Plasmonics: Application-oriented fabrication

Part 3. Fabrication methods

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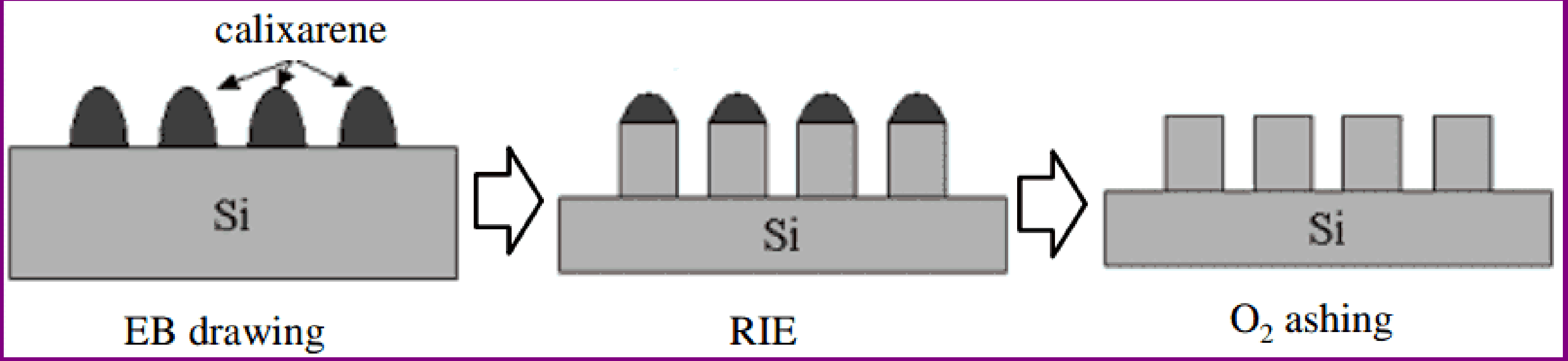
Motivation

- The first part - introduction to plasmonics
- The second part - analysis of fabrication problems for plasmonic devices
- This part - application of different methods in fabrication of plasmonic devices

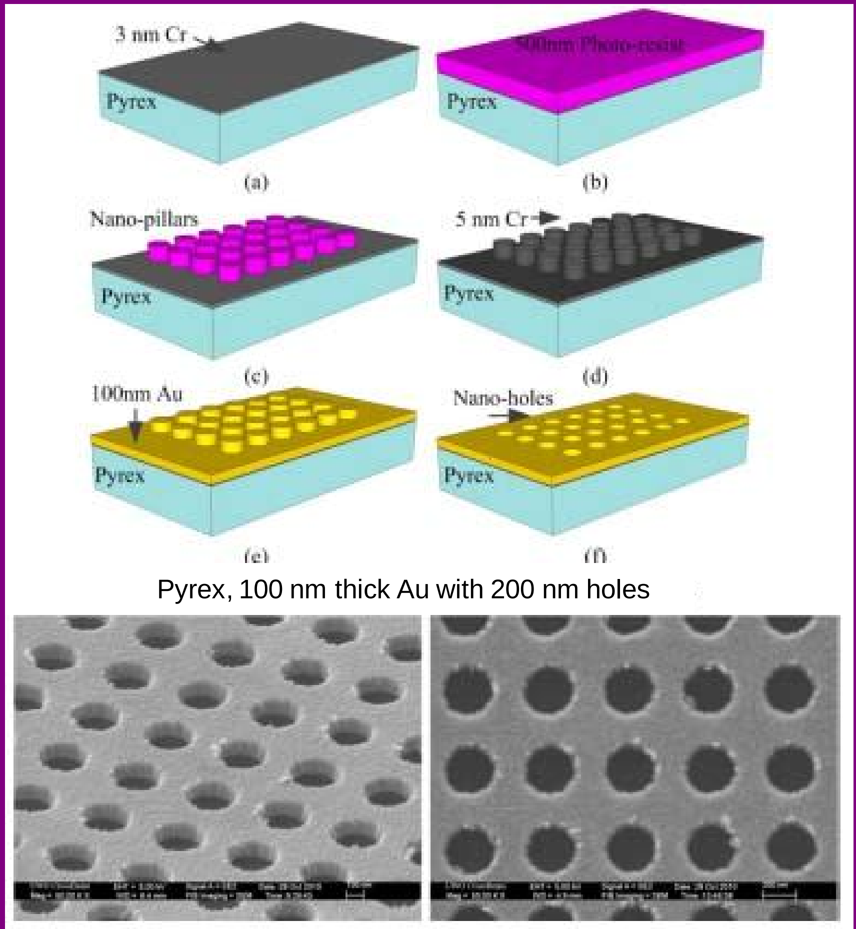
Electron beam lithography (EBL)

- Electron beam drawing at 30 keV. Conductive substrate is mandatory
- Pitch 18x18 nm for calixarene (negative, resolution 2.5 nm, 15 nm thick) and 40x50 nm for ZEP 520 (positive, resolution 10 nm, 70 nm thick)
- After RIE only pitch 25x25 nm, dot size decreased from 15 nm mask to 9 nm in Si, heigh 20 nm. Deep RIE is problematic.
- For metal patterning EBL is mainly accompanied by lift-off due to problems with metal etching. Adhesion layer for Au and Ag is mandatory.
- Alignment problems during fabrication of multilayer devices



S. Hosaka et al., Appl. Phys. Lett. 89, 223131 (2006)

Nanohole array by EBL

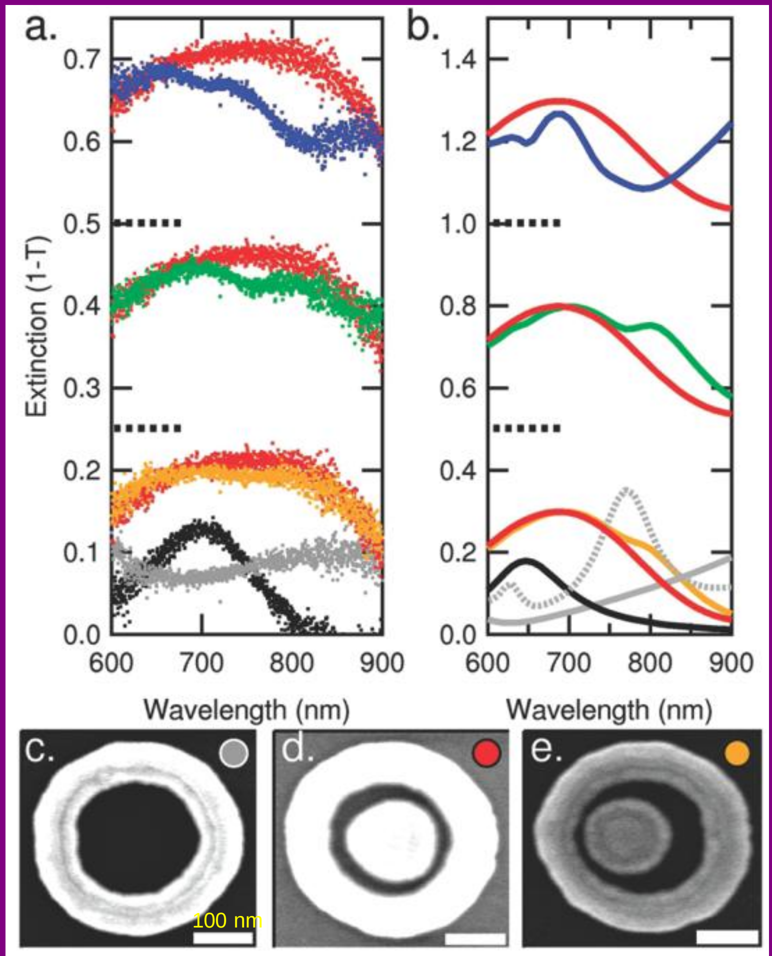


- Deposition of a conductive layer (3 nm of Cr or Ti) to avoid substrate charging.
- 500 nm photoresist (Negative Tone) was spin-coated and soft-baked on the conductive layer.
- Pattern of nano-hole arrays was written with the EBL machine
- (LEO, 1530 e-beam lithography) and followed by development. The adhesion layer (5-10 nm of Ti) was deposited
- Deposition of a 100 nm gold layer.
- Sacrificial mask layer (PR pillars) was lifted off

