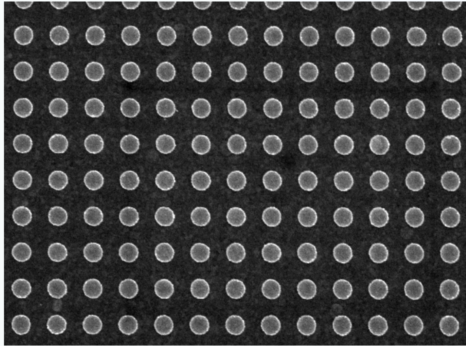
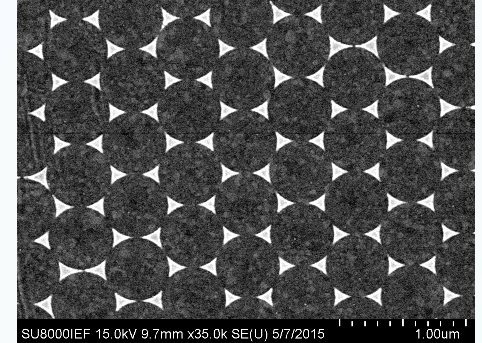
Ecole Thématique « Plasmonique Moléculaire et Spectroscopies exaltées »



Grégory BARBILLON



Surface Nanostructuring for bioplasmonics

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Outline

1. Conventional Lithography
2. Unconventional Lithographies
3. Conclusions

1. Conventional Lithography

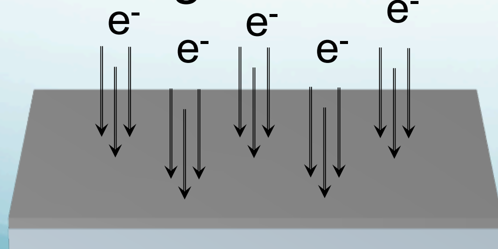
Electron Beam Lithography (EBL)

Fabrication Process with EBL

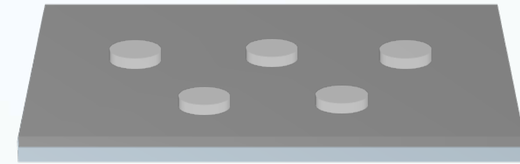
1- Cleaned SiO_2 Substrate

2- Deposition of PMMA by spin-coating

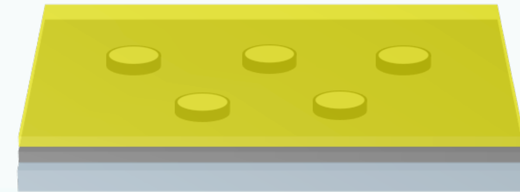
3- Pattern Design with electron beam



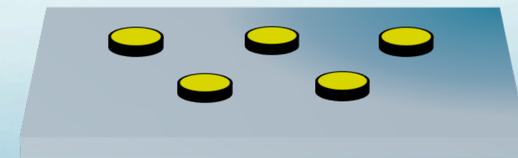
4- Development in solution MIBK/ISO



5- Evaporation of gold layer (30 nm)



6- Gold disks after lift-off process in acetone

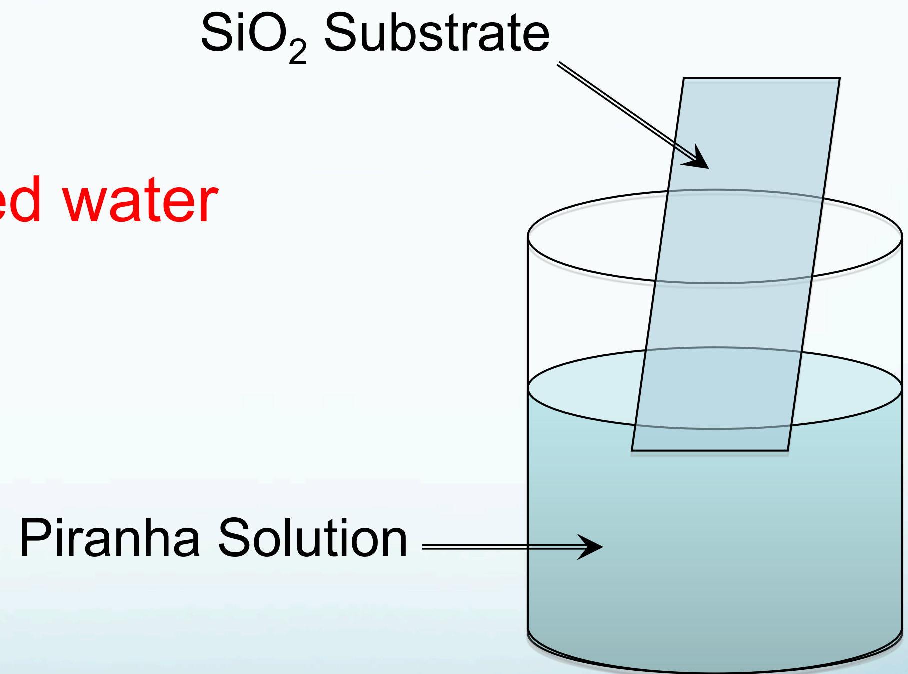


Step 1: Clean Substrate

1- Dipping in Piranha (3:1 H_2SO_4 (98%), H_2O_2 (30%)) solution during 30 min

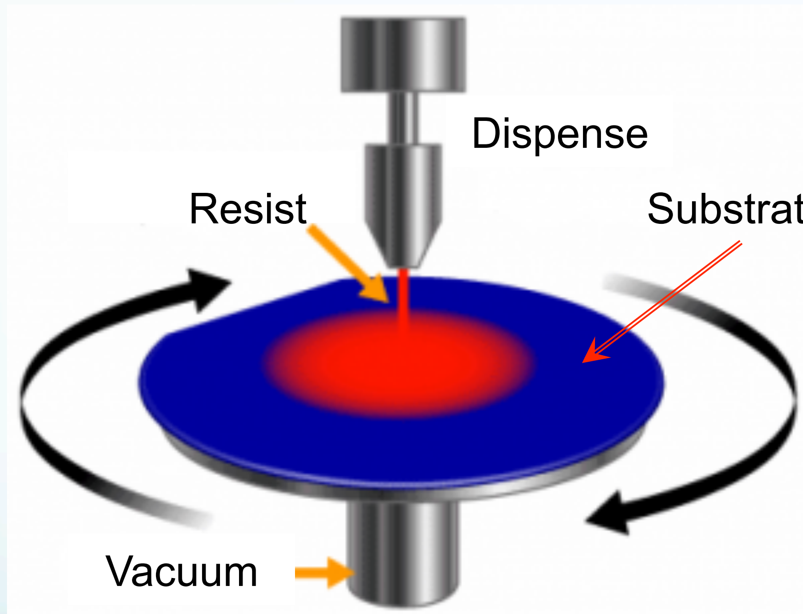
2- Rinsing abundantly with deionized water

