

Nanofabrication methods for Plasmonics

G. Lérondel

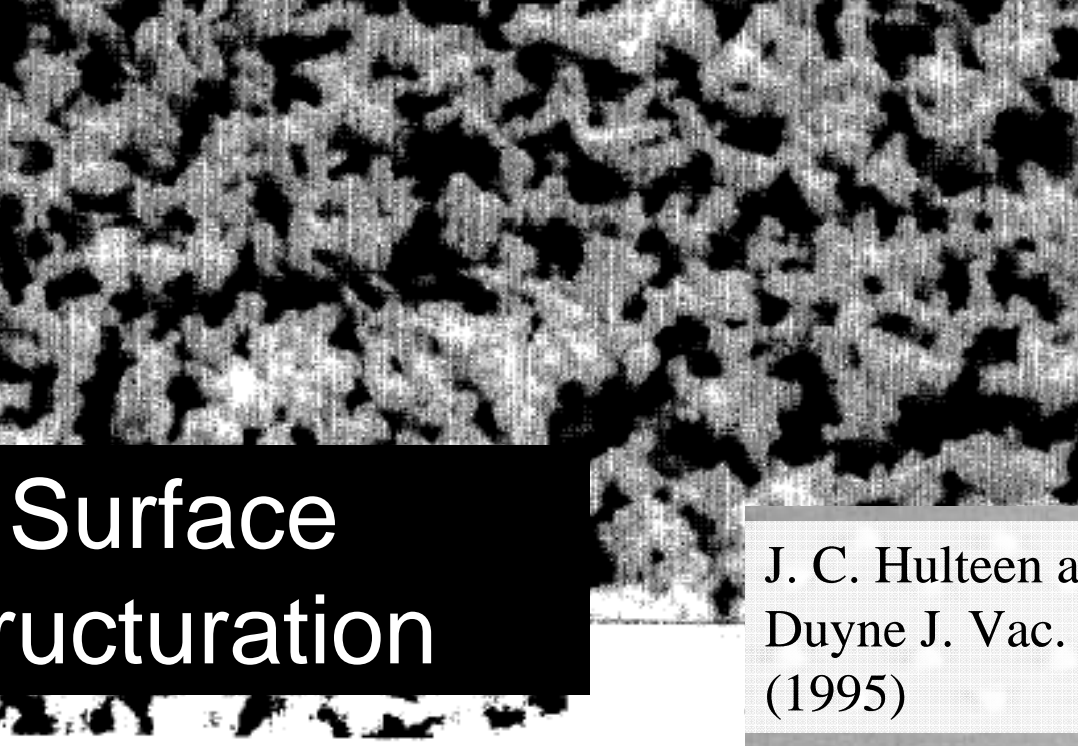
J. Plain and S. Kostcheev

Laboratory for Nanotechnology and Optical Instrumentation
ICD

History

Lithography

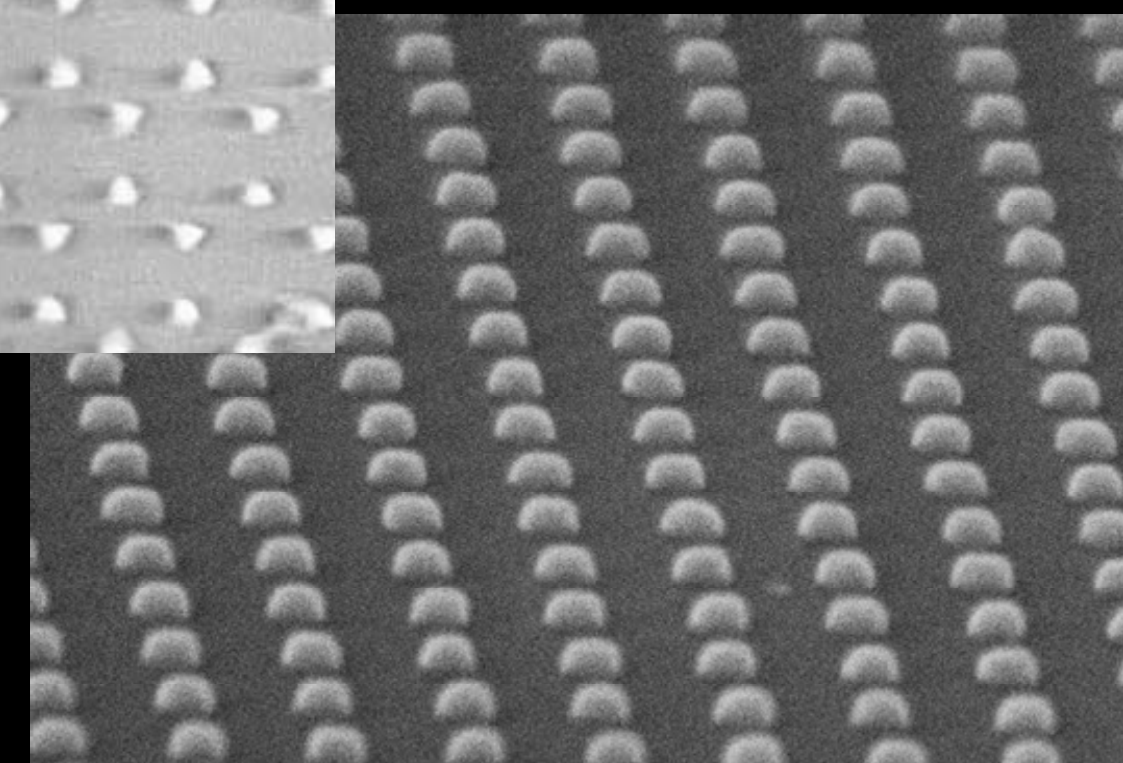
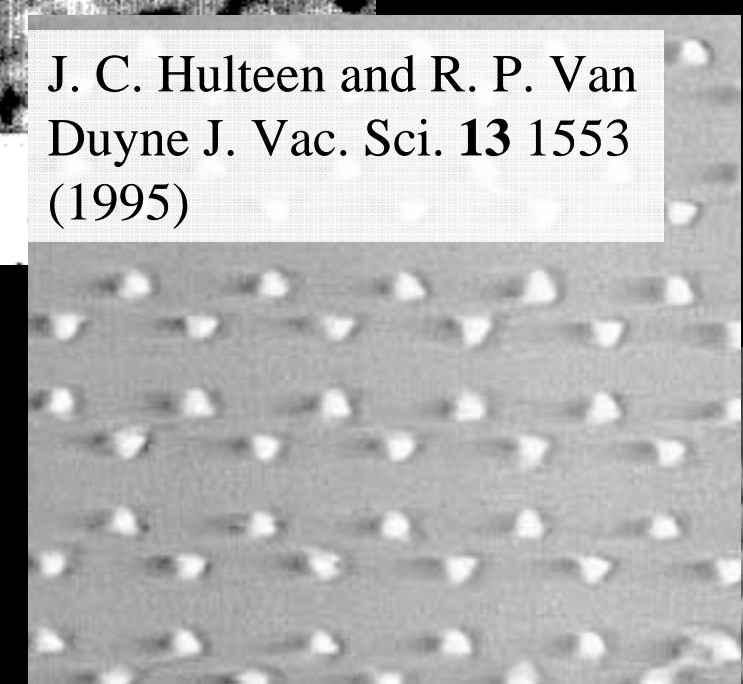
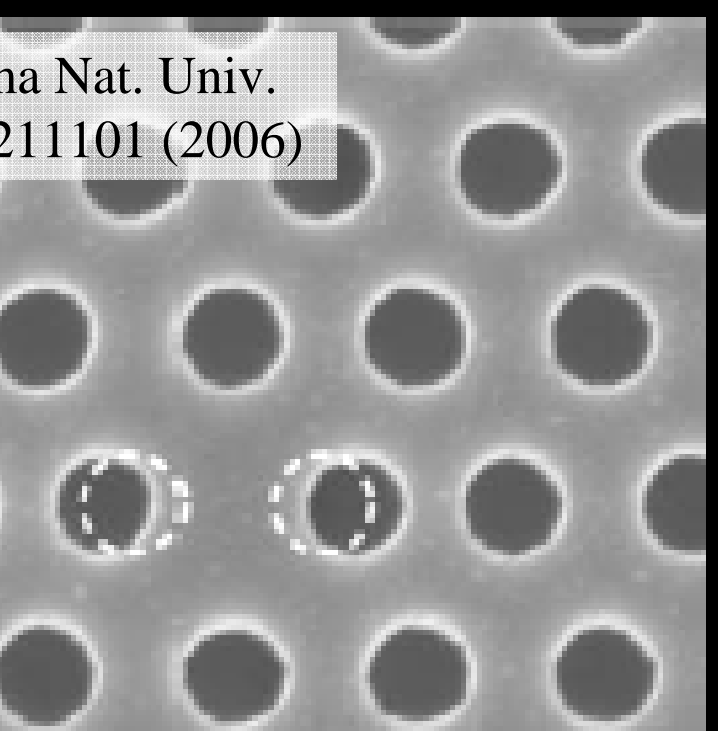
Surface Structuration



J. C. Hulteen and R. P. Van
Duyne *J. Vac. Sci.* **13** 1553
(1995)

Nanofabricatio

na Nat. Univ.
211101 (2006)

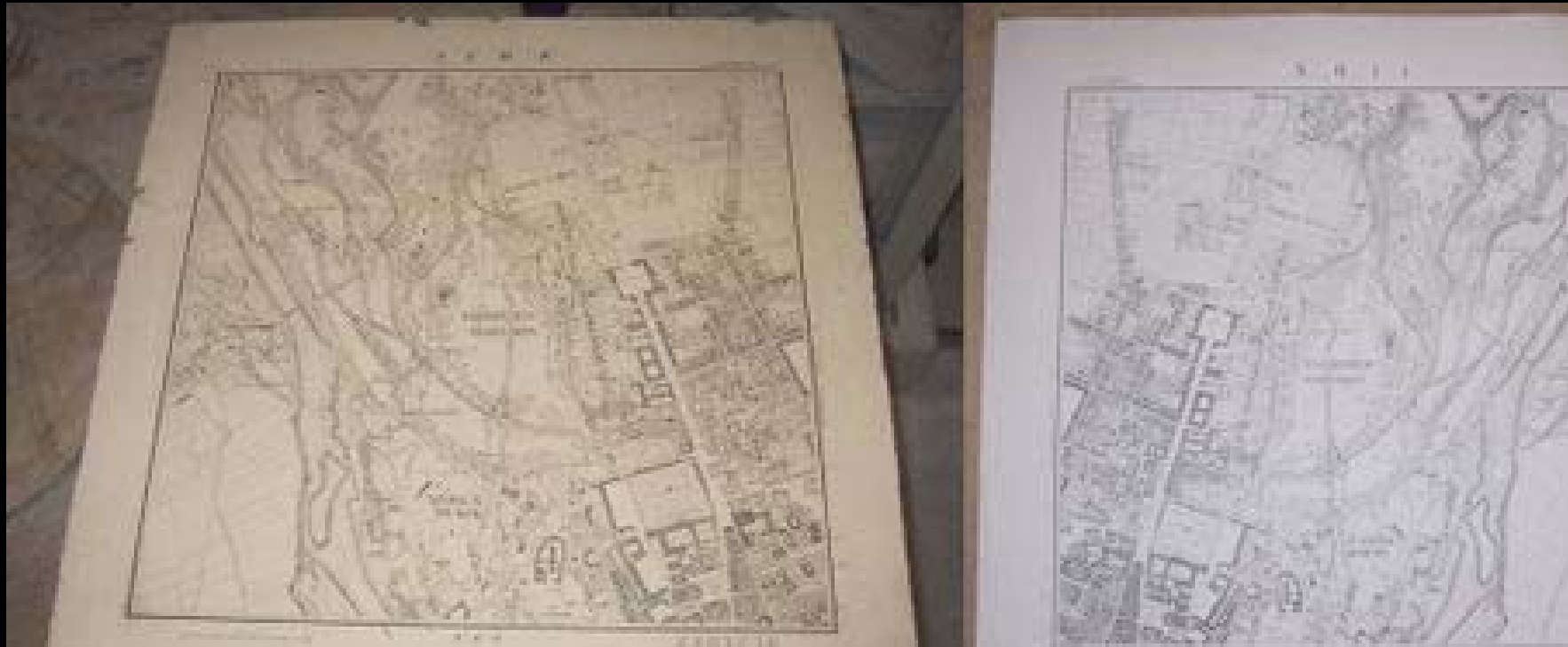


Lithography

Media :

Lithography is a printing process that uses **chemical processes** to create an **image (inv. 1796)**.

Lithography stone and mirror-image print of a map of Munich.



Lithography

Micro and nanoelectronics

Gate width

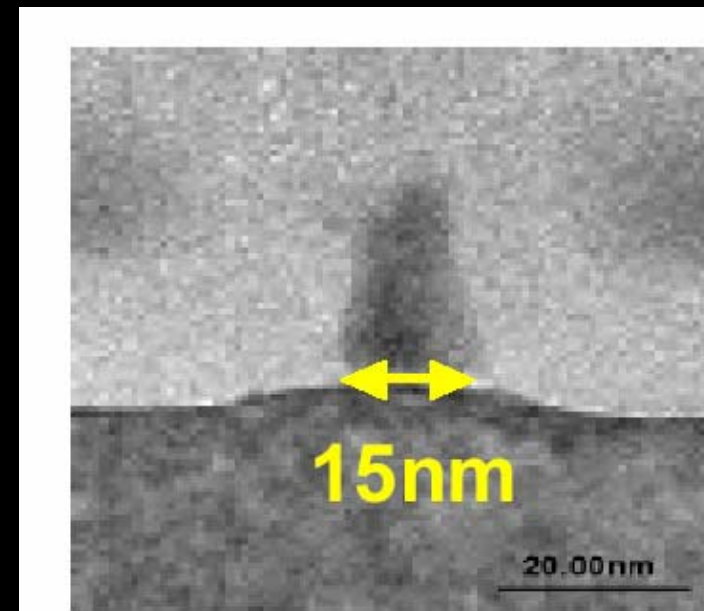
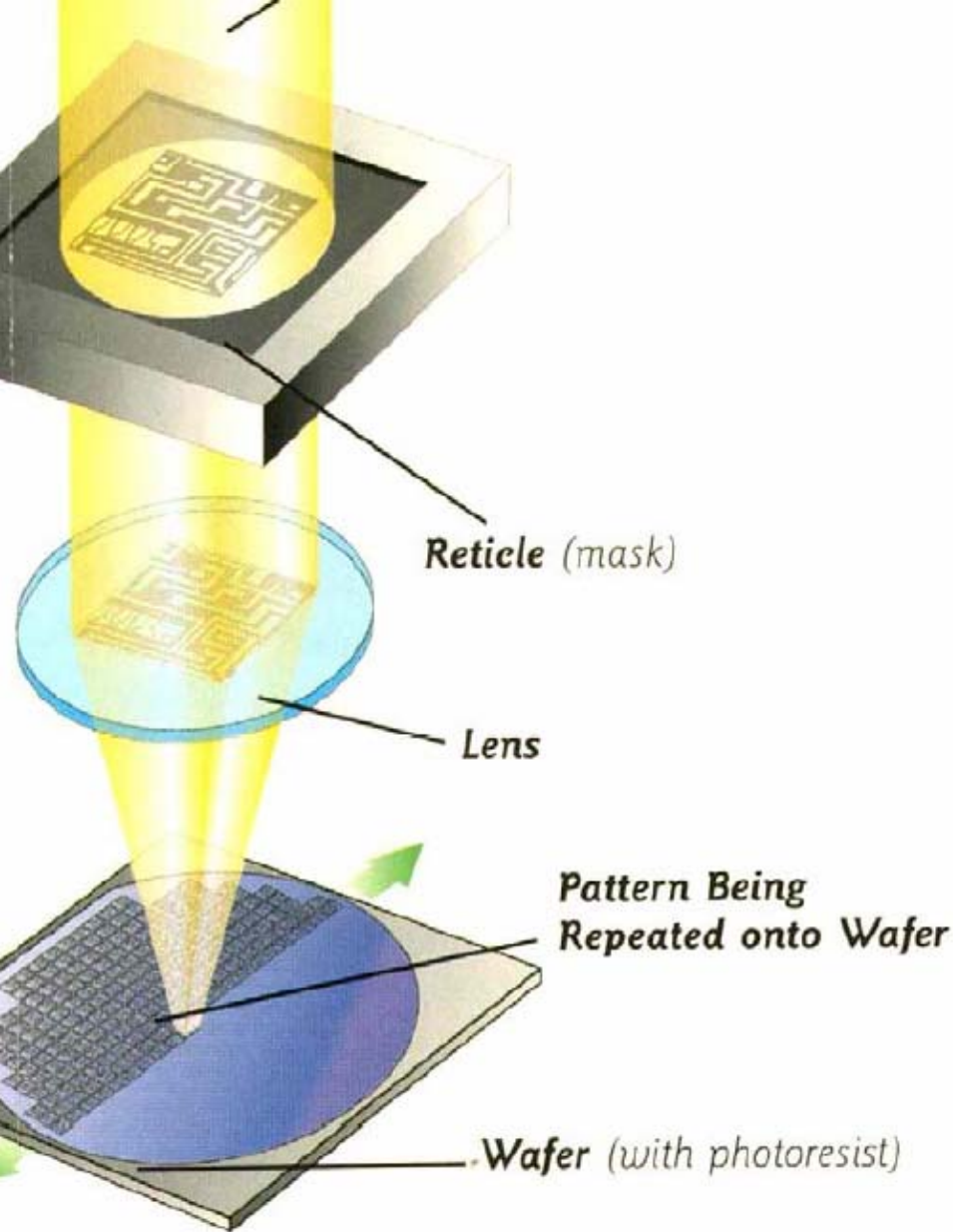
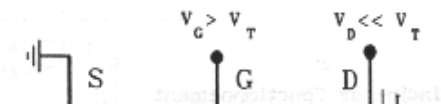


Figure 5: TeraHertz transistor with 15nm gate width

1mm in 1970



Inkjet lithography

E-beam lithography

I-beam lithography

Laser writing

Interference lithography

Self assembling

NA assisted lithography

Lithography glossary

Dip pen lithography

SNOM lithography

Embossing

Imprint

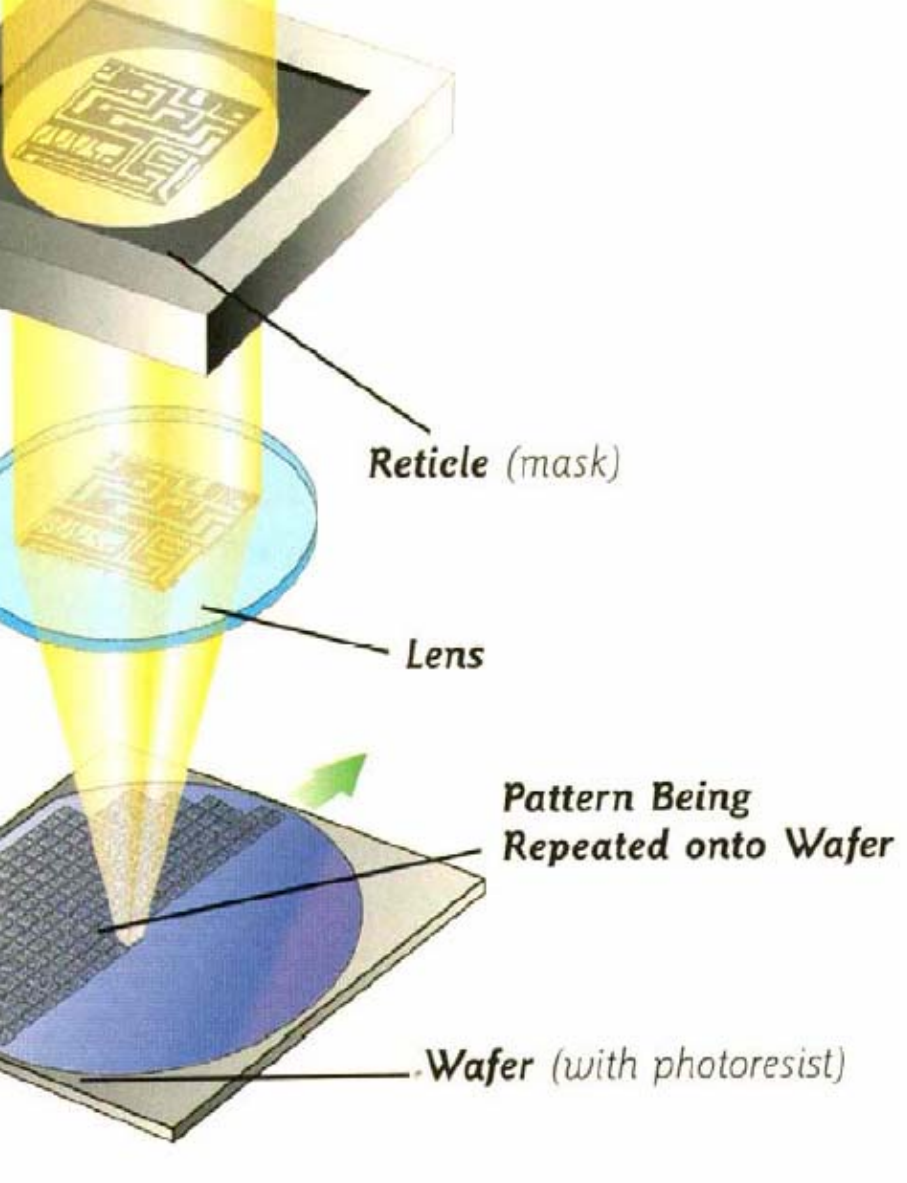
DIE CAIBE IBE

Content

- Introduction
- Conventional techniques
- Alternative techniques
- Emerging techniques and fourth coming issues
- Plasmonics for nanofabrication

Conventional Techniques

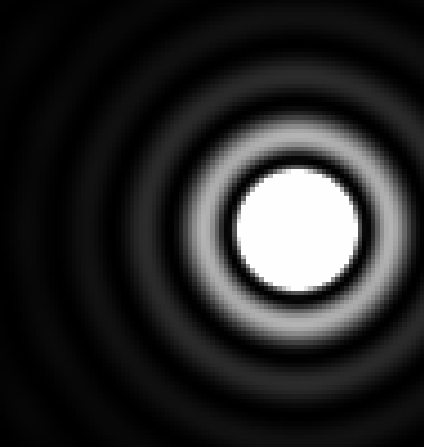
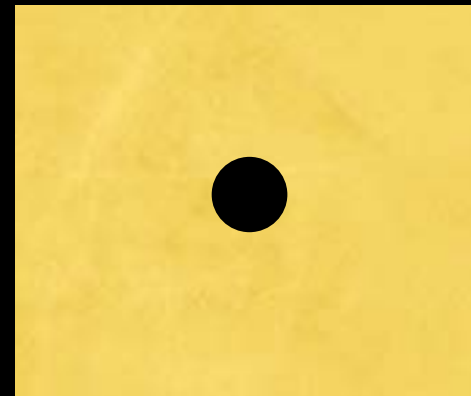
Photolithography



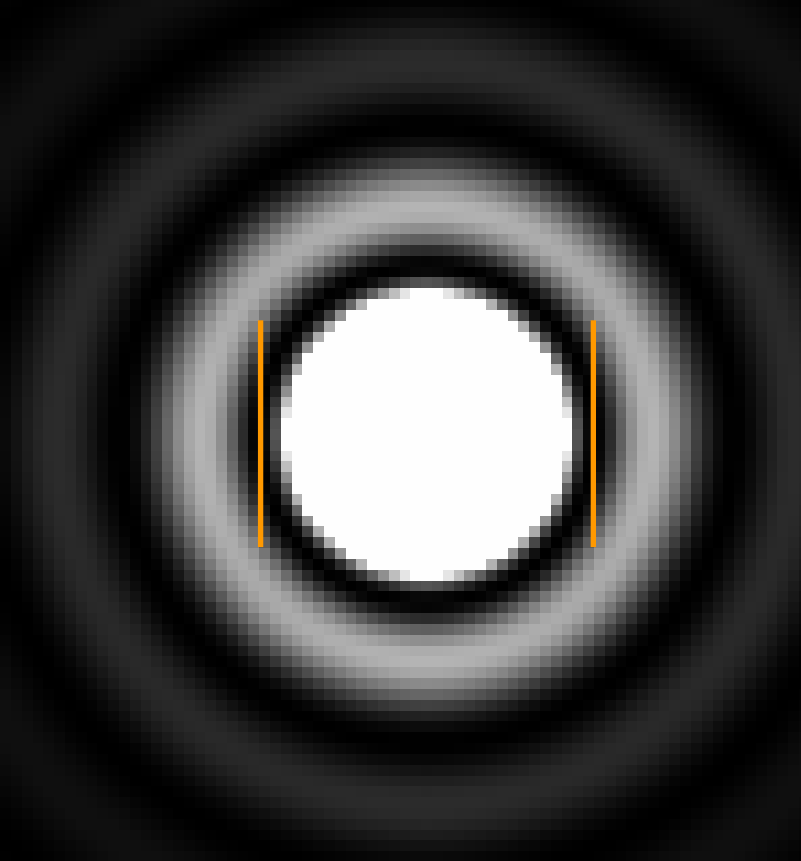
Projection type



Diffraction limited



Resolution



$$a_{\min} = 1.22 \frac{\lambda}{n \sin \theta}$$

on theory for a pinhole

$$E_0 \left(\frac{2J_1(ka \sin \theta)}{ka \sin \theta} \right)^2$$

Bessel function of the first kind

How to reduce a_{\min} ?