19 December 2011 / Vol. 19, No. 27 / OPTICS EXPRESS 26186

Ring structures by EBL

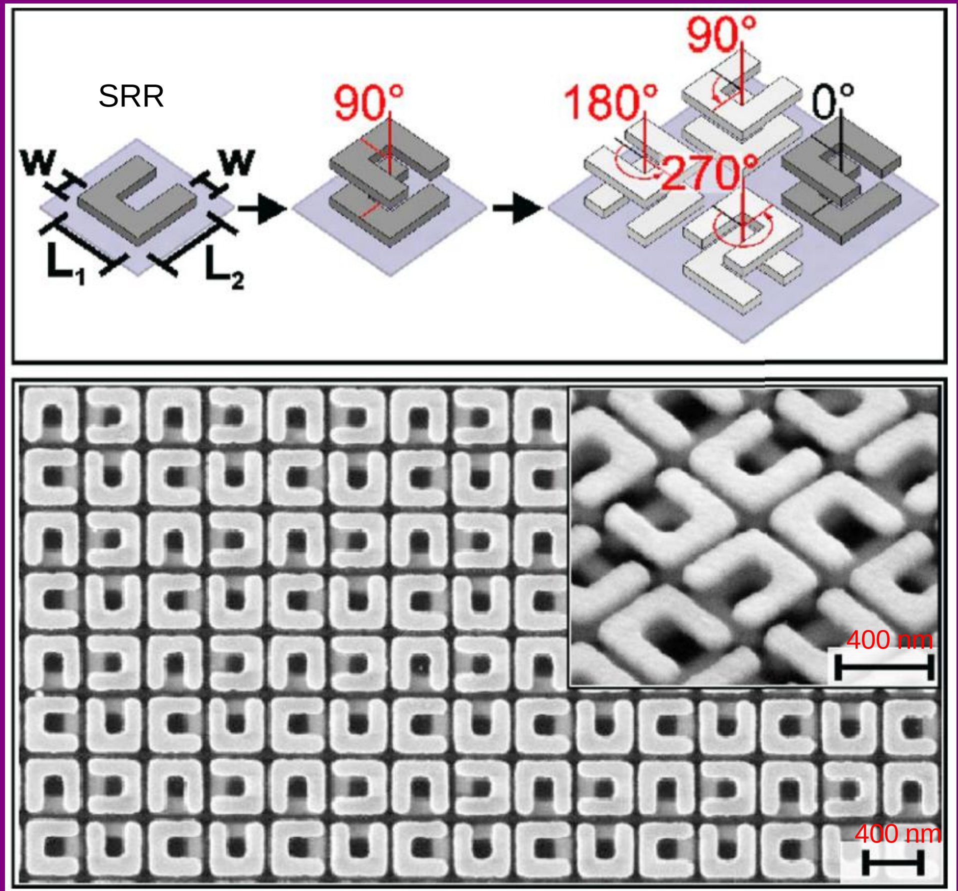
Measured Simulated



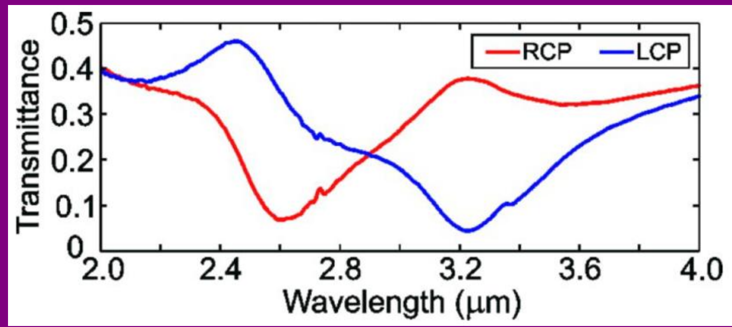
- Gold on thin glass slides (0.15 mm thick) coated with 10 nm ITO.
- Sputtering a nominally 50 nm Au/4 nm Ag film.
- An etch mask was created by EBL using a negative-tone hydrogen silsesquioxane (HSQ) resist.
- Xe ion milling of Au

ACS Nano 2010, 4, 1664–1670

Metamaterial on double layer of SRR



Left-handed and right-handed circular polarization, normal incidence



Two successive electron-beam-lithography steps and an intermediate planarization process via a spin-on di-electric. Planarize the sample via a 500-nm-thick spacer layer of commercially available spin-on dielectric (IC1-200, Futurrex, Inc.) and a subsequent thinning via reactive-ion etching to 85 nm.