3- Dry with N_2 gas (gun)



Step 2: Spin-coating of the resist

1- Spin-coating of the positive/negative-tone resist

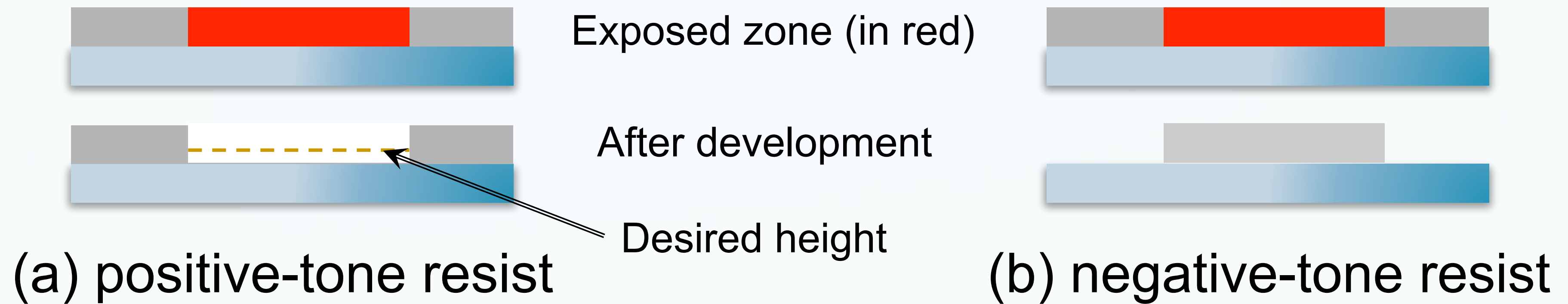


(a) Principle scheme of spin-coating

(b) Examples of spin-coating tool

2- Slight annealing for removing the solvent of the resist on hot plate at 180°C for 60-90s.

Step 2: Spin-coating of the resist



(a) positive-tone resist

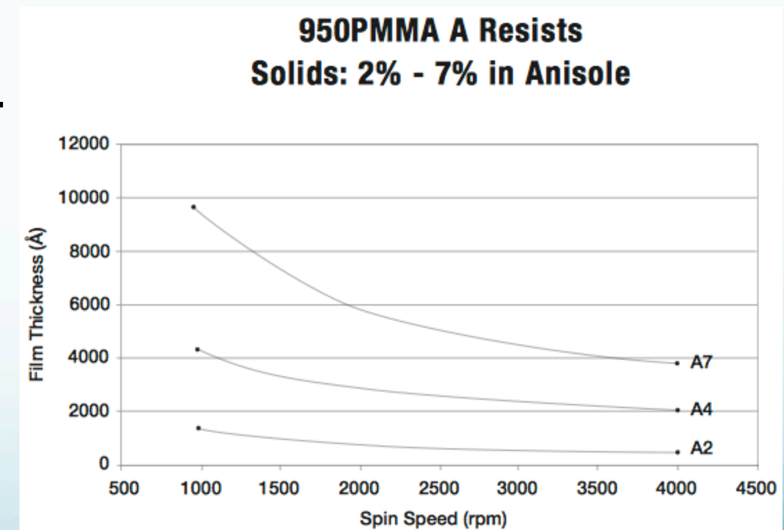
(b) negative-tone resist

Rule for good lift-off of nanostructures (NS):

Resist thickness = 3 x Desired height of NS

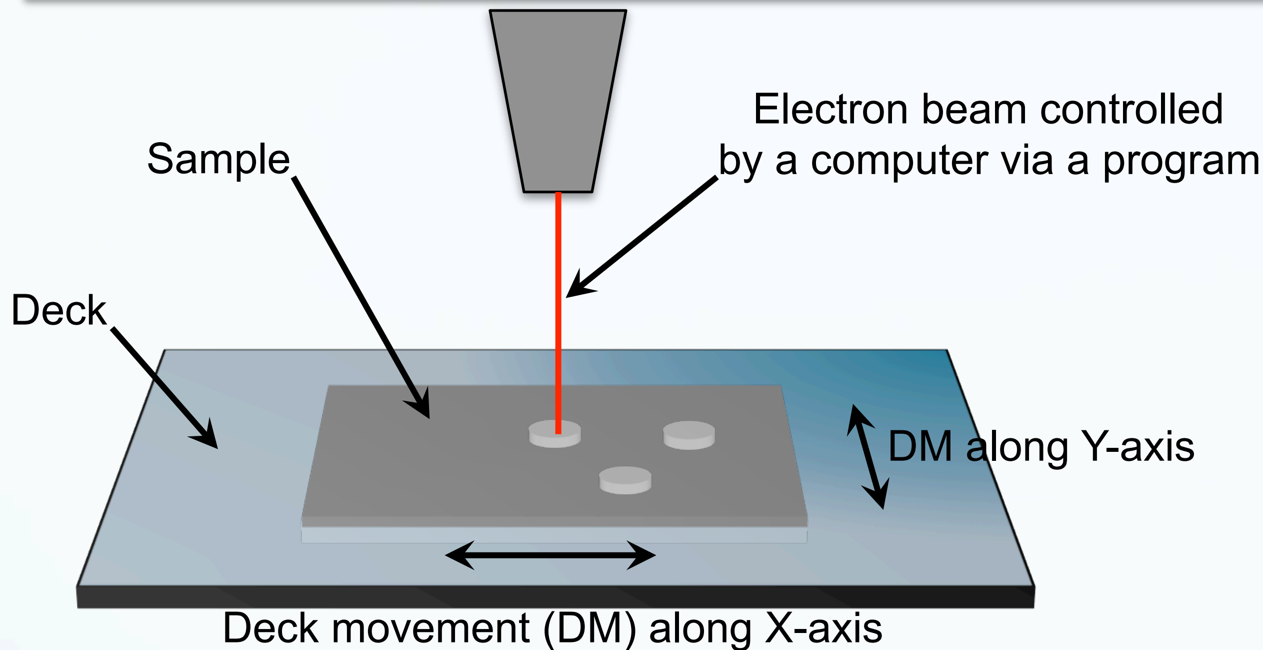
Important parameters:

- Spin speed
- Acceleration
- Time



(c) Spin-coating of PMMA: Thickness vs speed

Step 3: Pattern design with e⁻ beam



(a) Patterning of the sample

(b) Commercial EBL

Parameters to be set:

- Program of pattern
- Set the electron beam (focus…)
- Acceleration Voltage of electrons (typically 20-30 kV or 80-100 kV)
- Dose (via the current intensity used)