Solution

What is the smallest aperture you can obtain exposing in air a photoresist using a green laser ($\lambda = 515\text{nm}$) and a microscope objective of $\text{NA} = 0.5$?

$$a_{\min} = 1.24 \mu\text{m}!!!$$

Reduce Wavelength

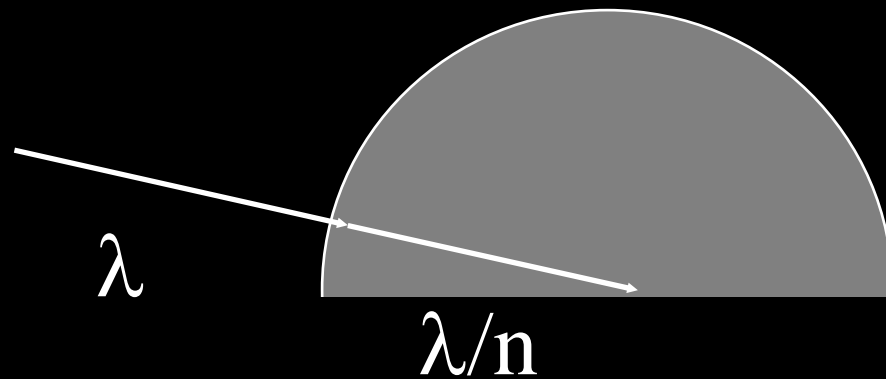
$$a_{\min} = 1.22 \frac{\lambda}{n \sin \theta}$$

Immersion lithography

Increase $\theta \sim \pi/2$ ($a_{\min} = 0.62 \mu\text{m}$)

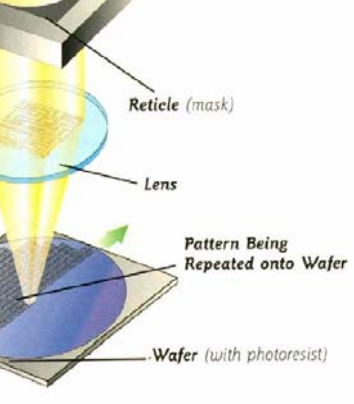
Liquid... water ($a_{\min} = 0.47 \mu\text{m}$)

Solid Immersion Lenses (SIL)



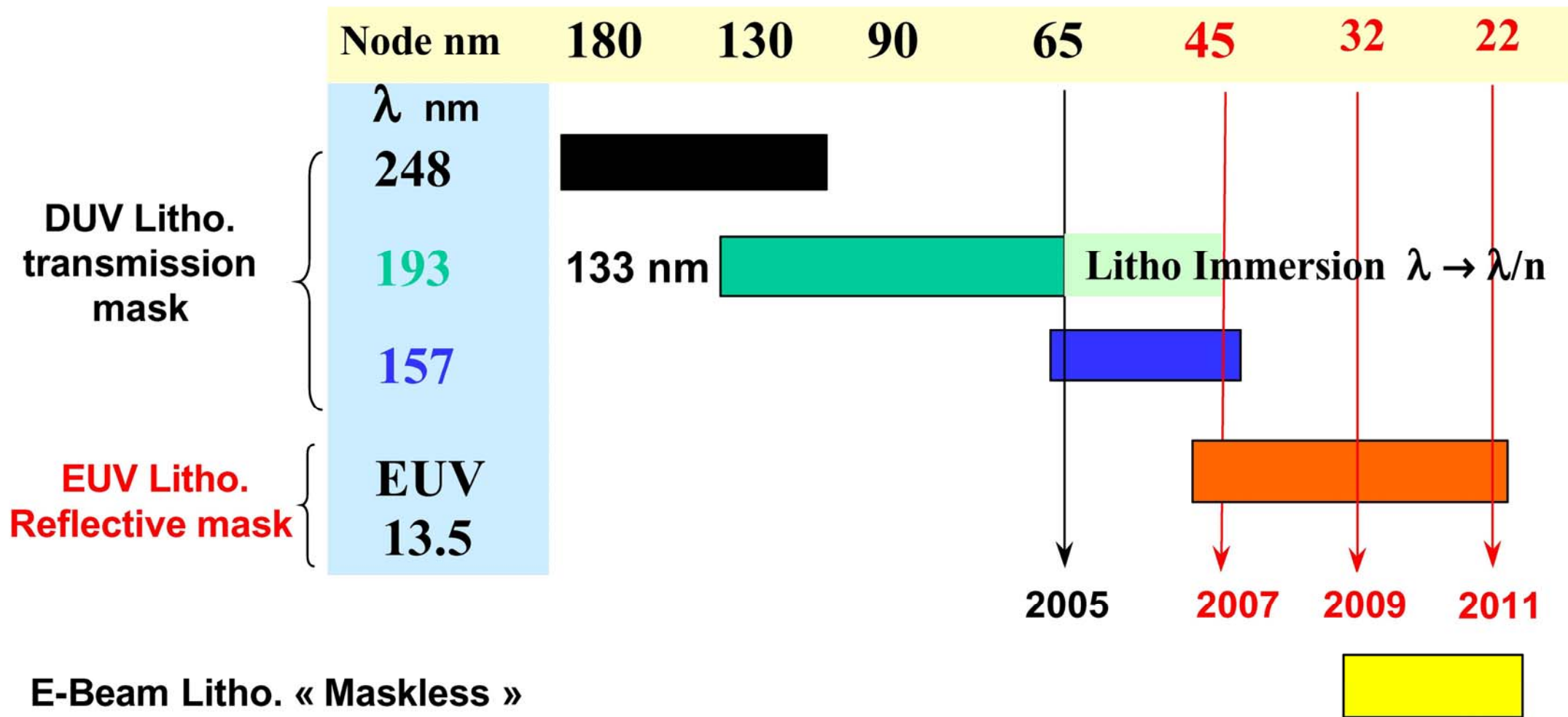
(Si_3N_4 $n = 2.5$)

$a_{\min} = 0.19$



Photolithography

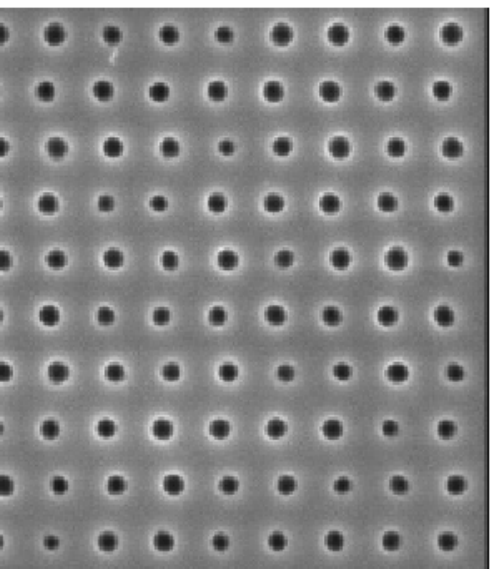
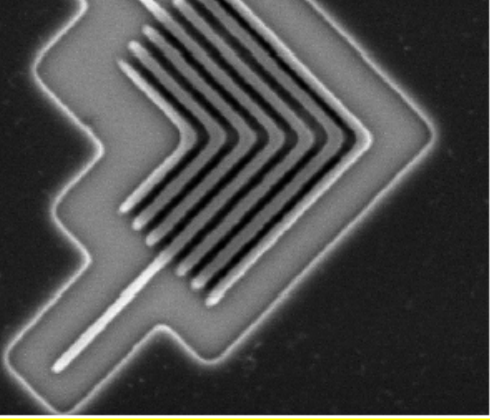
UV, DUP, EUV (X rays)...



EUV lithography

<http://www.xraylith.wisc.edu/ngl/in>

Soft X rays (10nm) $a_{\min} = 10\text{nm} !$



n lines and contacts patterned with a 0.1NA prototype EUV exposure tool

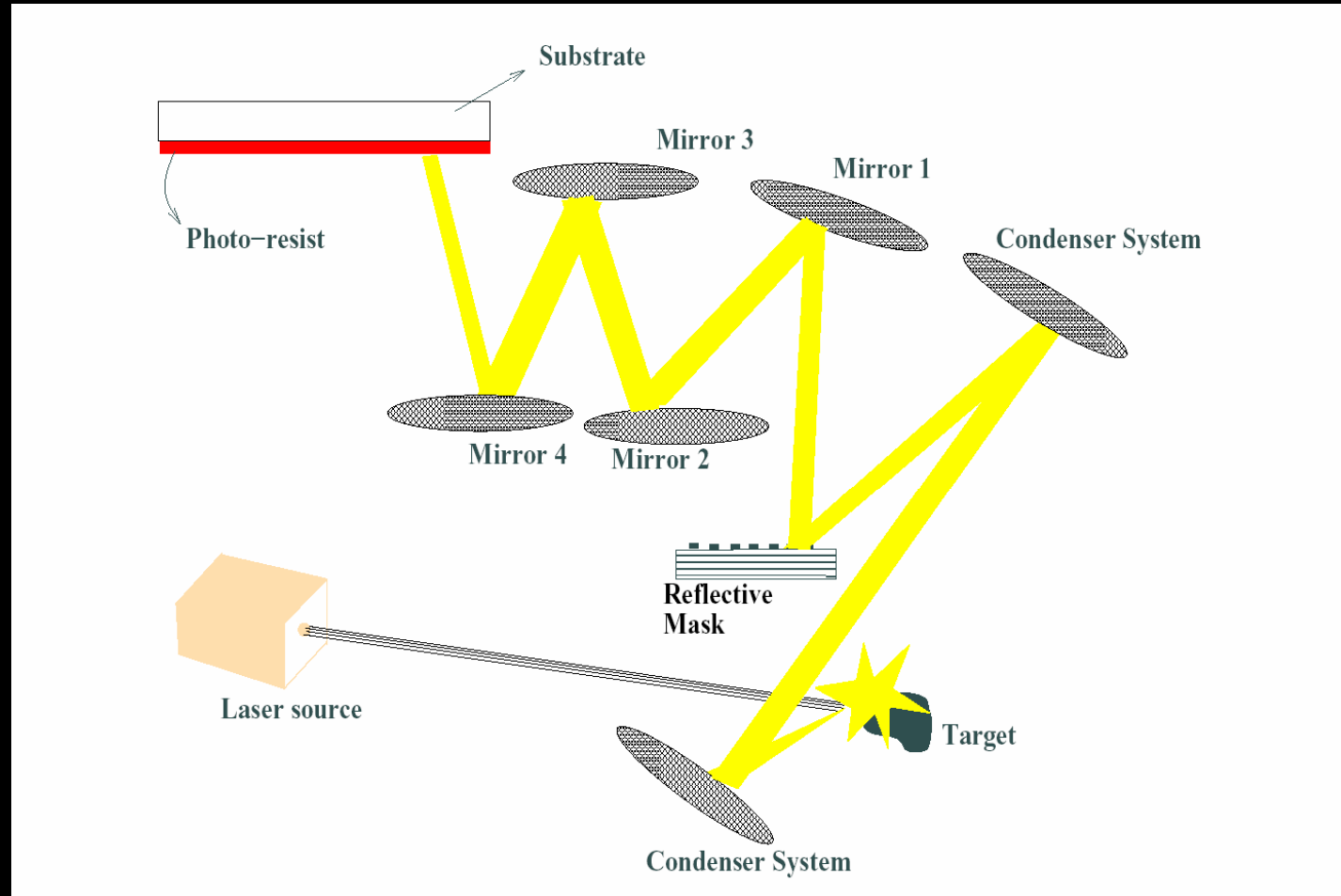
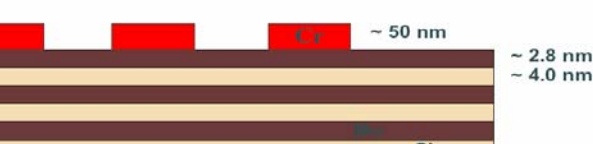
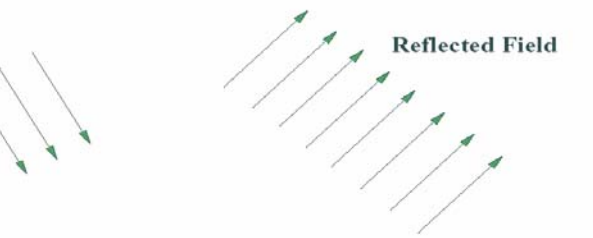


Figure 1: An artist's rendition of the proposed EUVL system (after Hawryluk A.M [7])

Issues:

Reflection

$$= \frac{h}{mV} = \left(\frac{h}{p} \right)$$

photons

Wave-particle duality

e^- : alternative to light i.e. photon

NR

$$\lambda = \frac{1.226}{\sqrt{E}}$$

with E in eV and λ in nm

$$\lambda = 1.2 \cdot 10^{-2} \text{ nm (E : 10 keV)} < r_0$$

$$\theta = 10 \text{ mrad}$$

R (E > 100 keV)

$$\lambda = \frac{1.226}{\sqrt{E(1.602 \cdot 10^{-19} \text{ J})}}$$

$$\lambda = 3.7 \text{ pm (E : 100 keV)}$$

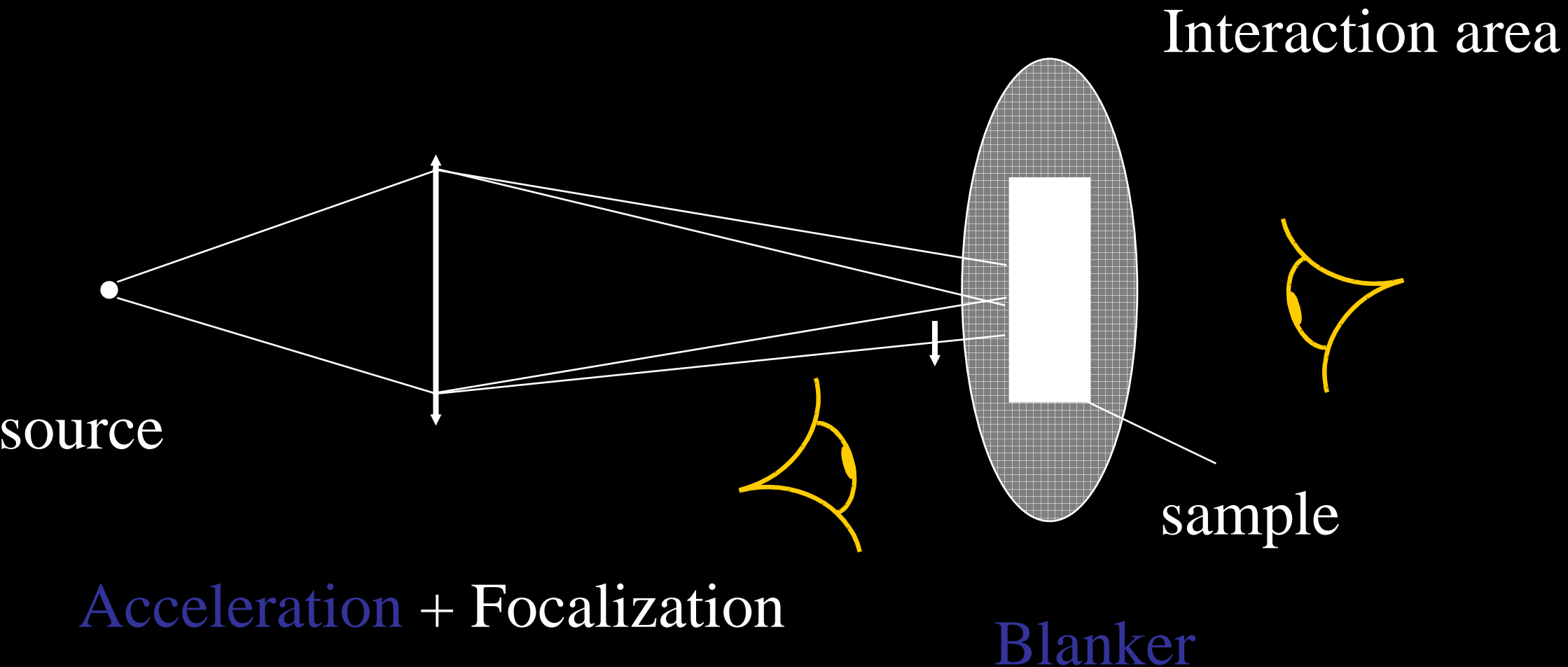
Instrumentation

Electron microscope
(Textbook material)

Electron beam lithography

Electron microscopy

Electron microscope : optical microscope



Source and e⁻ gun

Thermoelectronics emission - (heating: T)

Tungsten filament

Lanthanum Hexaboride LaB₆ filament

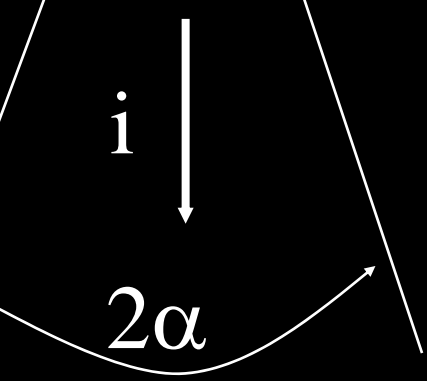
Field emission (electric field induced) – cold emission

Combined

Objective: create an e⁻ pencil that will be then used to

image (expose) the sample surface:

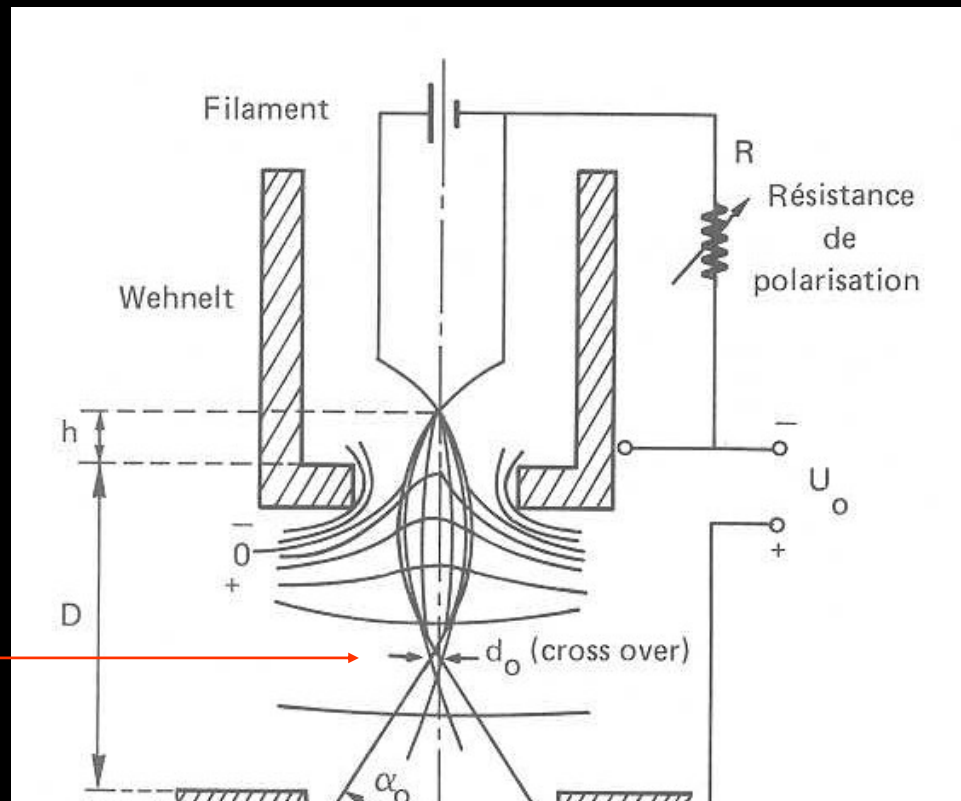
Probe (brightness and size)



$$\beta = \frac{4i}{\pi^2 \alpha^2 d^2}$$

and e⁻ g

Thermoelectronic emission



Real source

Field emission

Tungsten monocrystalline tip ($r=0.1\mu\text{m}$)

Emission through tunneling

e^- density

(Fowler-Nordheim)

$$J = A \frac{E^2}{W_s} \exp\left(-B \frac{W_s}{E}\right)$$

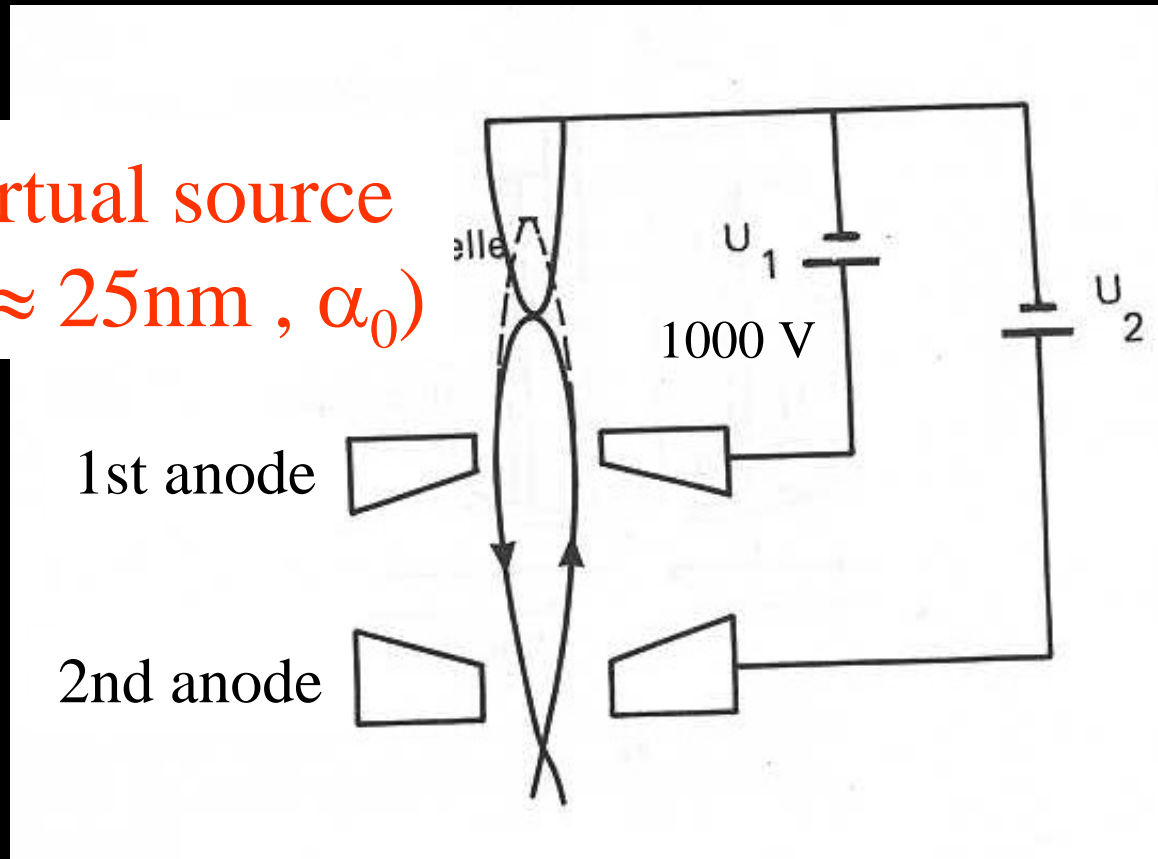
$A=1.4 \cdot 10^{-6}$ $B=4.510^7$ et $E=10^8$

Brightness

$$\beta = \frac{J_0 e U_1}{\pi \Delta}$$

10^9 A

Virtual source
($d_0 \approx 25\text{nm}$, α_0)



Different types of gun

Cathode	Radius of curvature (μm)	Temperature (K)	Cross-over diameter (μm)	Density J_0 (A/cm^2)	Brightness β ($\text{A}/\text{cm}^2/\text{sr}$)	Working time (h)
W	100	2700	50-150	1-2	$2-10 \cdot 10^4$	10-100
W pointe	1	2700	10-20	5	$2 \cdot 10^5$?
LaB ₆	1-10	1900	5-10	50-100	$1-10 \cdot 10^6$	$qq \cdot 10^2$ h
FE	0,1	300 - 1200	0,025	$1-10 \cdot 10^4$	$1-10 \cdot 10^8$	$qq \cdot 10^3$ h

W

LaB₆ (high vacuum)

FE (weak probing intensity, ultra - vacuum)



(electro-)magnetic lenses

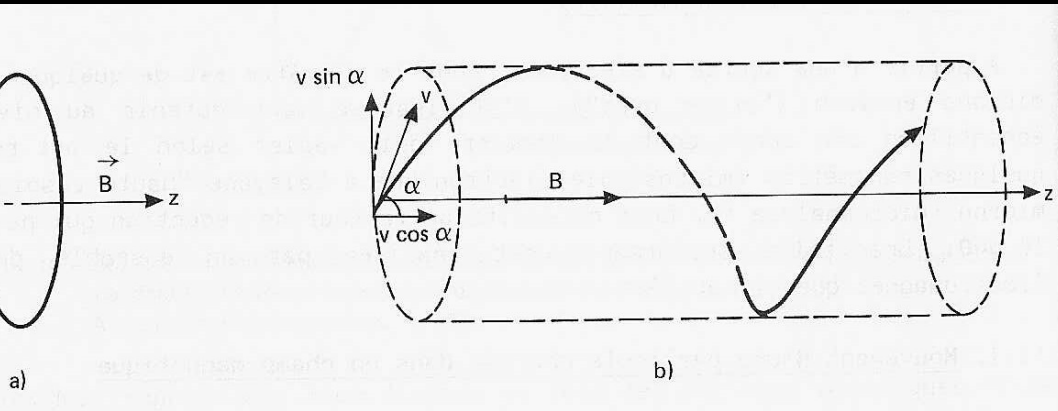
$$\vec{F} = -e \vec{v} \wedge \vec{B}$$

Goal : image the « cross over » on the sample
(size reduction 10 000)

Magnetic field

e^- speed module and energy are constant, only
their trajectory varies

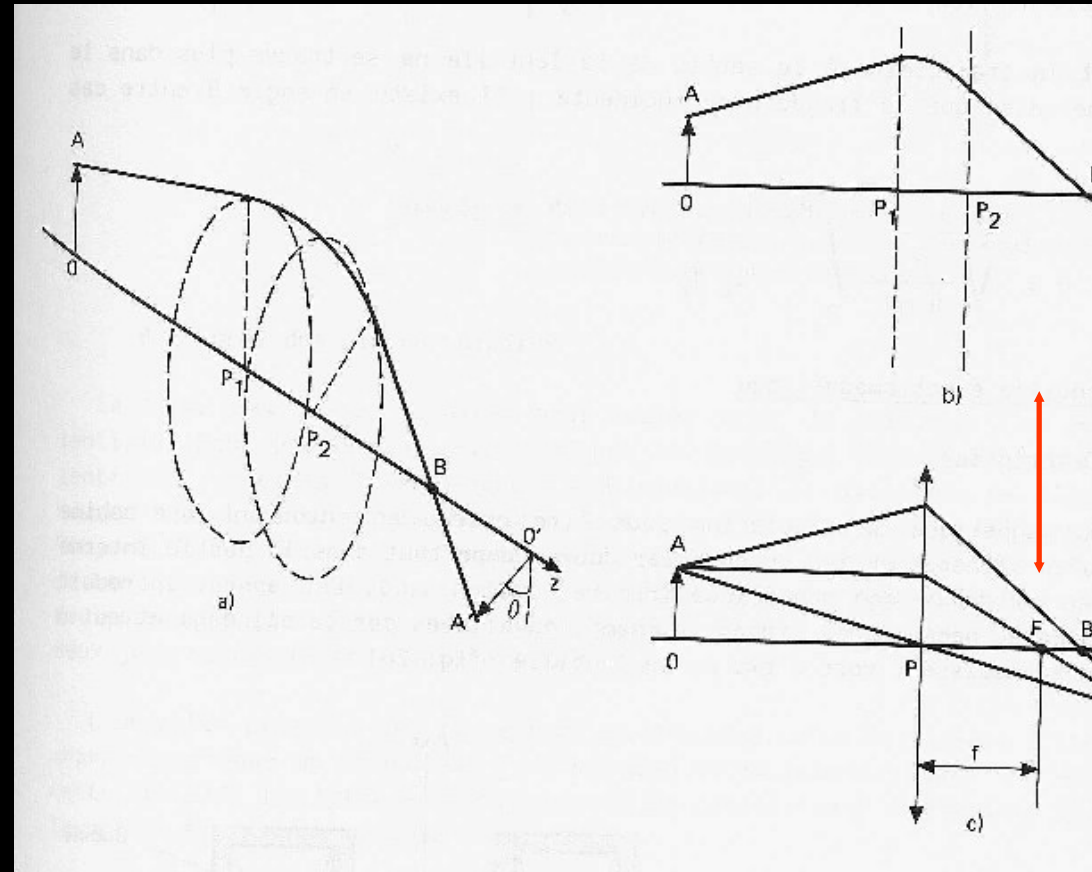
e^- in a magnetic field



Uniform field

$$R = \frac{mv \sin \alpha}{eB}$$

Rapid variation of radial component of the field

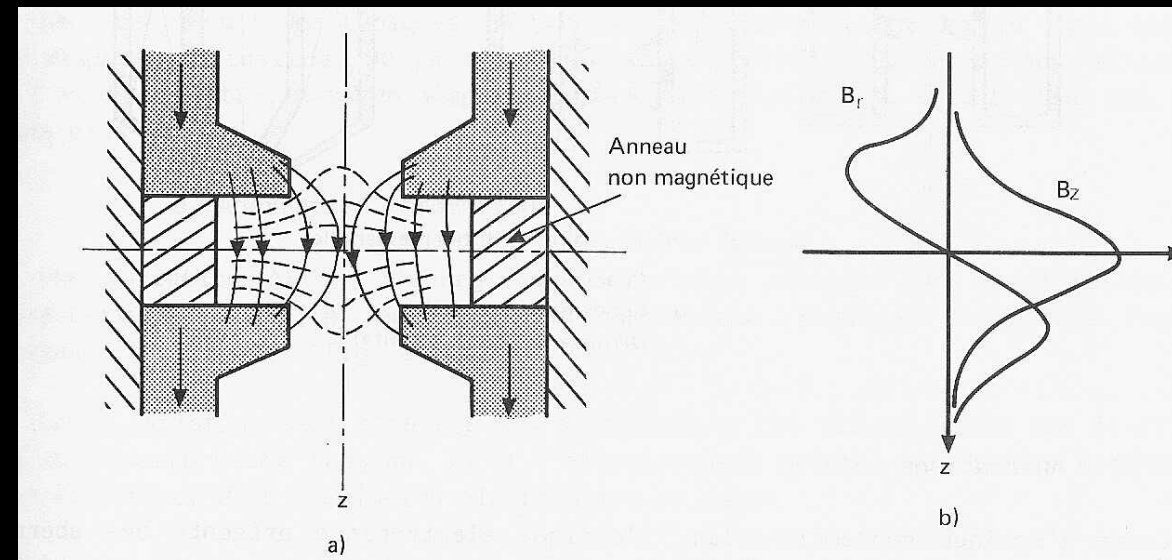
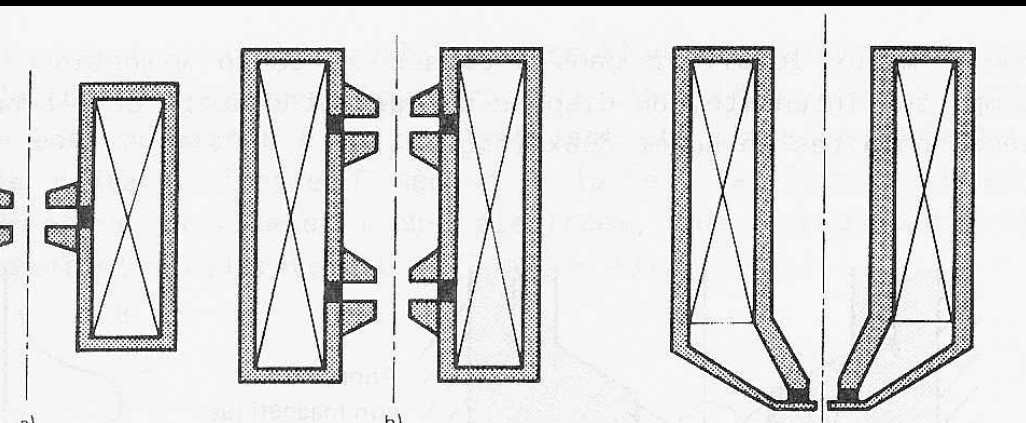


$$\frac{1}{f} = \frac{e}{8mU} \int_{P_1}^{P_2} B_z^2 dz \approx \frac{e}{8mU} B^2 L$$