100 μm × 100 μm area

A glass substrate covered with a 5 nm thin film ITO

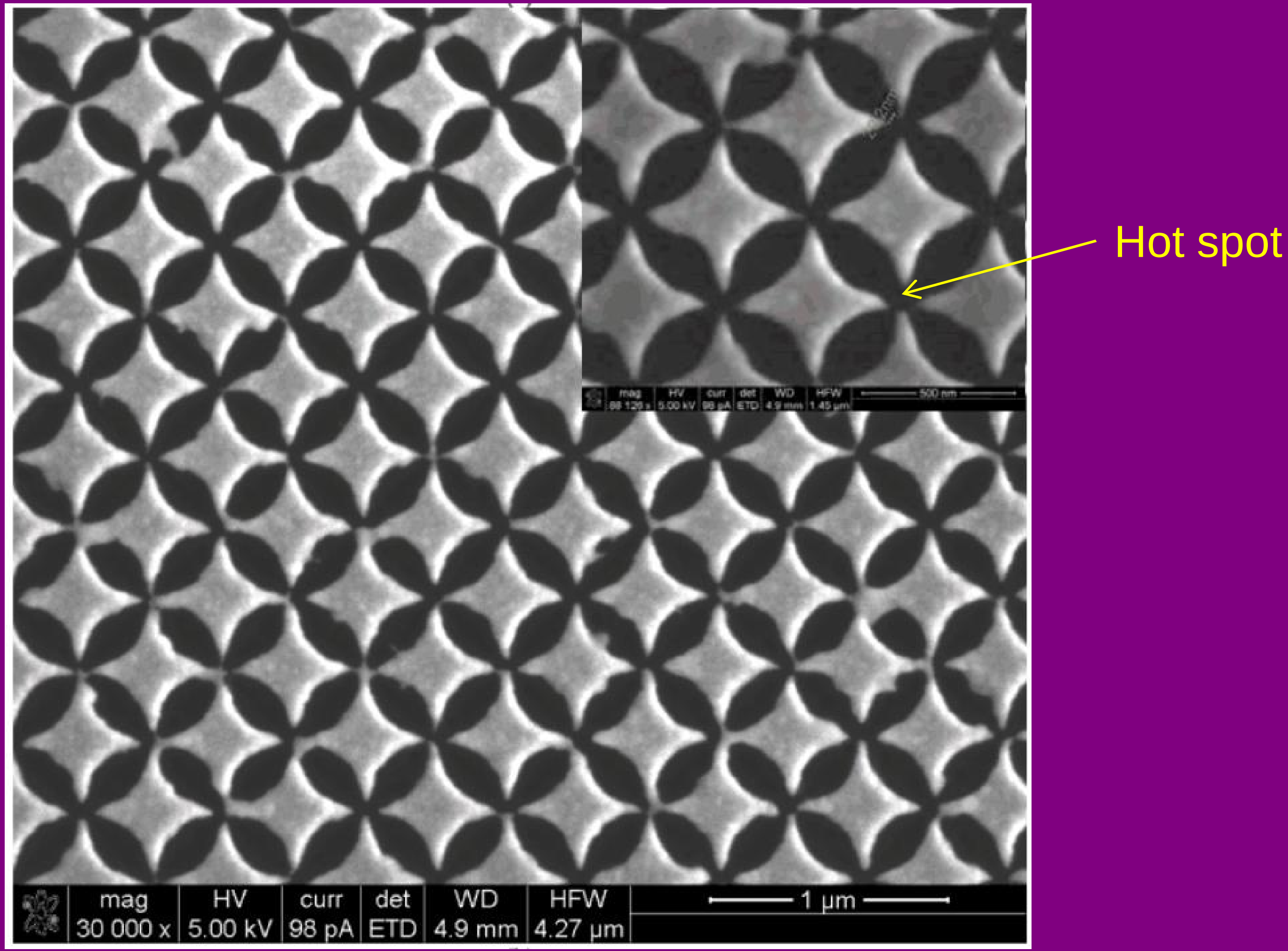
Au resonators

May 15, 2010 / Vol. 35, No. 10 / OPTICS LETTERS

FIB

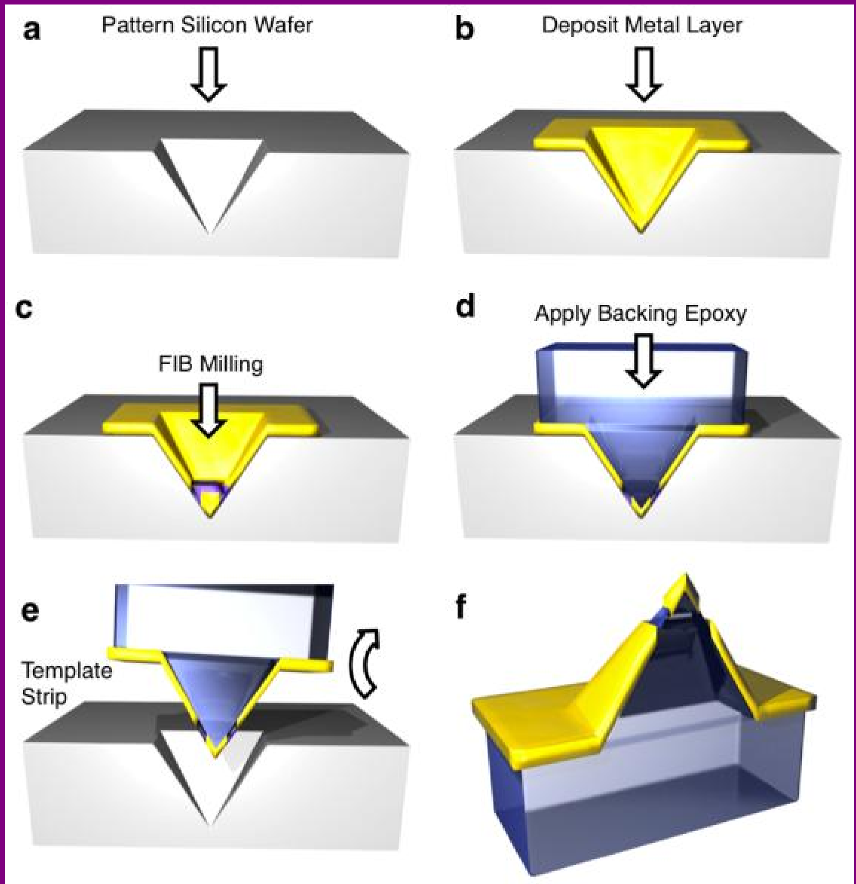
- FIB lithography is superior to EBL:
  - Higher resolution
  - Higher resist sensitivity
- Additionally to EBL:
  - Local ion beam etching (subtractive lithography)
    - 3D patterning
  - Local deposition of materials (additive lithography)
  - Local ion implantation
    - 3D patterning
  - Local ion-induced mixing
  - Direct patterning of hard mask layers
- Multi-beam systems
- Conductive layer on the substrate is mandatory
- Redeposition of sputtered material on the sample