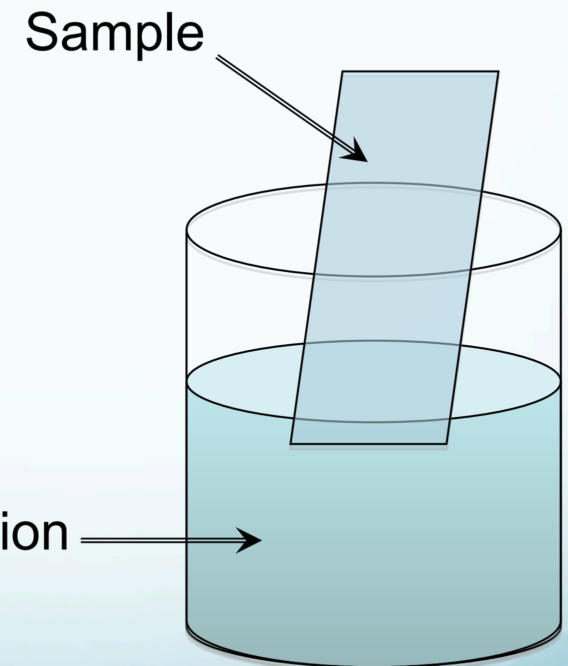
Step 4: Development in MIBK/ISO

1- Development of exposed zones during EBL

PRODUCT	COMPOSITION	RESOLUTION	SENSITIVITY / THROUGHPUT
M/I 1:1	1:1 MIBK to IPA	high	high
M/I 1:2	1:2 MIBK to IPA	higher	medium
M/I 1:3	1:3 MIBK to IPA	very high	low
MIBK	MIBK	low	high

Our choice

2- Dry the sample with N_2 gun



Scheme of the sample development

Step 5: Evaporation of metallic layer

Rotation

Sample

e^-

Crucible

Electron gun

Materials to evaporate:
Au, Ag,Ti, Cr, Pd,…

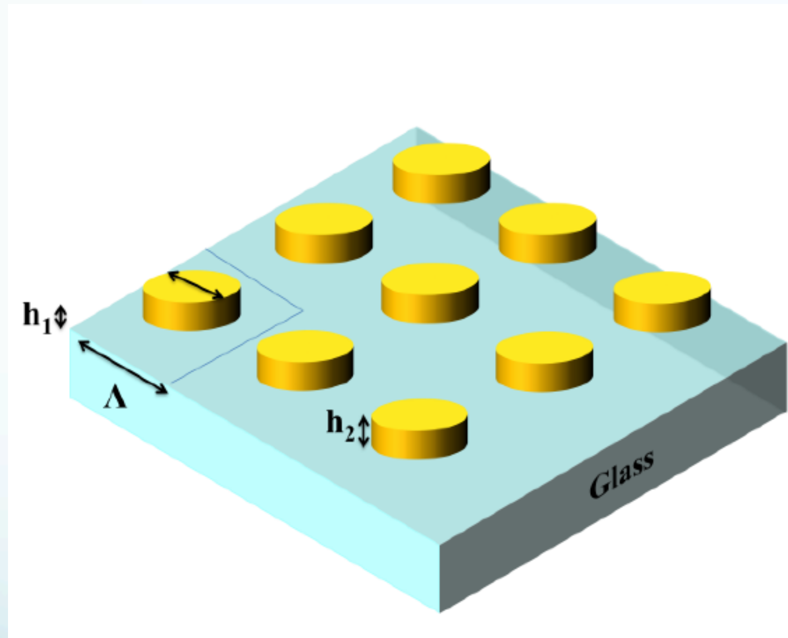
(a) Principle of Electron Beam Evaporation (EBE)

(b) Example of commercial EBE tool

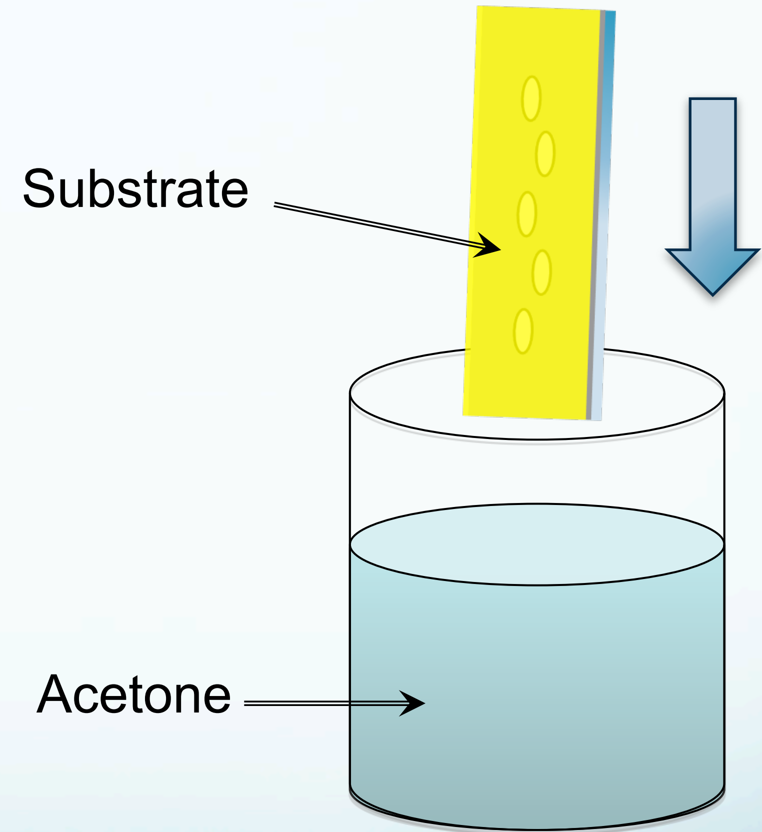
Parameters to be set:
- Vacuum
- Speed of deposition (nm/s)