(electro-)magnetic lenses

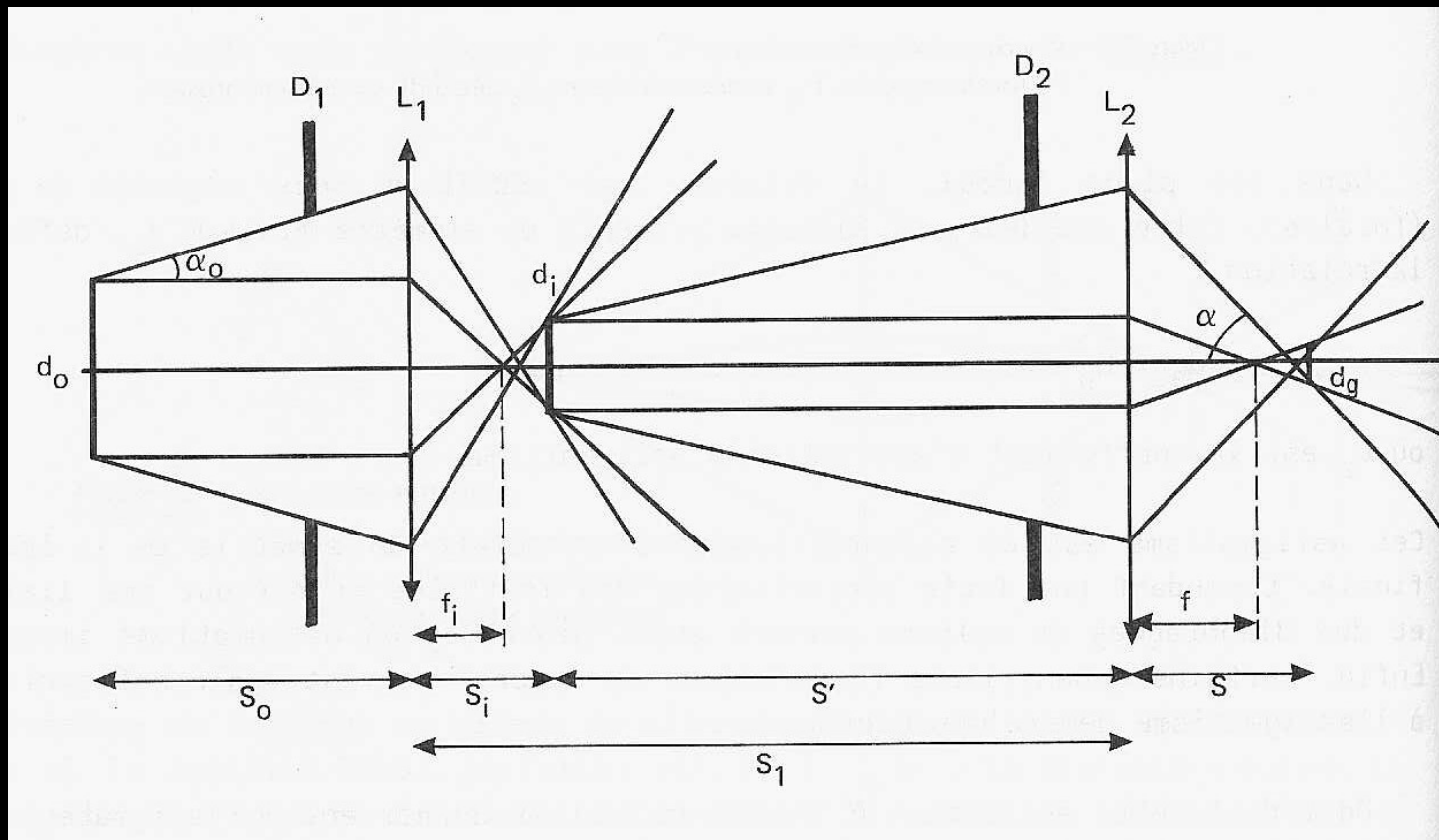
Solenoid surrounding by pure Iron

$$\frac{1}{f} \approx K = \frac{N^2 I^2}{V^*}$$



Beam diameter

Source + 2 electronic (magnetic) lenses



$$\frac{d_0}{d_g} = M_1 M_2 = -$$

$M = 50$ and 10

$S_0 = 20\text{cm}$, $S_1 = 30\text{cm}$ and

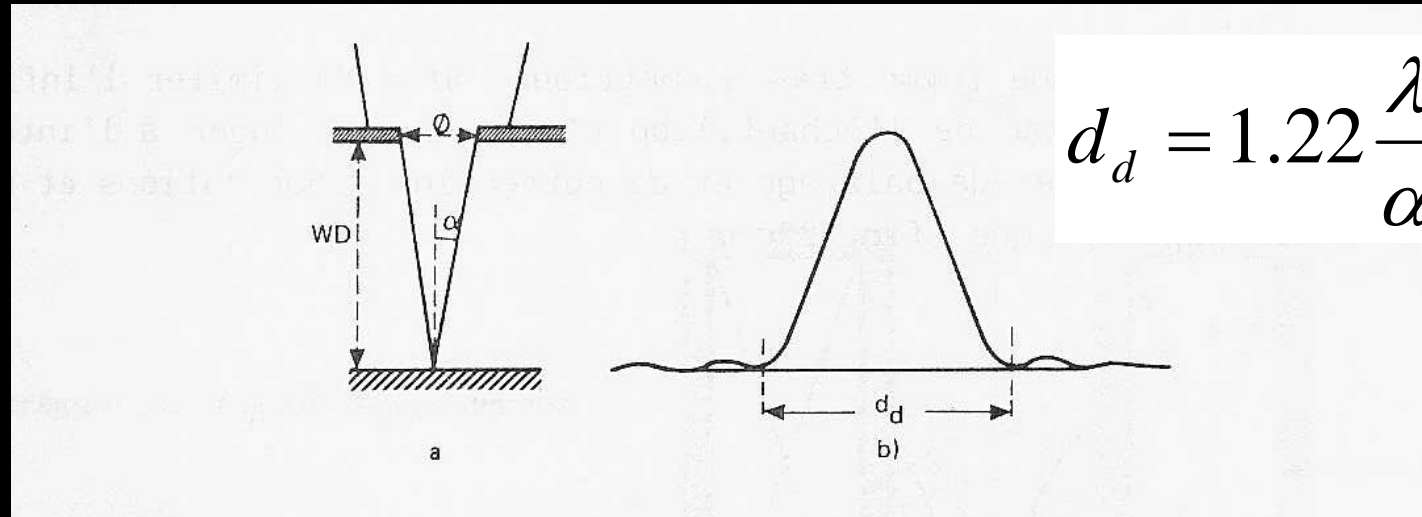
$d_g = 0.5\mu\text{m}$

with a 3rd lens

$\Rightarrow M = 1000$ et 10

Abserrations

Diffraction



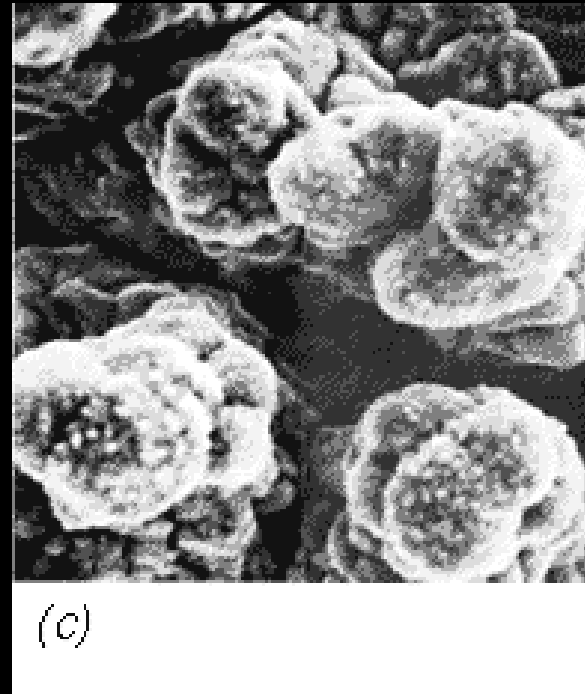
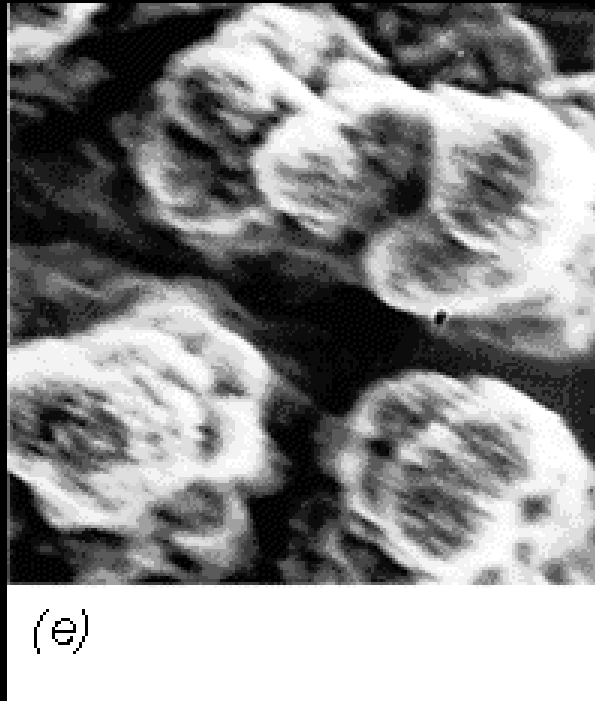
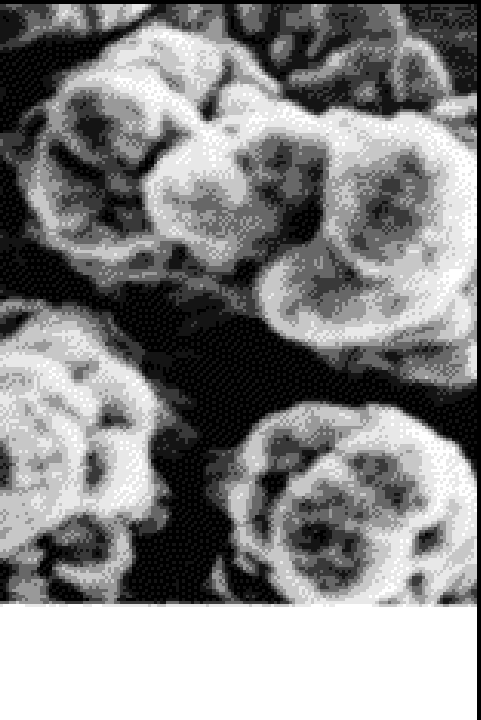
$d_d = 5.2 \text{ nm}$ with $WD = 25 \text{ mm}$, $\lambda = 8.6 \cdot 10^{-3}$ ($E_0 = 20 \text{ keV}$) et $\Phi = 1$

Chromatic (ΔE)

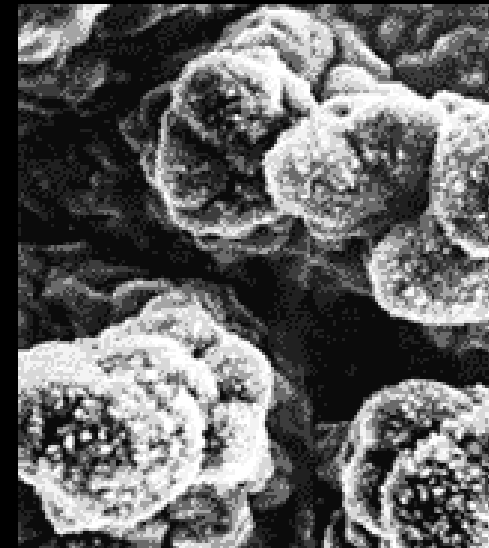
Large $\alpha = \text{small } d$

Spherical ... small α !

Stigmatism...



Focalized with correction
Focalized without correction
Unfocalized without correction
Unfocalized with correction



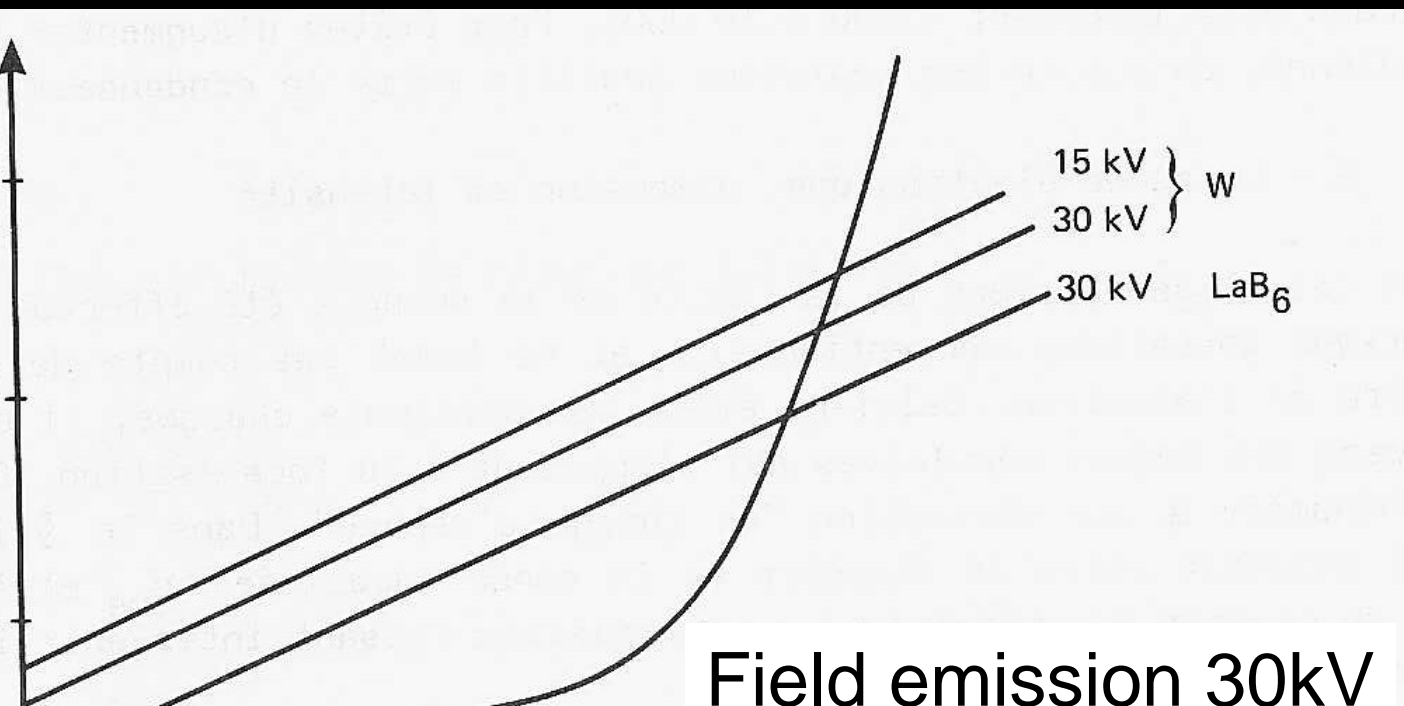
$$d^2 = \frac{1}{\pi^2 \beta \alpha^2} + \frac{1}{4} C_s^2 \alpha^0 \quad (+ \text{ast})$$

the beam

$$d^2 = \sum_i d_i^2 \quad (\text{independent phenomena})$$

Thermoelectronic Emission

$$d \propto i_0 \quad (U \text{ and } \beta)$$



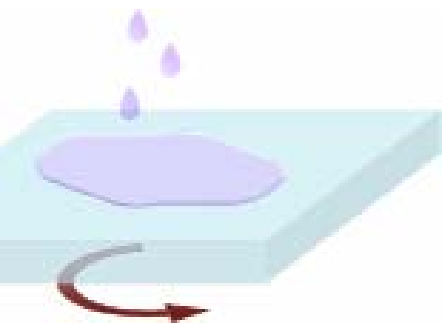
α_{optimum}

$d_{\text{opt.}} \sim \text{a few nanom}$

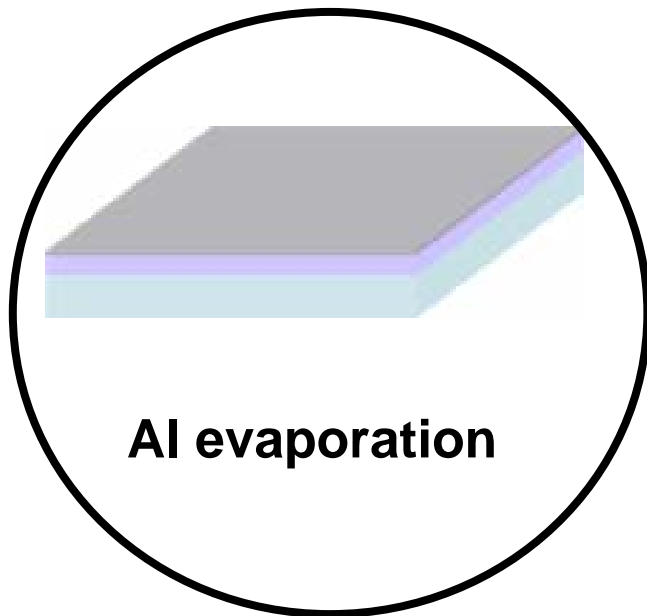
Lithography

Electron beam lithography

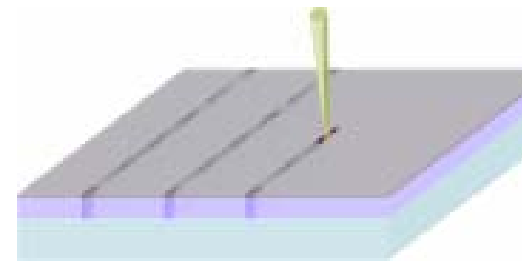
LED array fabrication process



PMMA spin-coating



Al evaporation



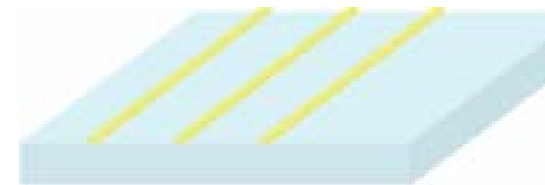
Exposure



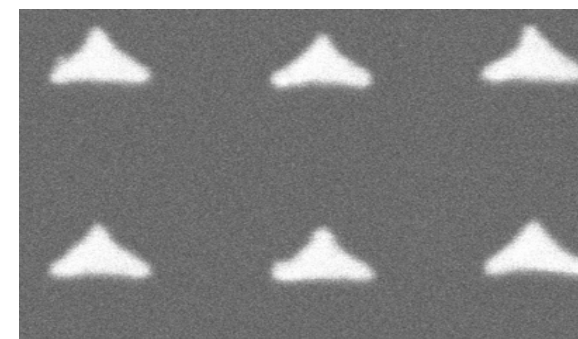
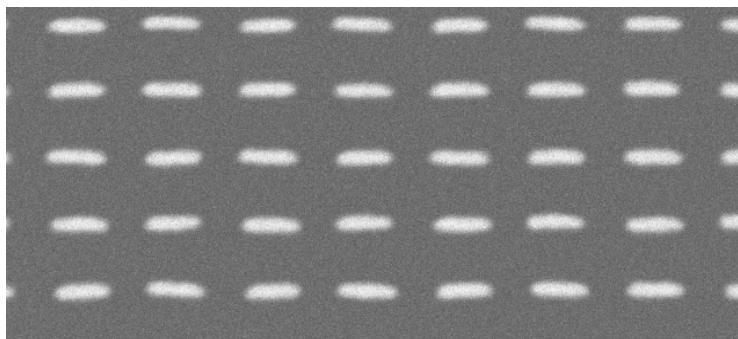
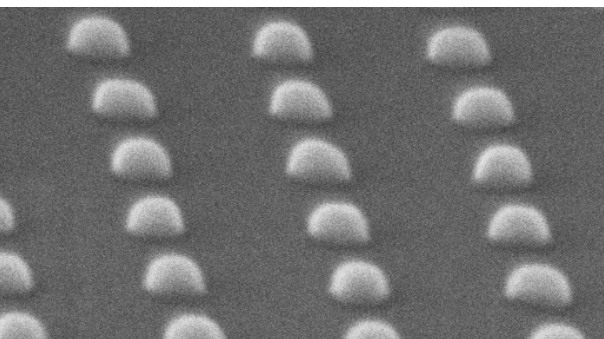
Development (MIBK:IPA)



Metal evaporation

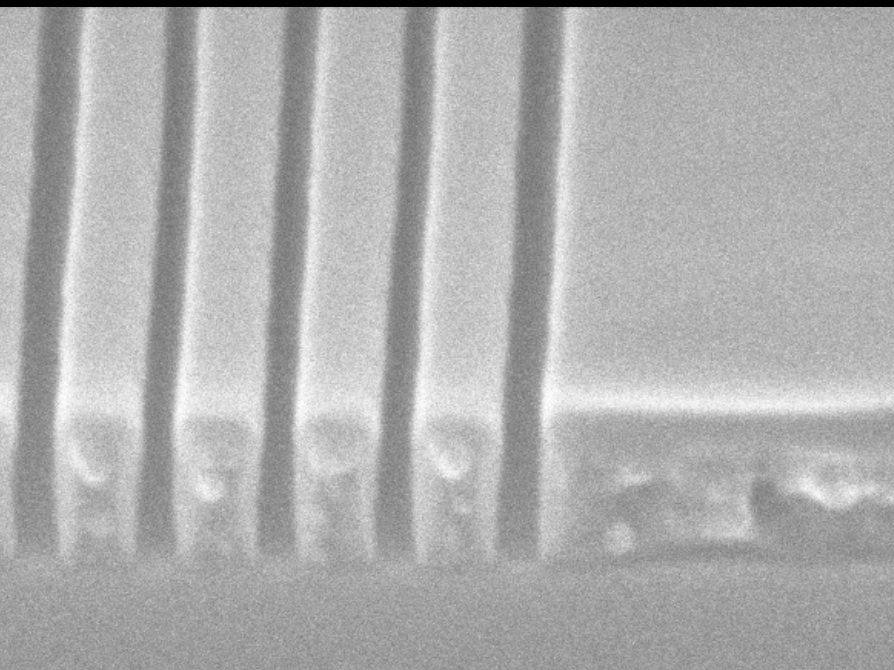


Lift-off (acetone)

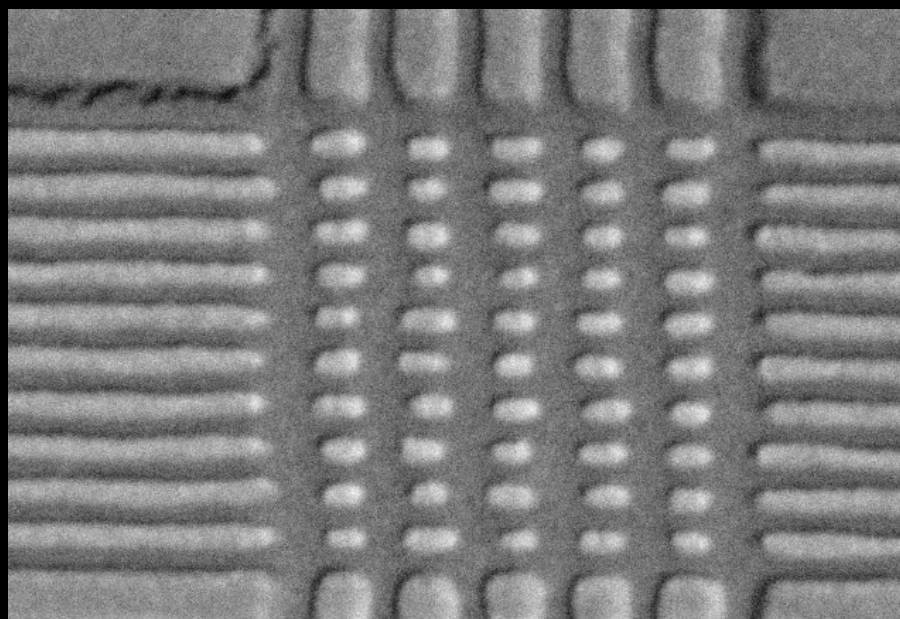


Test patterns

Lines and dots...