FIB, Au, thickness 60 nm



Nanofabrication, InTech, 2011, p. 247

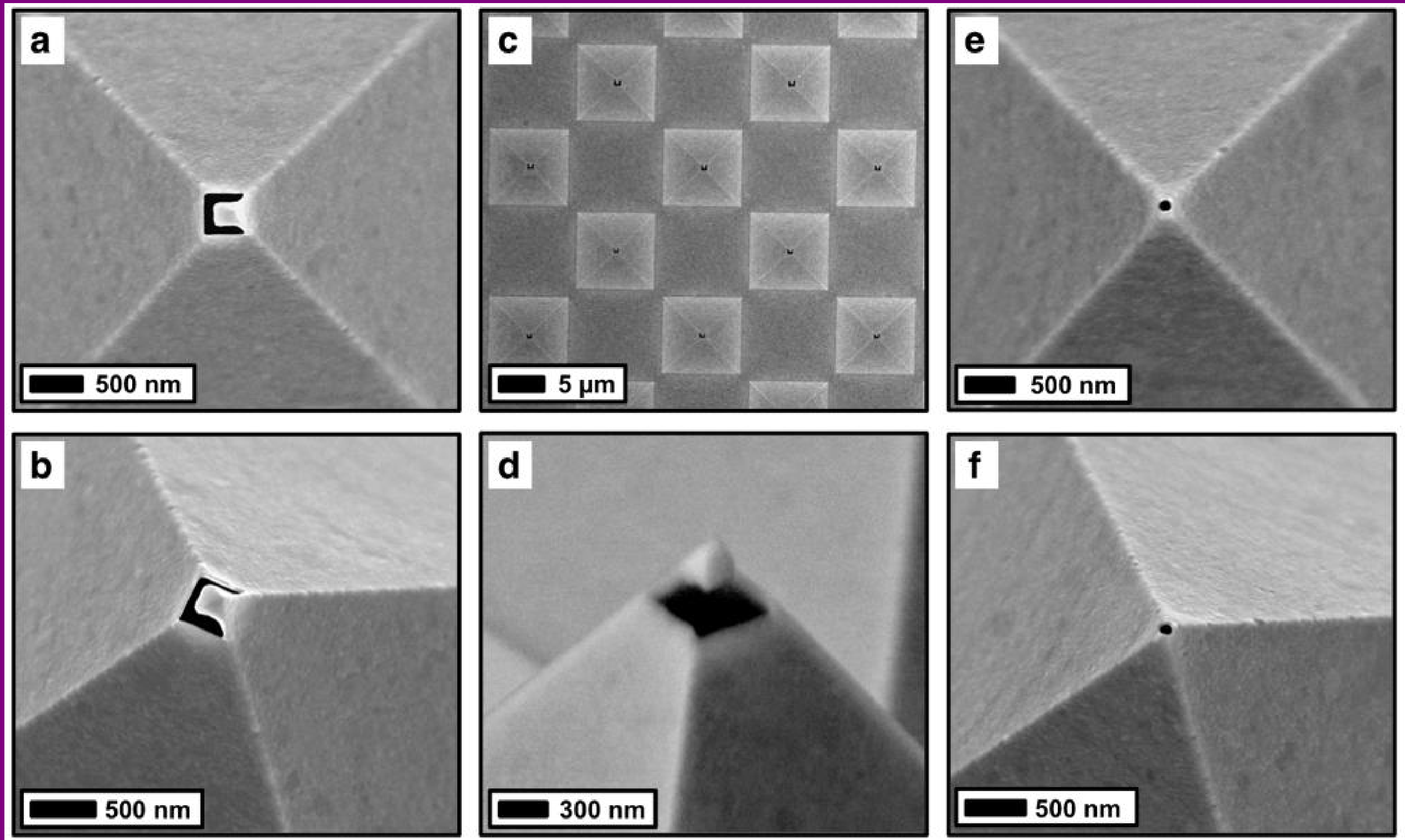
FIB patterning of nonplanar substrate



- (a) anisotropic KOH etching with an SiO_2 mask.
- (b) A 200 nm-thick Ag layer is deposited.
- (c) FIB milling is used to define the tip aperture shape (backside of the tip to avoid damage).
- (d) An optical epoxy layer is applied.
- (e) The pyramid with an integrated aperture is stripped from the template on demand.
- (f)The final hollow tip retains an ultrasharp tip untouched by the FIB

SCIENTIFIC REPORTS | 3 : 1857 | DOI: 10.1038/srep01857

Plasmonic nanofocusing structures by FIB

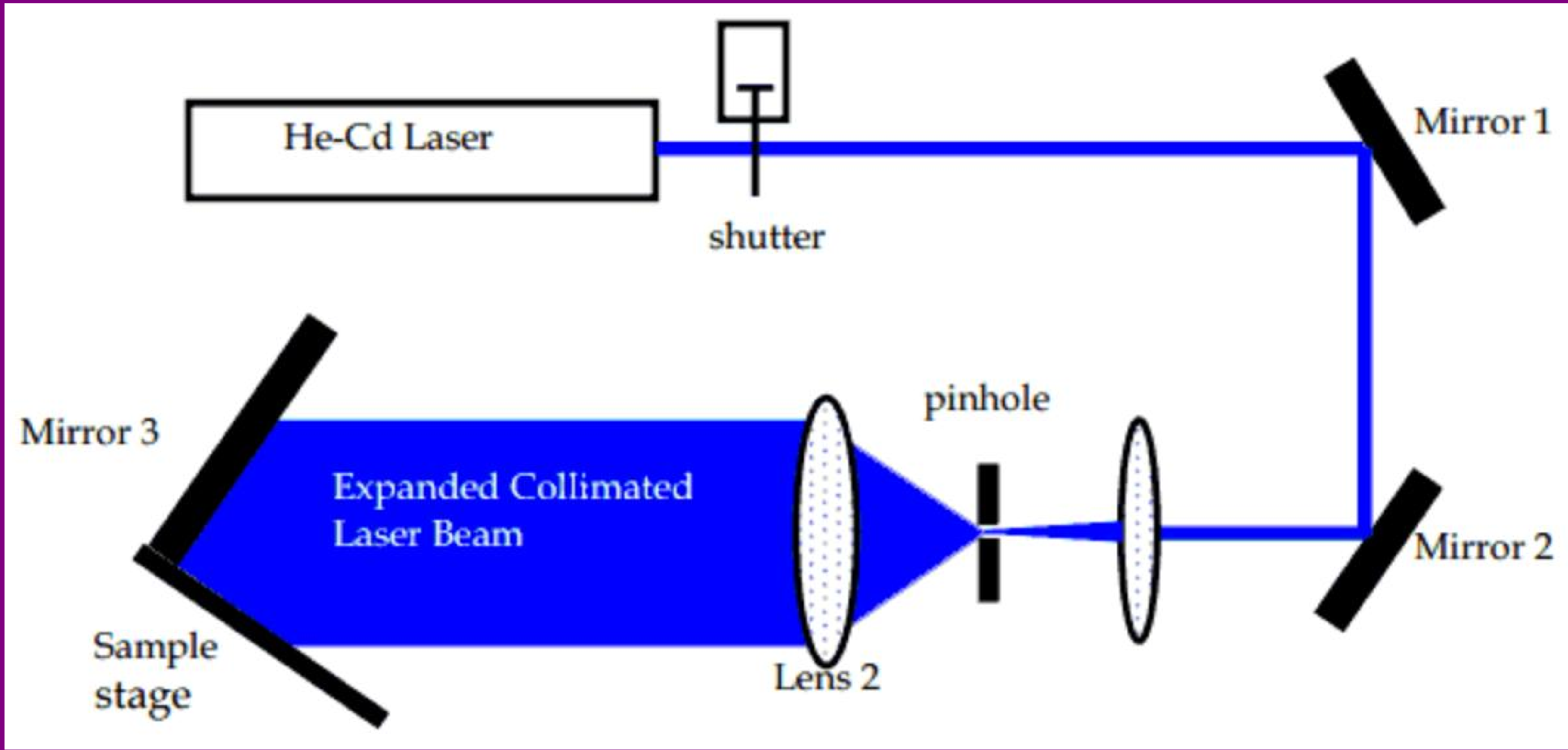


SCIENTIFIC REPORTS | 3 : 1857 | DOI: 10.1038/srep01857

Interference lithography (IL)

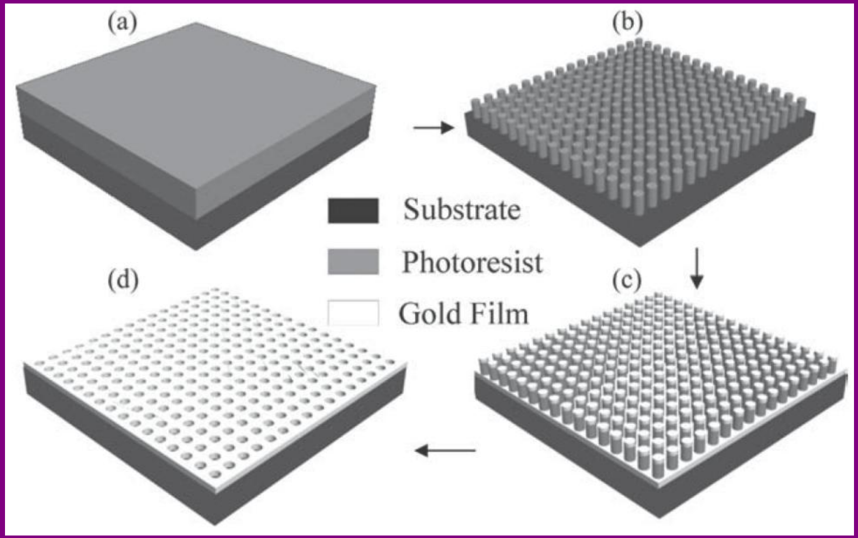
- Wafer scale
- High laser power, more than 1 W
- Laser coherence length more than 1 m
- Transparent substrate or absorbing layer below light sensetive layer (mask)
- PR patterning above metal is impossible
- Critical dimensions are limited by laser wavelength, but not less than 20 nm
- Limited to patterning arrayed features only with narrow range of size to spacing ratio