Step 6: Lift-off process in acetone

1-Dipping in acetone during several hours
2-Dry the sample with N_2 gun

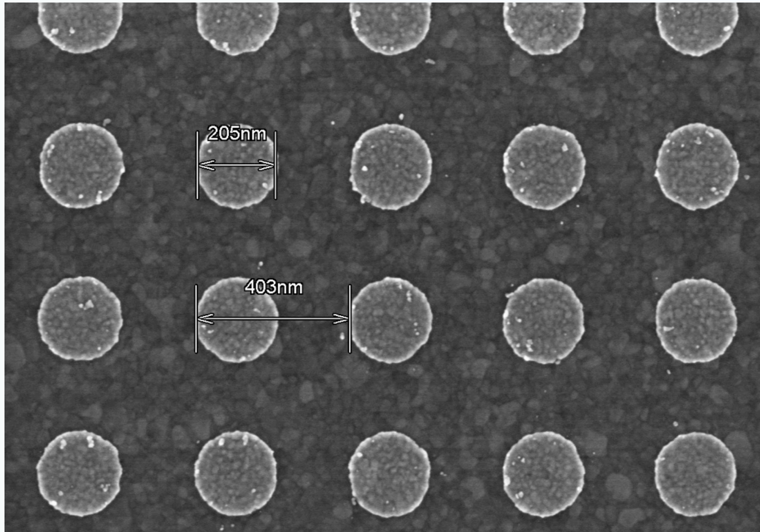


(a) Metallic nanostructures on glass substrate obtained after lift-off

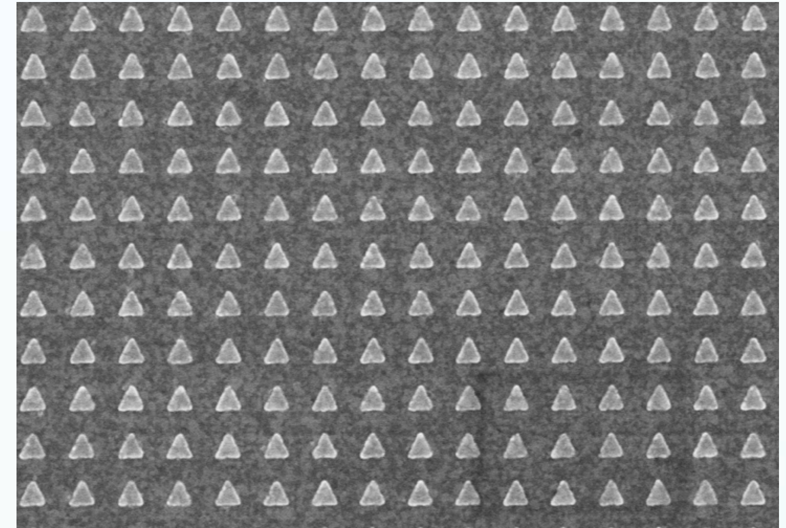


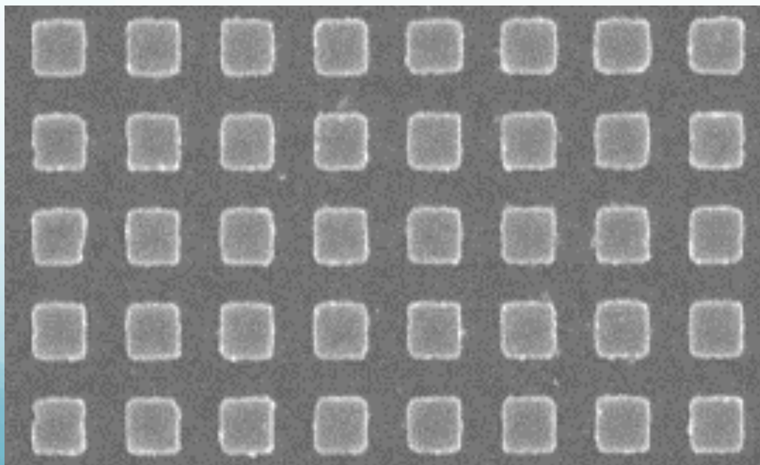
(b) Lift-off process

Examples of nanostructures



(a) Gold nanodisks


(b) Gold nanotriangles


(c) Gold nanosquares

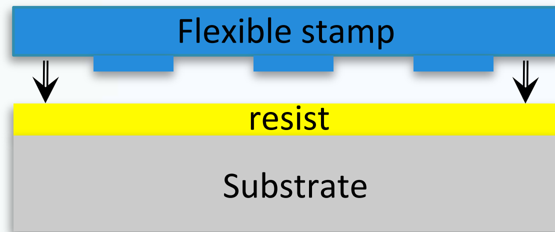
M. Sarkar *et al.* ***ACS Photonics*** 2015, 2, 237-245.
J.F. Bryche *et al.* ***J. Mater. Sci.*** 2015, 50, 6601-6607.
J.F. Bryche *et al.* ***Plasmonics*** 2016, 11, 601-608.

2. Unconventional Lithographies

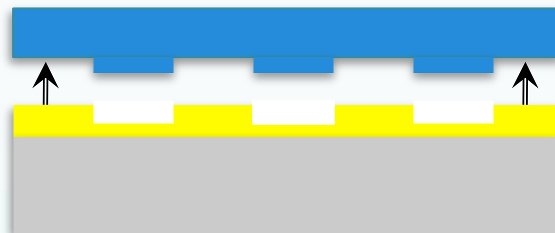
Soft UV Nanoimprint Lithography (UV-NIL)

Fabrication Process with UV-NIL

1. Fabrication of soft stamp and Press Stamp

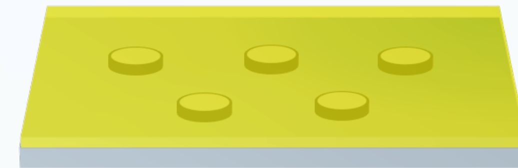


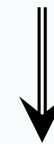
2. Imprint with UV light and Release Stamp



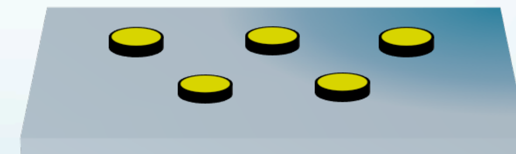
3. Reactive Ion Etching process
of residual thickness

4. Evaporation of gold layer (30 nm)



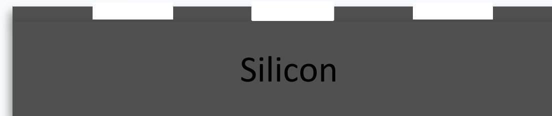


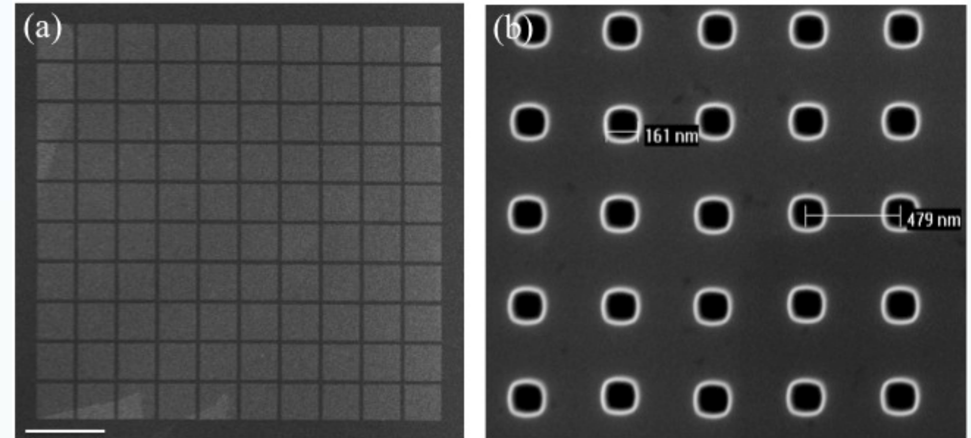
5. Gold disks after lift-off process in acetone