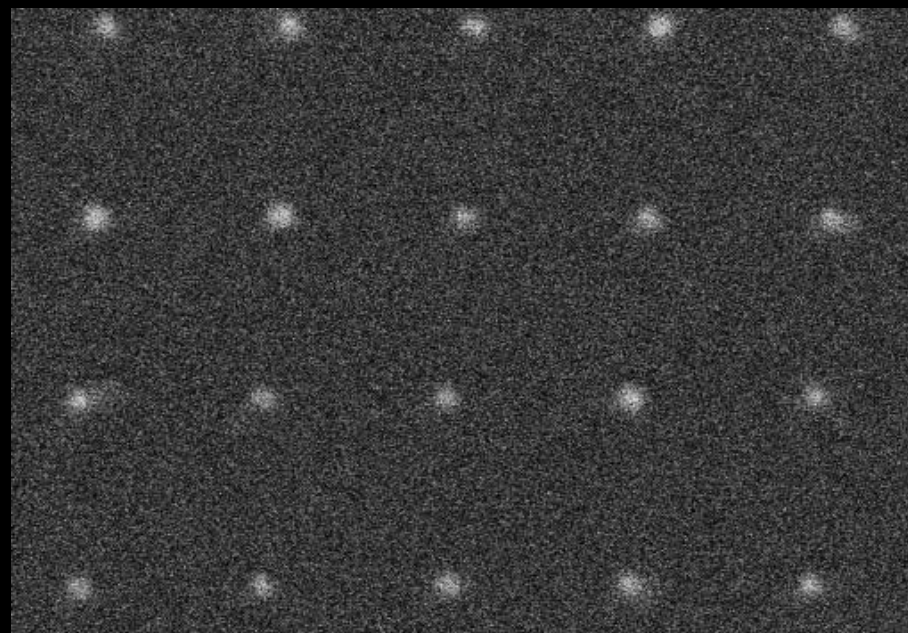
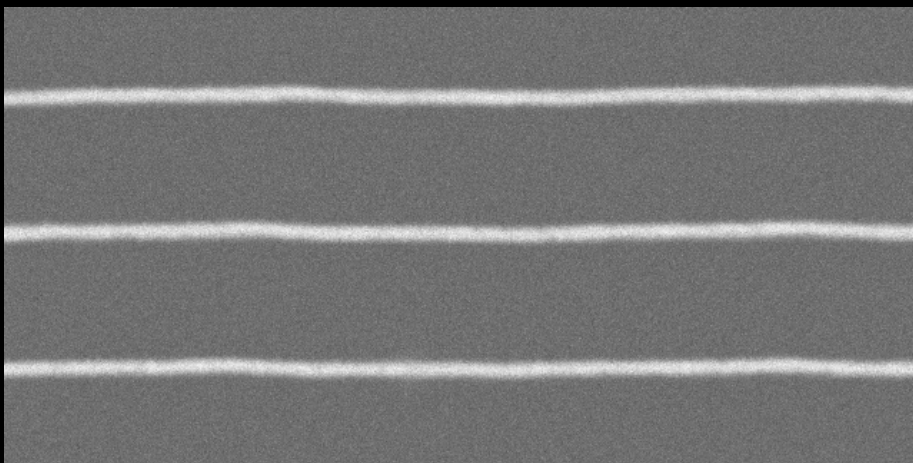


10-Jul-02 LNIO WD 3.7mm 20.0kV x100k 500nm



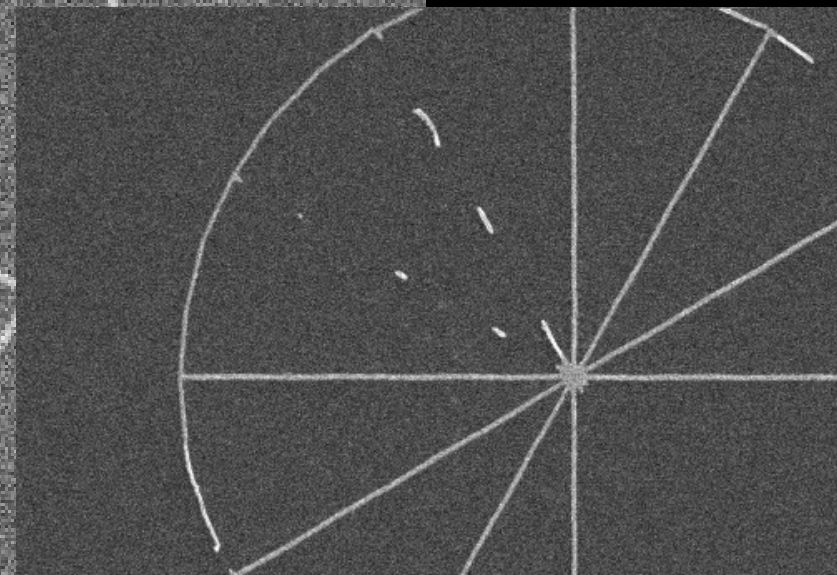
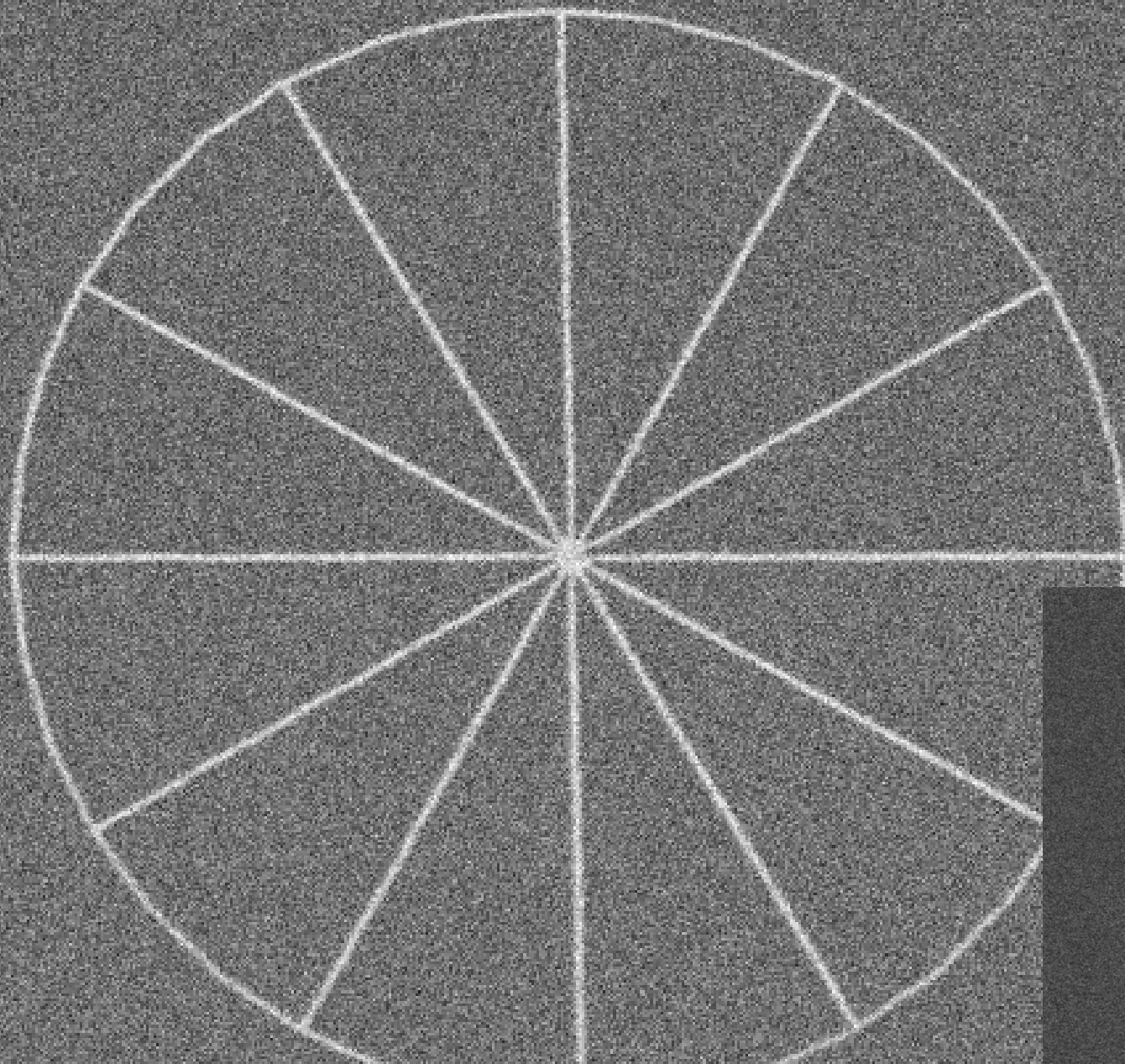
SE 08-Feb-01 LNIO WD 7.5mm 20.0kV x60k 500nm

Glass



Rest patterns

Wheel...

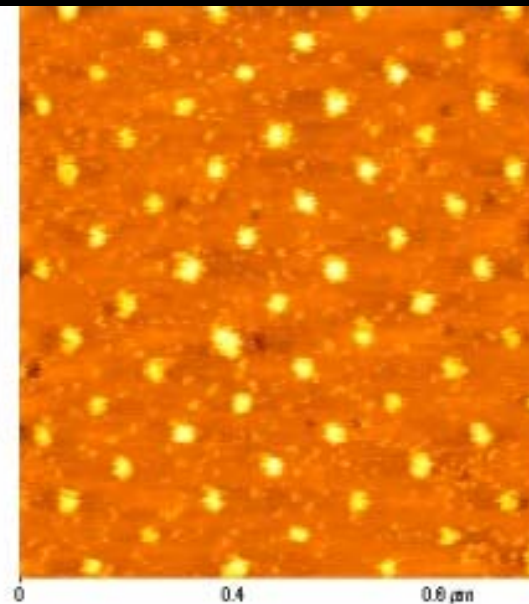
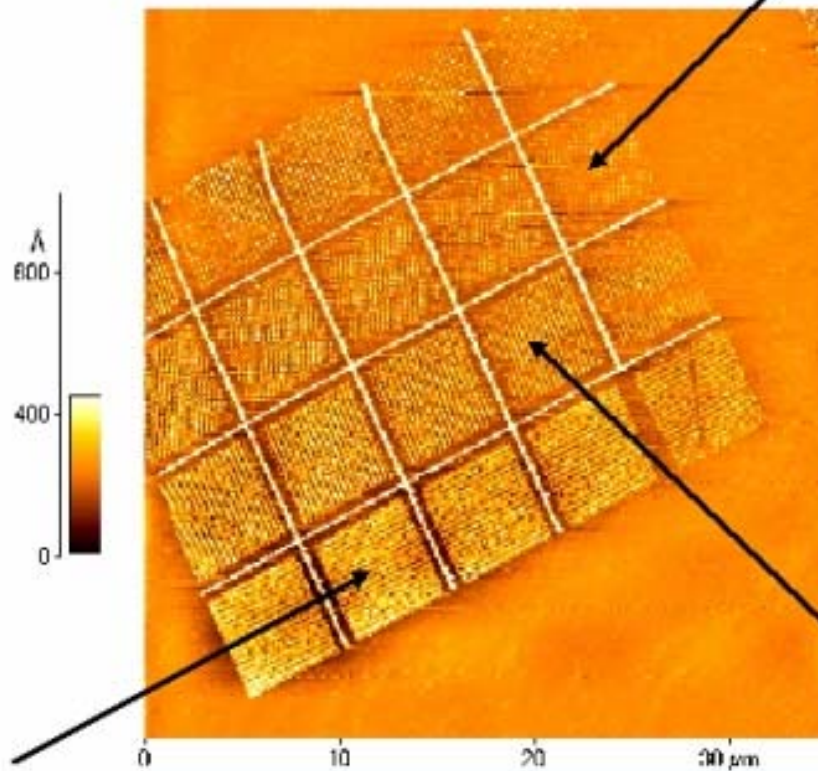
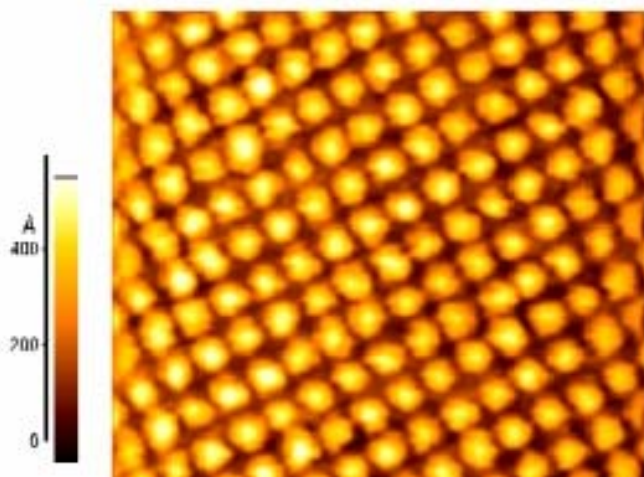


Patterned Study

On glass

Dot spacing

c-c 75 nm dia. 50 nm

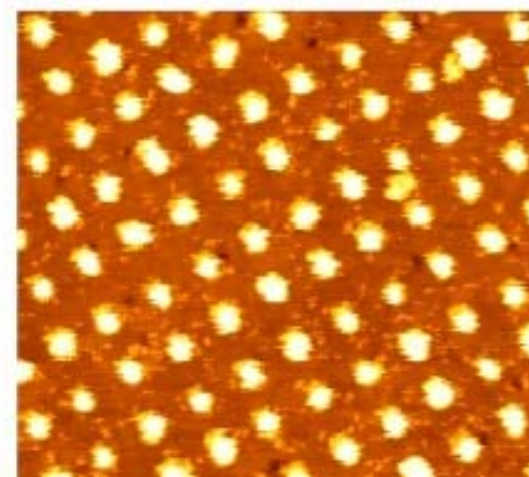


c-c 125 nm dia. 35 nm

c-c 100 nm dia. 40 nm

Dose

Dot height: 25 nm



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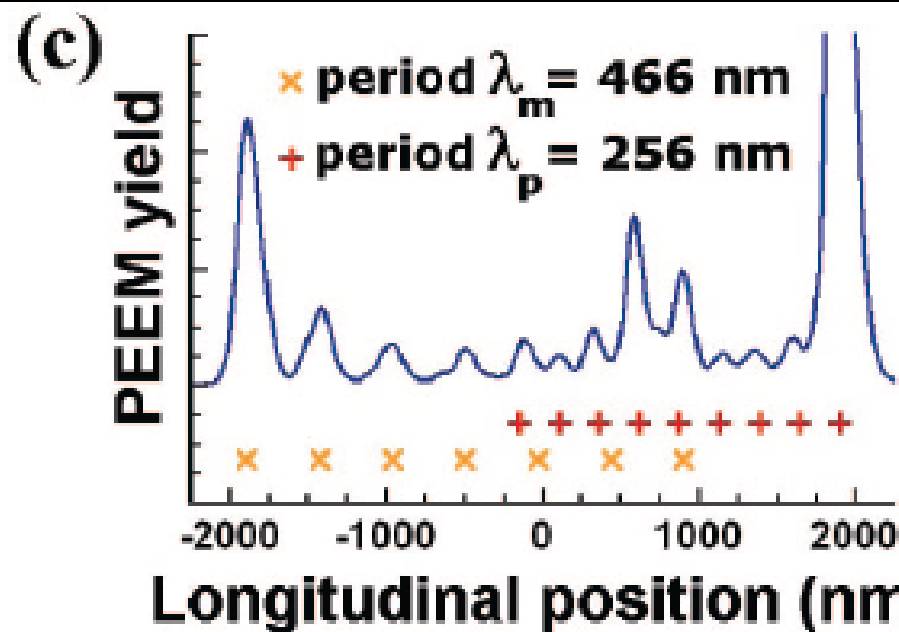
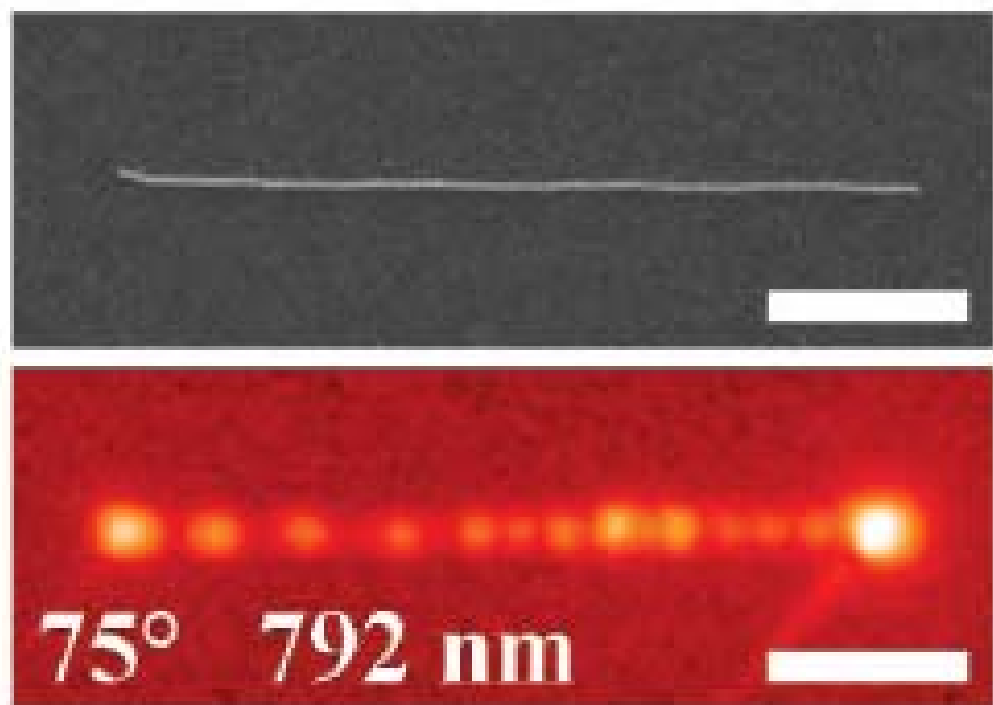
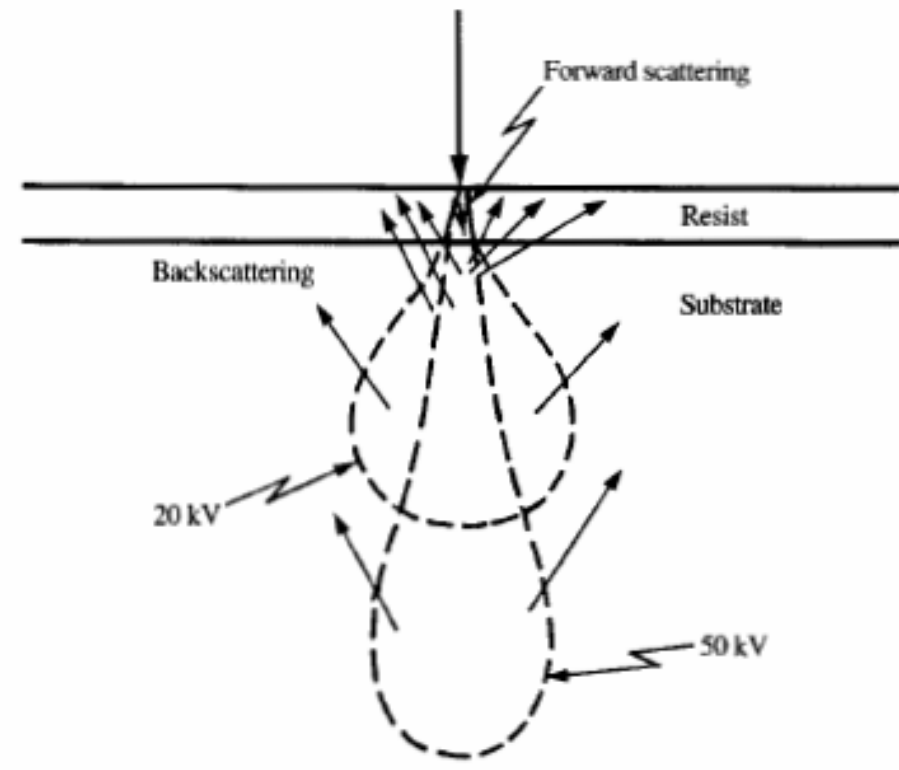
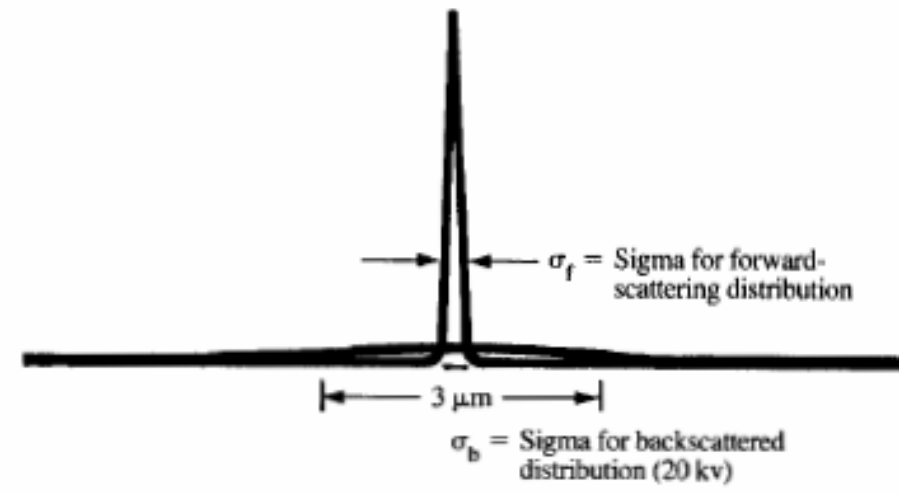


Figure 1. Off-resonant single Au nanowire investigation. (a) TEM picture of a 4 μm long nanowire. (b) PEEM near field image (grazing incidence $\alpha = 75^\circ$, p polarization, excitation wavelength $\lambda_0 = 792$ nm, incident power $P = 110$ MW/cm²). Longitudinal resolution is 41 nm:¹⁹ color scale is logarithmic. (c) Plot of PEEM yield versus longitudinal position (nm). Orange 'x' markers indicate the period $\lambda_m = 466$ nm and red '+' markers indicate the period $\lambda_p = 256$ nm.

Beam size < 1nm
 (Acceleration Voltage)
 Resist thickness

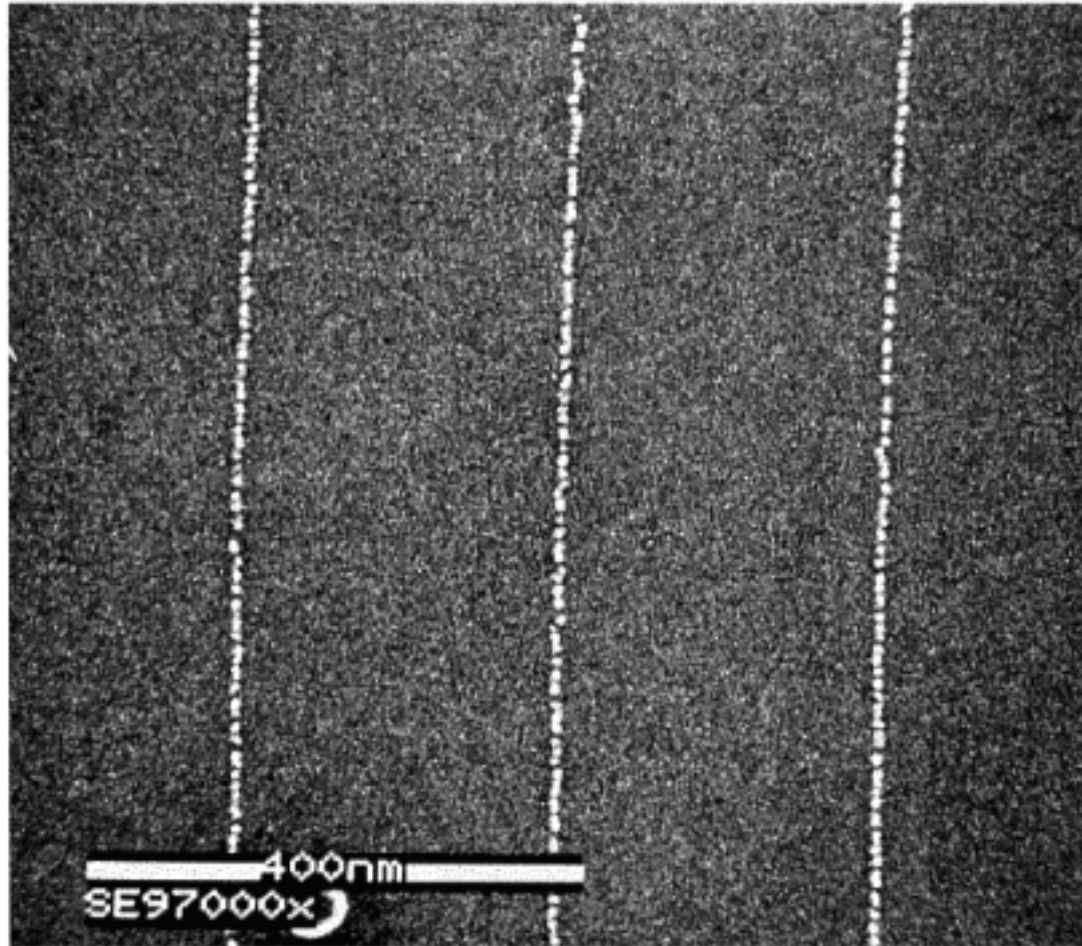


beam lithography: resolution limits and applications

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L. Couraud, H. Launois

structures et de Microélectronique (L2M / CNRS), 196, avenue Henri Ravéra, BP107, 92225 Bagneux Cedex, France

a)



b)





SS

Crucial Role of the Adhesion Layer in the Plasmonic Fluorescence Enhancement

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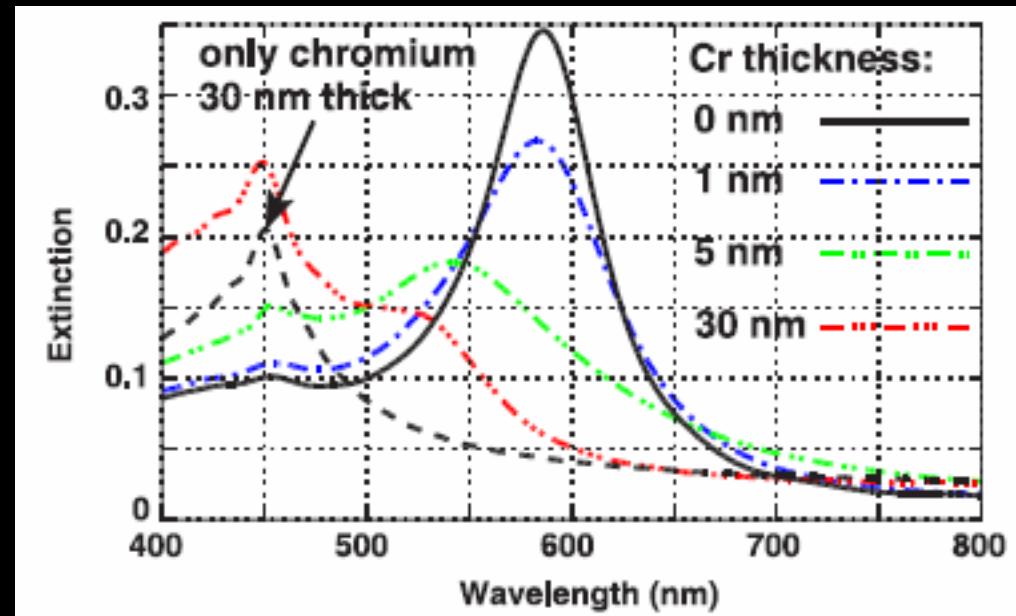
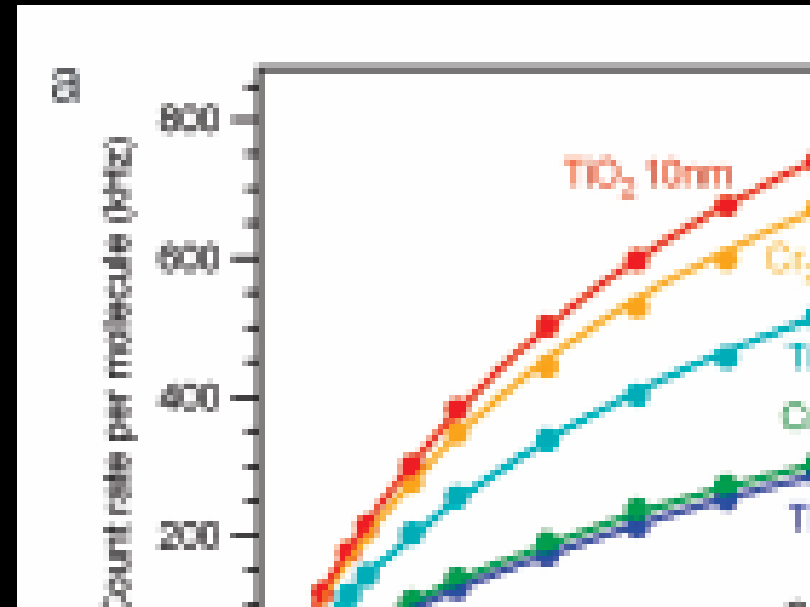