IL:
Lloyd's mirror configuration

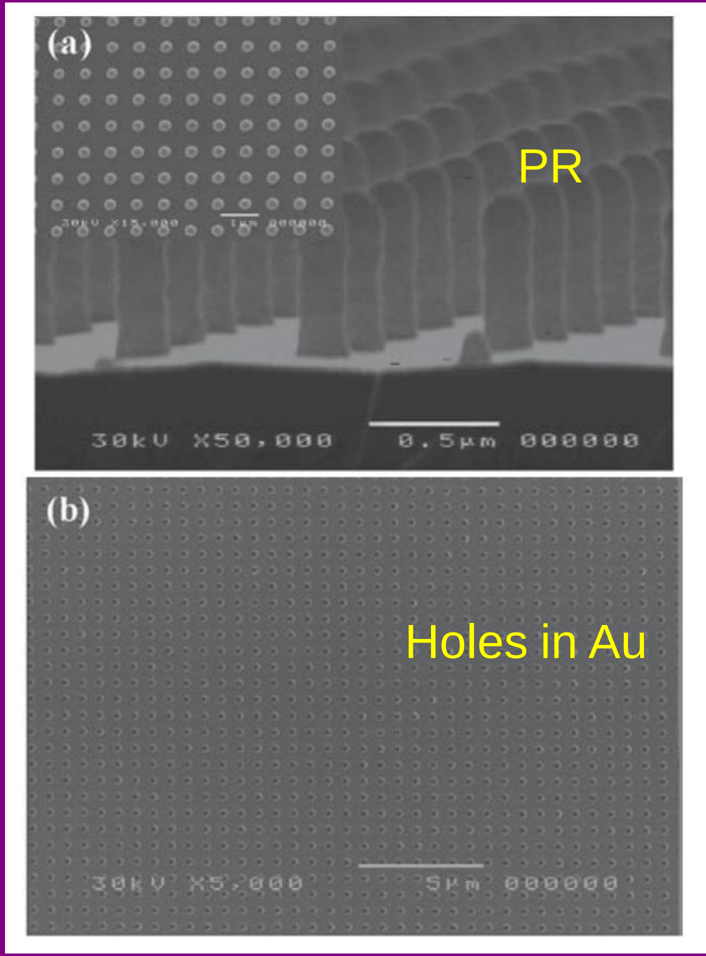


Nanofabrication, InTech, 2011, p. 256

Large area nanoholes by IL

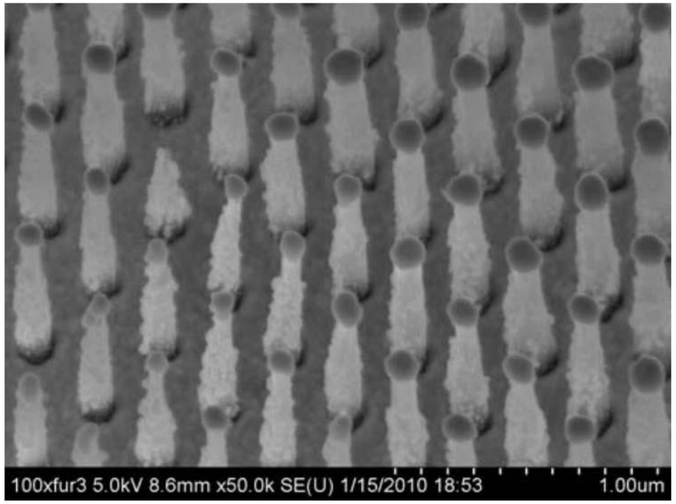


Glass, PR is 0.6 μm thick, λ=458 nm, 300 mW
Pillars dia 240 × 600 nm, pitch 700 nm
Pattern 2 x 2 cm^2, Au is 100 nm thick
Biosensing arrays, anode of solar cells.
Limitations: only transparent substrate, Au thickness < h/3, fixed ratio dia to pitch, limited area, low reproducibility

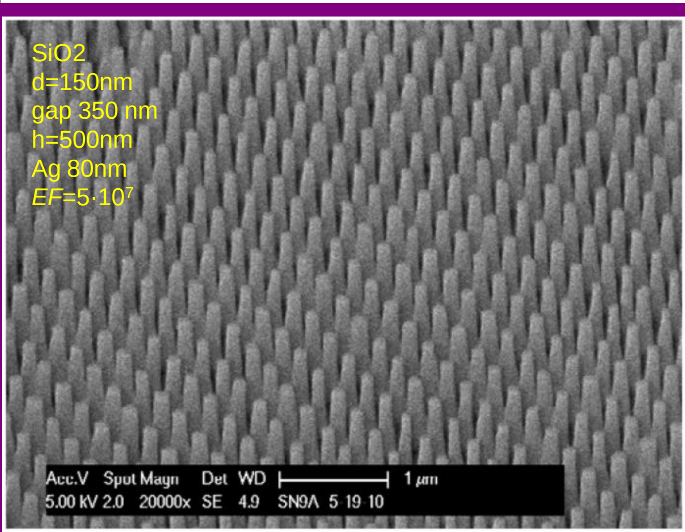


Adv. Funct. Mater. 2010, 20, 3918–3924

Pillars by IL



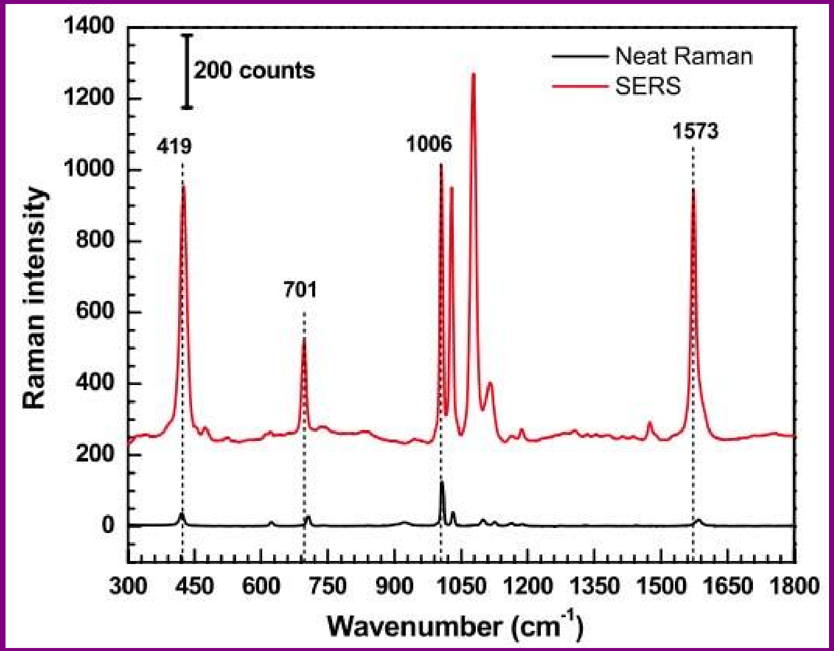
- Really uniform through the wafer
- Reproducible
- Undulation on the sidewalls after the Bosch process
- Powerful laser (1-5 W) with large coherense length
- Only transparent substrate due to interference with reflected light

