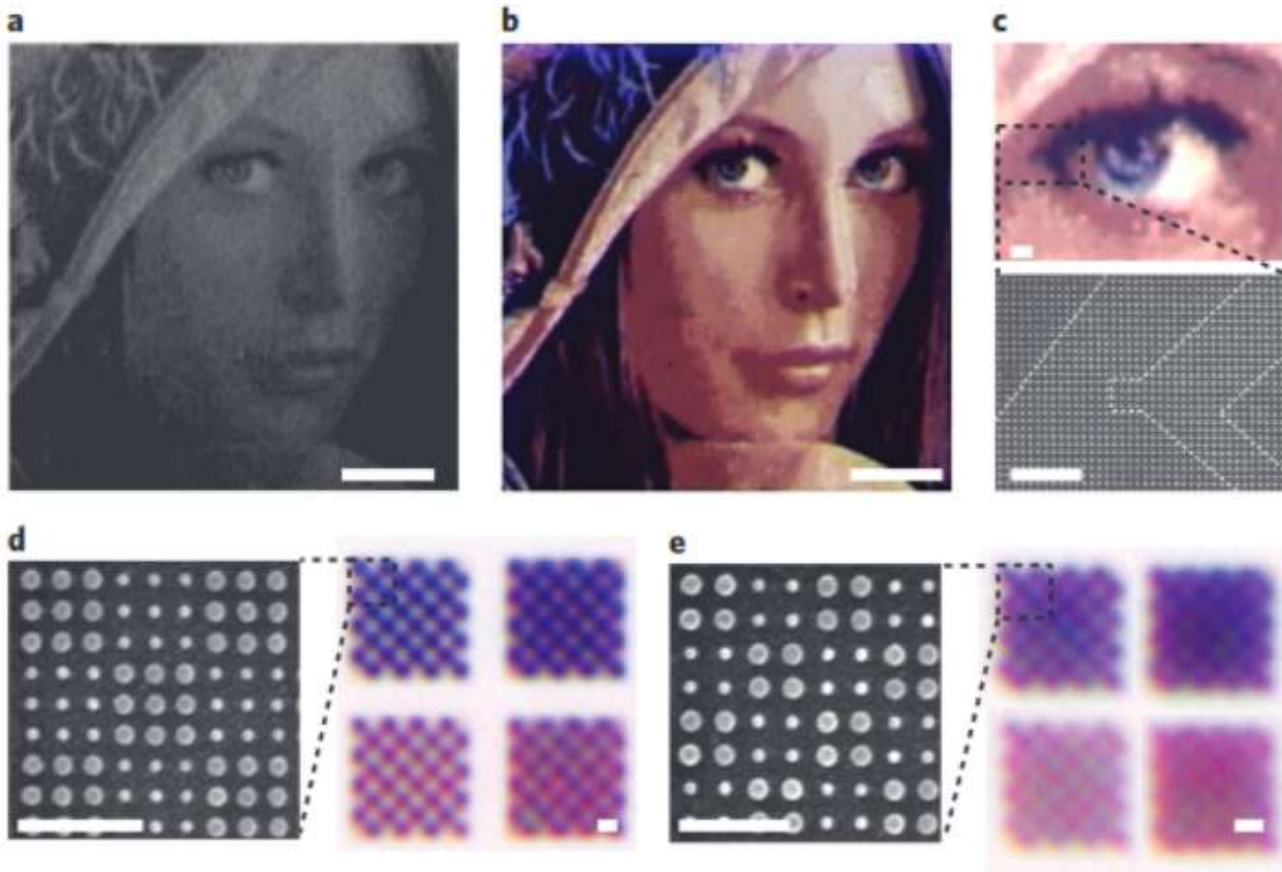
Kuznetsov, Miroshnichenko, Brongersma, Kivshar & Luk'yanchuk, [Science 2016](#)



The color is controlled by the shape and the size of nanostructures

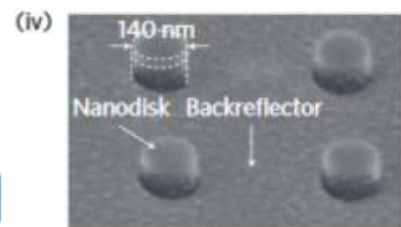
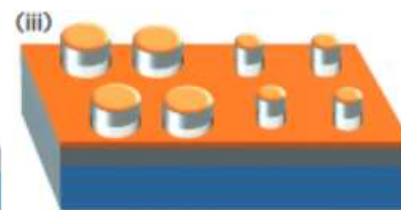
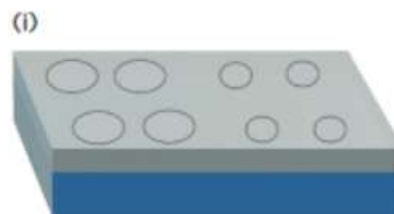
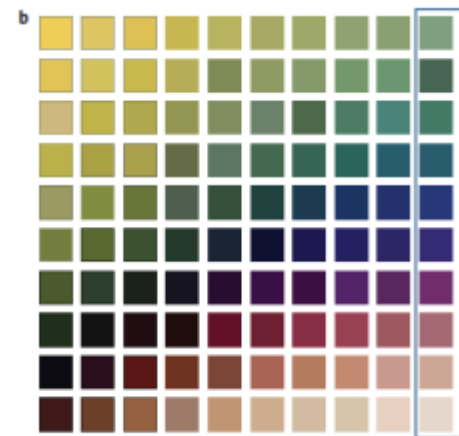
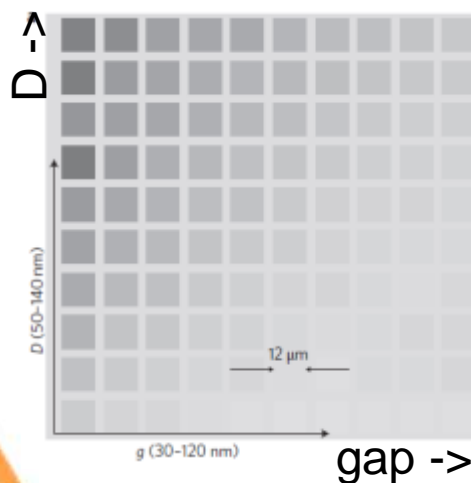
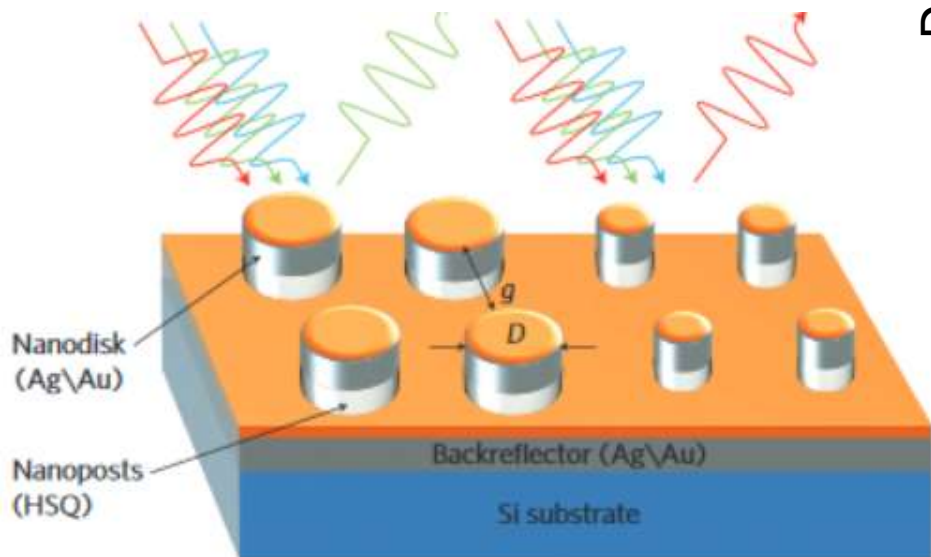
# Plasmonic color printing

NATURE NANOTECHNOLOGY DOI: 10.1038/NNANO.2012.128



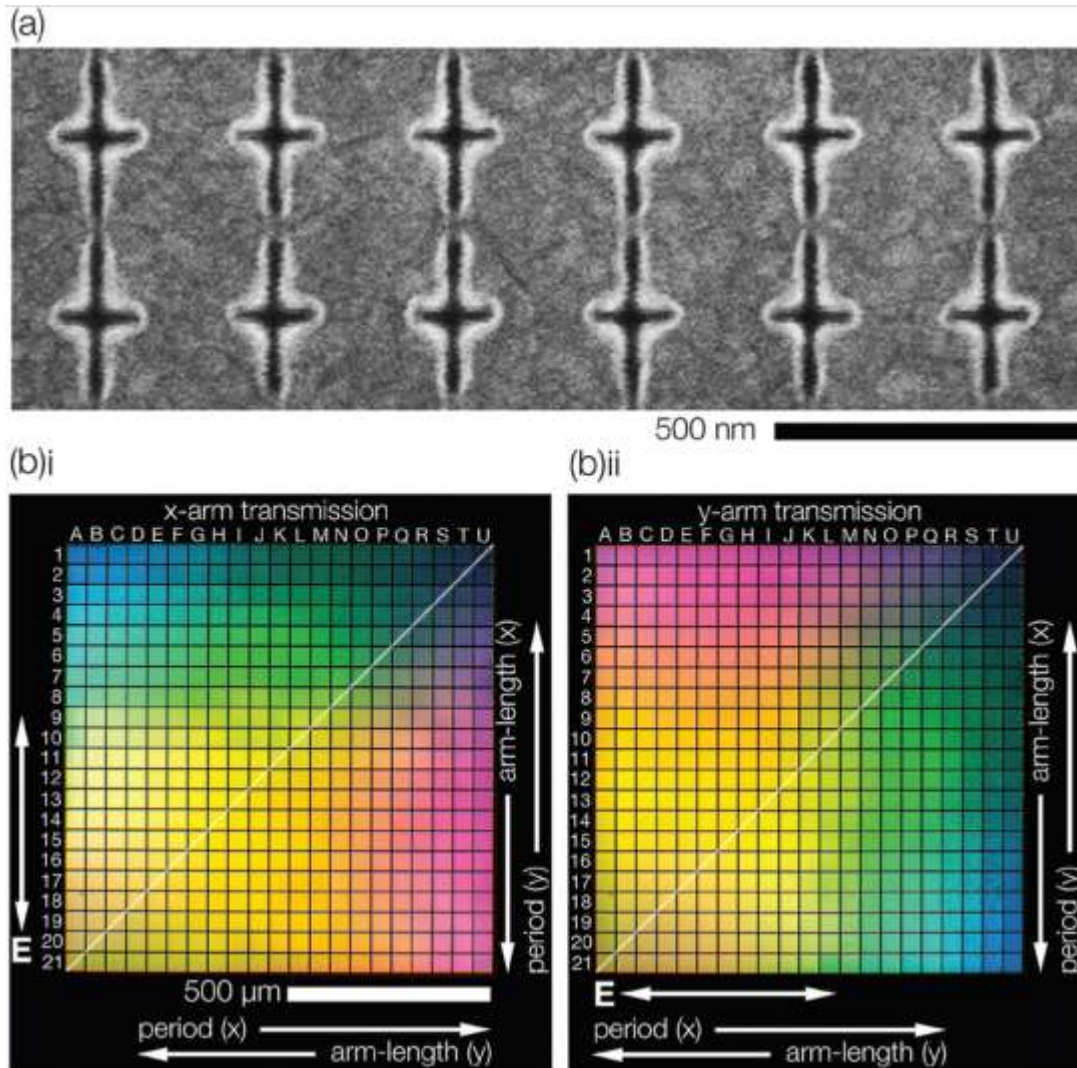
Joel Yang 2012

# Plasmonic color printing



Kumar, Duan, Hegde, Koh, Wei & Yang  
 Nature Nanotechnology, 7, 557–561 (2012)

# Plasmonic Dual-State Nanopixels

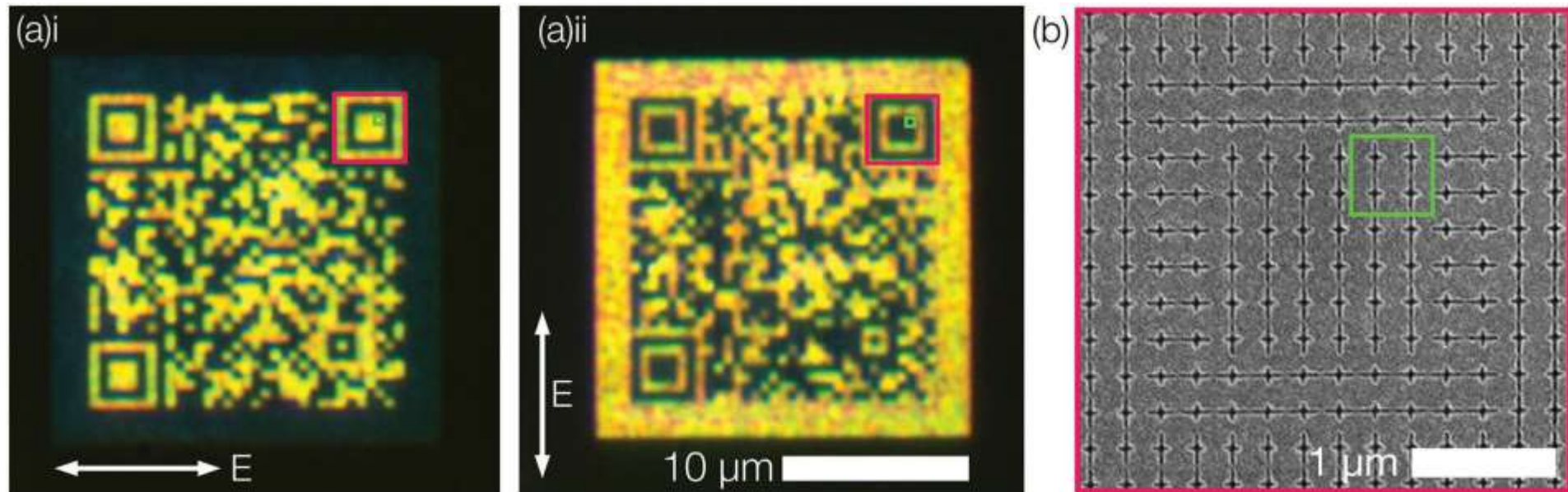


Nanofabrication using :  
metal-evaporation of aluminum film  
electron-beam lithography  
reactive ion etching  
and  
inductively coupled plasma deposition