Figure 7. Extinction spectra for a gold cylinder (diameter 100 nm, height 50 nm) calculated for different chromium intermediate layer thicknesses: 0 nm, 1 nm, 5 nm and 30 nm, respectively. The extinction spectrum for a 30 nm high chromium cylinder is also presented.



of dispersion properties of
ans of the critical points

templated lithography

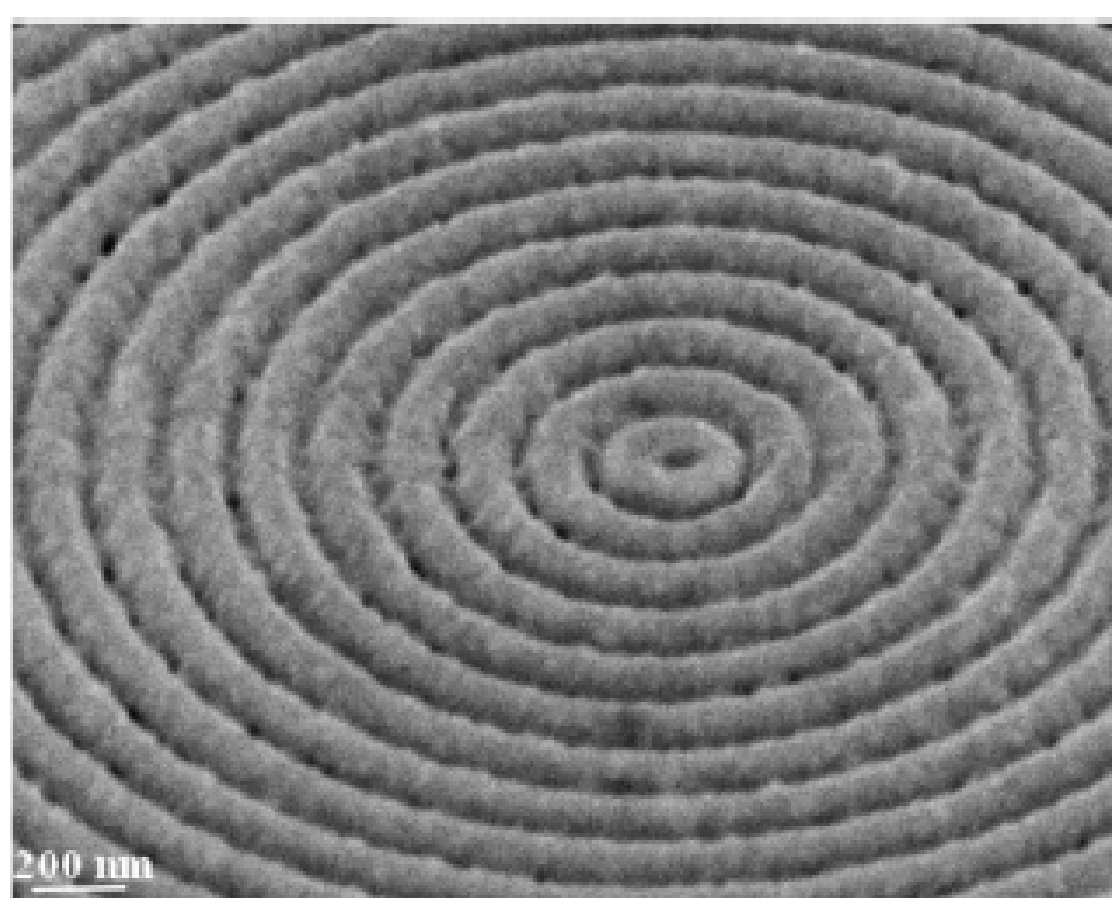
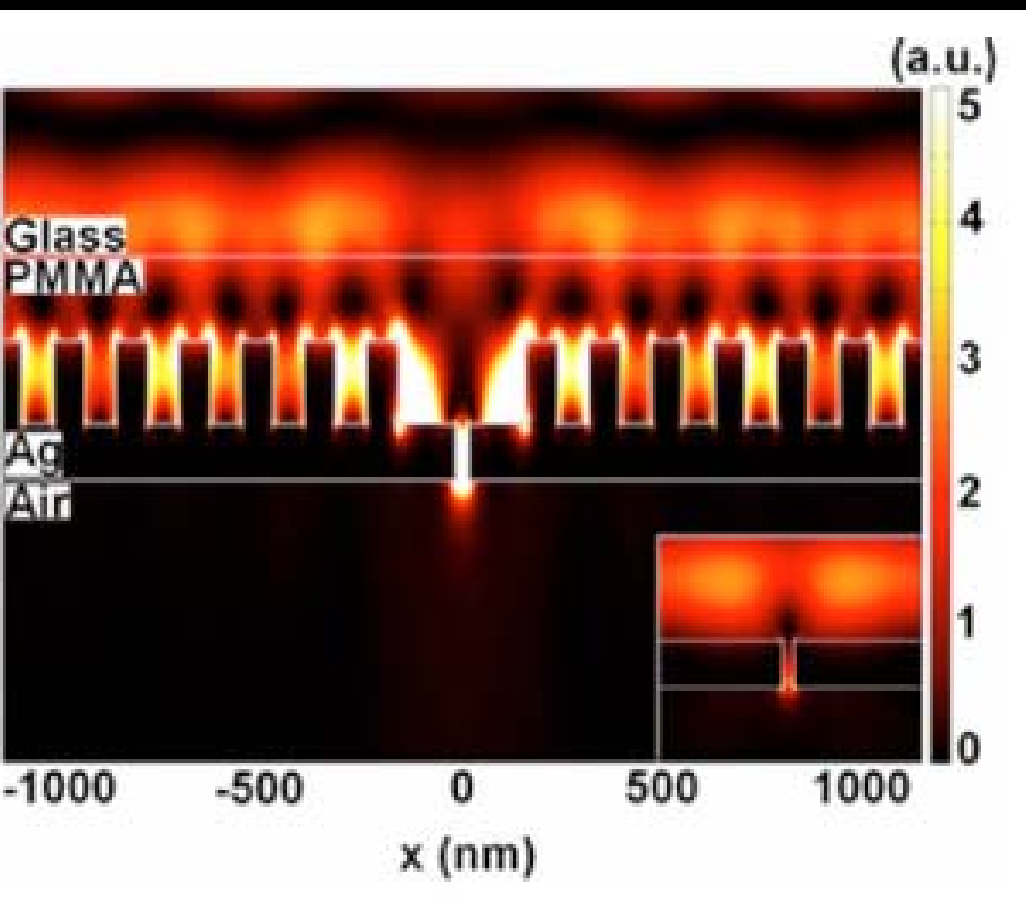


FIG. 3. Top view (scanning electron microscopy image) of the structure. The dimensions of the Bragg gratings are $a = 165$ nm.

on meta

PMMA structuring

or

Lift-off of dielectric structures (SiO_2)

on

metallic films

Focused Ion Beam

Important technique for the realization of « test » samples

Principle: id. SEM but with heavy charged particles (ions) ...

...Direct writing (physical process)

Drawback: possible contamination and redeposition

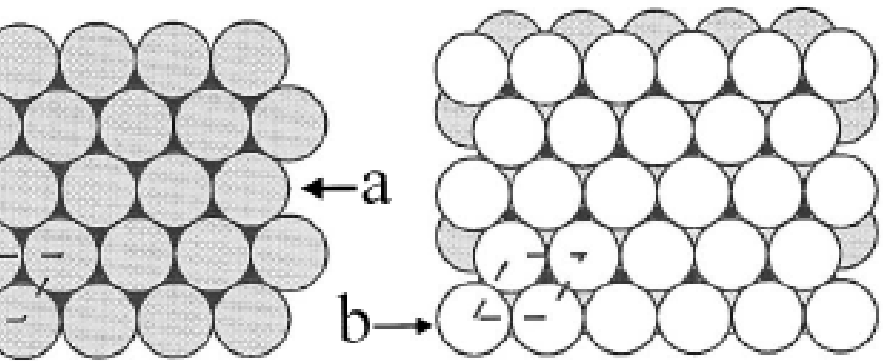
Examples of structure : See T. Ebbesen presentation

Alternative methods

Surface chemistry

Lithograp

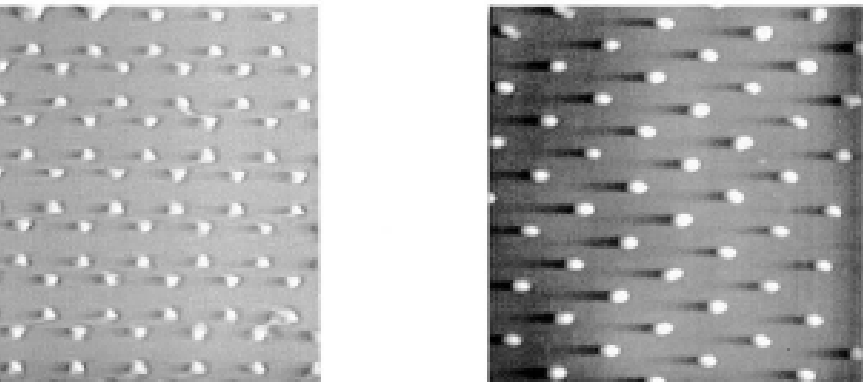
D.



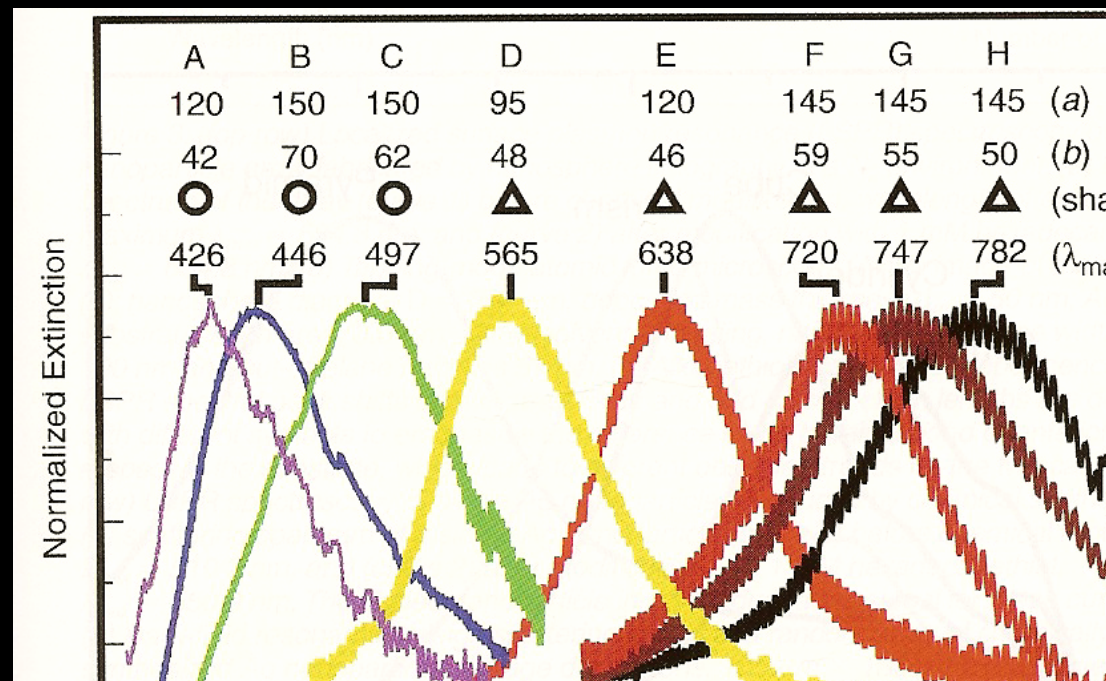
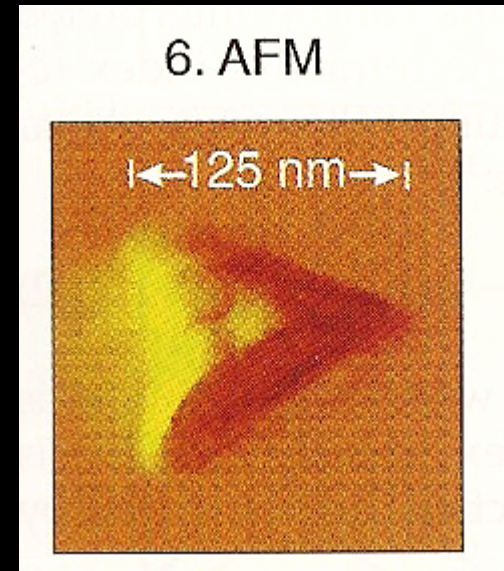
E.



F.



Schematic diagrams of single-layer (SL) and double-layer (DL) masks and the corresponding periodic particle array (PPA) surface. (A) $\sqrt{3} \times \sqrt{3}$ SL mask, dotted line=unit cell, a =first layer nano-particle diameter; (B) $\sqrt{3} \times \sqrt{3}$ SL PPA, 2 particles per unit cell; (C) $1.7 \times 1.7 \mu\text{m}$ constant



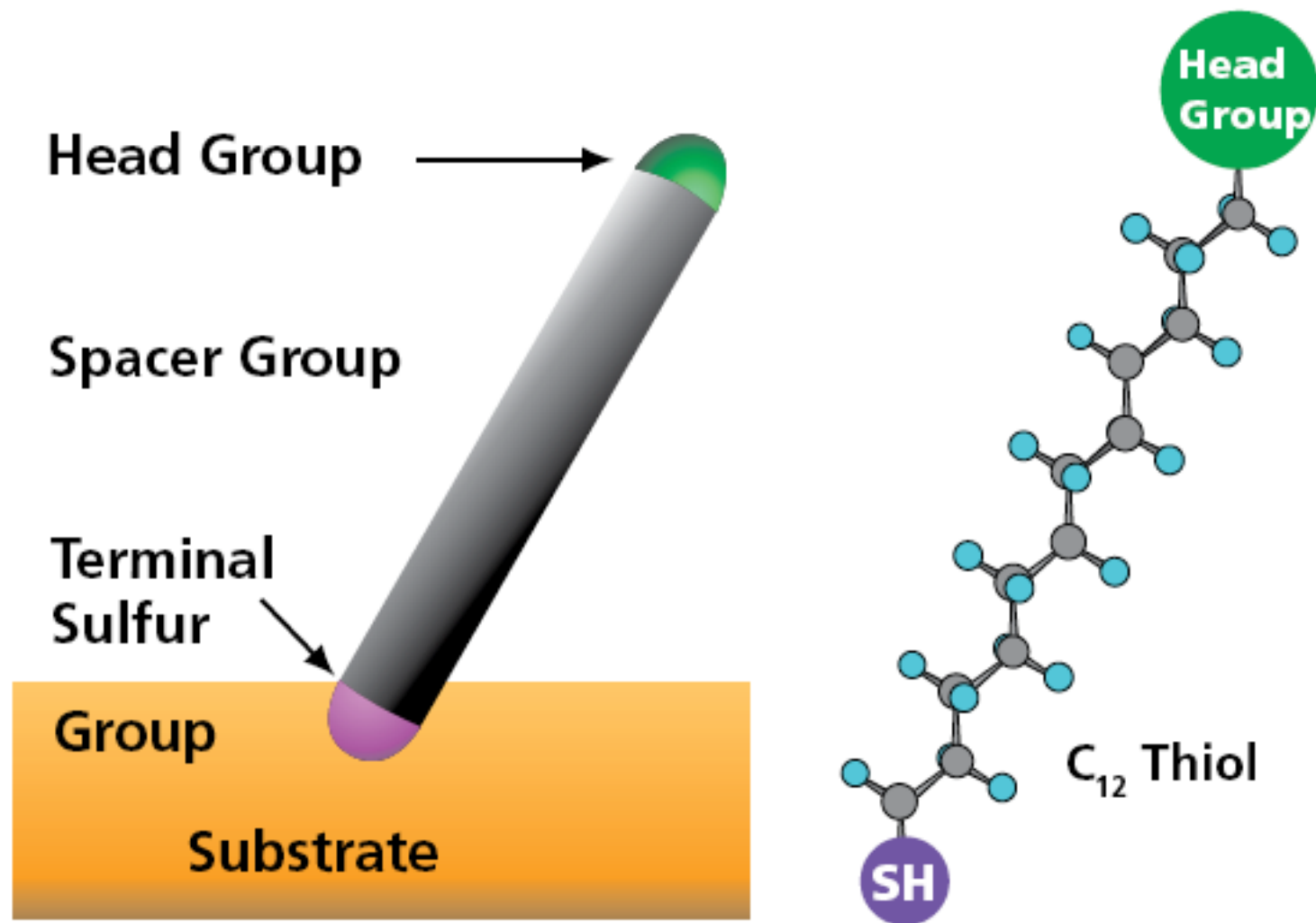


Figure 1. Schematic diagram of a thiol molecule.

The sulfur group links the molecule to the gold surface. The head group can be designed to provide virtually any surface chemistry, binding capacity, or property.

Au-thiolate ($\text{Au}_0\text{-S}$)

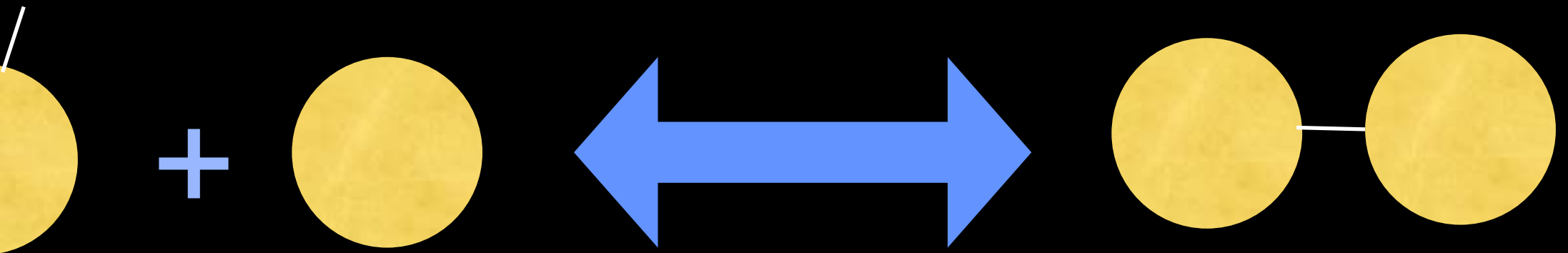
Binding energy of ($\text{Au}_0\text{-S}$)

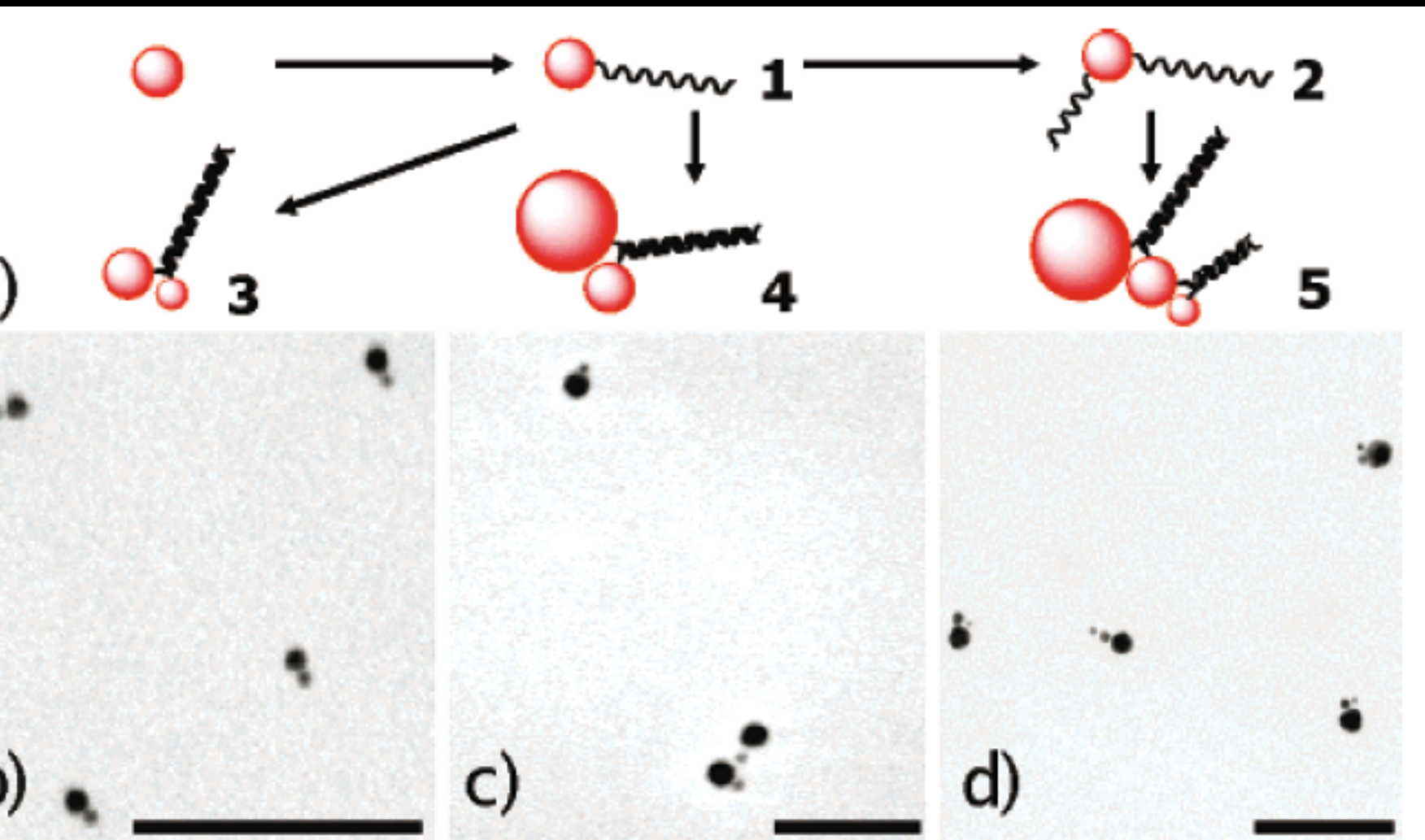
electrostatic interaction < ($\text{Au}_0\text{-S}$) < covalent bond

Table 3: Some head group examples useful for the applications

Application	Common Head Group
Non-fouling surfaces	PEG _n , Mannose
Specific binding receptors	Biotin, NTA, Peptide, Carbohydrates
Cell supports	Peptide
Molecular electronics	CH ₃ , SH
Microarrays	DNA, Peptide, PEG _n
Separations	NTA
Surface reactions	Azide, COOH, NH ₂ , OH, SH

From colloids to complex architectures





thiolated

Figure 1. (a) Nanoparticle assembly scheme. 8 nm diameter Au particles are attached to one 5' thiolated 100b ss-DNA molecule to produce building blocks 1. 1 is sequentially functionalized with a 5' thiolated 50b ss-DNA molecule to yield 2. Hybridization of 1 with 5 and 18 nm diameter Au particles monofunctionalized with the 3' thiolated complementary strand yields structures 3 and 4. 5 is obtained by hybridizing 3 with 5 and 18 nm diameter Au particles monofunctionalized with the 3' thiolated complementary strand.