Step 1: Fabrication soft stamp

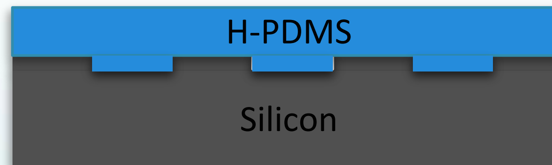
1. Master mold designed by EBL in PMMA
+ Transfer of patterns in Si by RIE (O_2 + SF_6)
+ Lift-off of PMMA





SEM images of master mold in Si:
(a) zone of 1 mm^2
(b) Zoom on a square

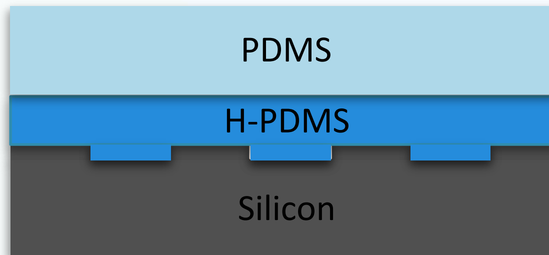
2. Hard-PDMS spin-coated (thickness 5-8 μm)



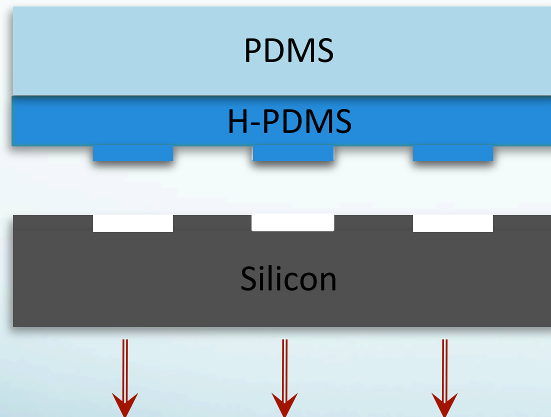
G. Barbillon *et al.* ***Microelectronic Engineering*** 2010, 87, 1001-1004.
G. Barbillon ***Micromachines*** 2012, 3, 21-27.
M. Cottat *et al.* ***Nanoscale Research Letters*** 2014, 9, 623.

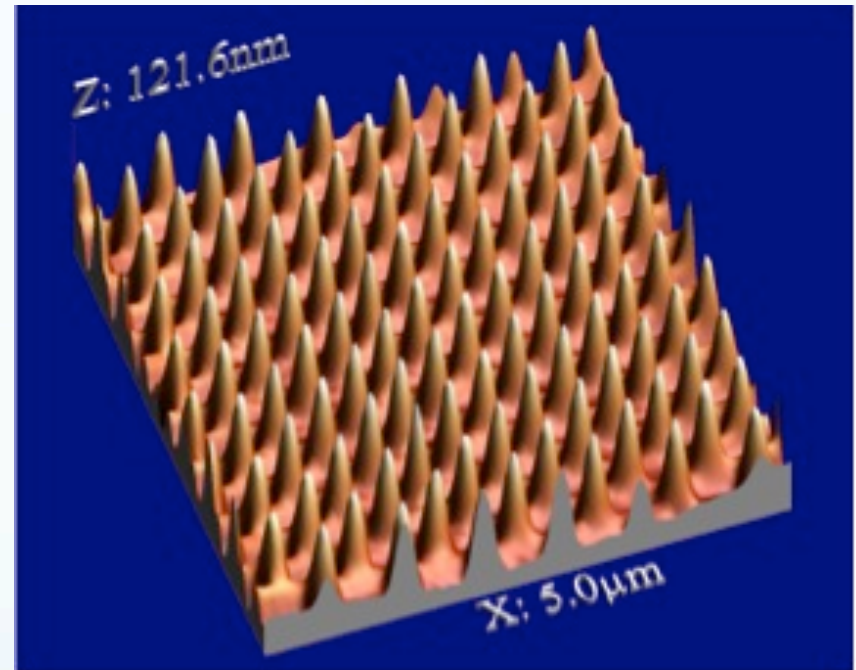
Step 1: Fabrication soft stamp

3. PDMS Casting (≈ 1.5 mm) and curing at 60°C during 24h



4. Bilayer Hard-PDMS/PDMS Stamp Release

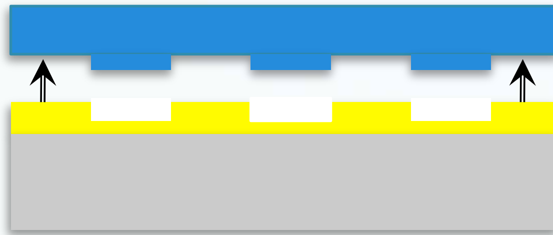




3D AFM image of PDMS stamp obtained

G. Barbillon *et al.* ***Book Chapter: Large Surface Nanostructuring by Lithographic Techniques for Bioplasmonic Applications*** in *Manufacturing Nanostructures*, 2014, 244-262.

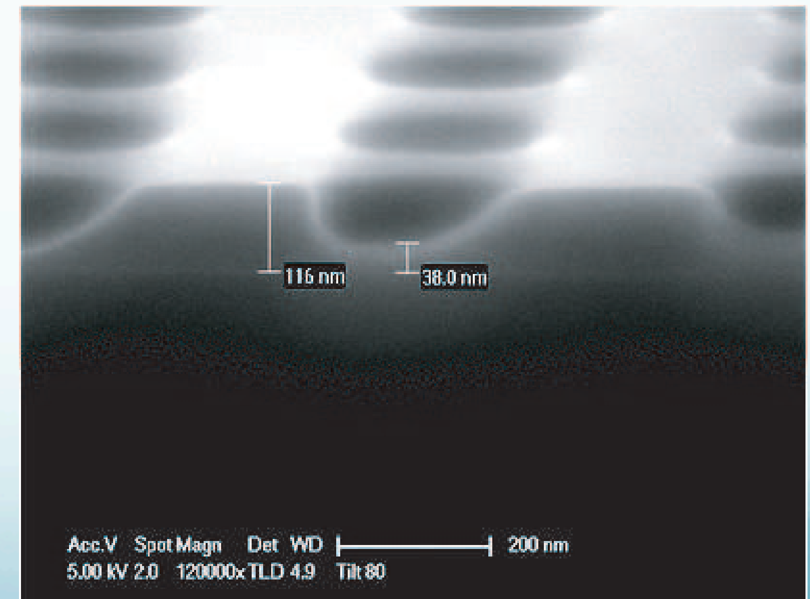
Step 2: Imprint with UV light & Release of stamp