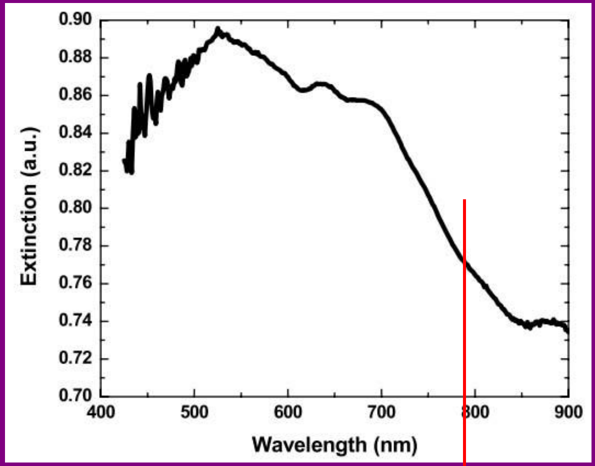


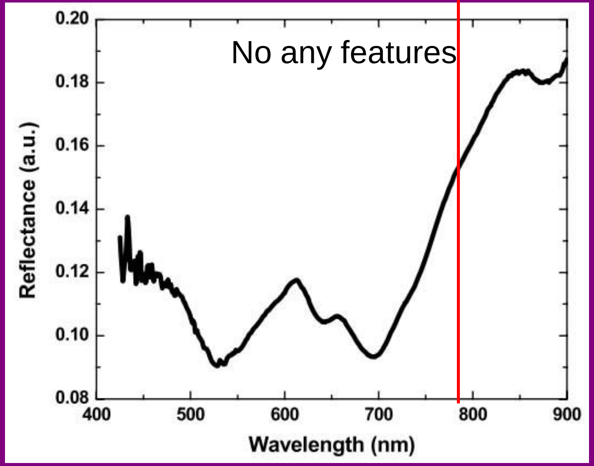
- 4 " SiO_2 wafer, 0.45 μm thick photoresist 413 nm wavelength, dose of ~ 40 mJ/cm^{-2} .
- The wafer is subject Bosch process, etched down for 500 nm
- Stripping the photoresist
- metal deposition by e-beam evaporation of an 80 nm thick film of silver at a rate of 0.1 nm/s, room temperature, a hemispherical mounting rotating at 50 rpm
- functionalized with a SAM of benzenethiol by submerged in 4 mM solutions of benzenethiol made with ethanol for 1 h

M. R Gartia et al., Nanotechnology, 21(2010) 395701 (9pp)

Pillar based substrate as a SERS substrate







Excitation at 785 nm, analyte is benzenethiol

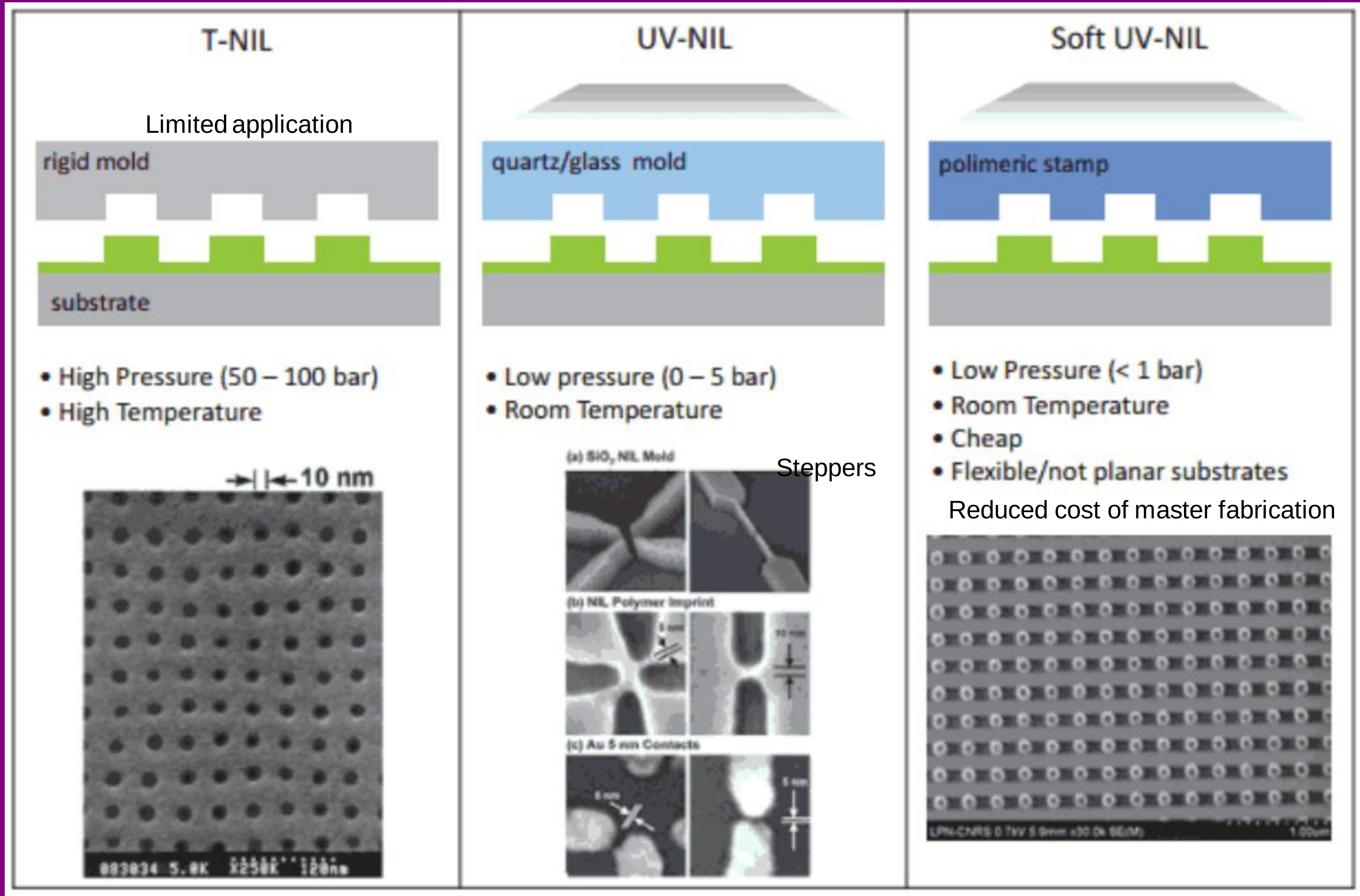
M. R Gartia et al., Nanotechnology, 21(2010) 395701 (9pp)

Nanoimprint Lithography (NIL)

- Thermal assisted (T-NIL), 50 nm pitch, 100C above Tg, 50-100 bar, 1995.
- microContact Printing (mCP), 1993
- UV-NIL, 5 nm features, 0-5 bar
- Soft UV nanoimprint lithography (Soft UV-NIL), sub-50 nm range