ADVANCED  
FUNCTIONAL  
MATERIALS

Heydari, Sperling, Neale, and Clark  
*Adv. Funct. Mater.* **2017**, 1701866

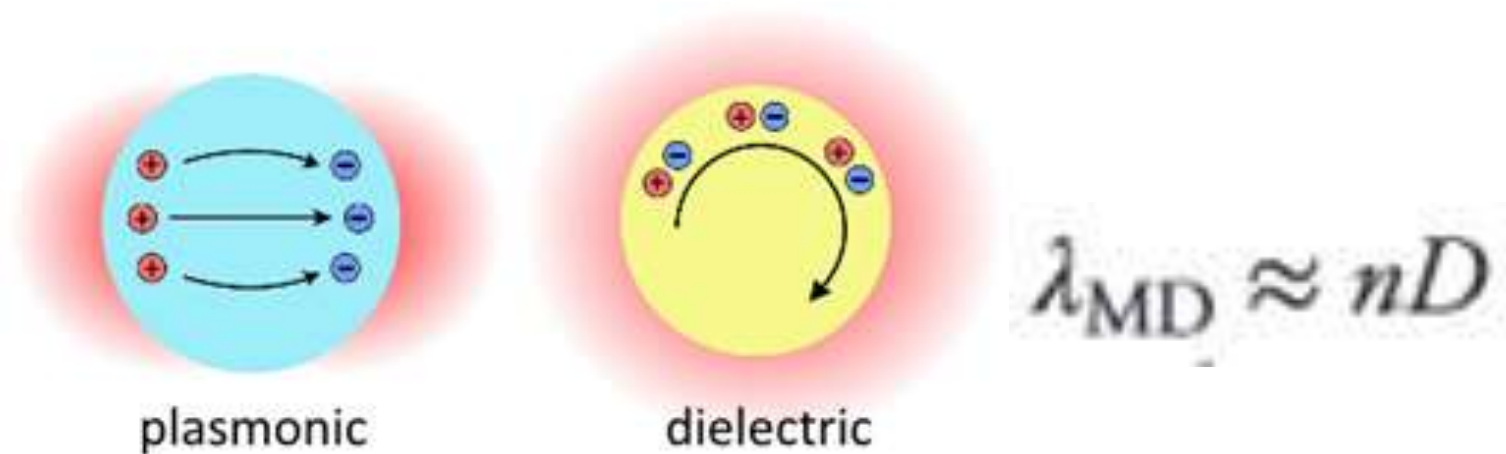
# Switchable QR-code



Bright-field and SEM images of a switchable QR-code

# Plasmonic and All-dielectric nanophotonics

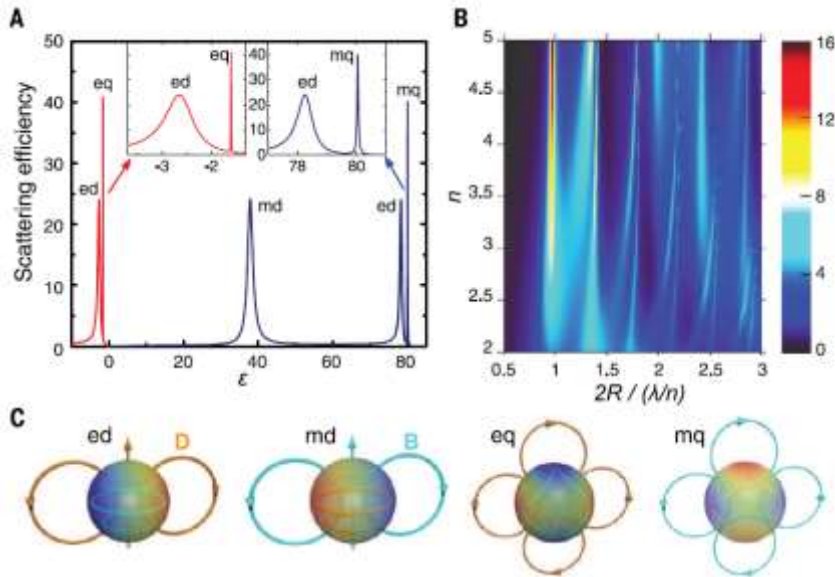
The spectral position of the MD resonance of a spherical particle is approximately defined by  $\lambda_{\text{MD}} \approx nD$  with  $n$  being the refractive index of the sphere and  $D$  its diameter



Baranov, ..., Evlyukhin, Chichkov

Optica, Vol. 4, Issue 7, pp. 814-825 (2017)

# Dielectric photonics

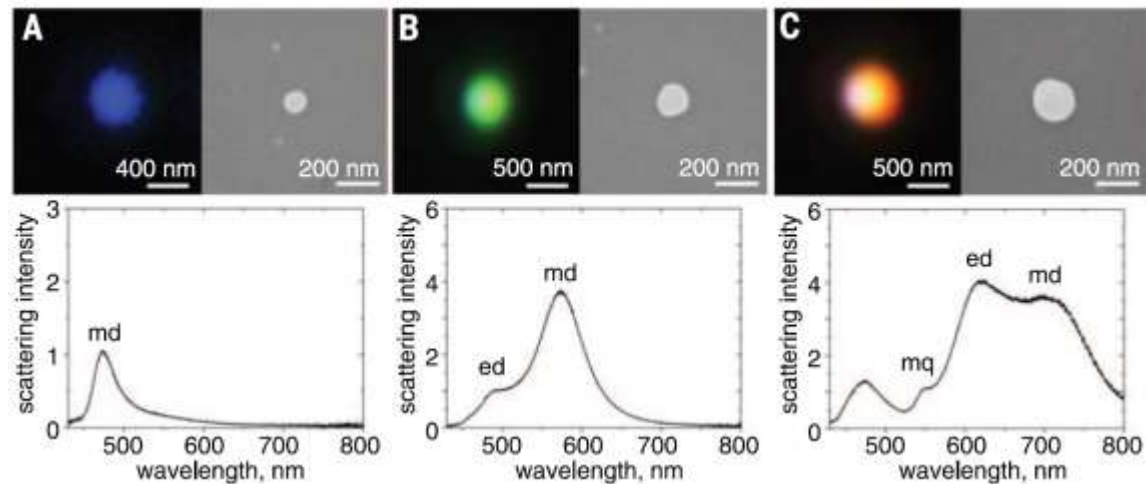


## Resonant dielectric nanostructures

Kuznetsov, Miroshnichenko, Brongersma, Kivshar & Luk'yanchuk, [Science 2016](#)

## Mie resonances

of a spherical particle



# Materials for dielectric photonics

Crystalline and amorphous Silicon  $n \sim 3.5$   
in the visible and near IR range

Low losses

Cheap

Robust

Chemically stable

Compatible with microelectronic processing

$$\lambda_{MD} \approx nD$$



# Amorphous Si resonators

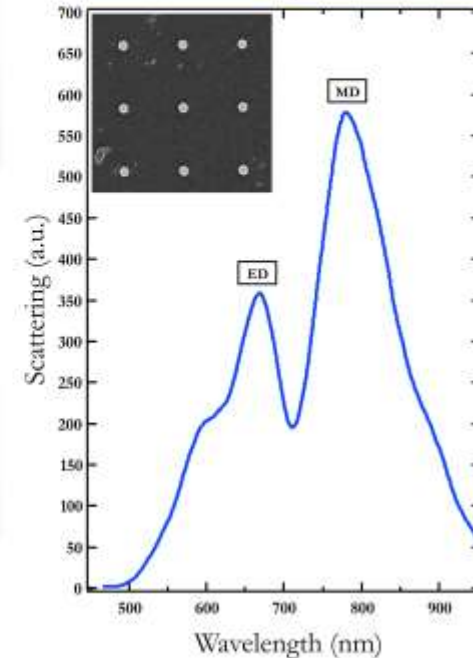
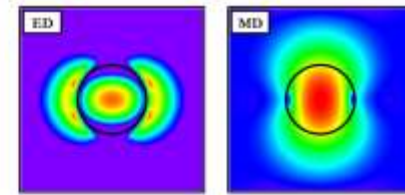
Gold mask on polycrystalline silicon



Alkaline etching



Silicon resonators on glass

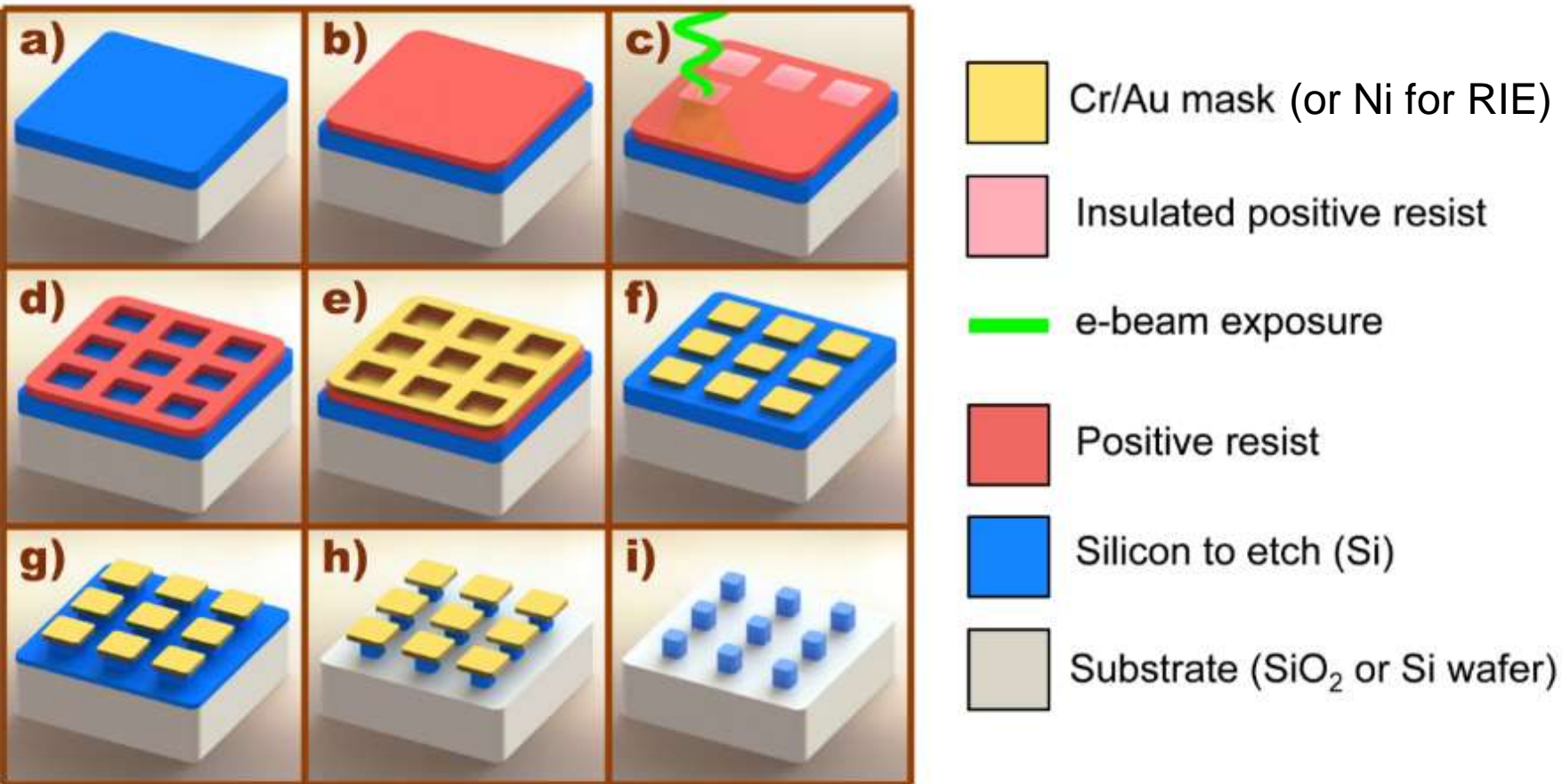


## Chemical Alkaline Etching of Silicon Mie Particles

*Julien Proust,\* Frédéric Bedu, Stéphane Chenot, Ibrahima Soumahoro, Igor Ozerov, Bruno Gallas, Redha Abdeddaim, and Nicolas Bonod\**

Advanced Optical Materials, **3**, 1280–1286, **Septembre 2015**

# Nanofabrication of silicon structures



WET ALCALINE  
or PLASMA RIE

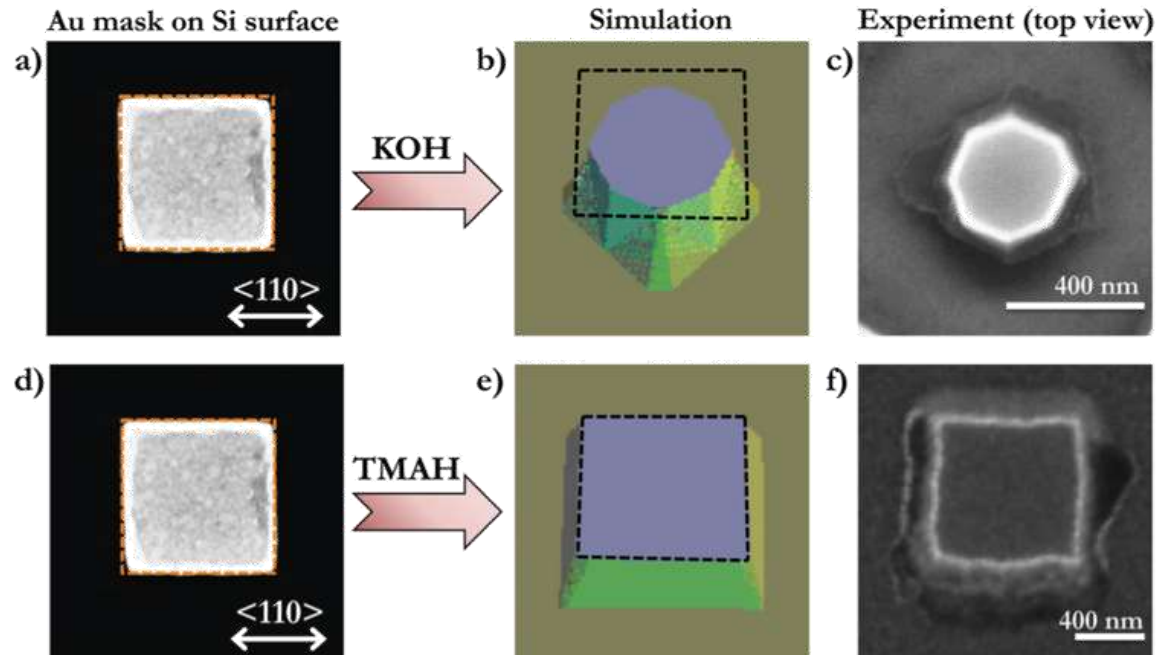
Control of the nanostructure shape and size

# Crystalline silicon nanostructures

KOH or TMAH ?

KOH  $\{110\} > \{100\} > \{111\}$

TMAH  $\{100\} > \{110\} > \{111\}$



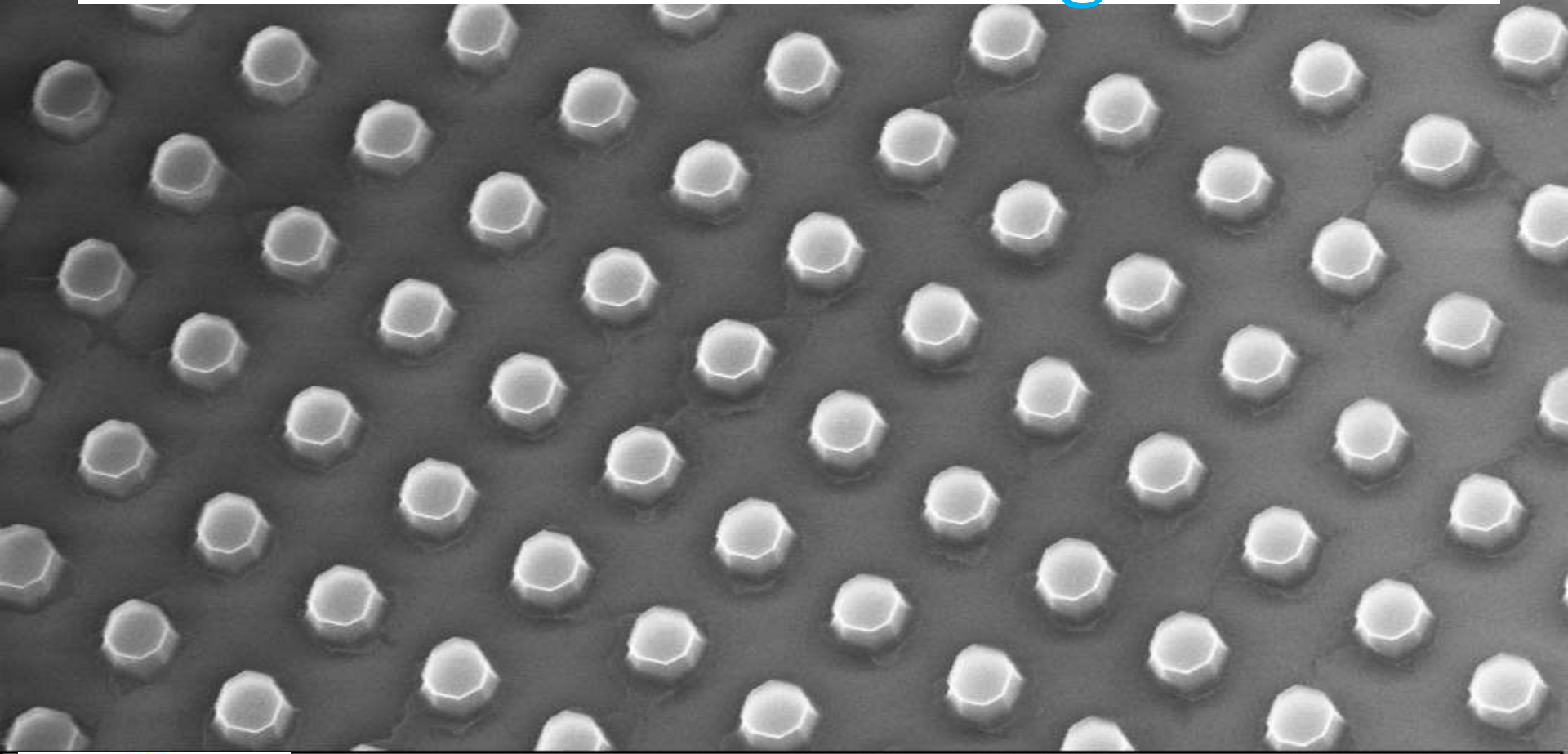
Selective chemical etching, Cr/Au mask

**ADVANCED  
OPTICAL  
MATERIALS**

J. Proust, F. Bedu, S. Chenot, I. Soumahoro, I. Ozerov, B. Gallas, R. Abdeddaim, and N. Bonod, *Advanced Optical Materials*, vol. 3, pp. 1280-1286, 2015.