Imprint in AMONIL deposited on a PMMA layer (on substrate):

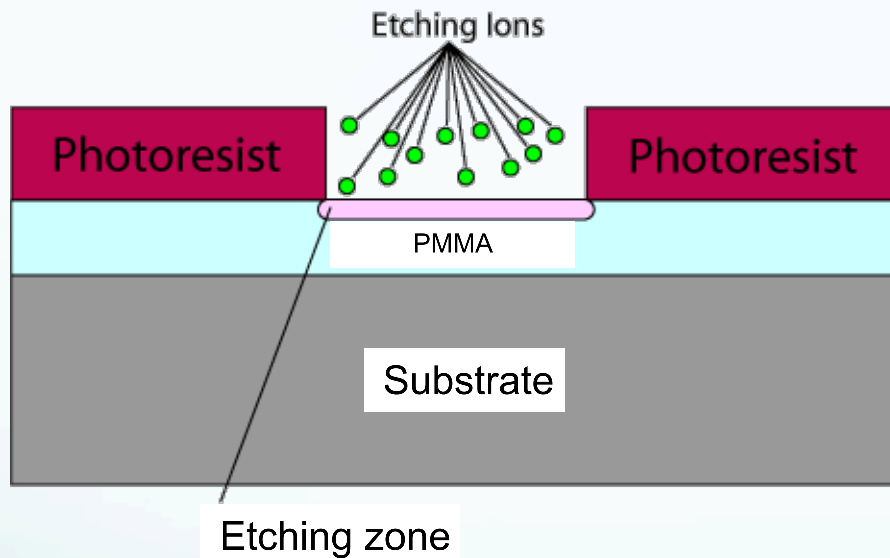
- UV light used: λ = 365 nm with 10 mW/cm^2 during 20 min
- Pressure used: P = 200 mbar.

SEM image of imprint AMONIL with a PMMA underlayer



G. Barbillon *et al.* ***Microelec. Eng.*** 2010, 87, 1001-1004.

Step 3: Reactive Ion Etching of Residual thickness



Principle scheme of RIE process

RIE process for AMONIL & PMMA:

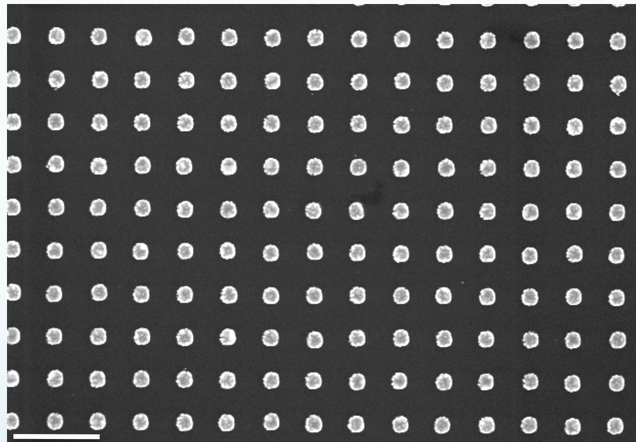
- Gases used for AMONIL:
  2 sccm O_2 & 20 sccm CHF_3
- Gases used for PMMA:
  10 sccm O_2
  v_{PMMA} = 80 nm/min,
  v_{AMONIL} = 30 nm/min

Commercial RIE tool

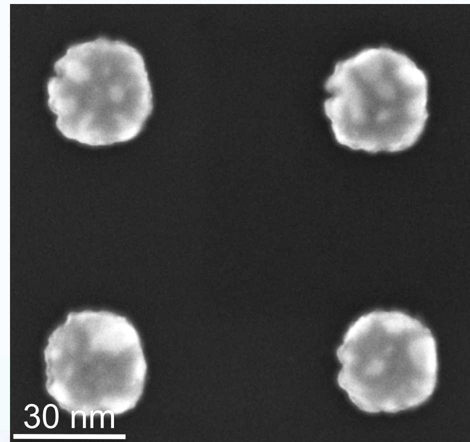
F. Hamouda *et al.* ***Microelectronic Engineering*** 2009, 86, 583-585.
G. Barbillon *et al.* ***Microelectronic Engineering*** 2010, 87, 1001-1004.
G. Barbillon ***Micromachines*** 2012, 3, 21-27.

Step 4 & 5: Evaporation of Au layer And lift-off in acetone

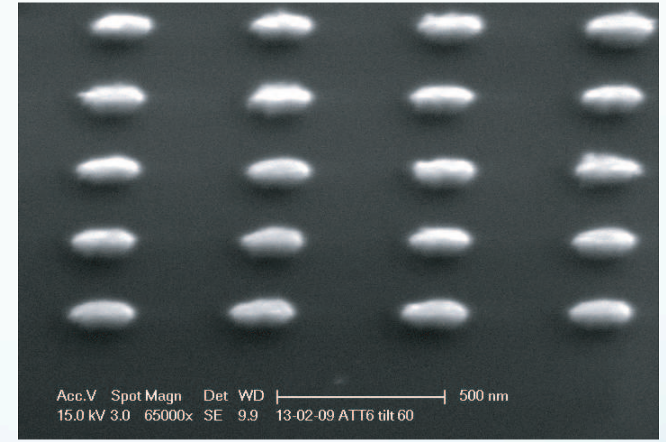
1-Evaporation with the technique previously described
2-Dipping in acetone during several hours
3-Dry the sample with N_2 gun



(a)



(b)



(c)

SEM images of gold nanodisks obtained with UV-NIL: (a) a zone of some mm^2 (scale bar = 150 nm), (b) diameter: ≈ 28 nm, and periodicity: 78 nm, and (c) diameter: ≈ 165 nm and periodicity: 500 nm

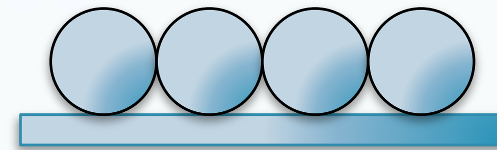
G. Barbillon *et al.* ***Microelectronic Engineering*** 2010, 87, 1001-1004.
G. Barbillon ***Book Chapter: Sub-30 nm Plasmonic Nanostructures by Soft UV Nanoimprint Lithography*** in *Updates in Advanced Lithography*, 2013, 197-208.