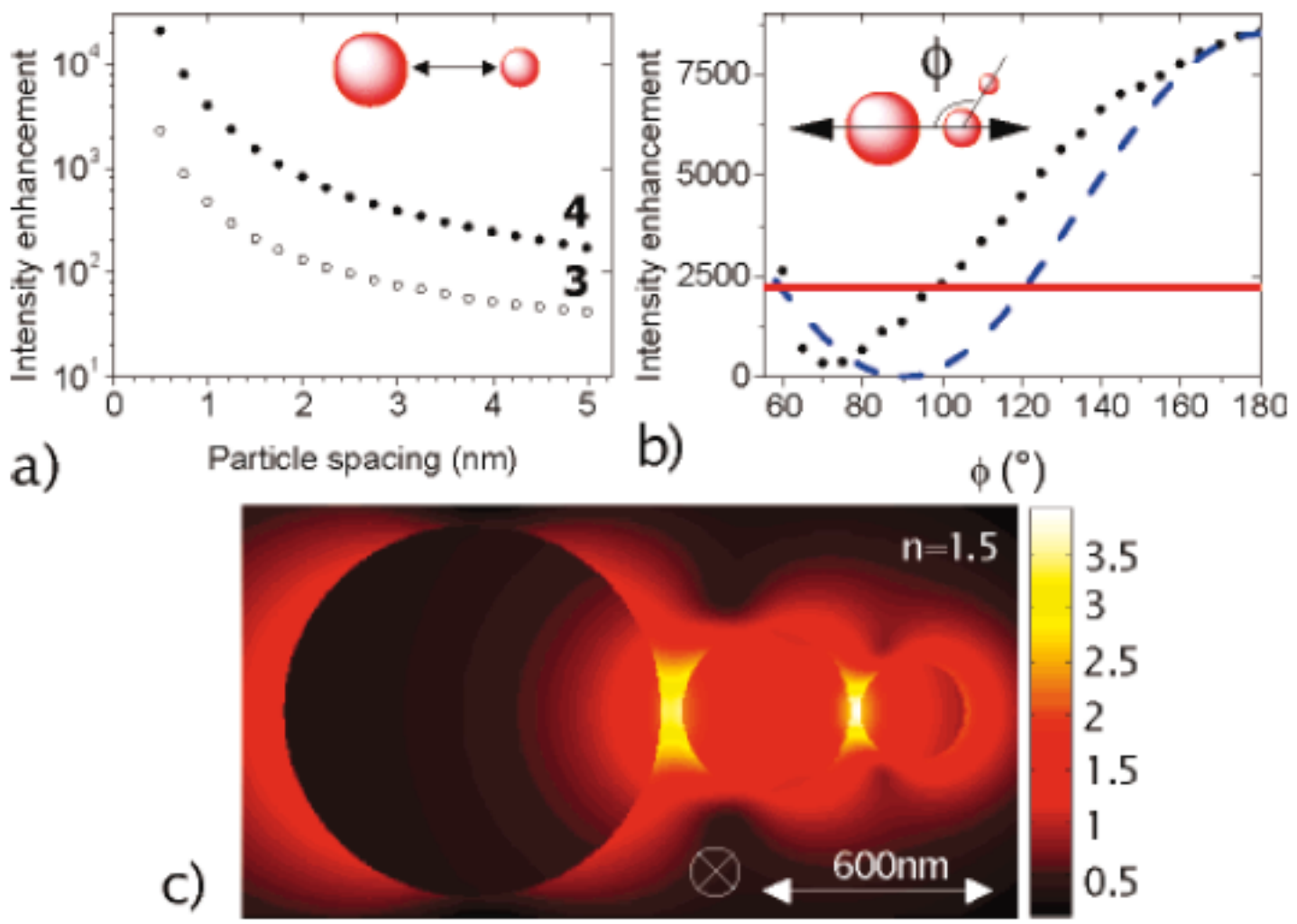
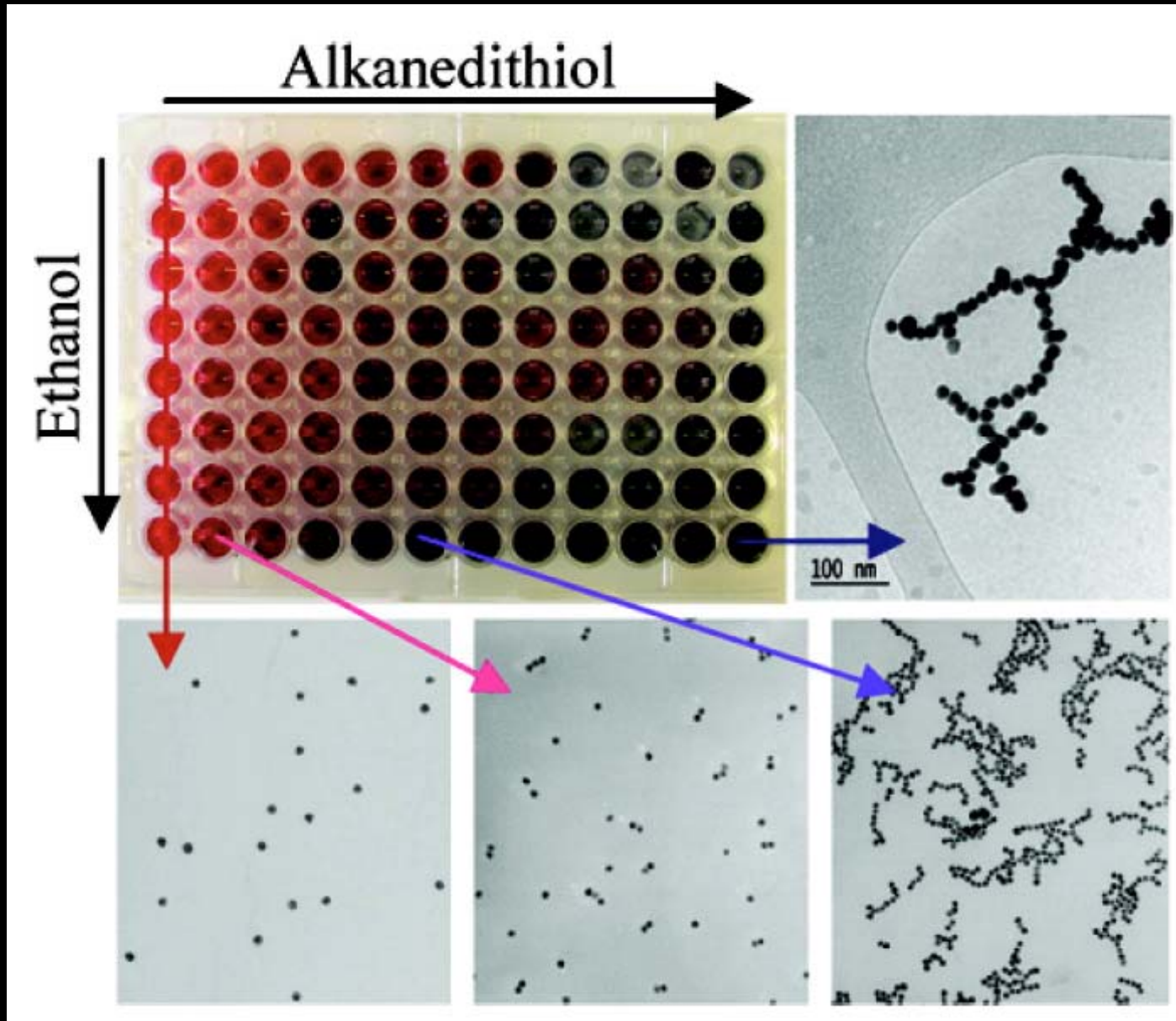
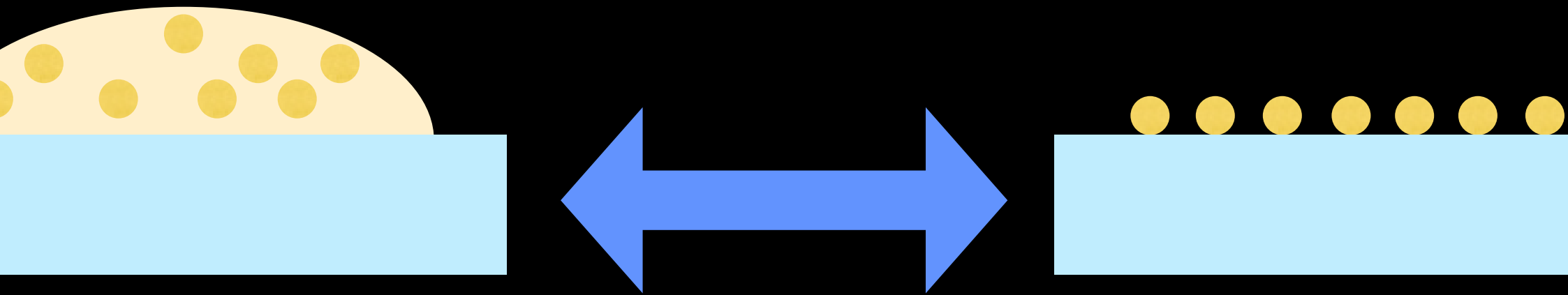
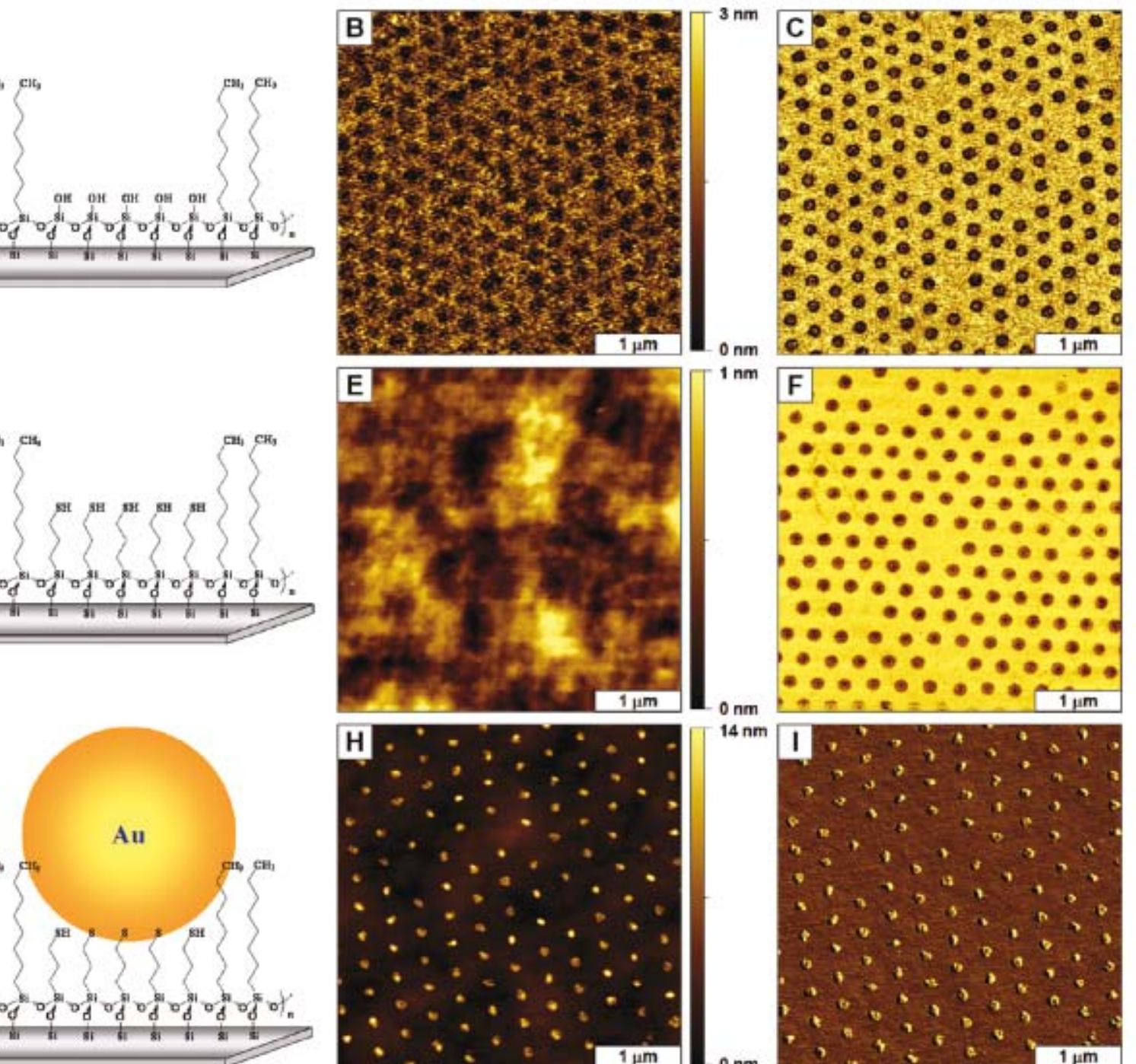


Figure 2. (a) Calculated maximum intensity enhancement (I^{enh}) in the gap of groupings 3 (○) and 4 (●) for particle spacings ranging from 0.5 to 5 nm ($n = 1.5$ dielectric environment). (b) Evolution of I^{enh} on the surface of the 5 nm particle in groupings 5 (1 and 0.5 nm spacings), for ϕ ranging from 60° to 180° and incoming polarization along the 8–18 nm particles axis. The red line corresponds to I^{enh} in grouping 3 for 0.5 nm spacing, and the dashed blue line is a $\cos^2(\phi)$ evolution. (c) I^{enh} (logarithmic scale) in aligned 18, 8, and 5 nm spheres with 1 and 0.5 nm spacings, respectively.



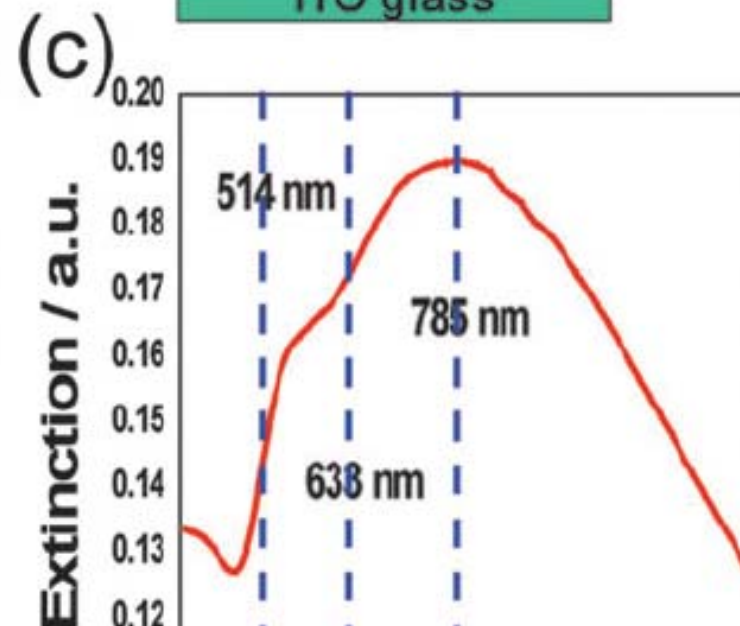
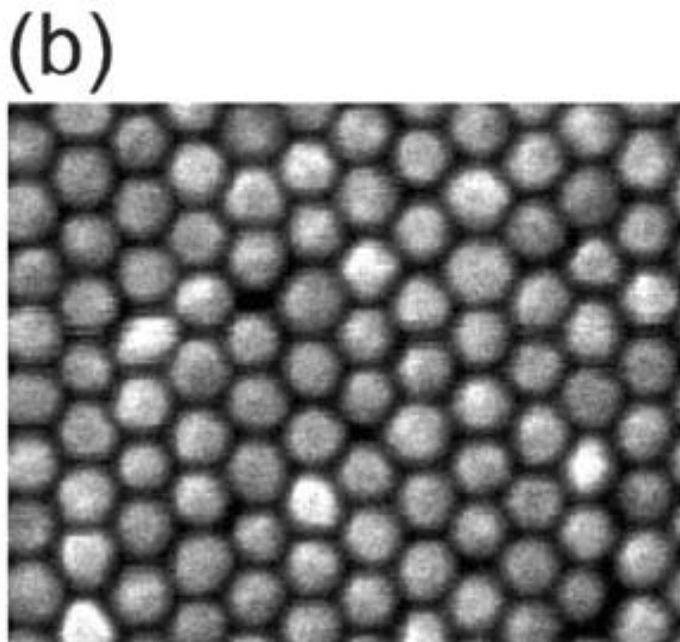
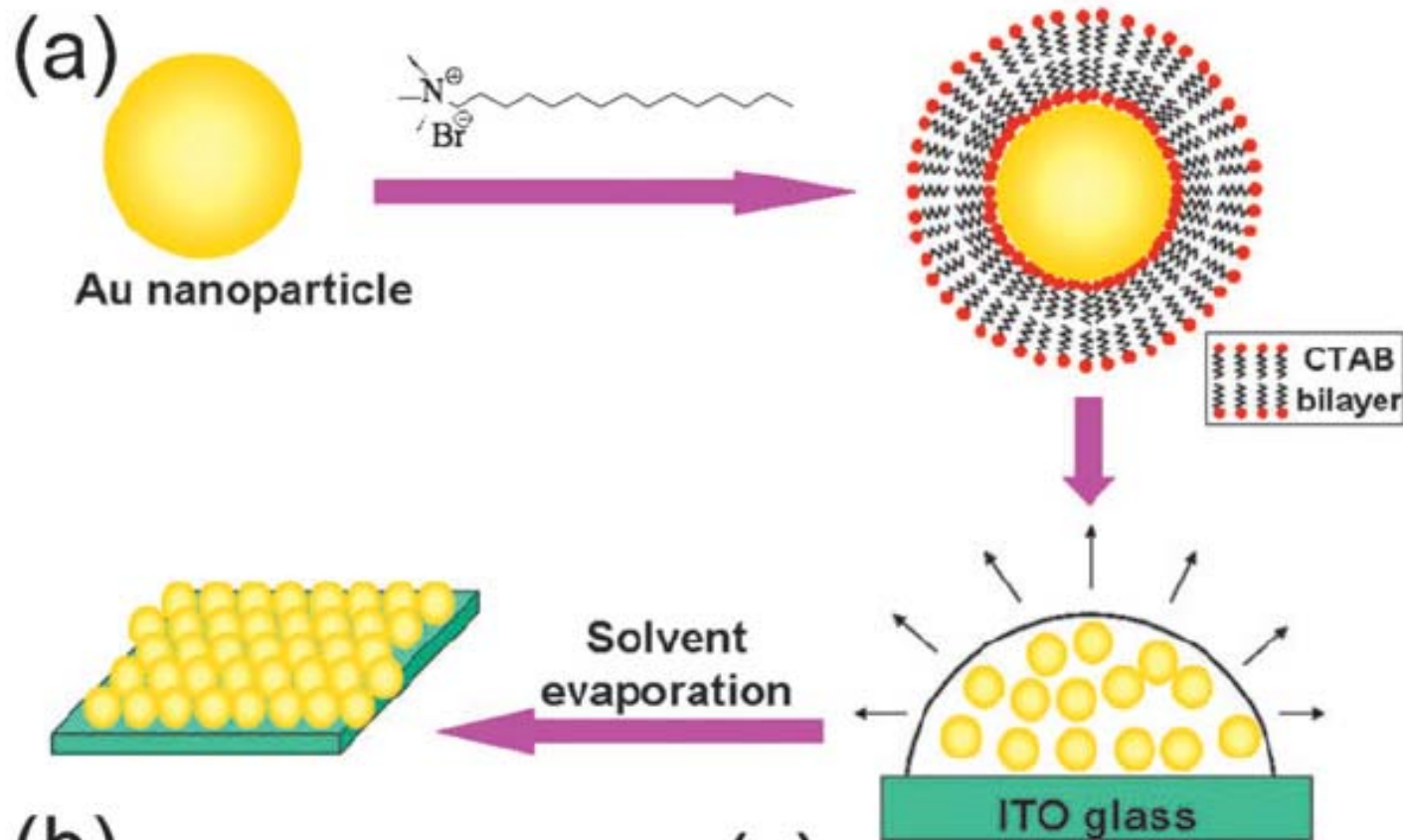
from colloids to complex architectures: 1D to 2D





Chemical nanopatterning

Pallandre et al. NanoLett 2006
 Plain et al. small 2006



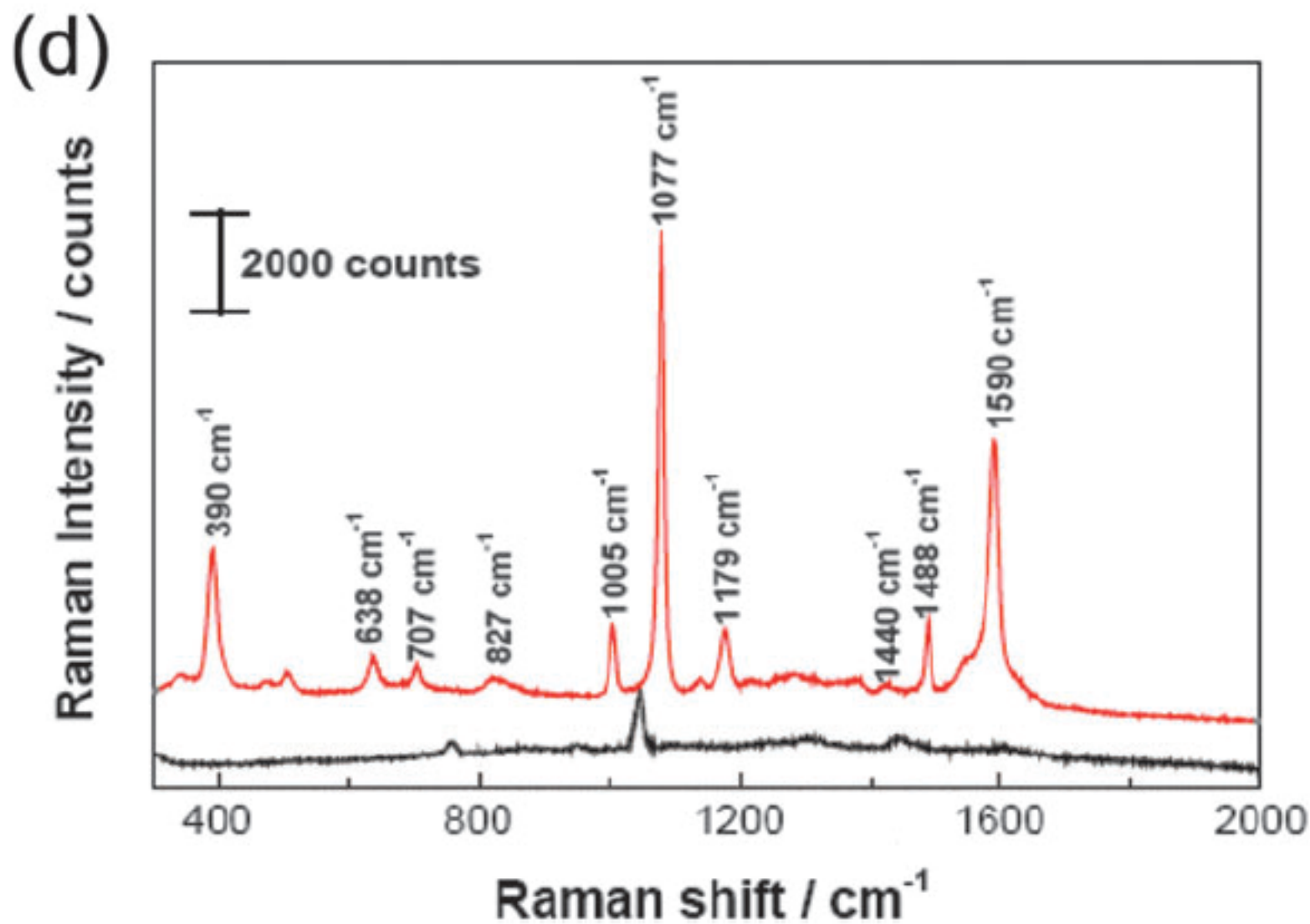
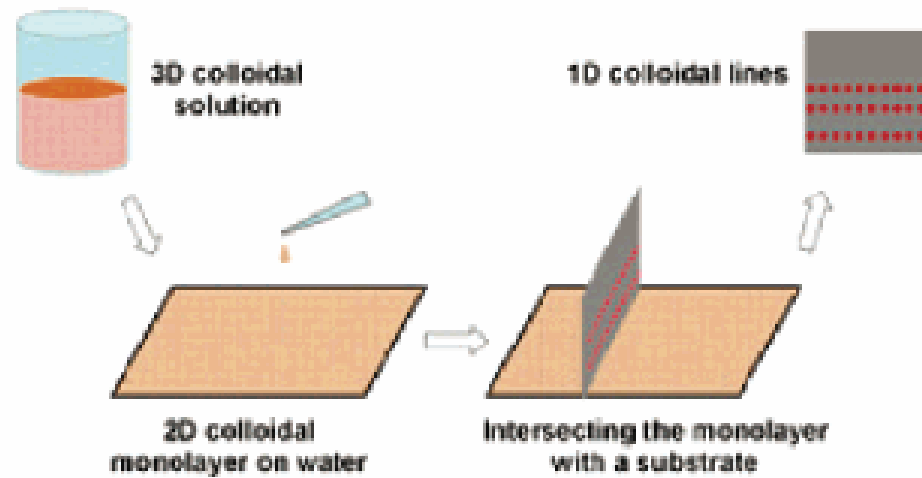
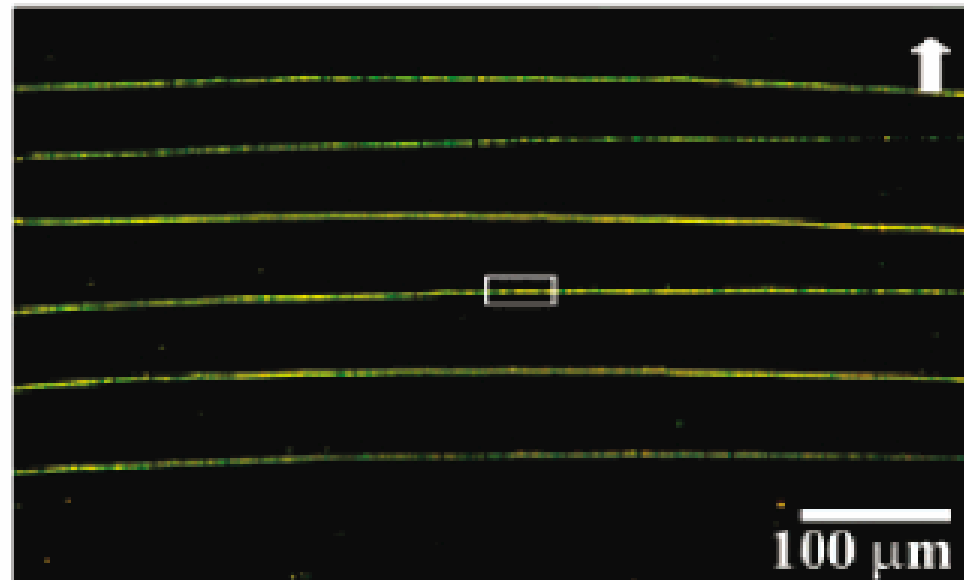


Fig. 9 (a) Schematic illustration of the fabrication of sub-10 nm gap Au NP arrays. (b) SEM image of a Au NP array on ITO glass. (c) Vis-NIR extinction spectrum of the NPs arrays (solid curve). (d) SERS spectra of *p*MA adsorbed on the Au nanosphere arrays. The red curve is a SERS spectra of *p*MA, and the black curve is the spectra of Au

a**b****c**

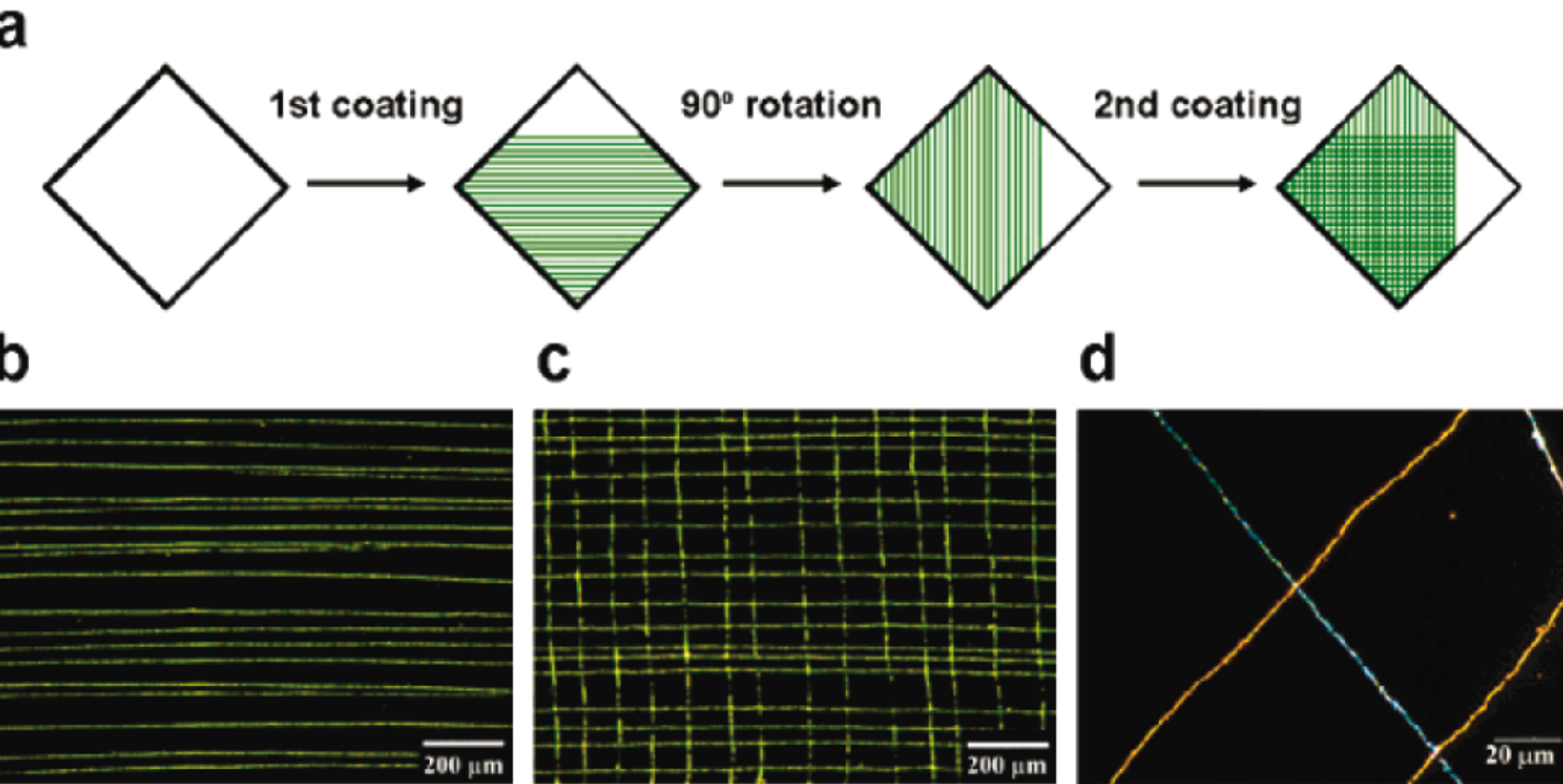
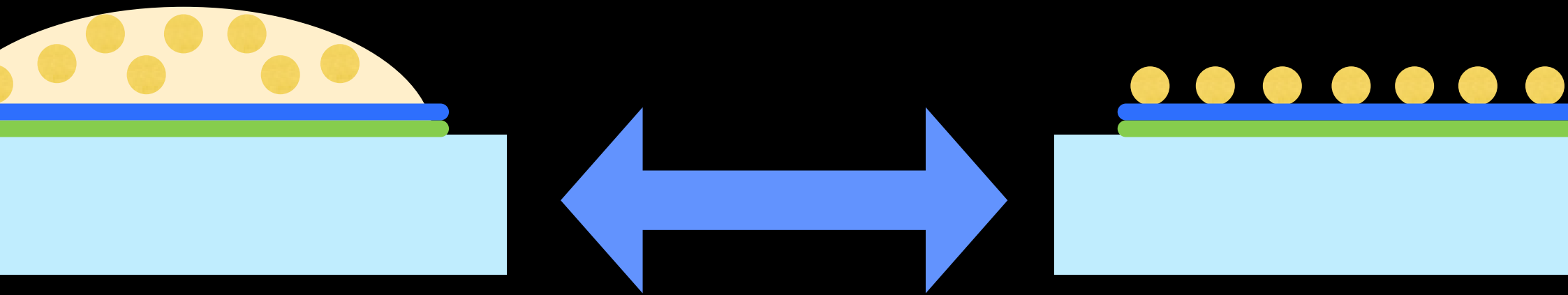
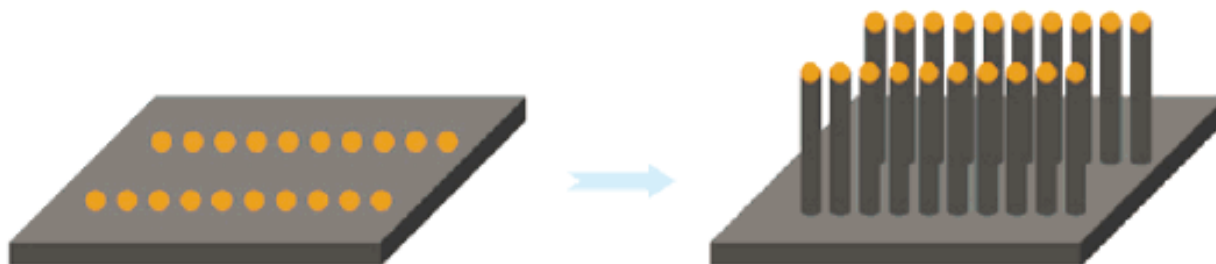


Figure 3. (a) Schematic diagrams illustrating the grid patterns obtained by two sequential crossed dip-coatings. Optical microscopy images showing (b) the Au single particle line pattern obtained by the first coating, (c) the grid pattern obtained by coating a second line perpendicular to the first one, and (d) hybrid Au-Ag grid pattern by two dip coating steps of Au and Ag nanoparticles, respectively.