# Crystalline silicon nanostructures

## Alcaline etching



1  $\mu$ m



Mag = 12.00 K X

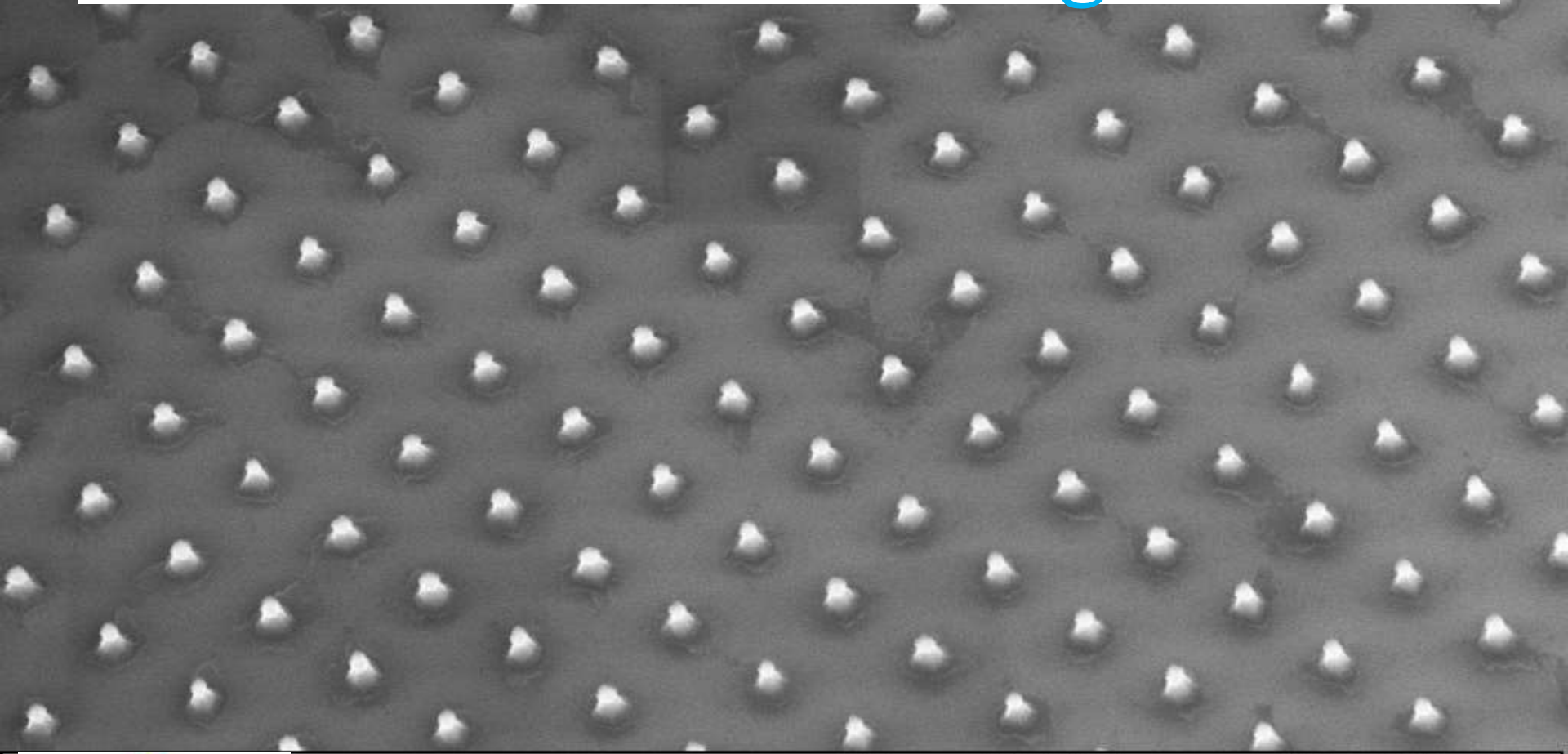
InLens

WD = 8.0 mm

EHT = 10.00 kV

# Crystalline silicon nanostructures

## Alcaline etching



1  $\mu\text{m}$



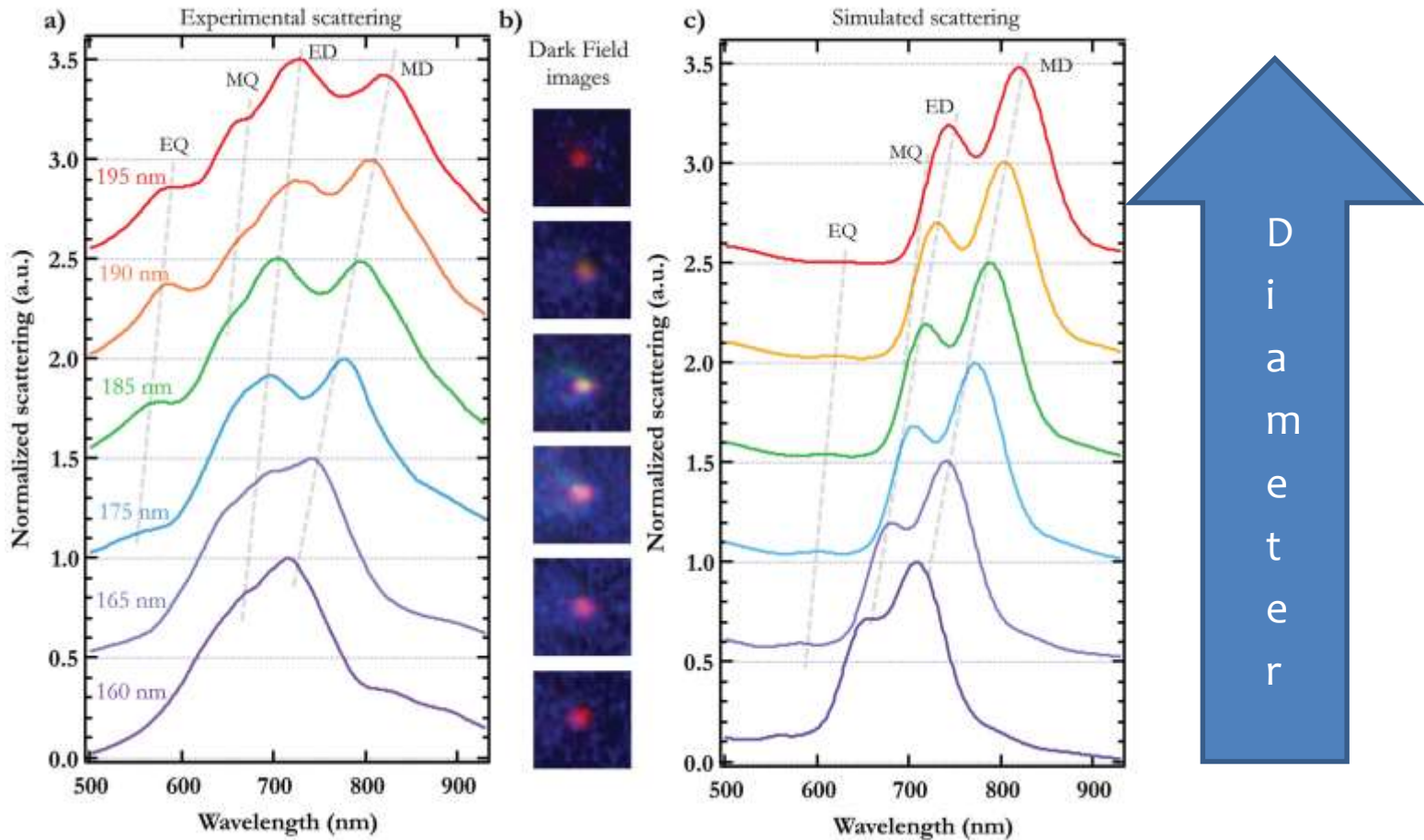
Mag = 12.00 K X

InLens

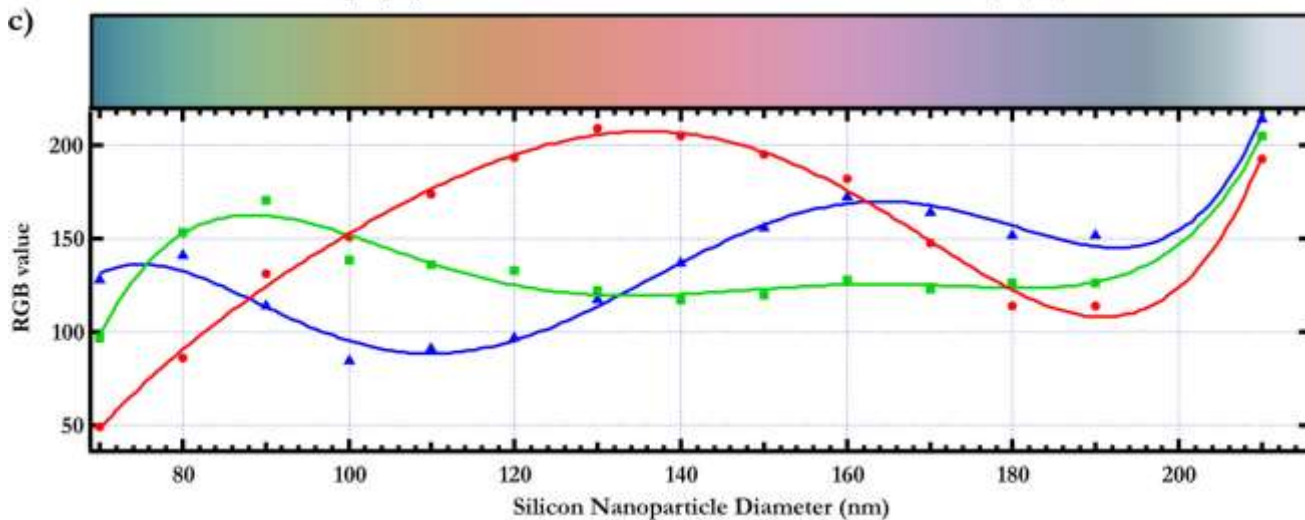
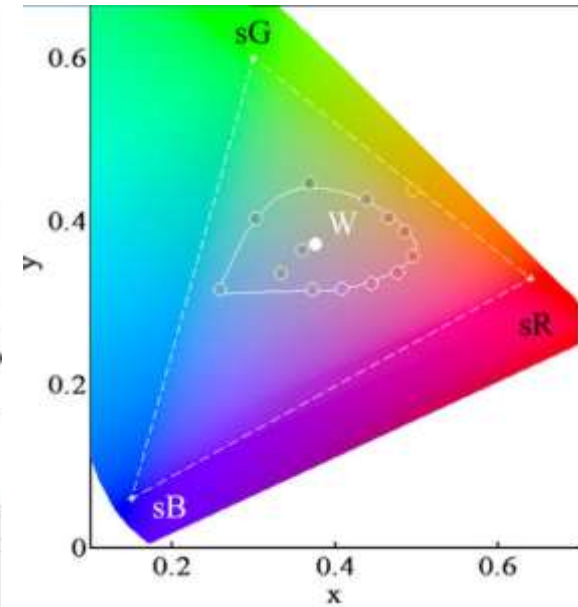
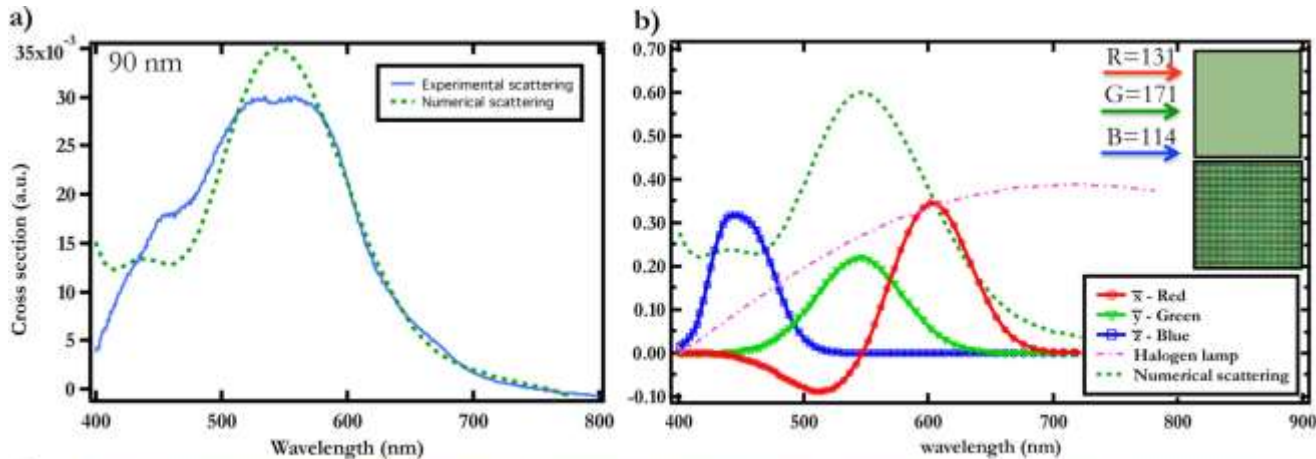
WD = 8.0 mm