Nanosphere Lithography (NSL)

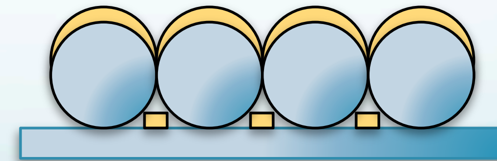
Fabrication Process with NSL

1- Cleaned SiO_2 Substrate

2- Deposit of nanospheres by spin-coating



3- Deposit of gold layer under normal incidence

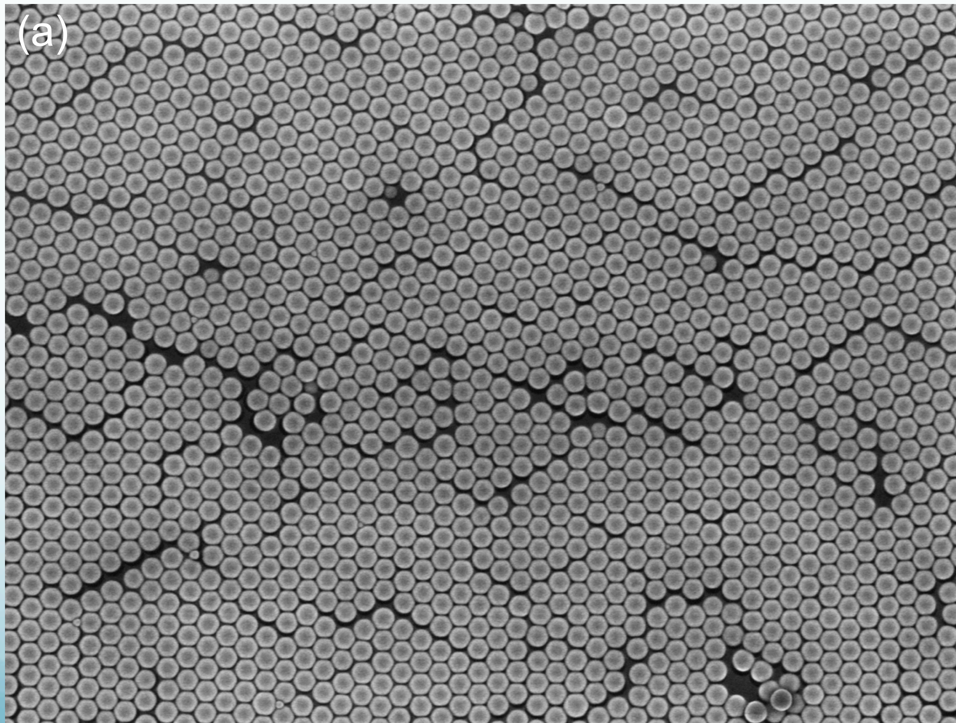


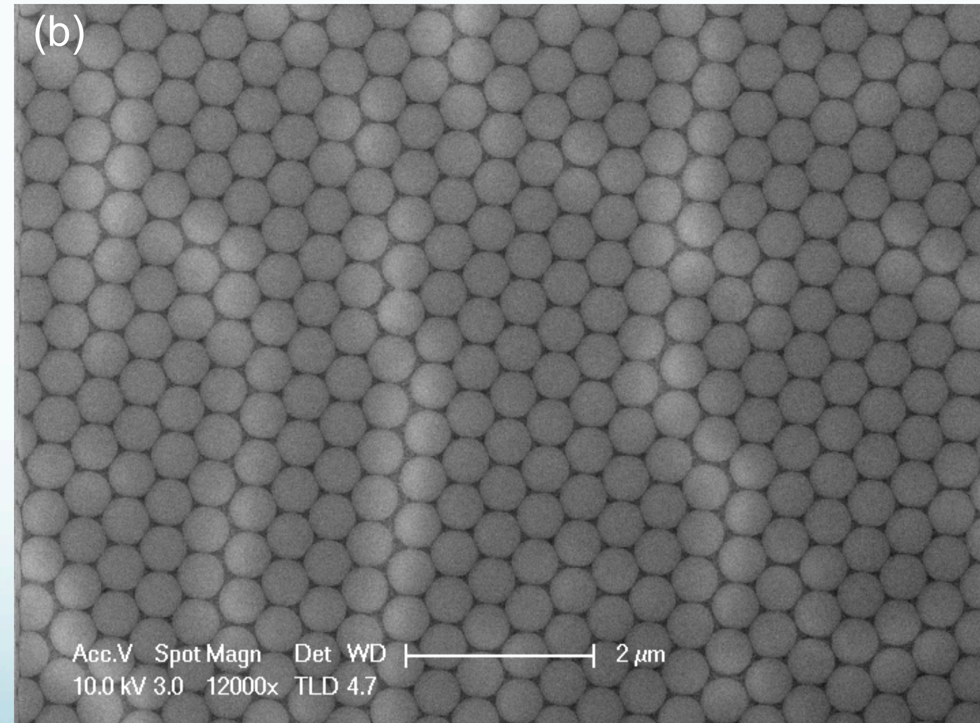
4- Gold nanostructures After removal of nanospheres