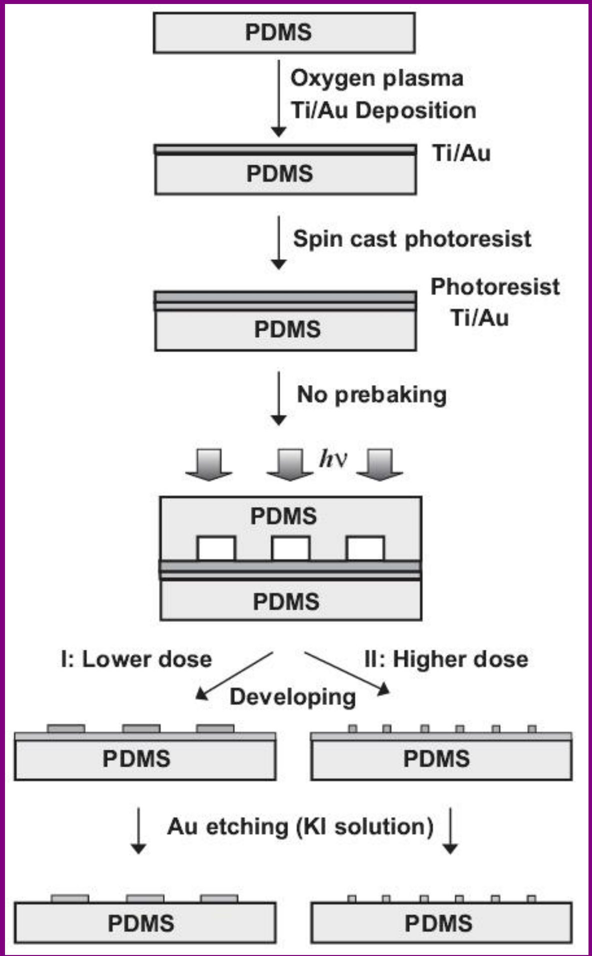
Nanoimprint

replicate features on a hard or soft stamp in a thermoplastic or UV-curable polymeric material by embossing or molding



Recent Advances in Nanofabrication Techniques and Applications, InTech, 2011, p. 140

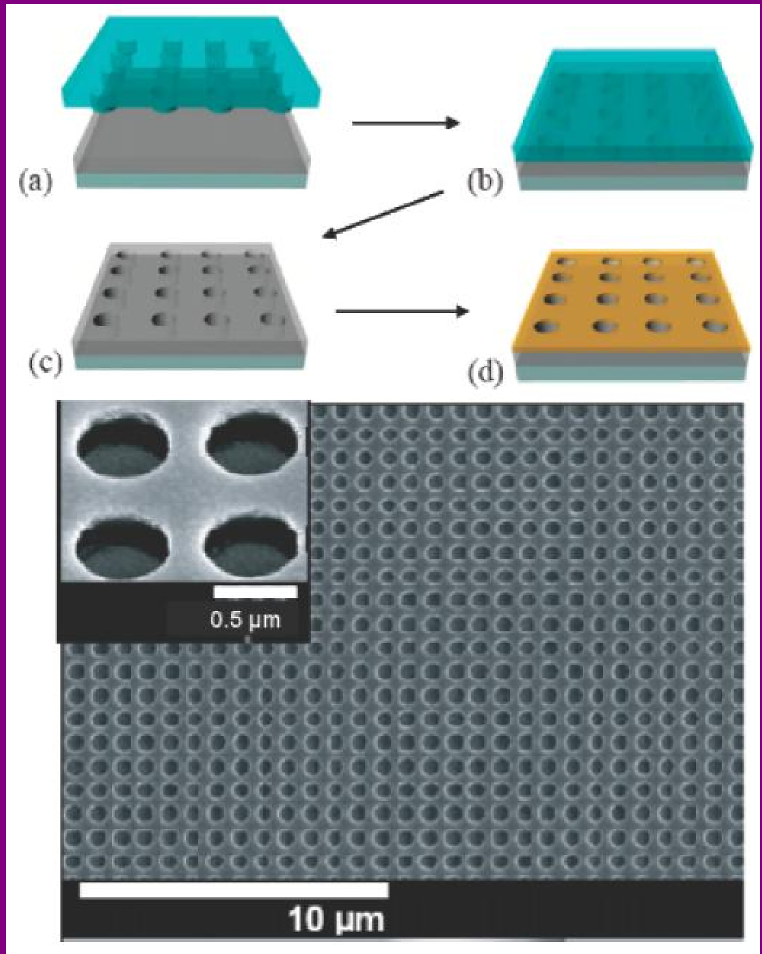
Soft lithography



Adv. Funct. Mater. , 2005, 15, 1435

- PDMS 4 mm thick
- Ti/Au 1/20 nm
- PR 400 nm
- PDMS mask was done on separate Si wafer with patterned PR by casting PDMS (4 mm thick, relief 400 nm).
- PDMS provides 180° shift (higher dose).

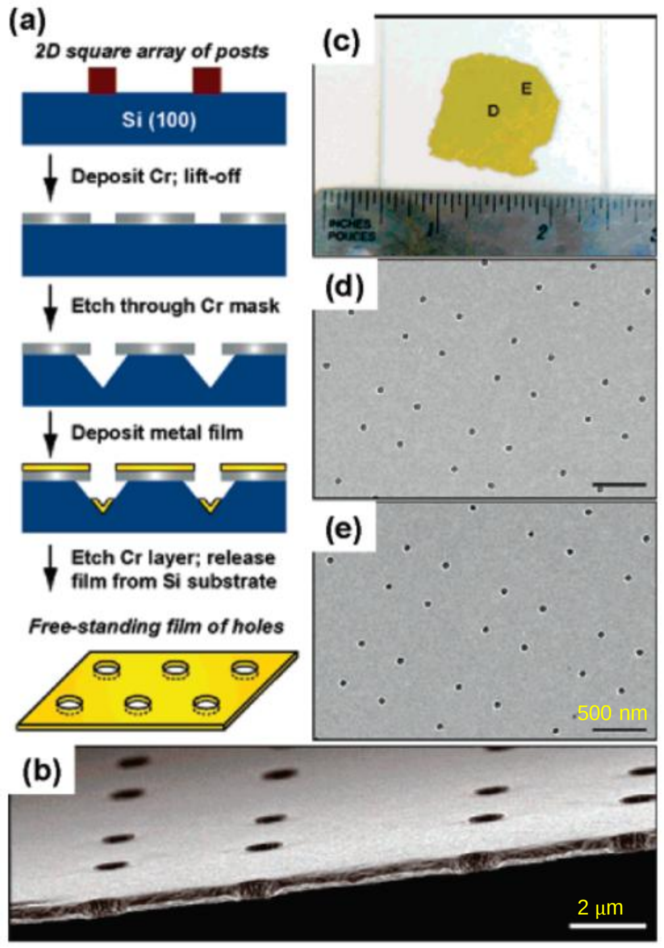
Plasmonic crystal by soft lithography



- Embossing a thin UV-curable polyurethane film with a composite *h*-PDMS/PDMS stamp
- Stamp consists of a thin layer of structured *h*-PDMS supported by a thicker planar layer of compliant PDMS. Provides mechanical stability and conformal contact with nonplanar surfaces
- UV-cure
- Remove stamp
- Au e-beam deposition, 50 nm