EHT = 10.00 kV

# Scattering from individual Si particles



# Colometry (amorphous silicon)

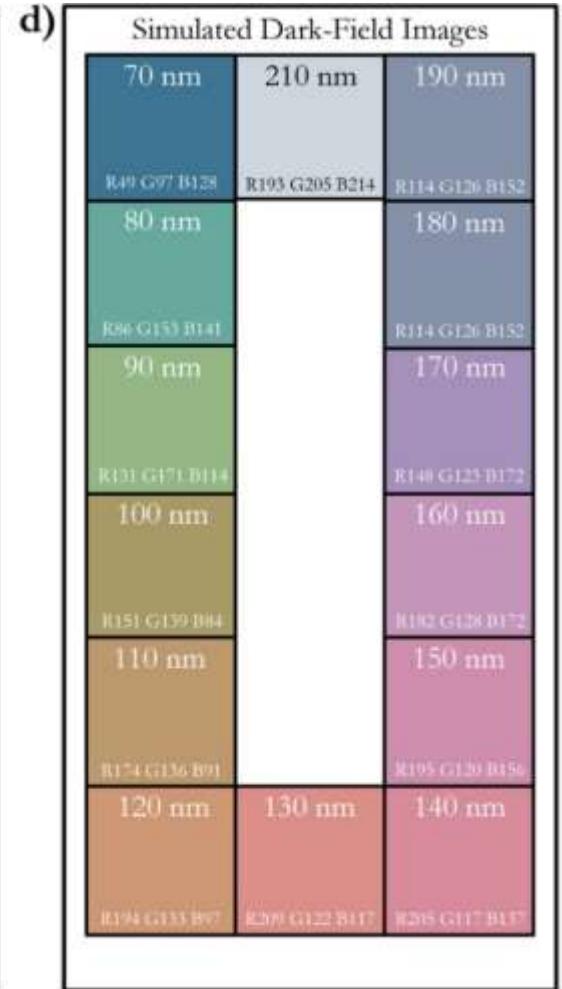
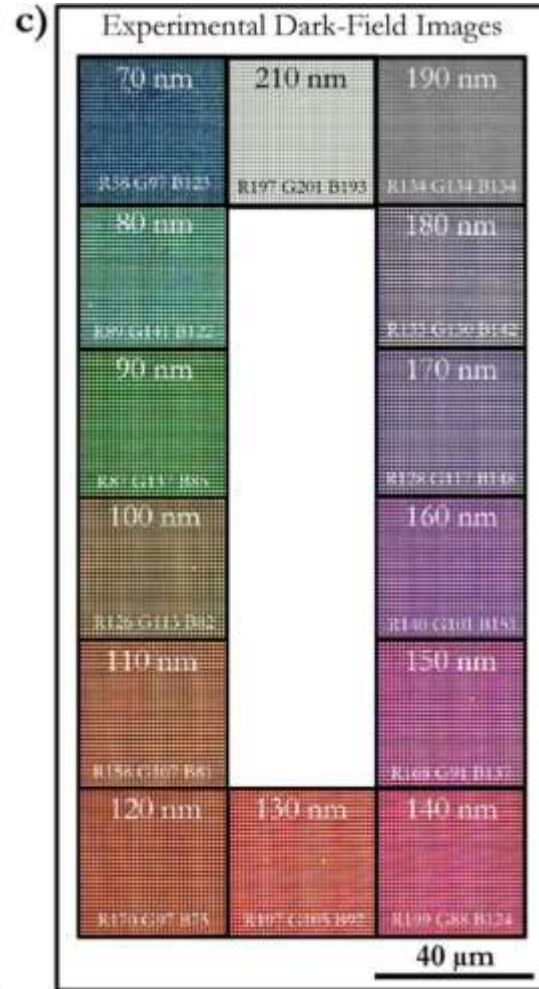
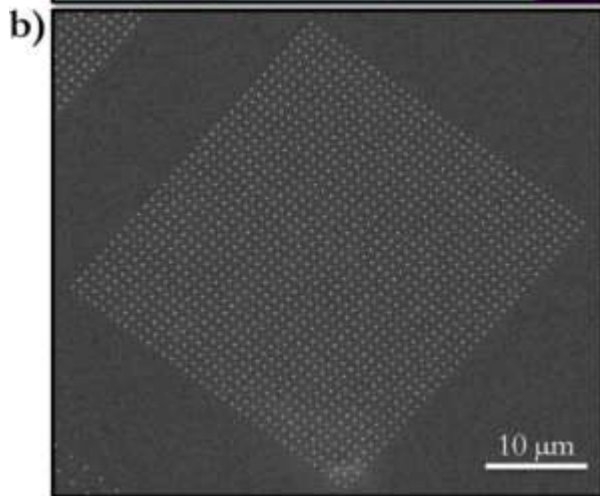
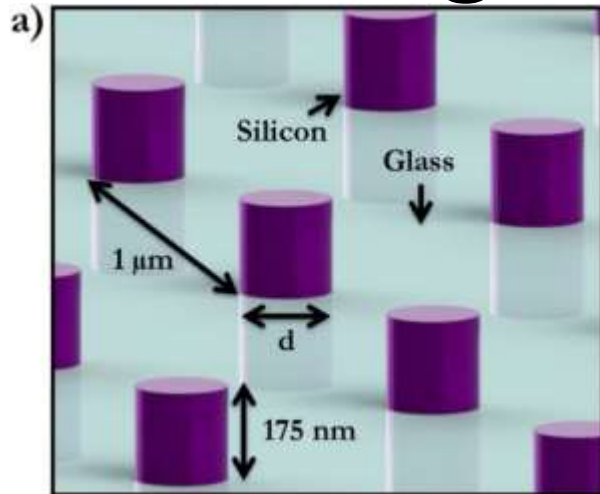


ACS NANO

All-Dielectric Colored Metasurfaces with Silicon Mie Resonators

Julien Proust<sup>†‡</sup>, Frédéric Bedu<sup>§</sup>, Bruno Gallas<sup>†</sup>, Igor Ozerov<sup>§</sup>, and Nicolas Bond<sup>††</sup>

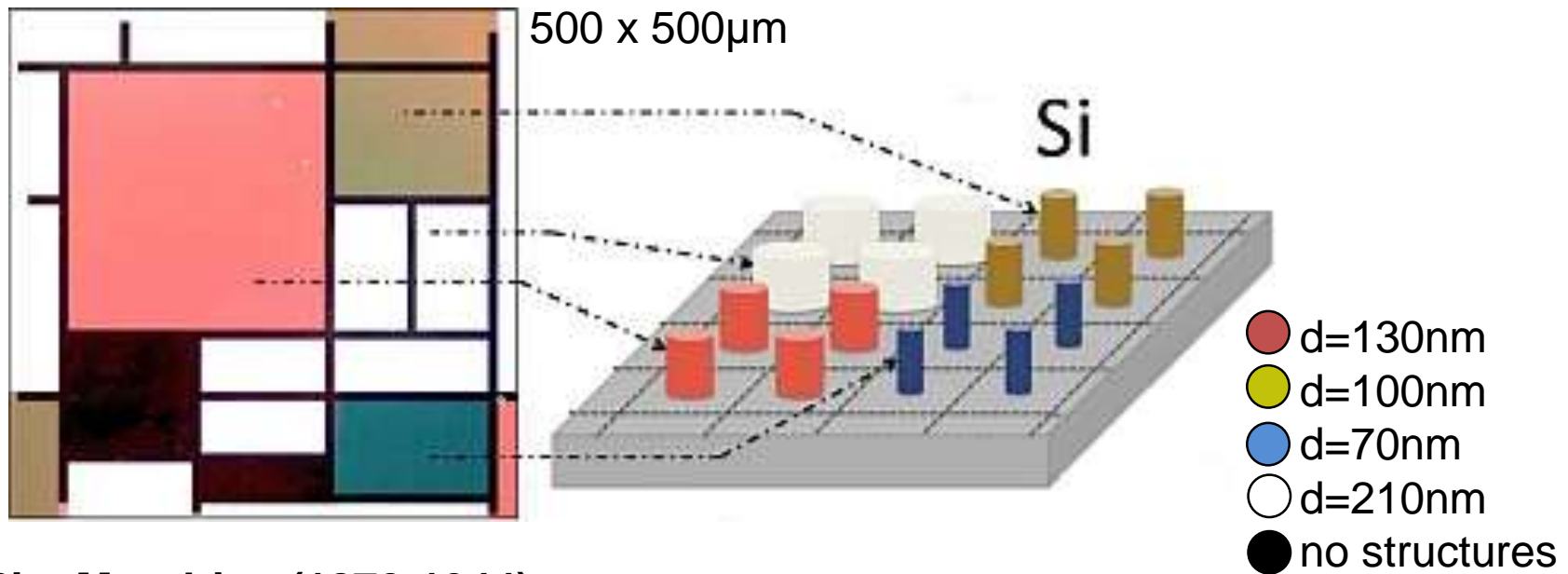
# Scattering from individual Si cylinders





# Amorphous silicon structures for nanoscale painting

Dark Field Microscopy

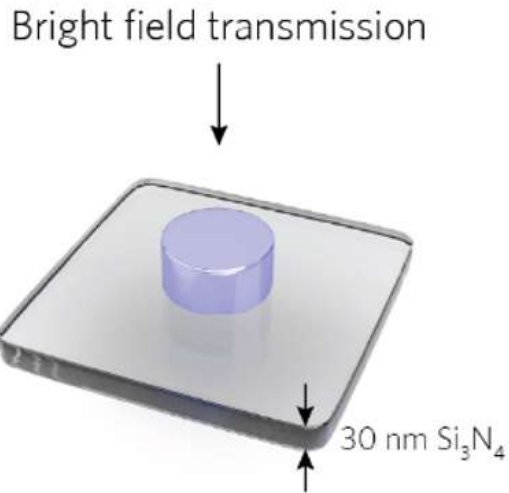
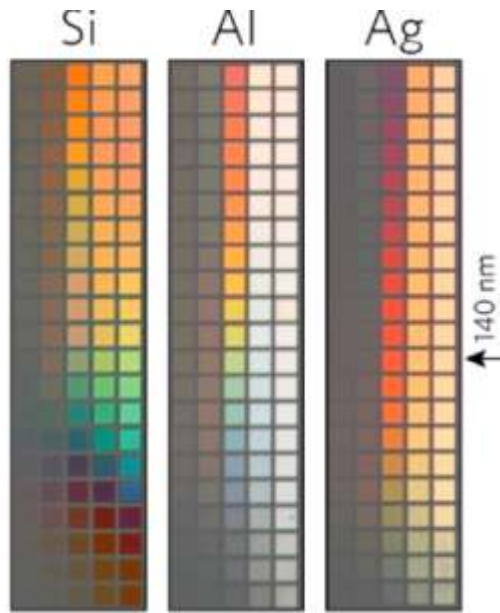
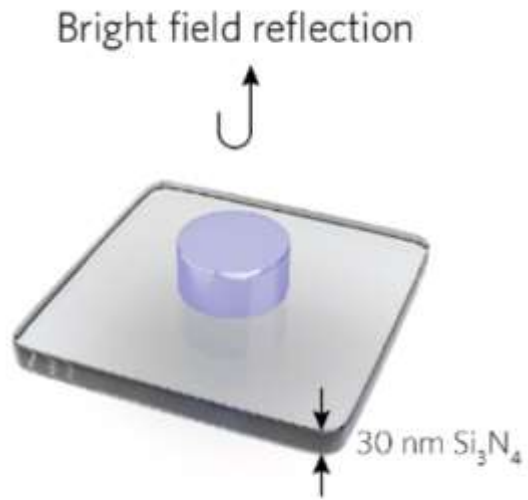


**Piet Mondrian (1872-1944)**

ACS NANO

All-Dielectric Colored Metasurfaces with Silicon Mie Resonators

Julien Proust<sup>†‡</sup>, Frédéric Bedu<sup>§</sup>, Bruno Gallas<sup>†</sup>, Igor Ozerov<sup>§</sup>, and Nicolas Bonod<sup>††</sup>



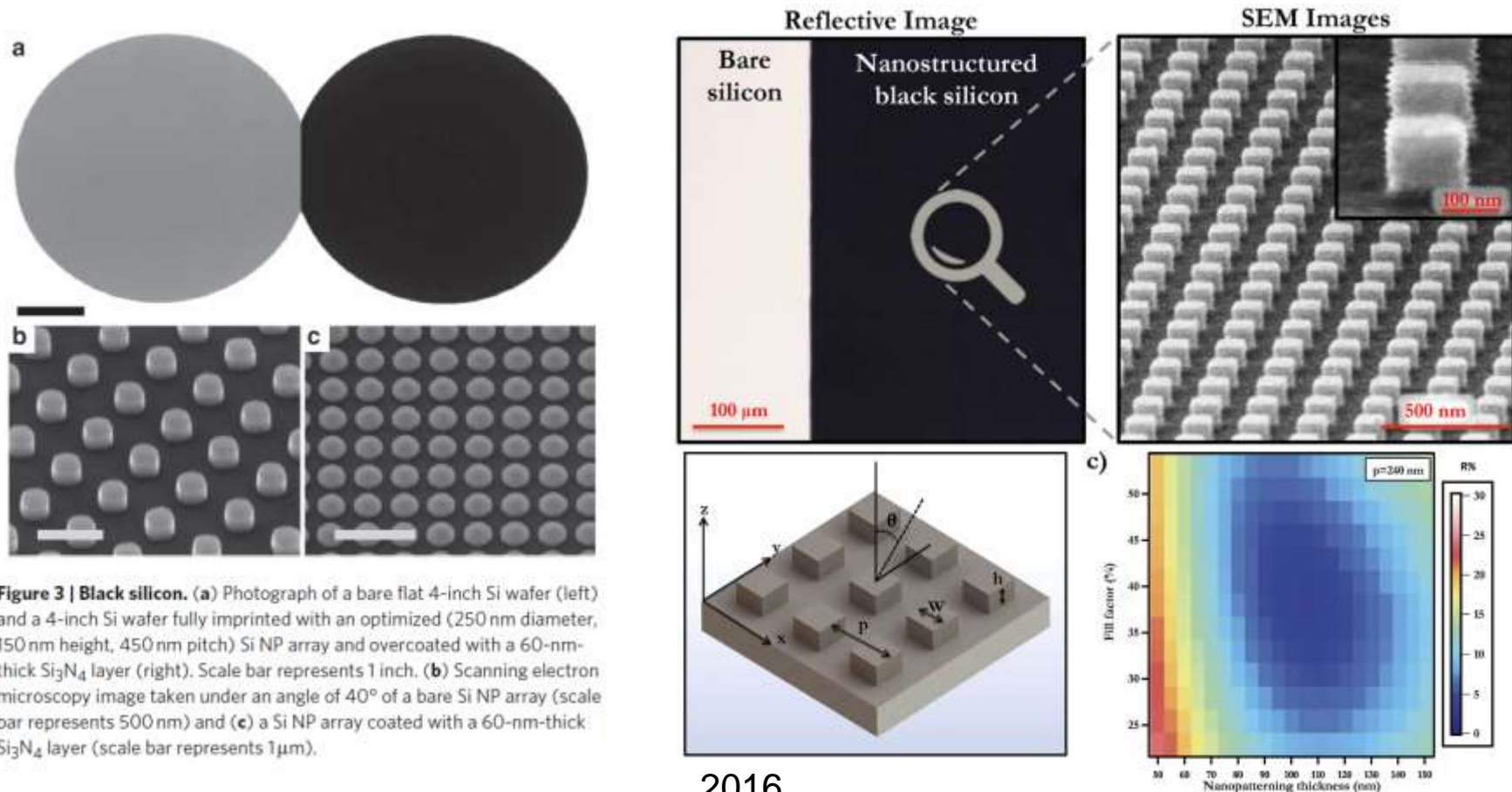
Edvard Munch, The scream (1863–1944)