Steps 1 & 2: Spin-coating of NS on cleaned substrate

1- Cleaning the substrate following the protocol previously described

2- Spin-coating of NS as previously described



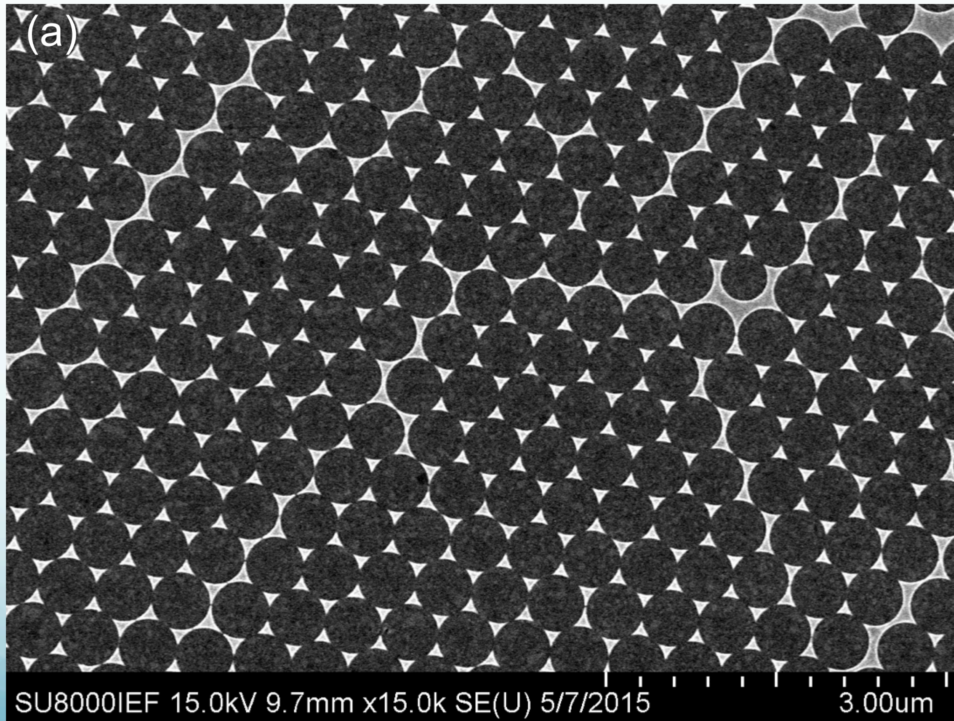


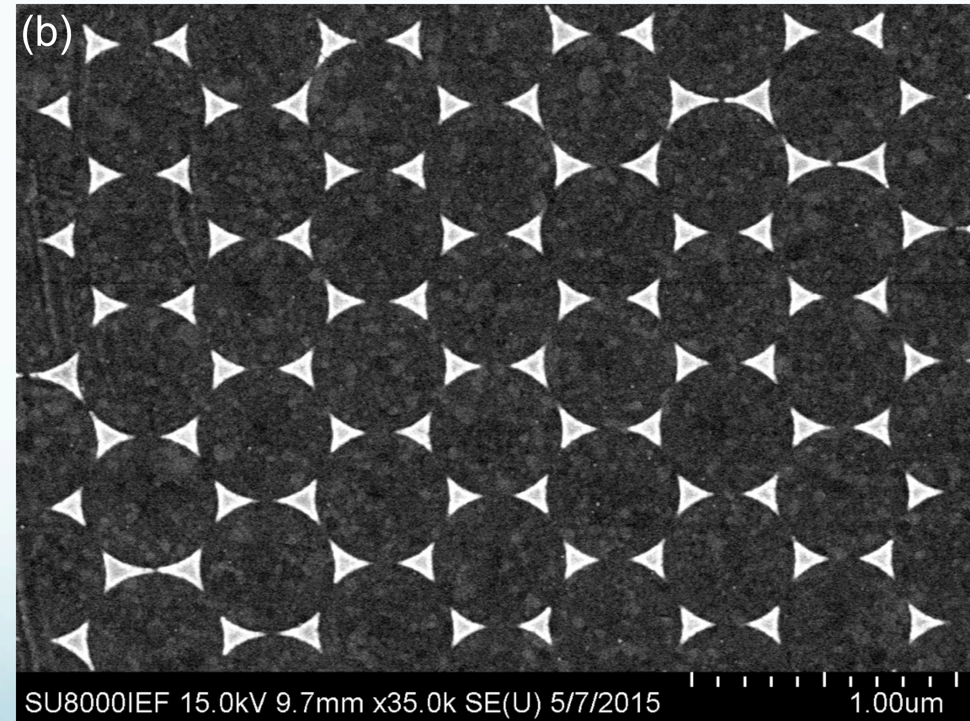
(a) and (b) SEM images of polystyrene beads (NS) deposited on substrate

Steps 3 & 4: Deposit of gold layer and the lift-off process

1- Deposit of metallic layer following the protocol previously described

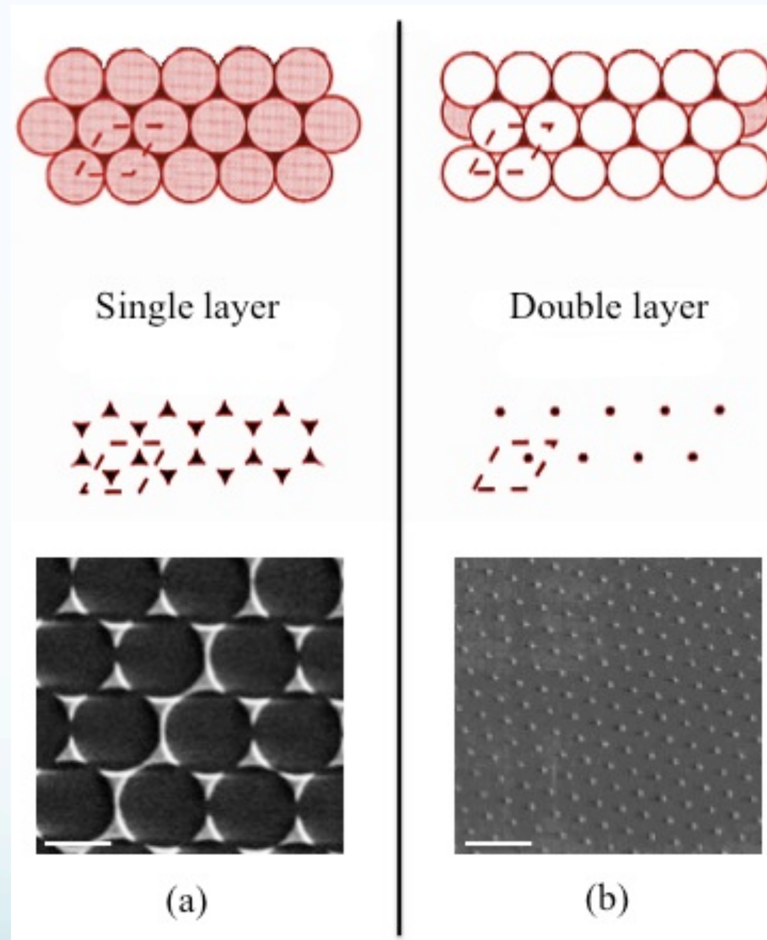
2- Lift-off process as previously described





(a) and (b) SEM images of gold triangular nanoprisms.

Single and double layer of NS



(a) Single layer of NS and (b) double layer of NS and SEM images of gold nanostructures associated to each case (scale bar = 400 nm for (a) and 1 μm for (b)).

3. Conclusions

Advantages/disadvantages

Techniques	Advantages	Disadvantages
EBL	- High spatial resolution - Various Shapes - Large surface patterning	- High cost - Writing time for large surface - Charge effects on insulating substrates - Mass production
Soft UV-NIL	- Writing time (imprint) - Large surface patterning - Imprint on corrugated substrate - Good spatial resolution - Mass production - Low cost	- Resolution < EBL resolution
NSL	- Low cost - Large surface patterning - Good spatial resolution - Mass production	- Defect presence in assembly of nanospheres - Resolution < EBL resolution

G. Barbillon *et al.* ***Book Chapter: Large Surface Nanostructuring by Lithographic Techniques for Bioplasmonic Applications*** in *Manufacturing Nanostructures*, 2014, 244-262.

Thank you for your attention

Merci pour votre attention

For any questions, do not hesitate to contact me:
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Personal email: gregory.barbillon@laposte.net