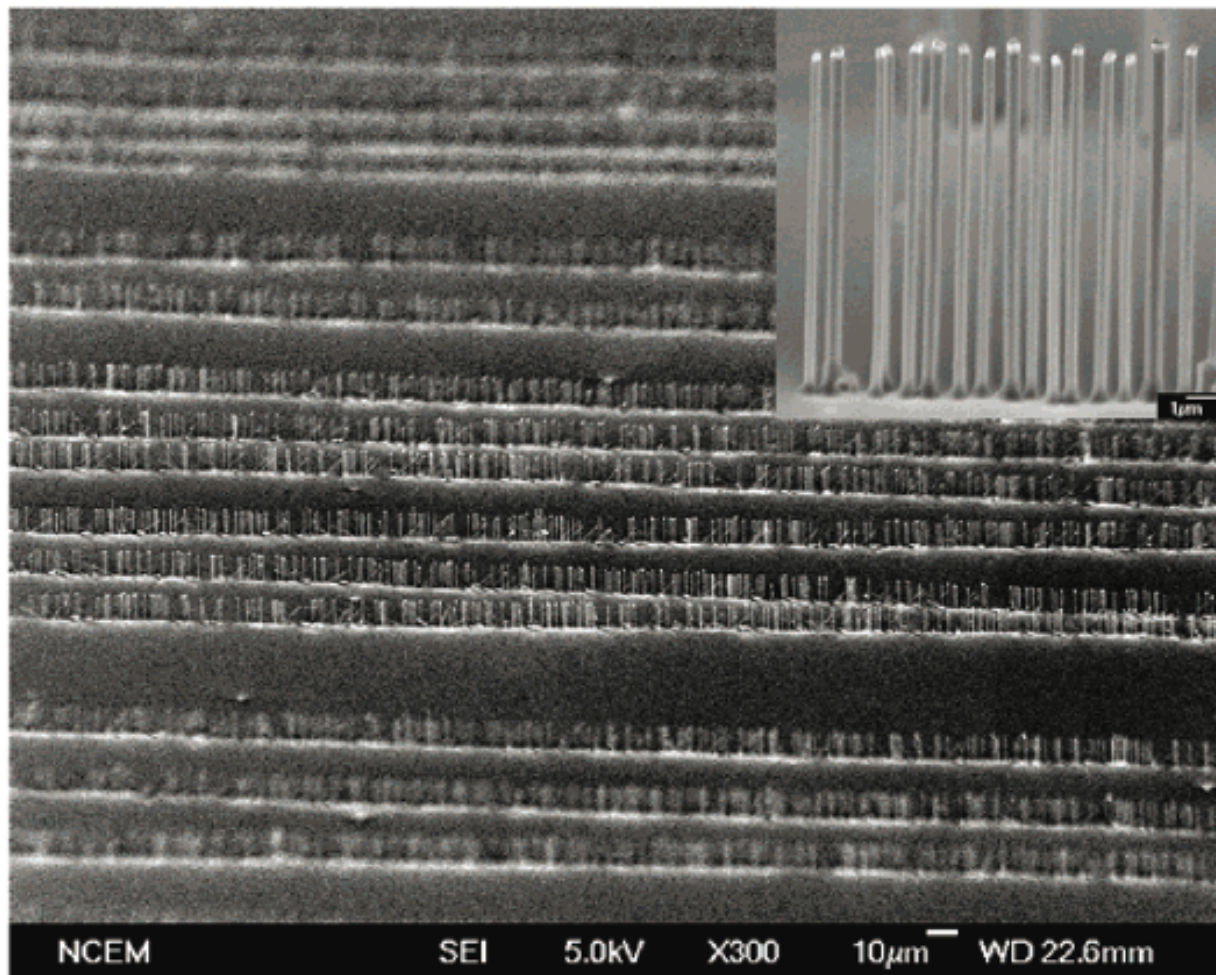
from colloids to complex architectures: 1D to 3D



a

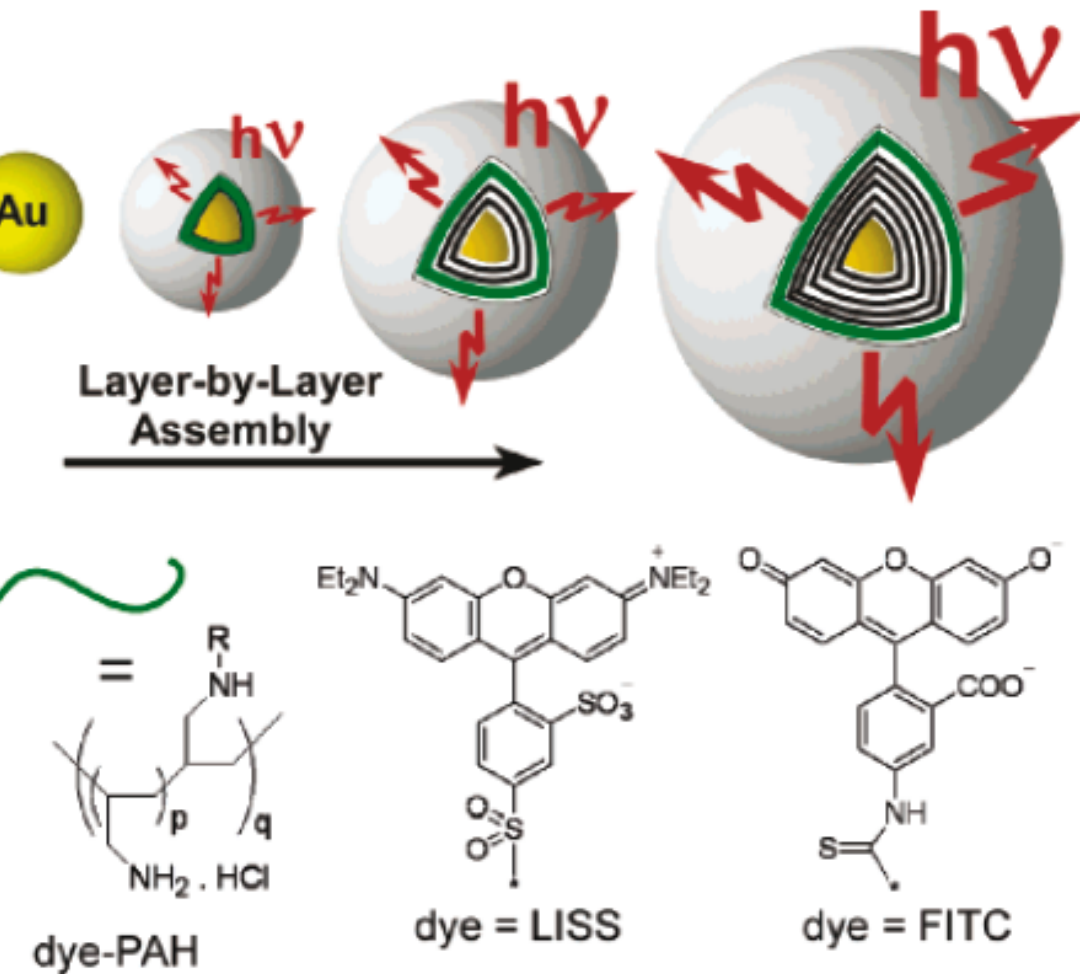


b

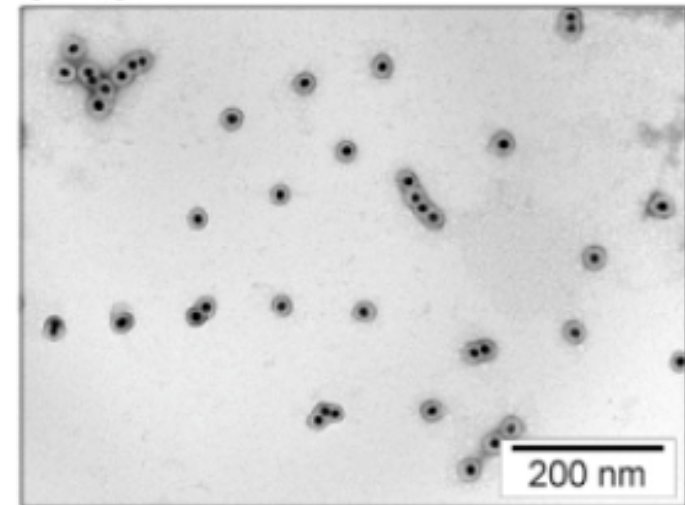


From colloids to hybrid architectures

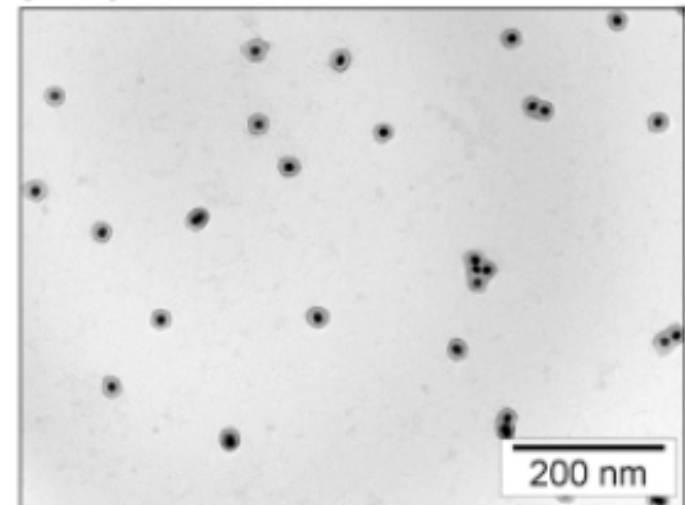
Figure 1. Layer-by-Layer Assembly for the Construction of Core-Shell Nanoparticles Containing Fluorescent Corona Layers^a



(1A)



(1B)



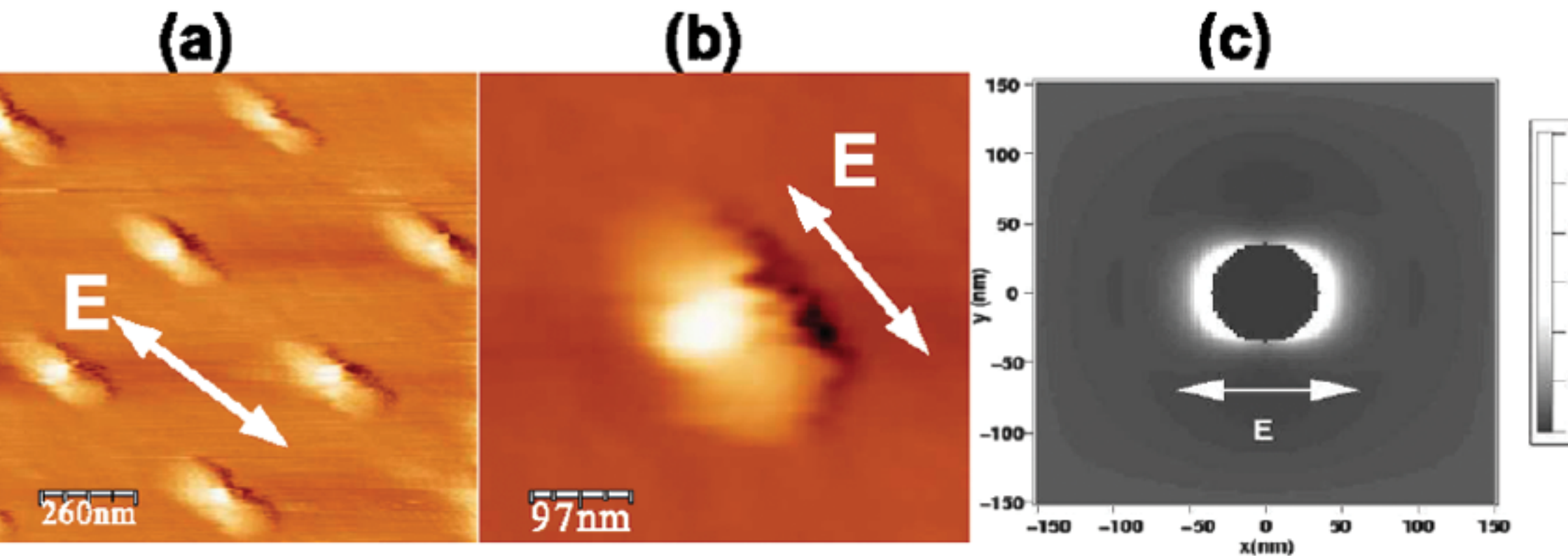
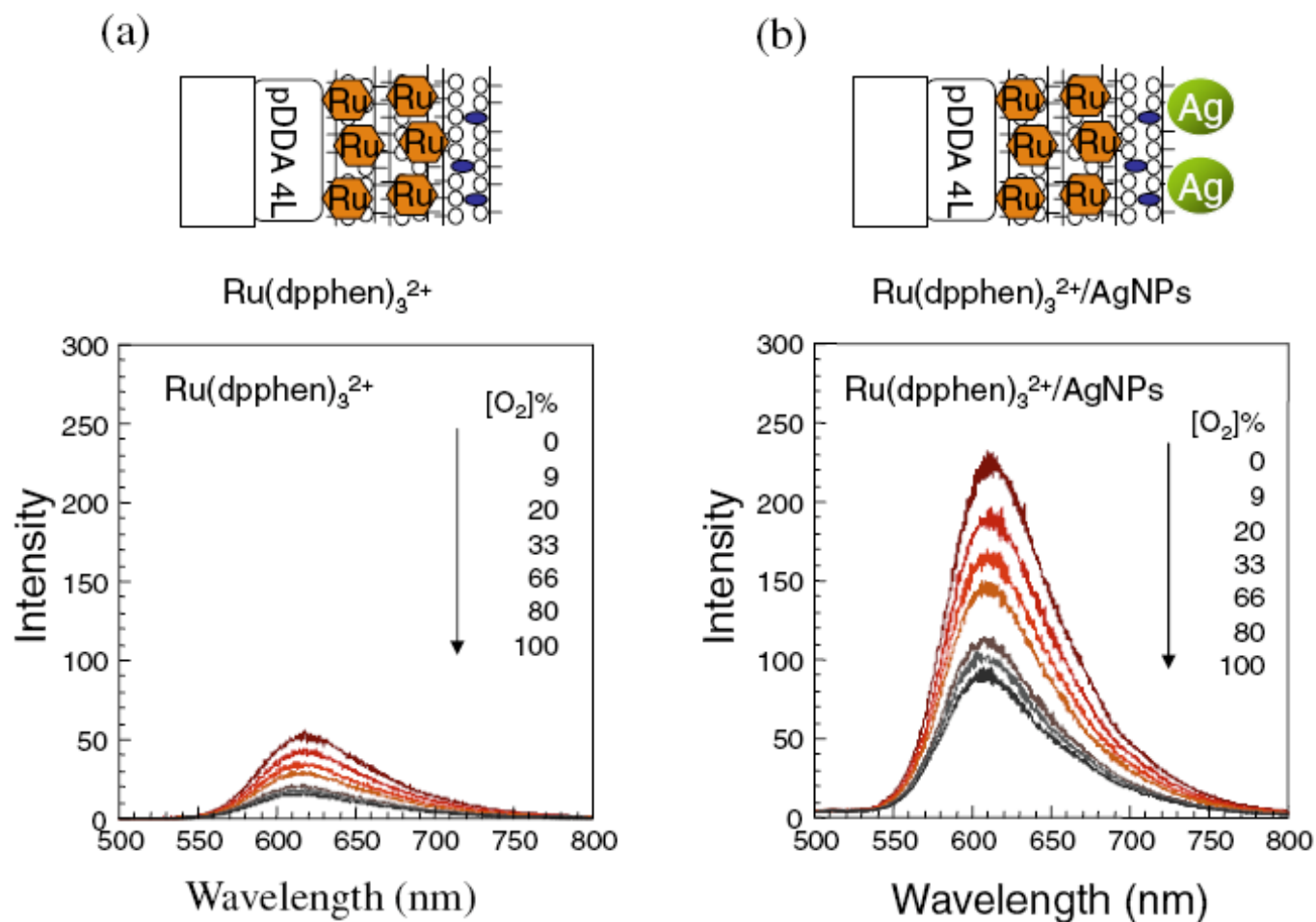


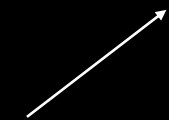
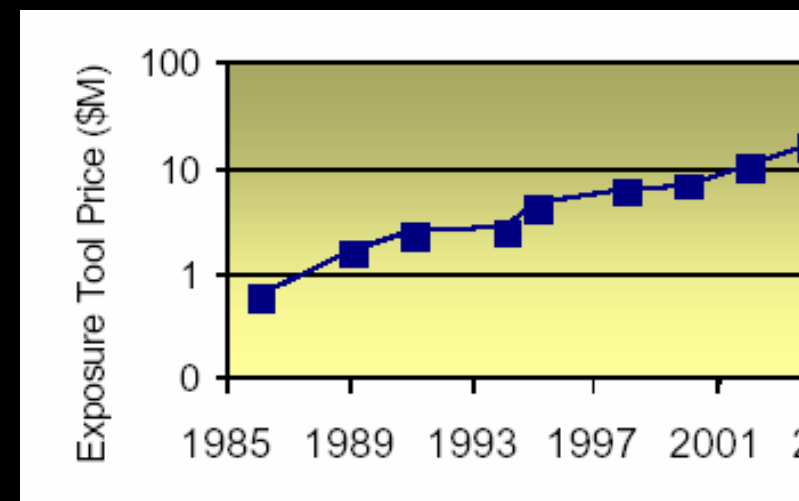
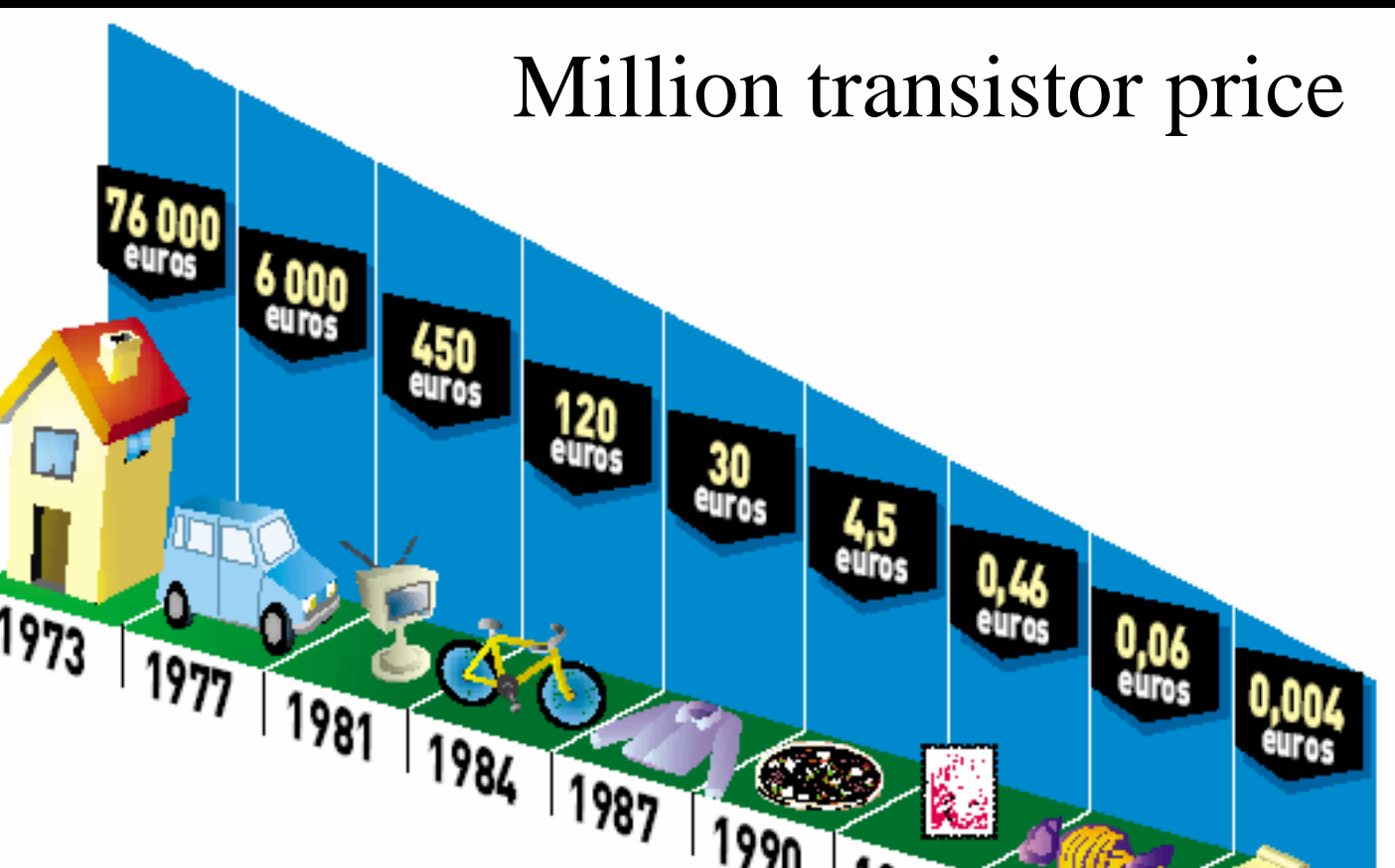
FIG. 2 (color). (a) and (b) AFM images recorded after irradiation and developing of the silver nanoparticles arrays covered with the photopolymerizable formulation. (c) Intensity distribution in the vicinity of an Ag particle embedded in the formulation as calculated by FDTD method ($\lambda = 514$ nm). The white arrow



9. Luminescence spectra of (a) four-layer p(DDA/Ru) nanosheets and (b) four-layer p(DDA/Ru) nanosheets + AgNPs. They were assembled on quartz slides.

Emerging methods
and
Fourth coming issues

How fast, how small and how large?
Solution : being able to write fast and small on a large surface, VLSI



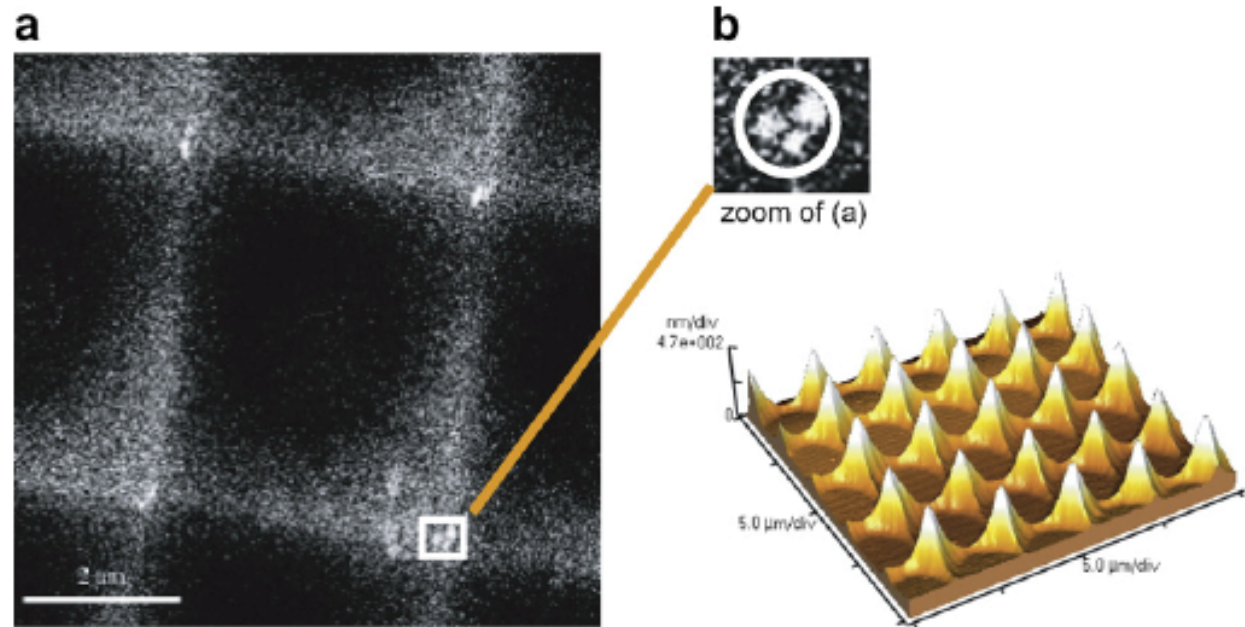
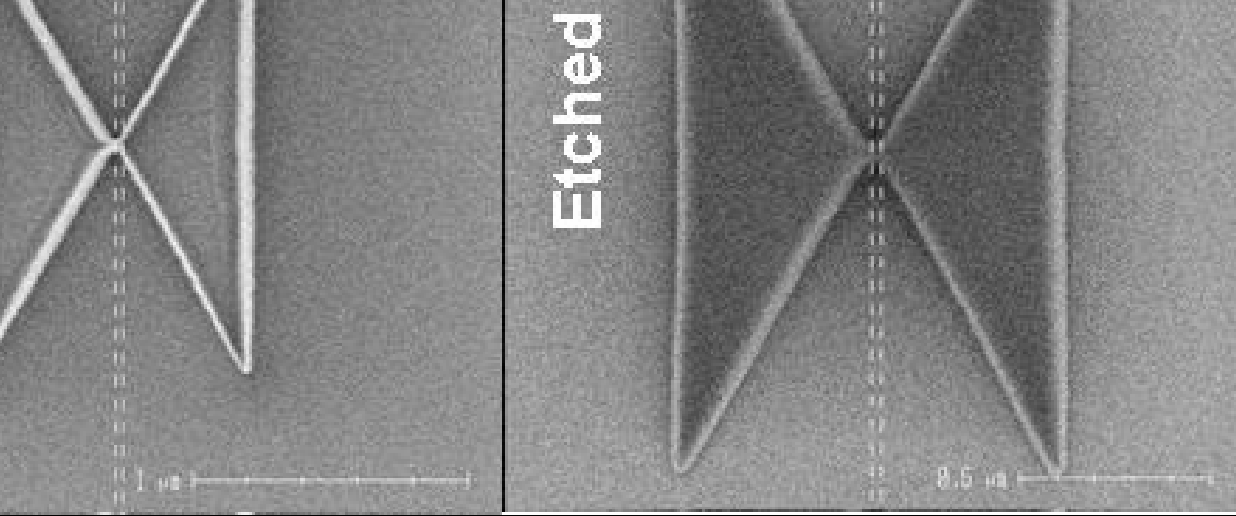


Fig. 2. (a) SEM image of integrated plasmonic glass nanotips (scale bar = 2 μm), (b) Top zoom of (a) SEM image of gold nanospheres (external circle = diameter of curvature of the nanotip apex = 160 nm) (b) bottom AFM image of glass nanotips array.