2017

Flauraud, Reyes,  
Paniagua-Domínguez,  
Kuznetsov, and Brugger

ACS Photonics

# Black Silicon Antireflective Coating



2011

Spinelli, Verschuuren & Polman

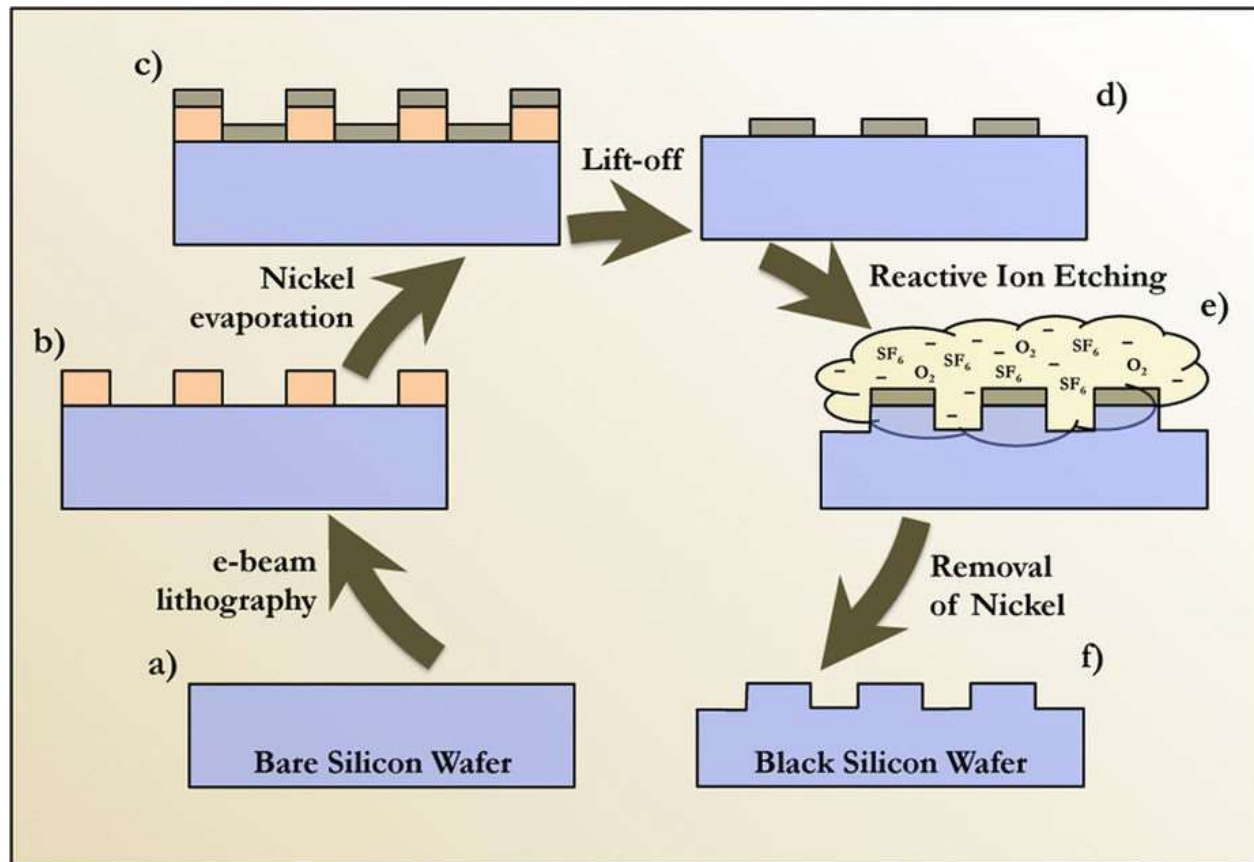
2016

Proust, Fehrembach, Bedu, Ozerov & Bonod

SCIENTIFIC REPORTS

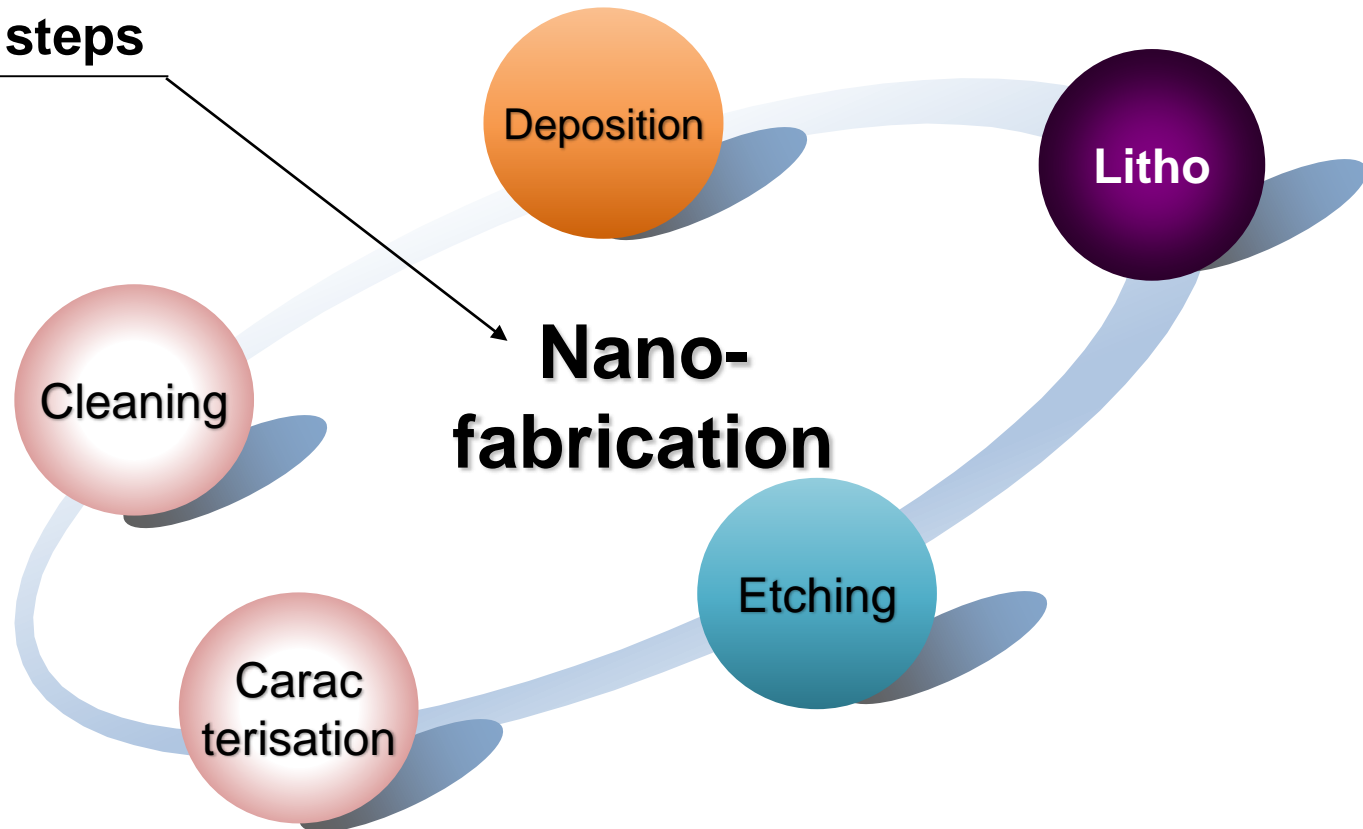
DOI: 10.1038/srep24947

# Black Silicon Antireflective Coating nanofabrication steps



# Top-Down Approach

Typical steps

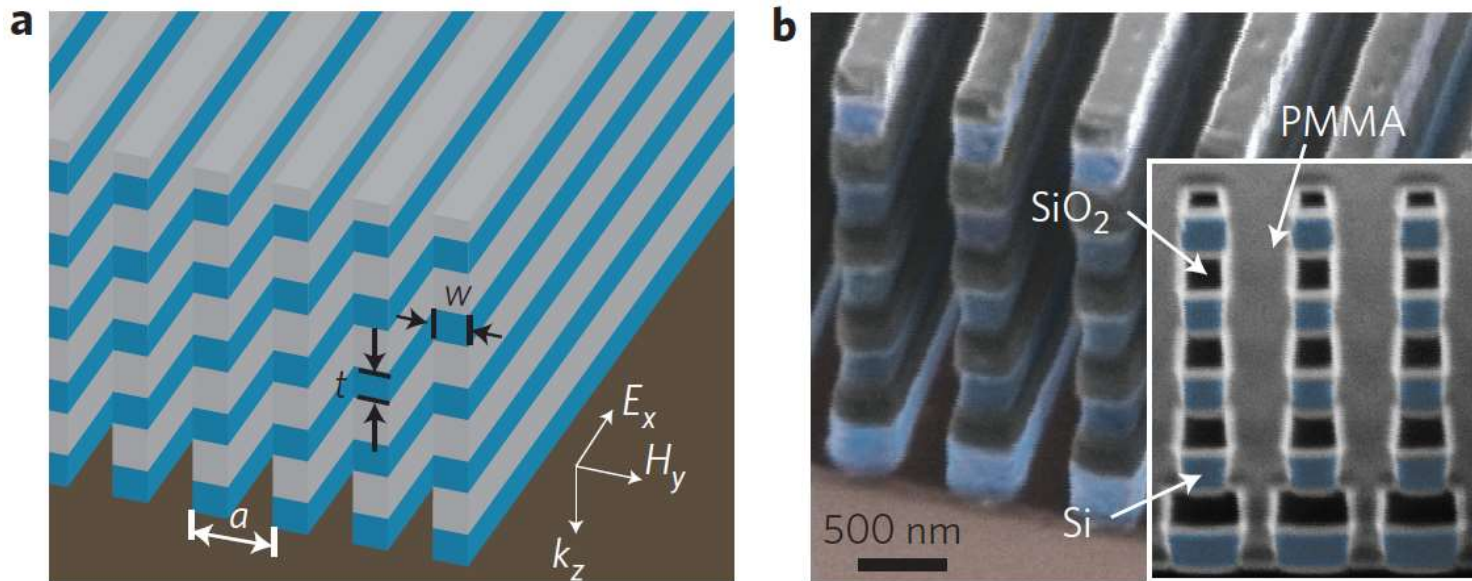


# All-dielectric zero-index optical metamaterial

## Realization of an all-dielectric zero-index optical metamaterial

Parikshit Moitra<sup>1†</sup>, Yuanmu Yang<sup>1†</sup>, Zachary Anderson<sup>2</sup>, Ivan I. Kravchenko<sup>3</sup>, Dayri P. Briggs<sup>3</sup>  
and Jason Valentine<sup>4\*</sup>

from  $\lambda = 1432$  nm to 1457 nm  
the permittivity is negative but the  
permeability remains positive



**Figure 1 |** Diagram and images of fabricated ZIM structure.

electron-beam lithography, and RIE were used to structure the multilayer film

# Nanoimprint Lithography

**Imprint Step 1: Press stamp**



Fabrication of master stamp

**Imprint Step 2: Remove stamp**



The resist is cured with UV light or thermally

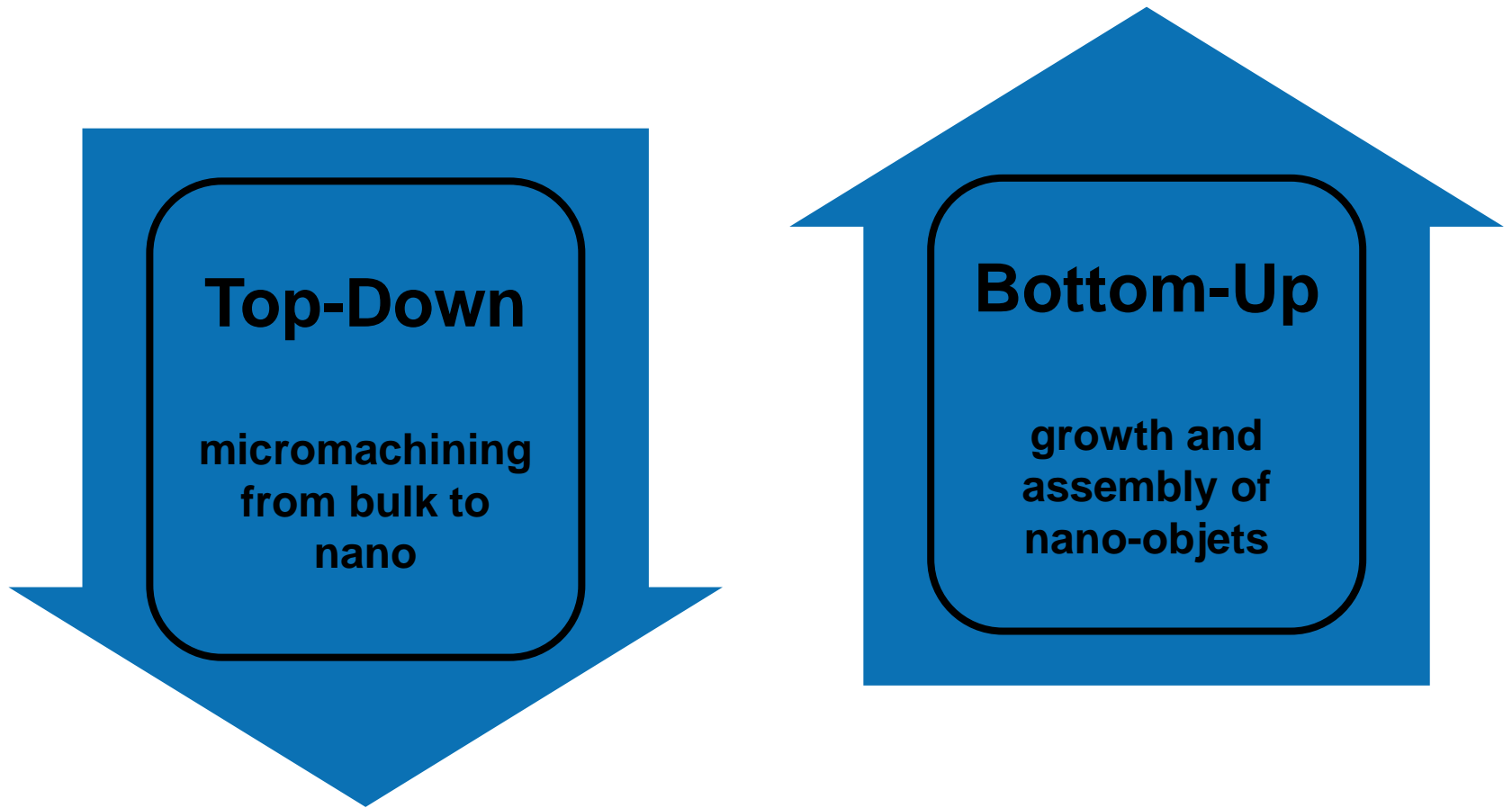
**Pattern transfer Step 1: Etch**



The remaining resist should be etched by RIE

Jung and Byun  
Biomed Eng Lett (2011) 1:153-162

# Nano- et micro- fabrication approaches

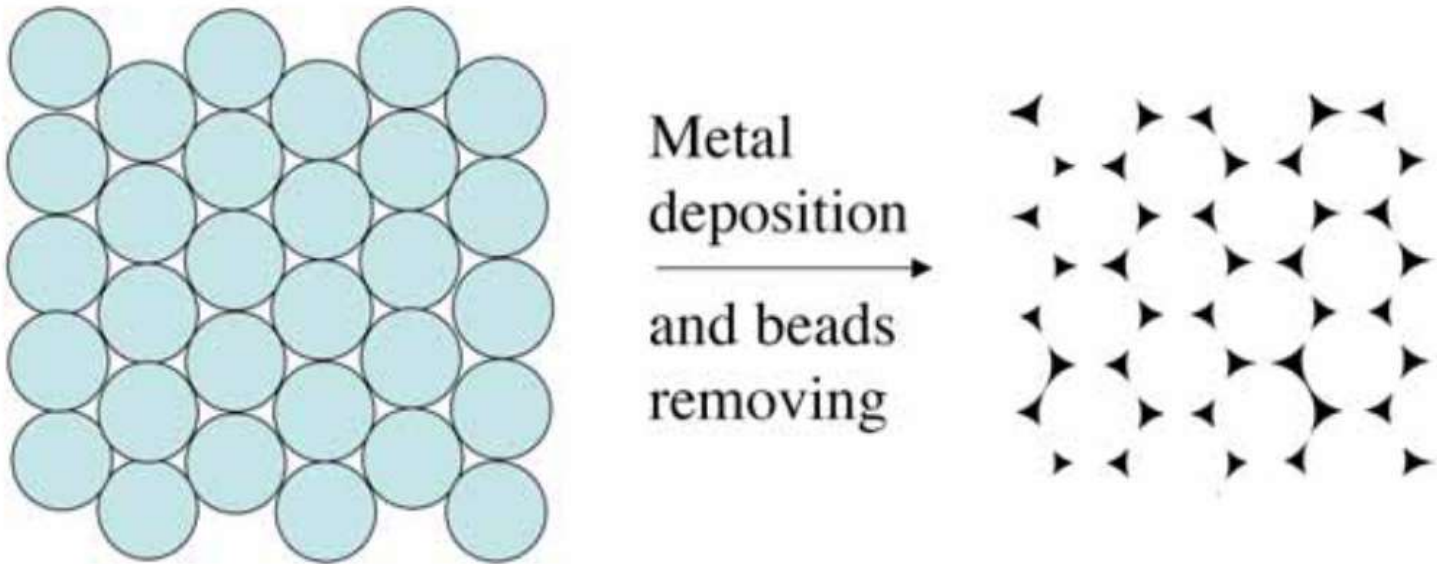




# Nanosphere Lithography

*Alternative Masks for Nanolithography*

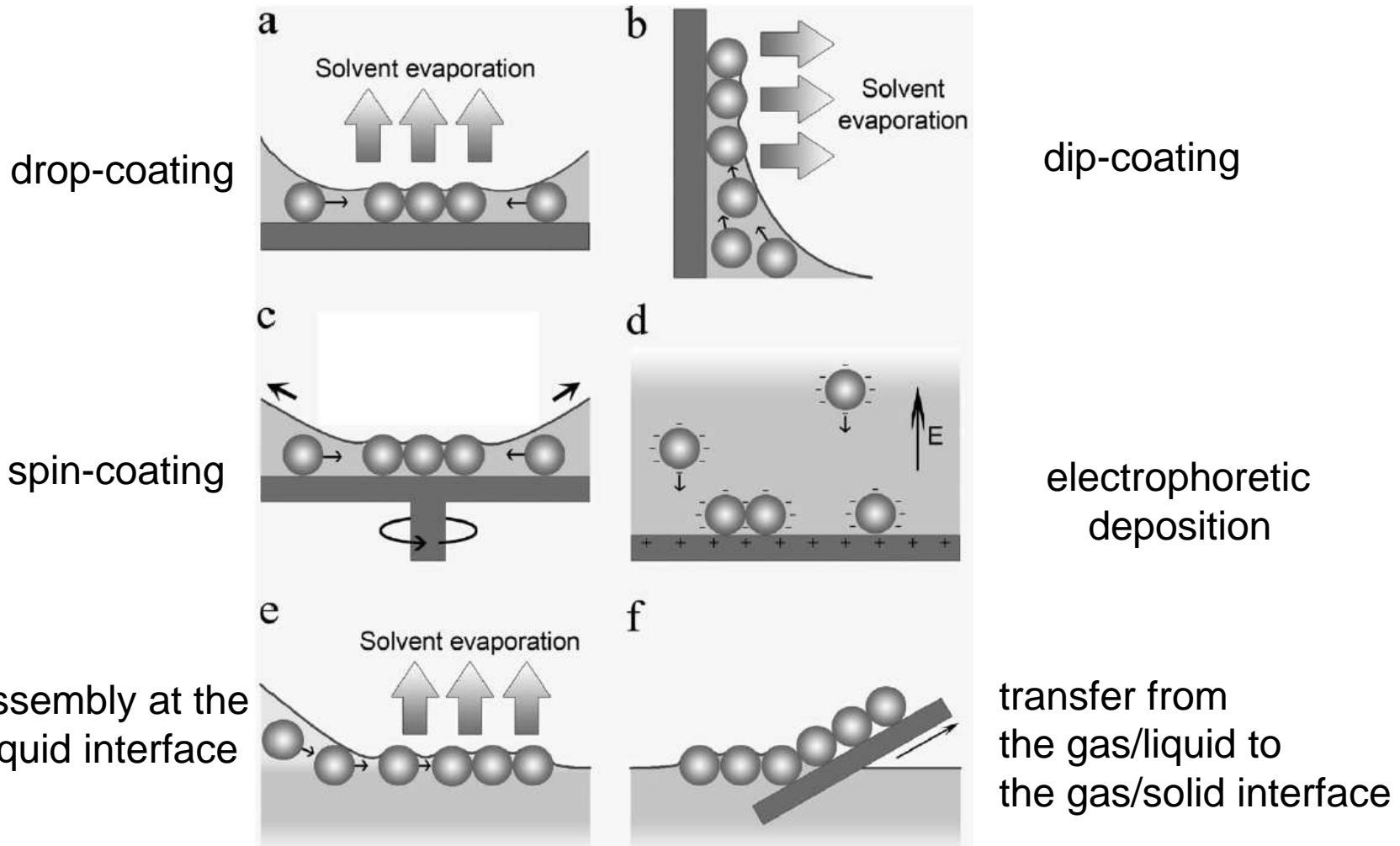
*The Open Physical Chemistry Journal, 2007, Volume 1*



**Fig. (1).** Schematic representation of nanosphere lithography.

D. Inger, 2007

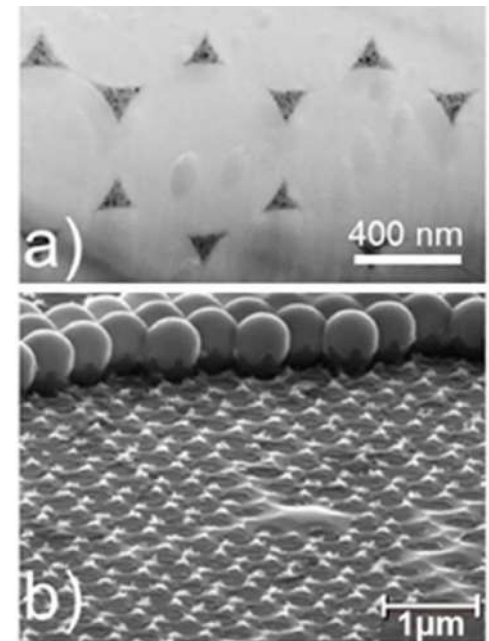
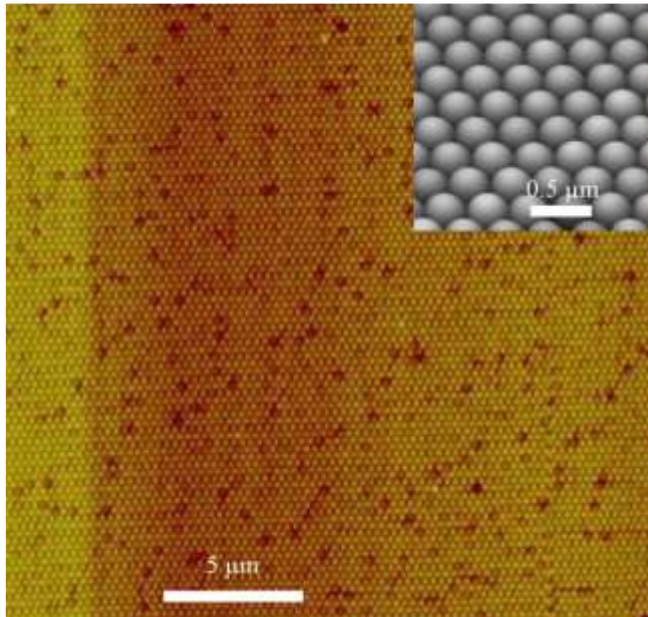
# Bead self-assembly strategies



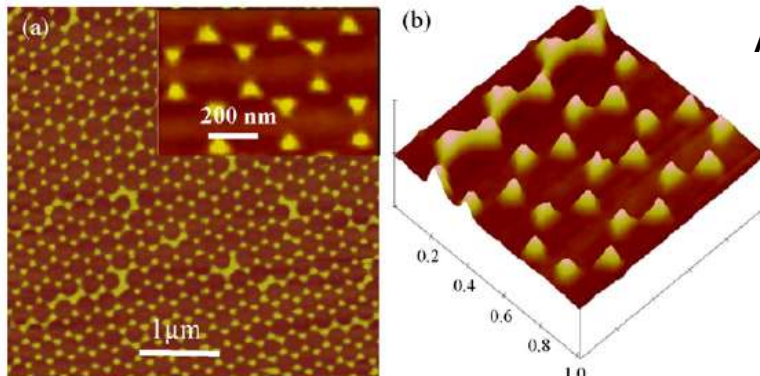
Ye and Qi, Nano Today (2011) 6, 608—631

# Nanosphere Lithography

## Evaporation Lift-off



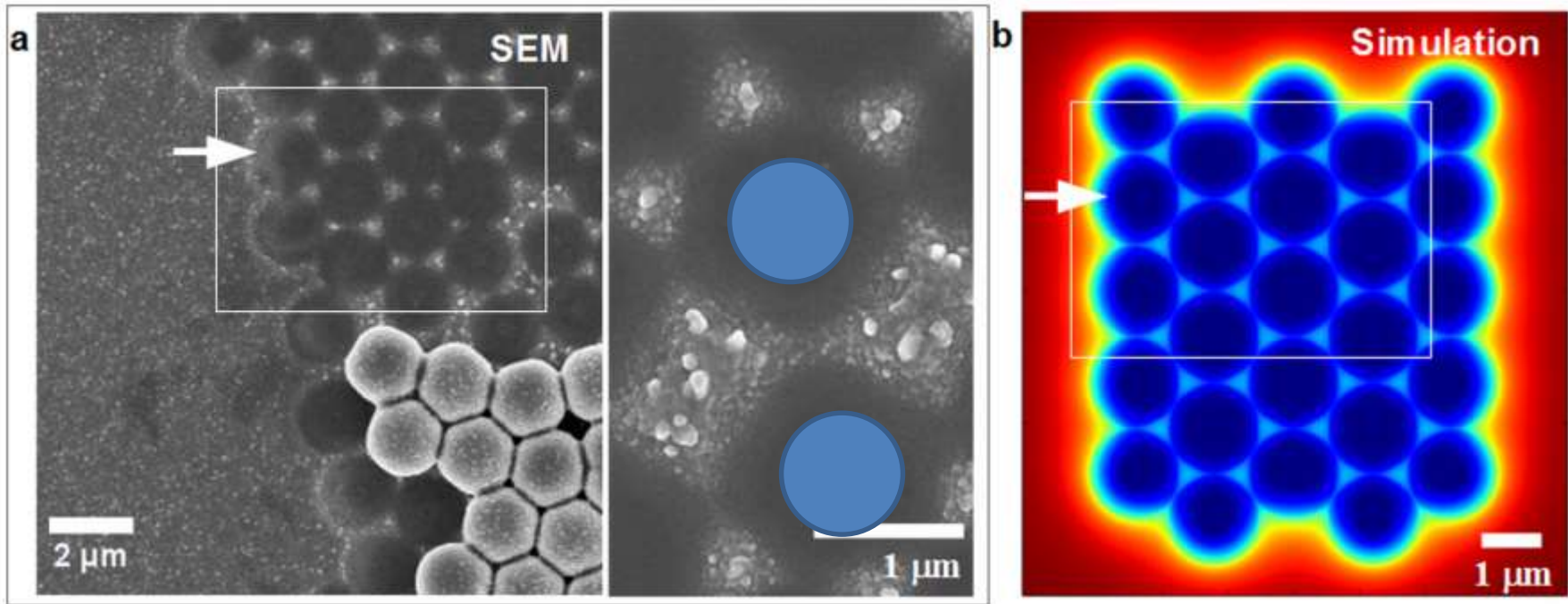
Silver  
Gold  
Nickel  
Aluminum



Jörg Linder SPIE  
10.1117/2.1201310.005154

Y. Song, H.E. Elsayed-Ali / *AppliedSurfaceScience* 256 (2010) 5961–5967

# Tuning pit-size with Al thickness



## Sputtering & Lift-off

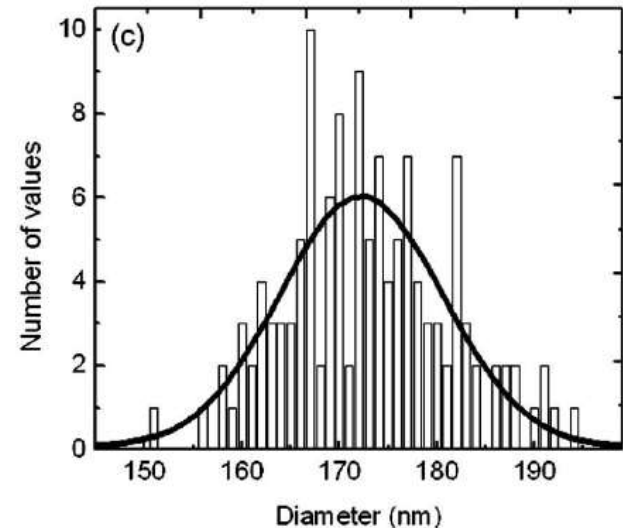
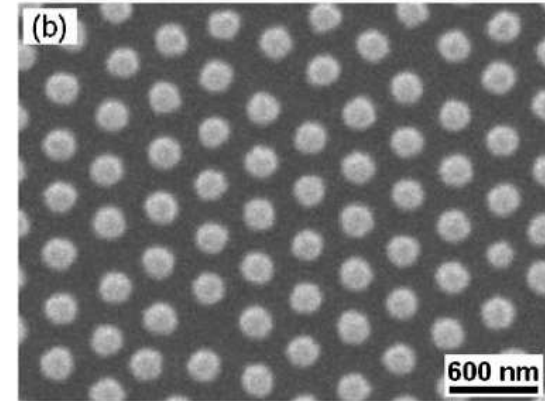
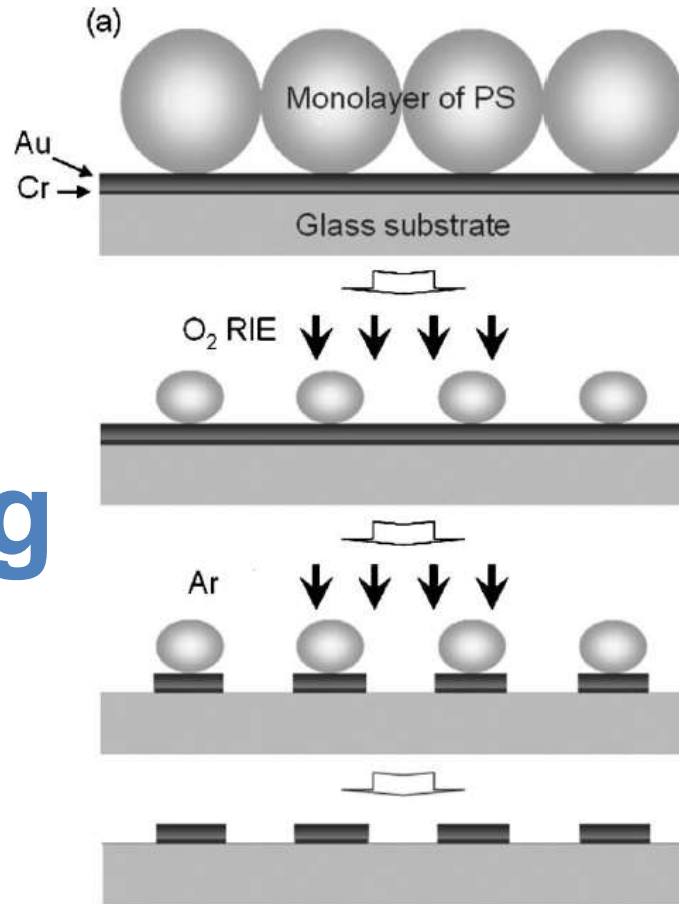
NANO LETTERS