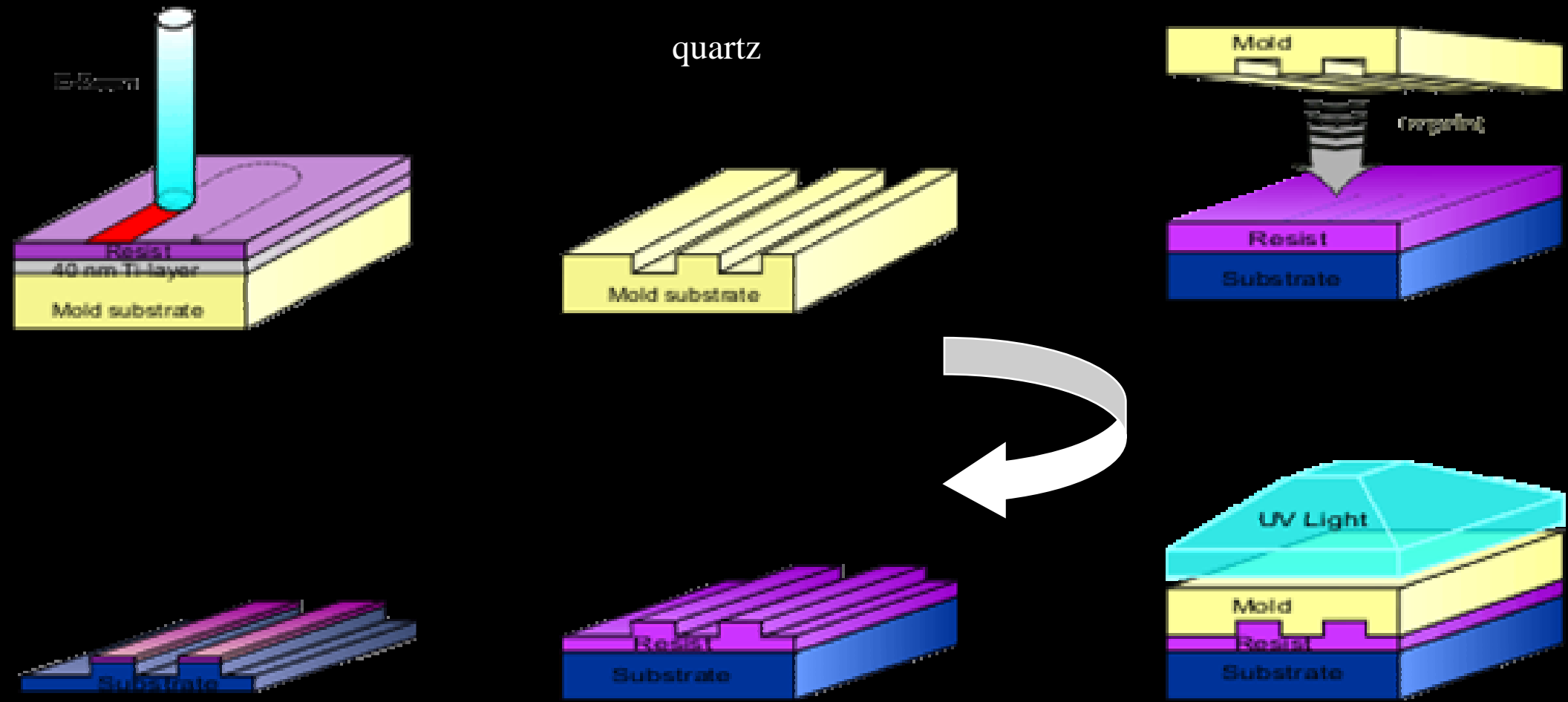
t (nm) at each modification step of the surface and the corresponding layer thickness (nm)

ion	LSPR shift (nm)	Effective thickness (nm)
A	8	1.28
A + PDDA	3	<1
A + PDDA + PSS	3	<1

1. Surface functionalization
(40 nm gold particle grafting)
2. Holographic patterning
3. Glass wet etching

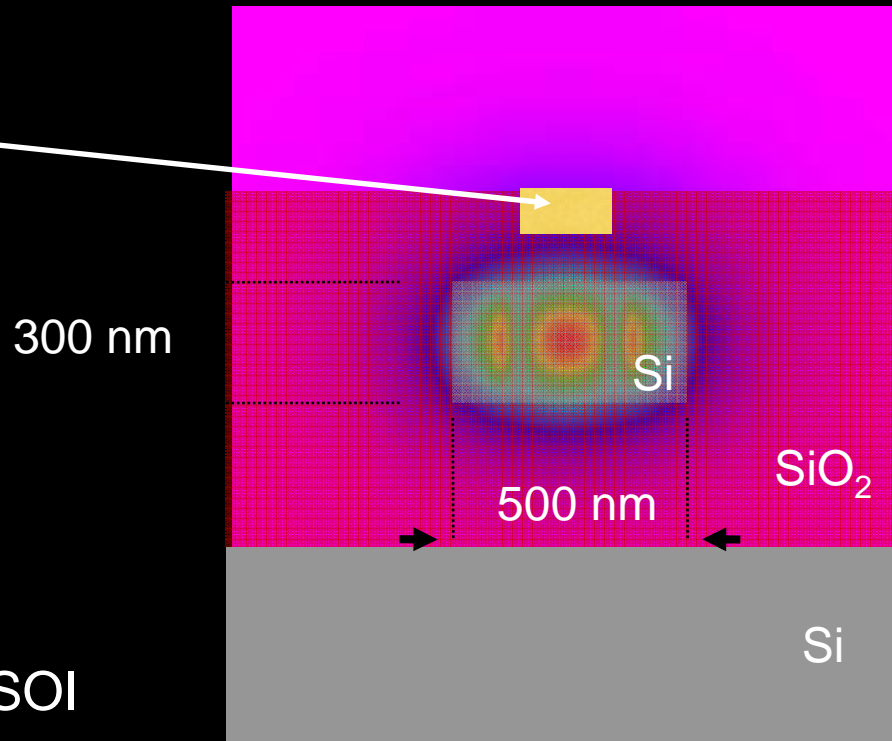


Courtesy of S. Landis CEA/LETI



Ultimate refractive silicon photonics

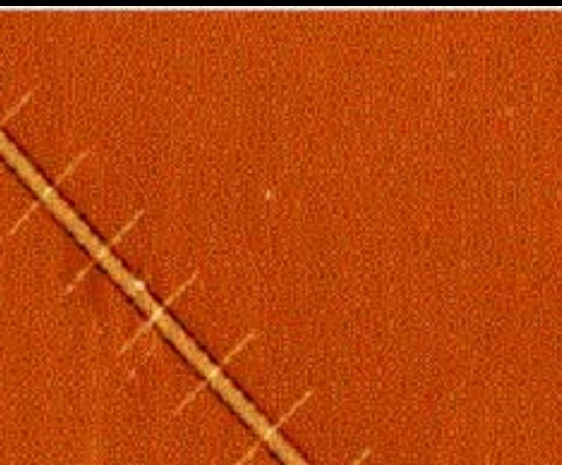
Plasmonic block



$$\Delta n > 2$$
$$E_{\text{surface}} < 1\% E_{\text{guided}}$$

SWIFTS

One of the first metallic structures realized on SOI waveguiding structure



PLACIDO ANR proje

See Poster session today M. Février p5

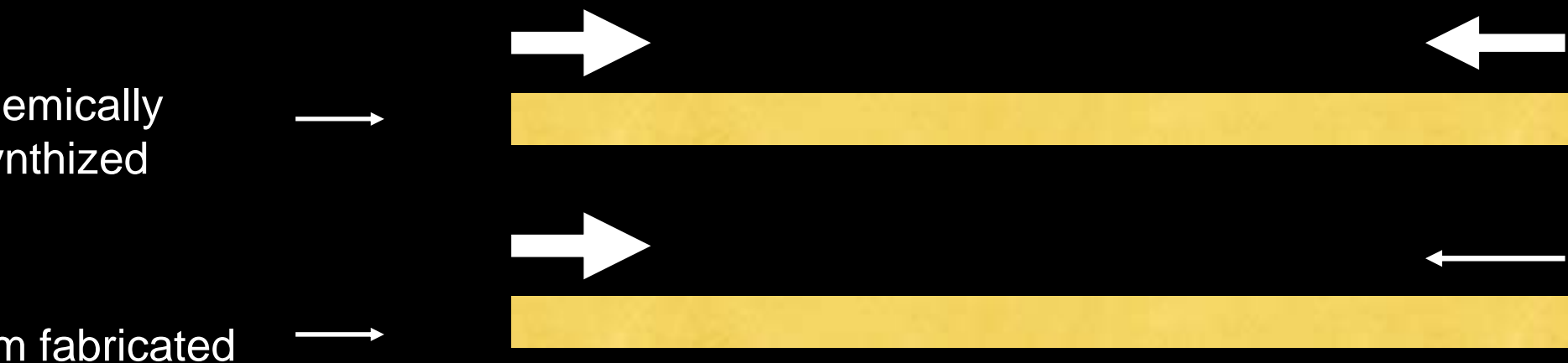
related issues

Gold \Rightarrow Copper

Alloy

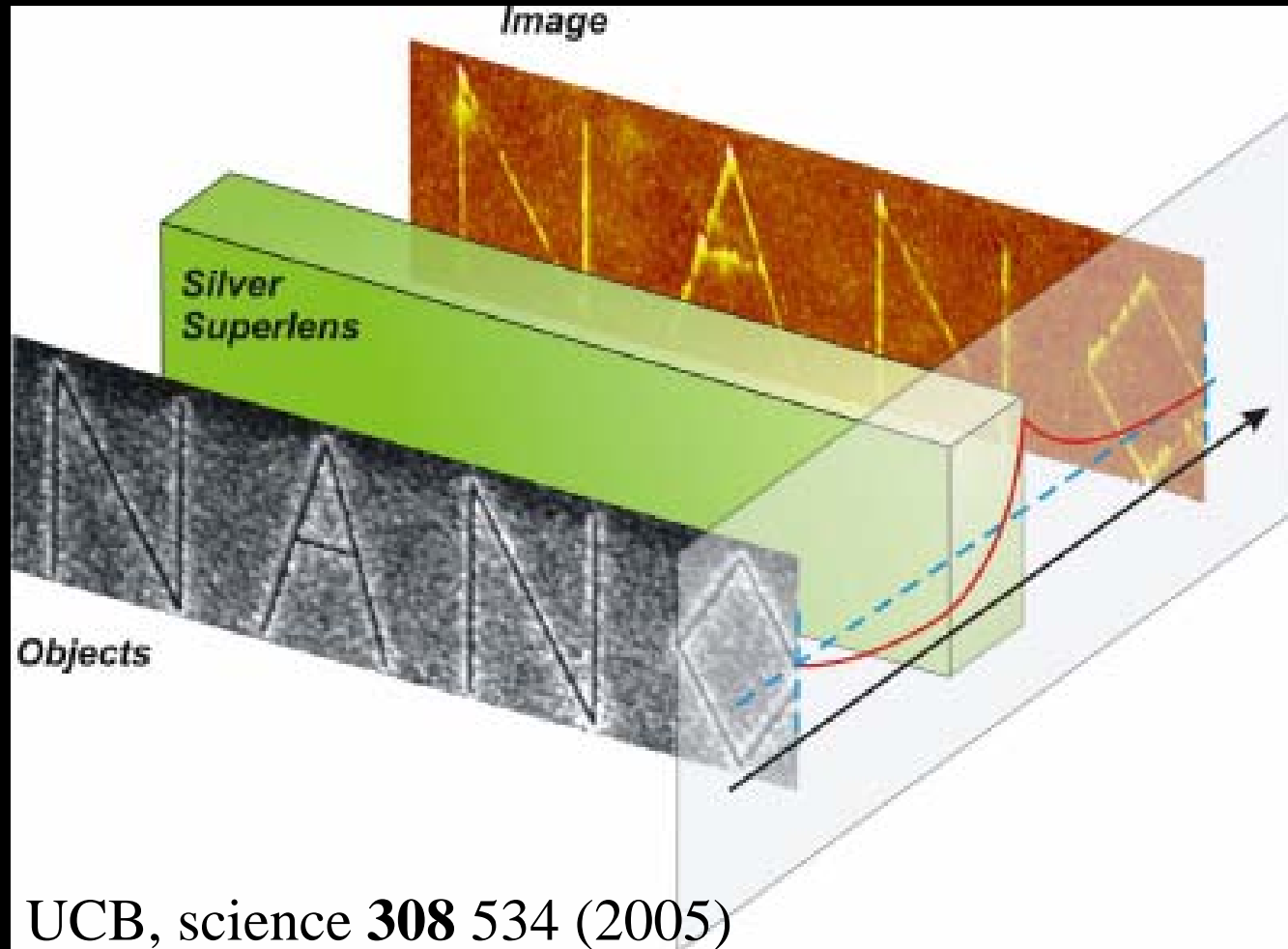
Crystal quality

Diltbacher et al. PRL 95, 257403 (2005)



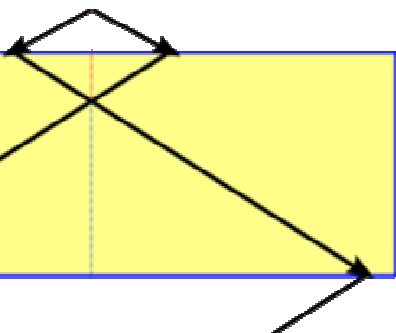
Plasmonics for nanofabrication

Superlens



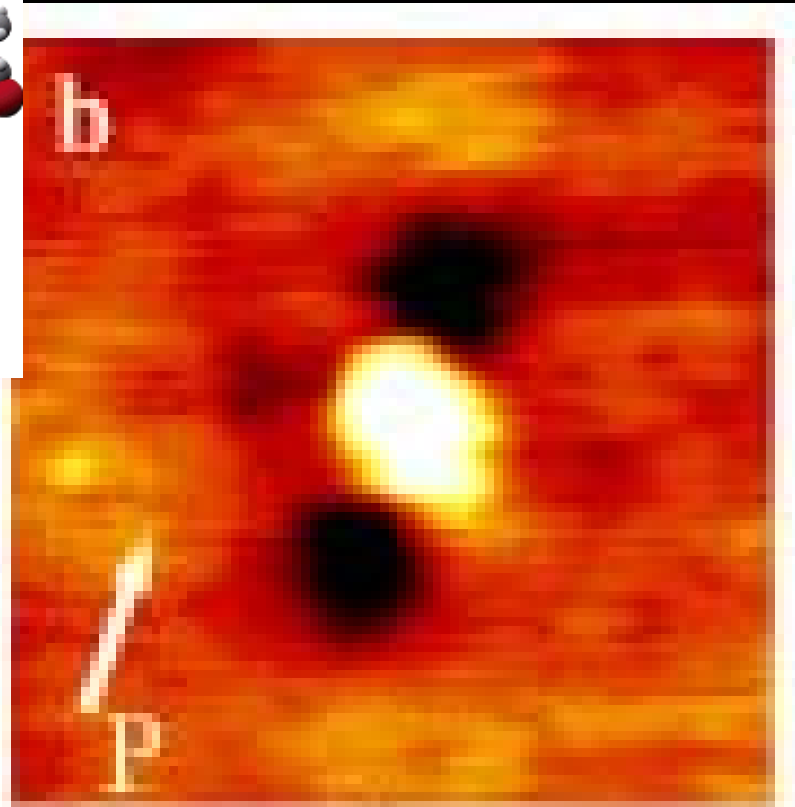
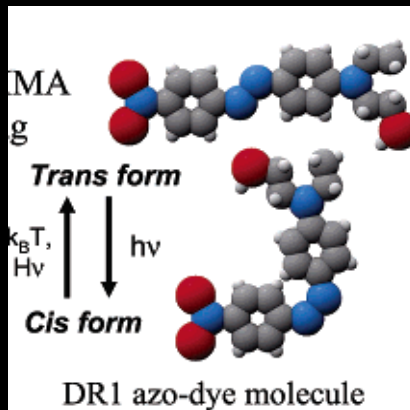
PRL **85** (2000)

Object focus



lithograph

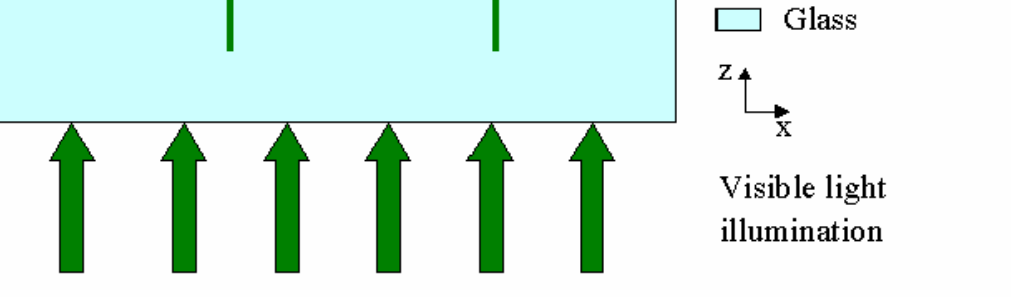
Localized plasmons assisted « lithography »



*LNIO – DPG PR
p107402 (2007)*

97 nm

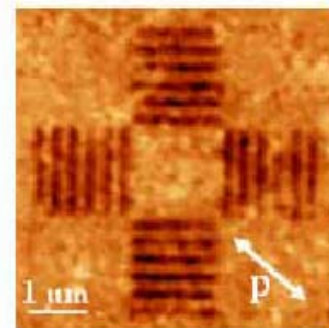
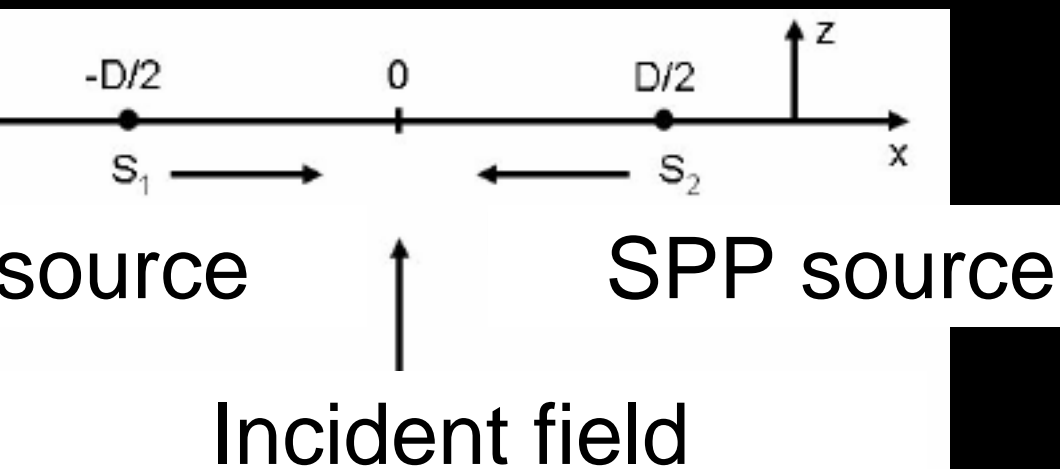
*IO – ANL - Northwestern
noletters 5 615 (2005)*



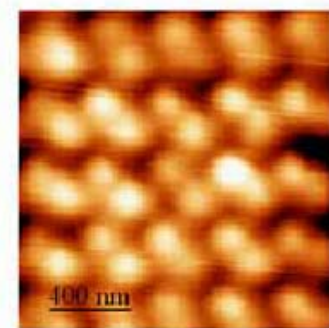
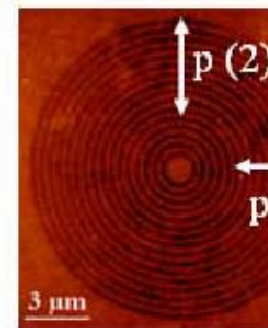
lithograph

Photons interferences printing

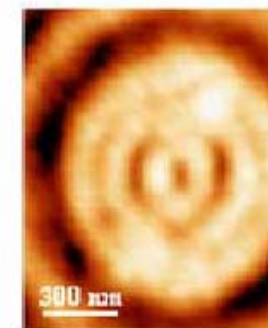
$$\lambda_{sp} = \lambda / \text{Re}(n_{\text{eff}})$$



(a)



(c)

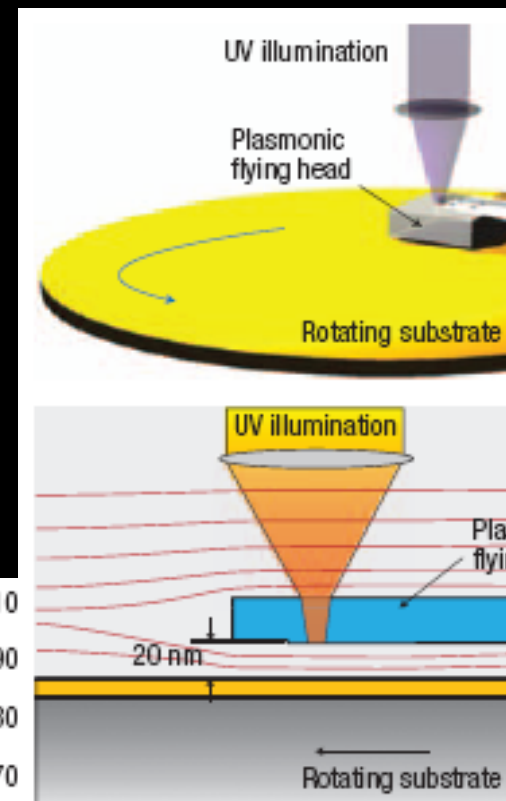
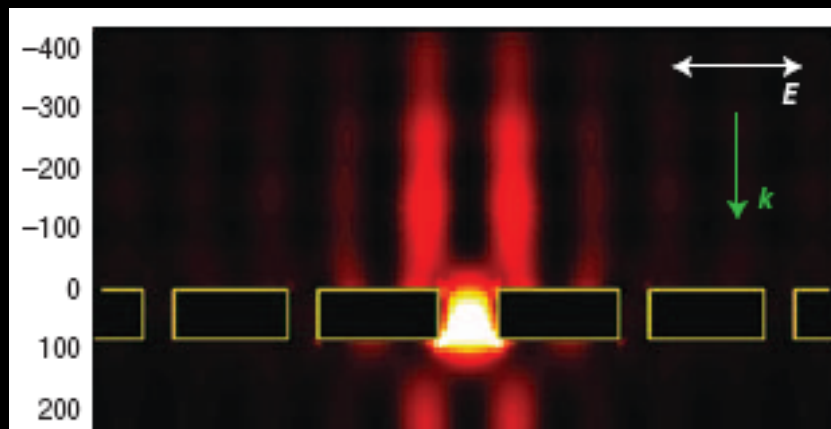
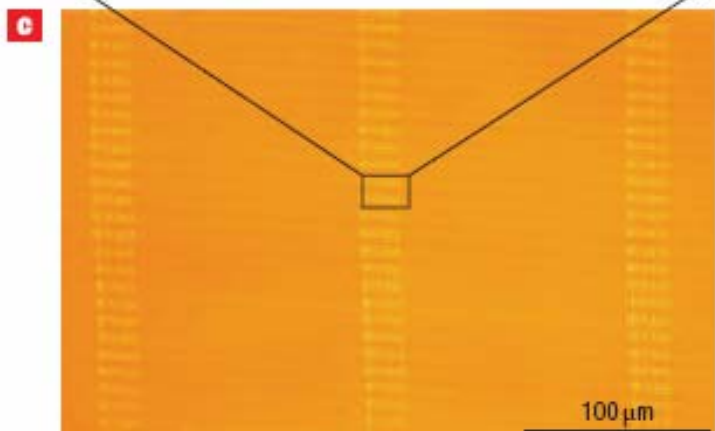
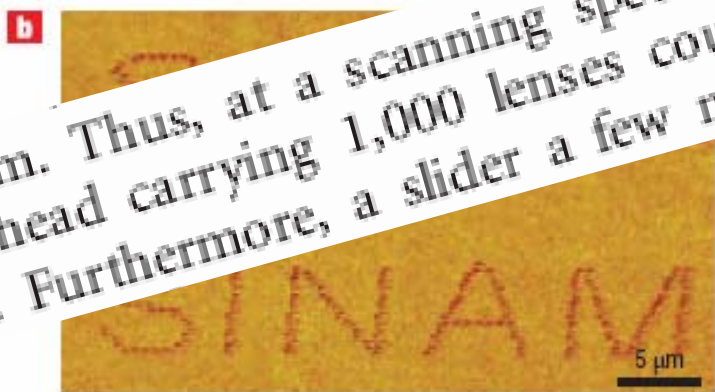
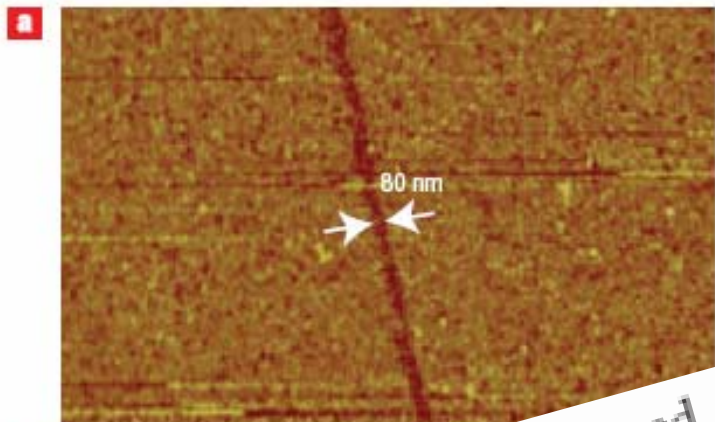


x 10⁴ (a.u.)



Plasmon lithography

nm. Thus, at a scanning speed of 10 m s^{-1} , a plasmonic
head carrying 1,000 lenses could write a 12 in. wafer in
n. Furthermore, a slider a few millimetres in size may take



Concluding remarks

Nanofabrication \Leftrightarrow plasmonics

Combination of techniques is required
including soft chemistry routes
and 3D nanoobjects assembly

Coming issues:

Silicon photonic integration

Elaboration of (hybrid) functional Materials

Thank you