Pi, Dillard, Alameddine, Benard, Wahl,  
Ozerov, Charrier, Limozin, Sengupta,  
Nano Letters, 15, 5178–5184 (2015)



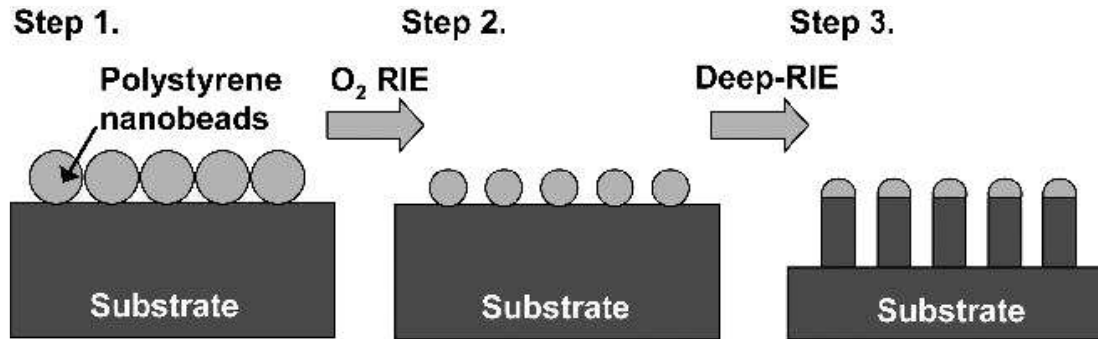
# Nanosphere Lithography

Zheng *et al.* J. Appl. Phys. 103, 014308 (2008)



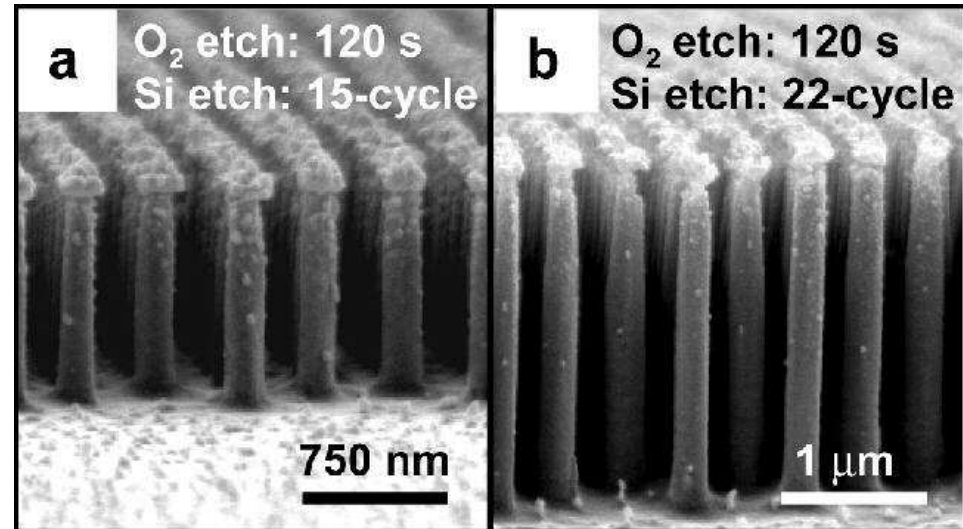
Etching  
of  
Gold

# Fabrication of nanopillars by nanosphere lithography

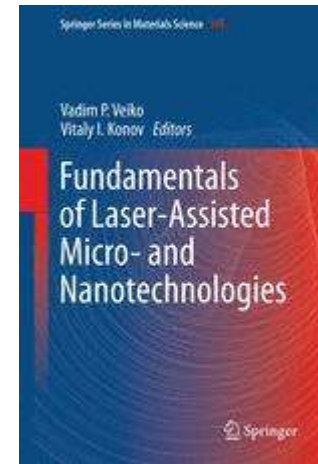
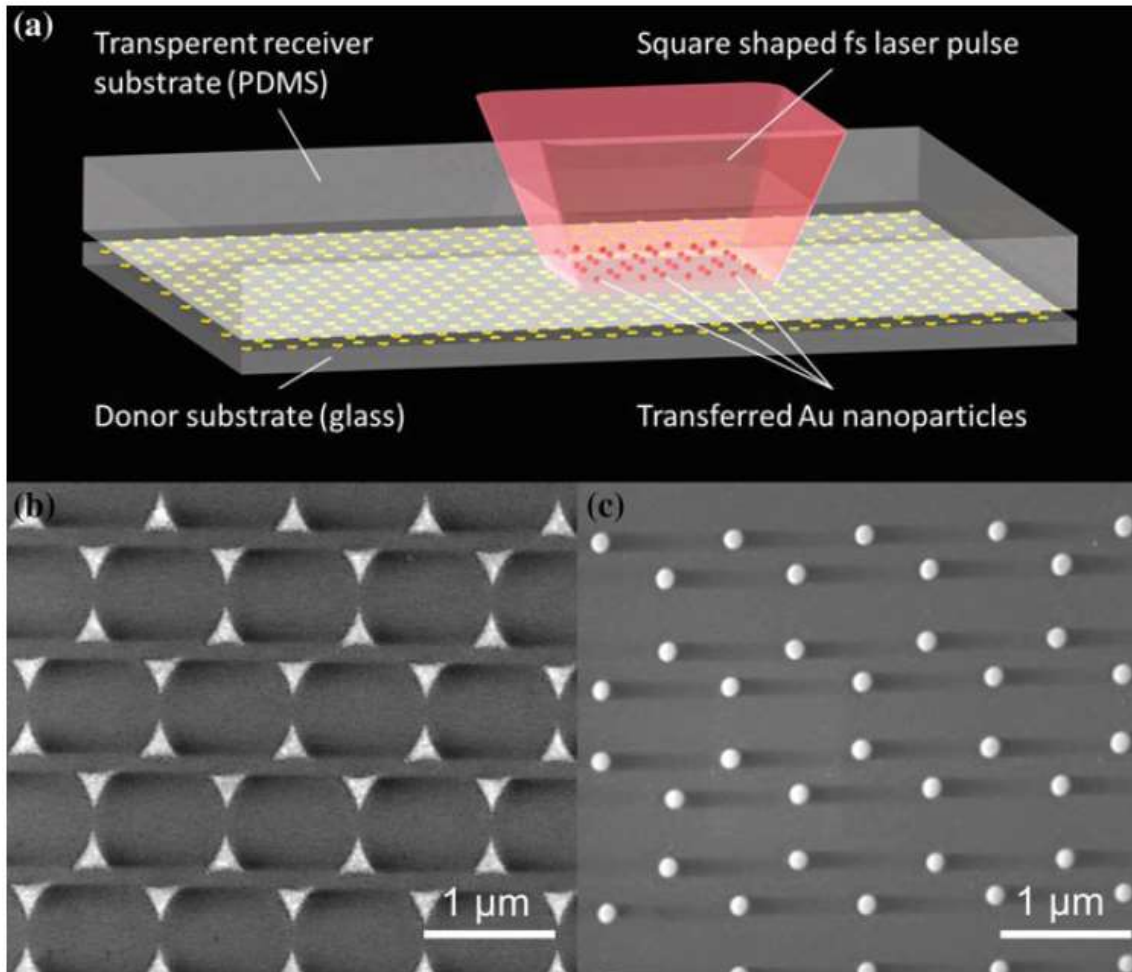


## Deep Etching of Silicon

Cheung et al.  
Nanotechnology **17** (2006) 1339–1343

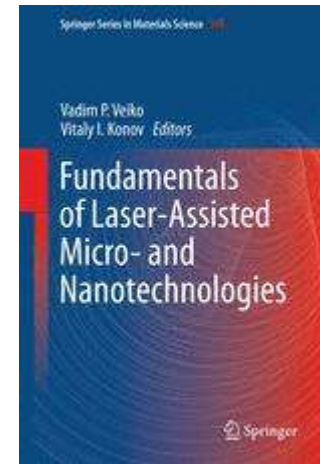
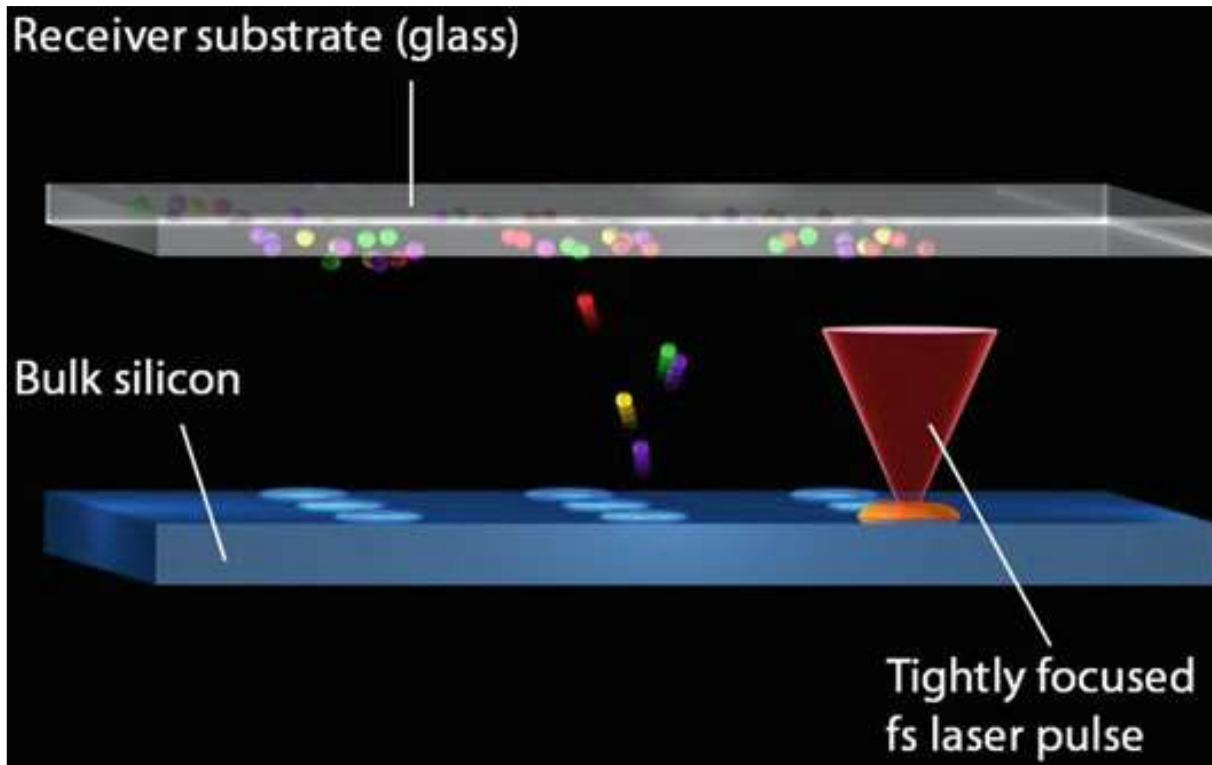


# Laser Generation and Printing of Gold Nanoparticles



**Barchanski, Evlyukhin,  
Koroleva, Reinhardt, Sajti,  
Zywietz and Chichkov  
2014**

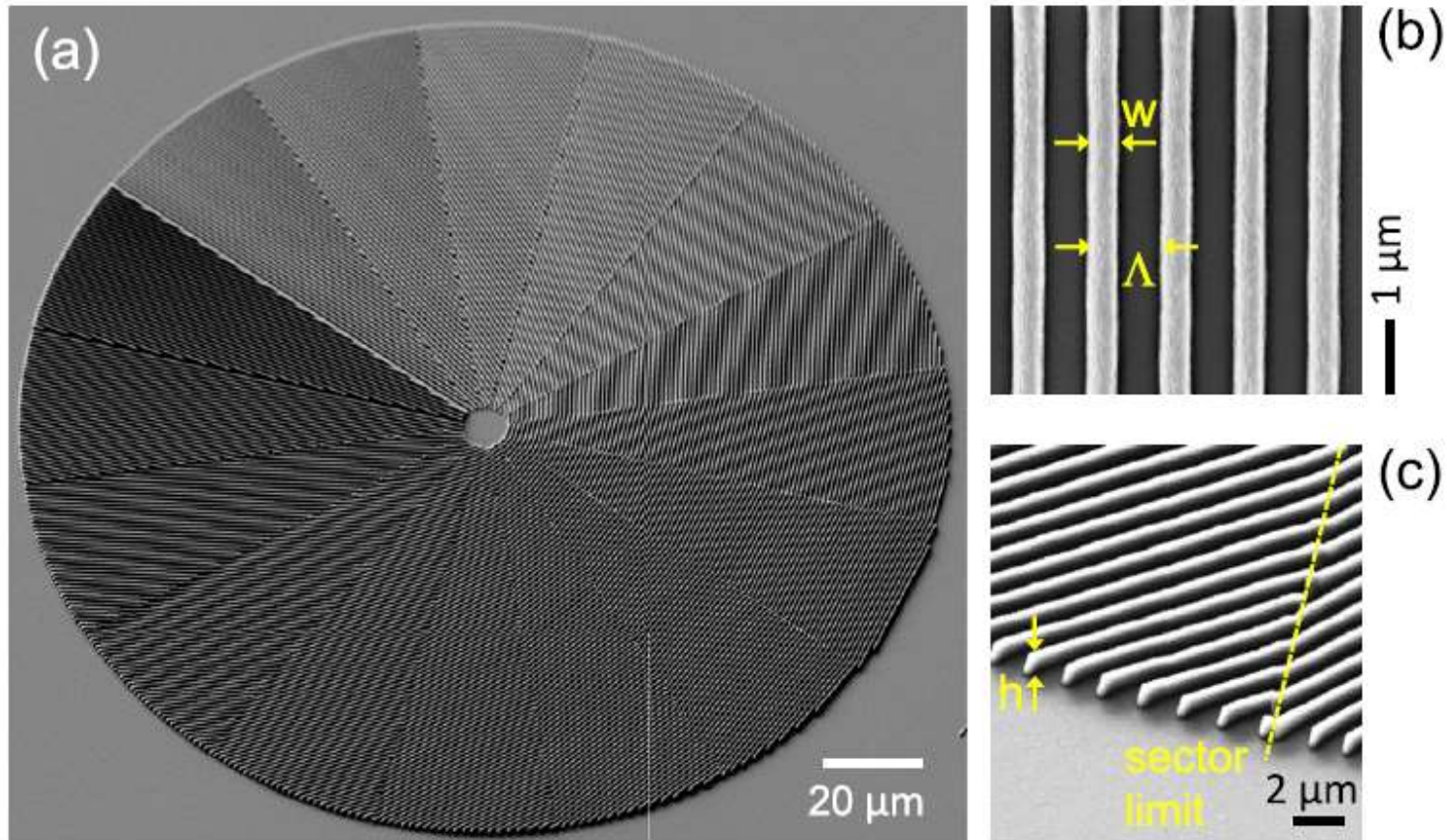
# Laser Generation and Printing of Silicon Nanoparticles



**Barchanski, Evlyukhin,  
Koroleva, Reinhardt, Sajti,  
Zywietz and Chichkov  
2014**



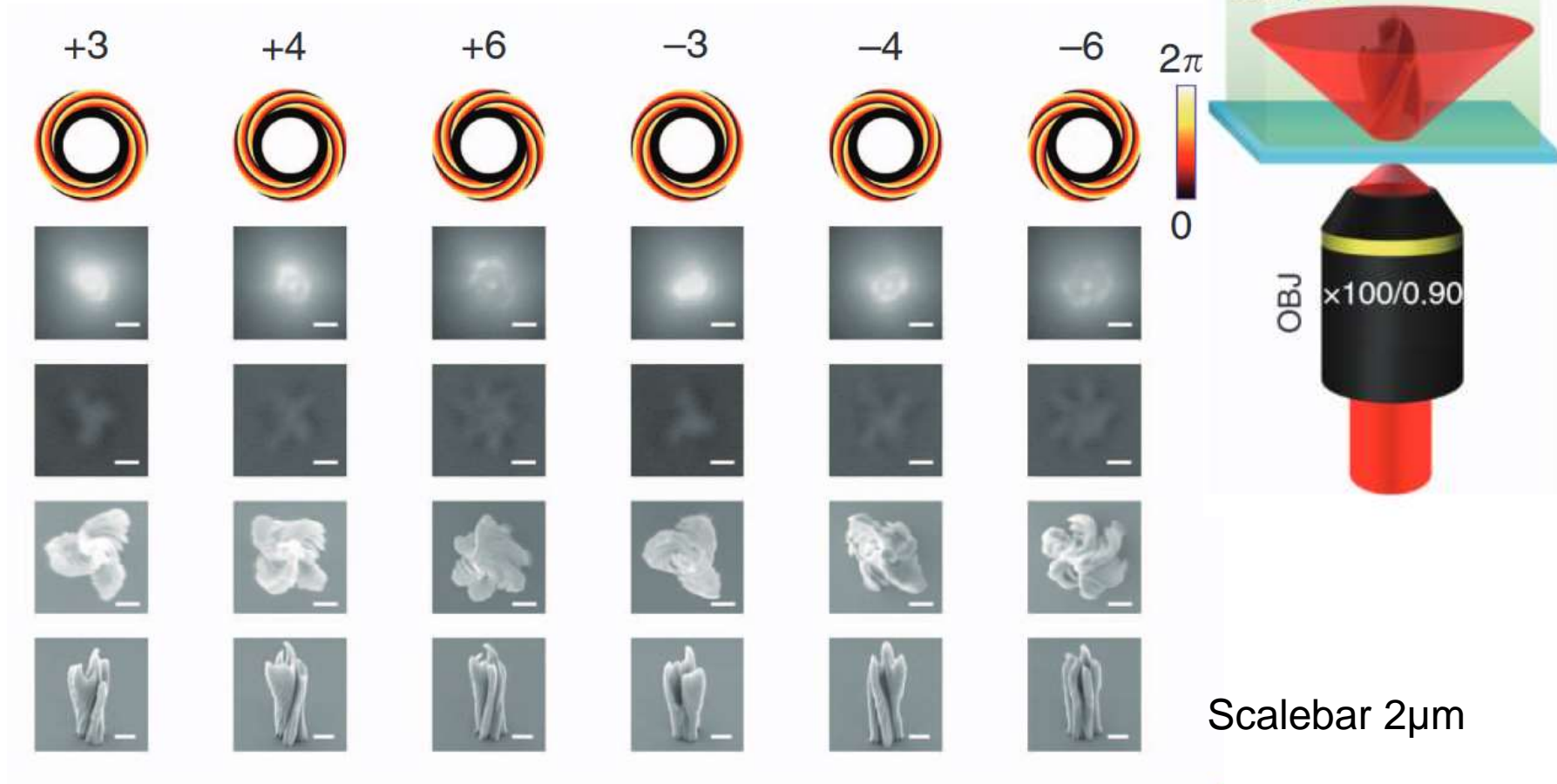
# Photopolymerisation direct laser writing in photoresists



**geometric phase optical elements**

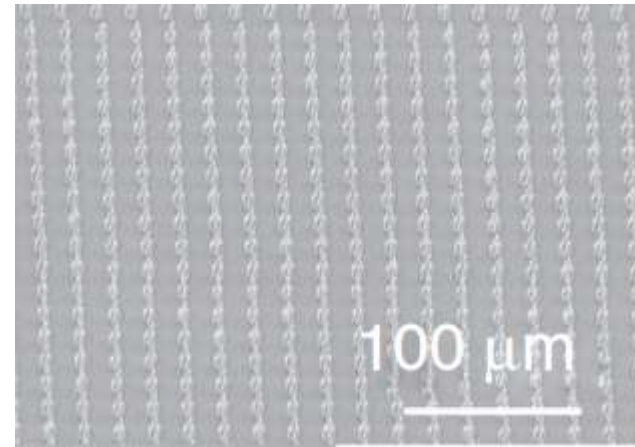
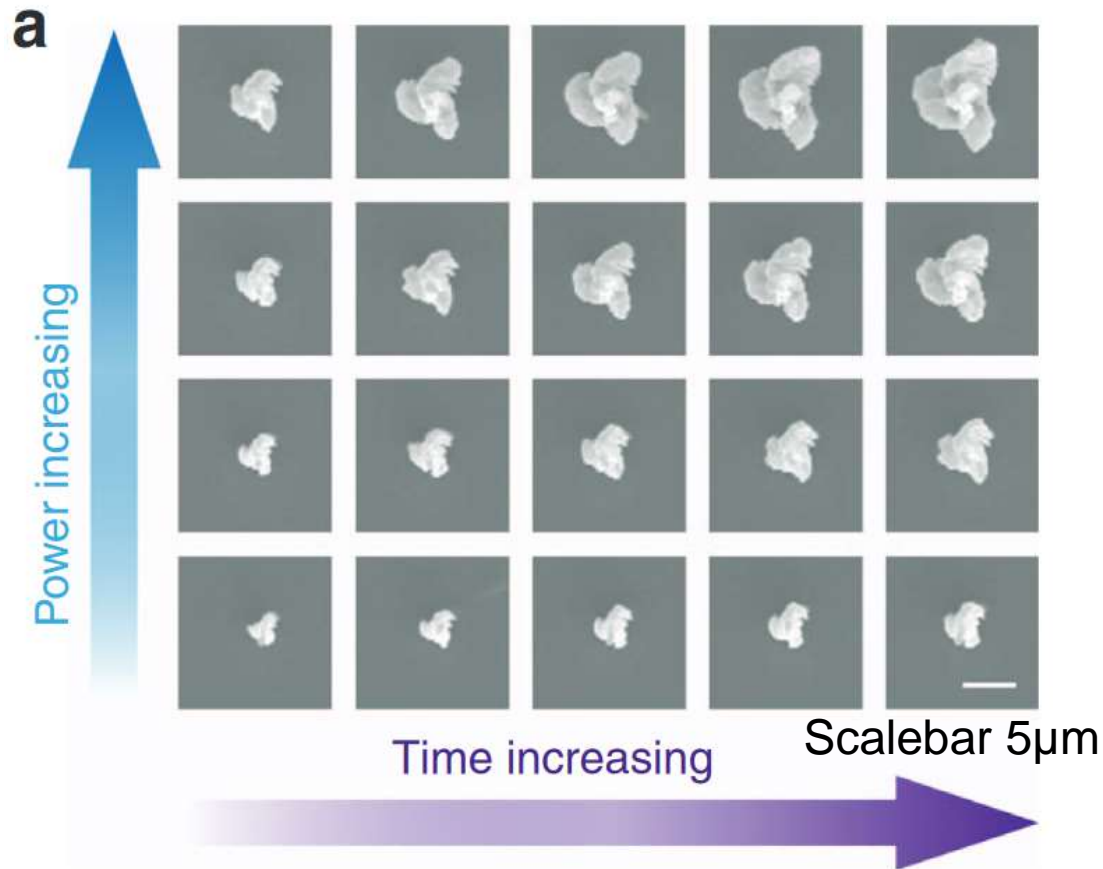
Wang et al. Appl. Phys. Lett. 110, 181101 (2017)

# Laser-assisted fabrication of 3D chiral microstructures



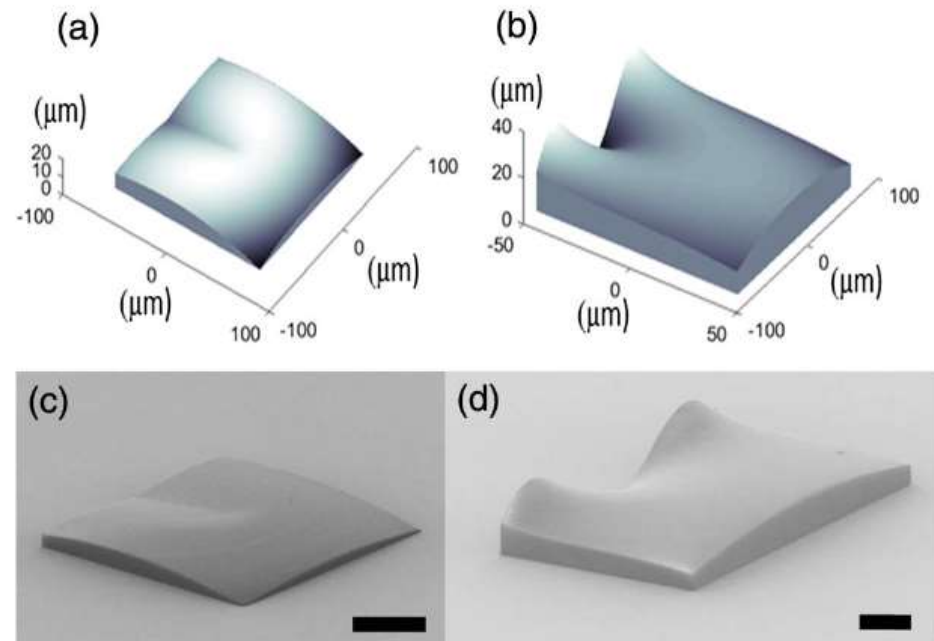
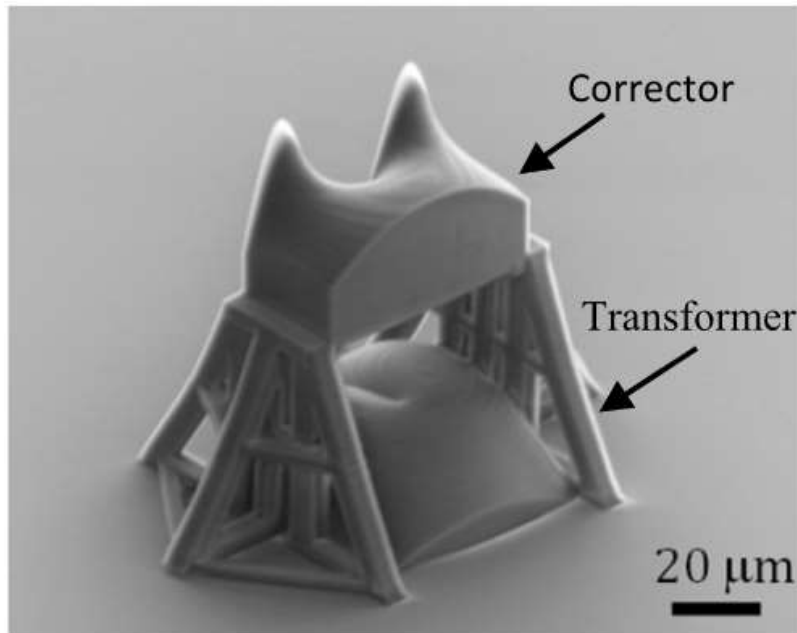
J. Ni et al. Light: Science & Applications (2017) 6, e17011

# Laser-assisted fabrication of 3D chiral microstructures



J. Ni et al. Light: Science & Applications (2017) 6, e17011

# Mode sorter for vortex beams produced by 3D laser printing



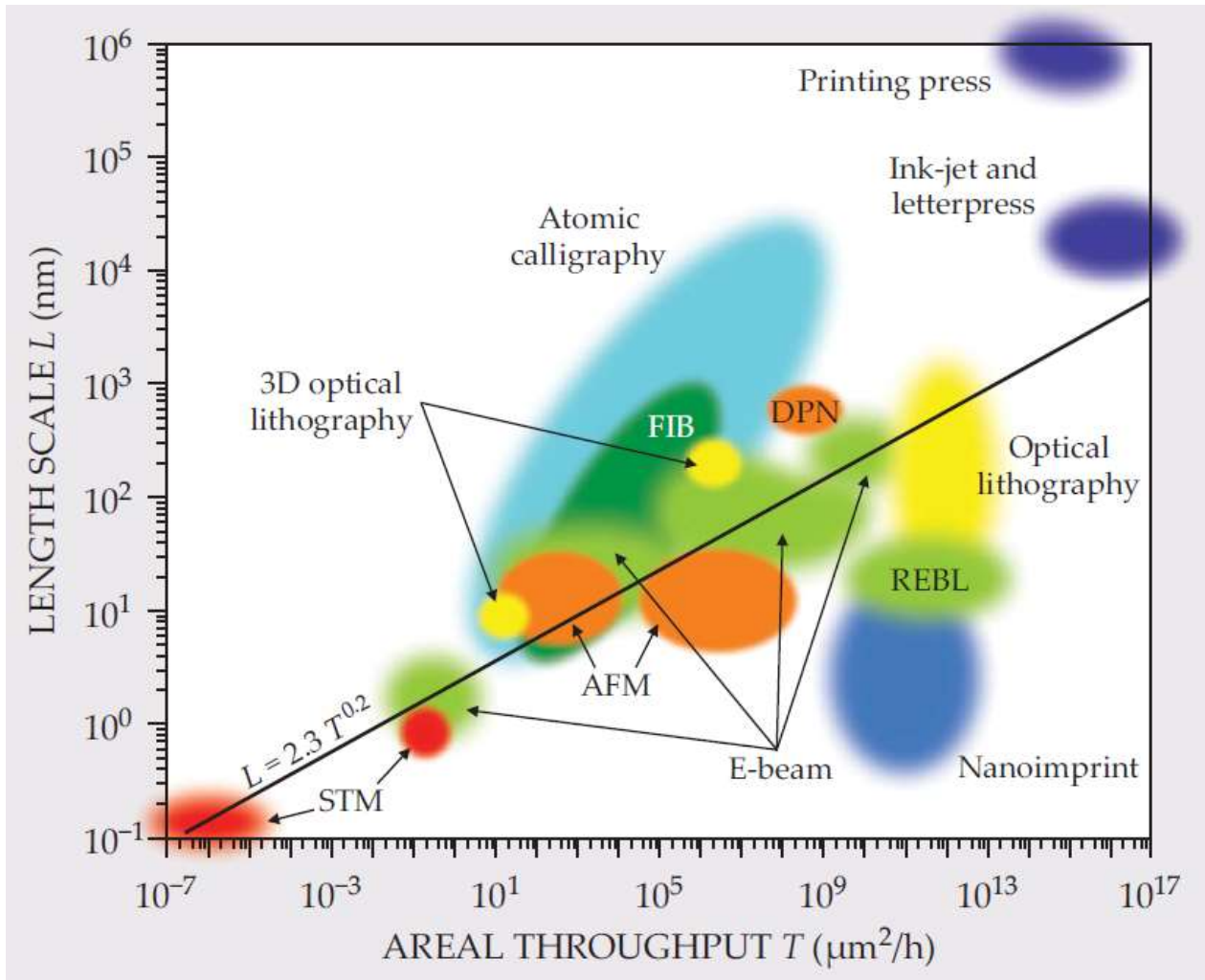
**Fig. 1.** Top: Theoretical (de)multiplexer designs of the (a) transforming and (b) correcting elements. Bottom: (c, d) SEM images of the above-fabricated elements. Scale bars are 25 μm.

LIGHTMAN et al., *Optica* 4 (2017) 605

S. Lightman et al. *Optica* (2017) 4, 6051

Scalebar 25μm

# Nanomanufacturing



Imboden and Bishop, **Top-down nanomanufacturing**, Physics Today **67**, 45 (2014)

# Conclusions

Nanofabrication deals with

Precision

Resolution

Process Speed

Area to be treated

Cost

2D layer by layer or 3D direct writing

Sometimes low-cost bottom-up methods give excellent results

# Acknowledgements



Frédéric BEDU



Benjamin  
DEMIRDJIAN



Julien PROUST



Yeon Ui LEE



Jeong Weon WU



Nicolas BONOD

Thank you for your attention!