Chem. Rev. 2008, 108, 494−521

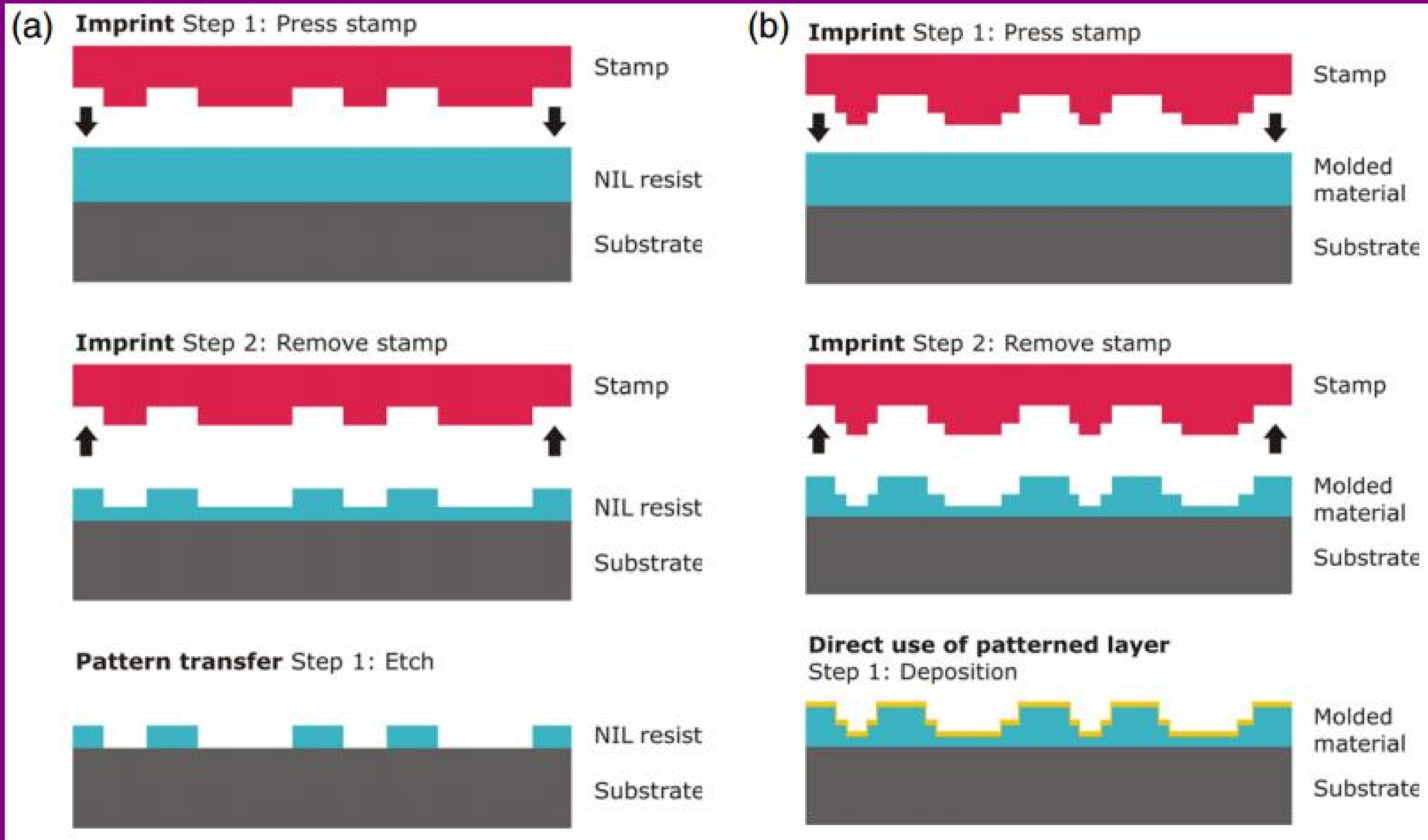
Large-area hole array by soft lithography



Chem. Rev. 2008, 108, 494−521

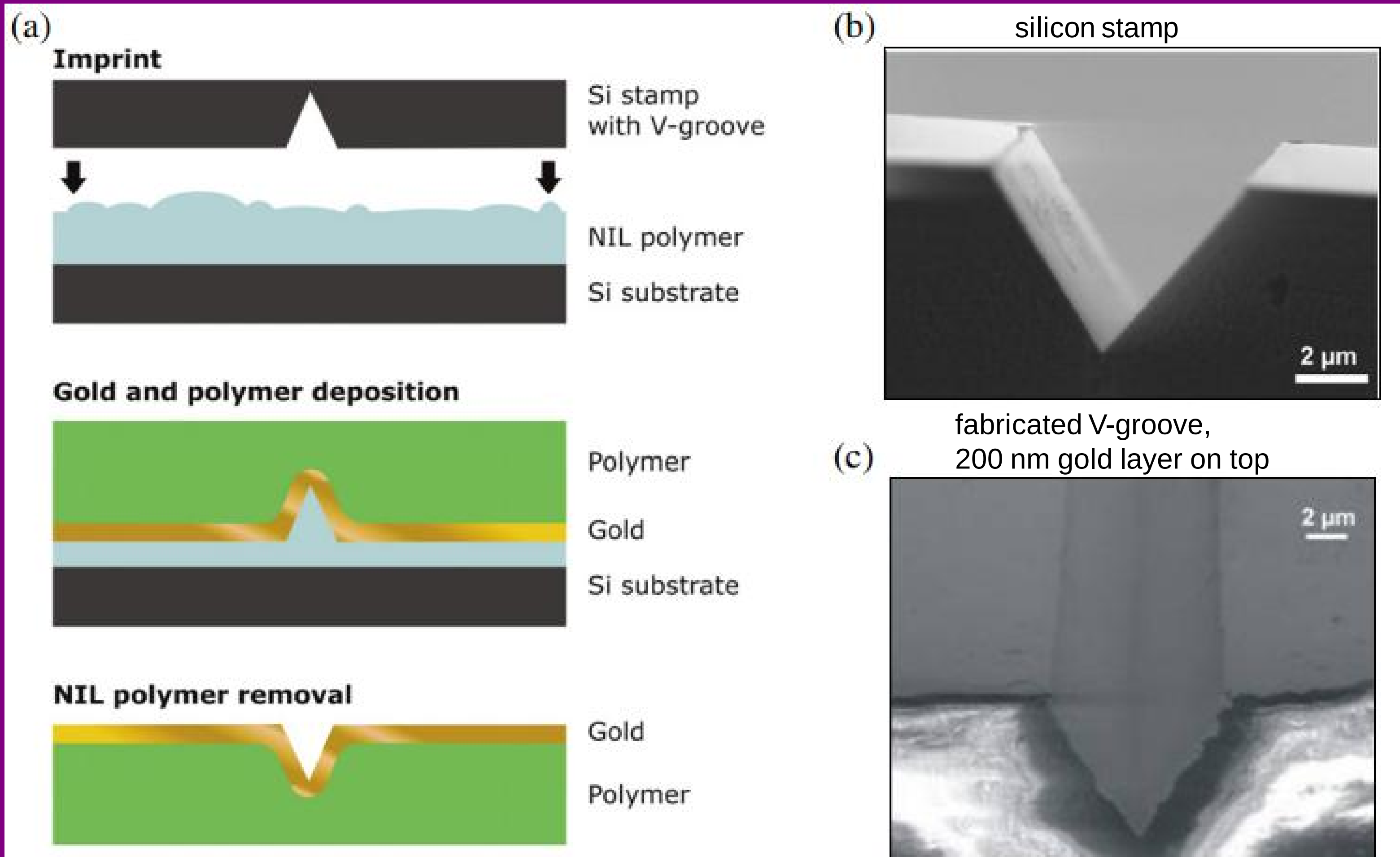
- An array of posts of positive photoresist with diameters of 250 nm is patterned by phase-shifting hotolithography using a conformable composite PDMS photomask
- A thin layer of Cr is then deposited by e-beam evaporation followed by removal of the photoresist posts
- The exposed Si is then anisotropically etched using a KOH/isopropyl alcohol (IPA) solution to produce pyramidal-shaped voids
- A layer of Au can then be deposited by e-beam evaporation

Nanoimprint for plasmonics



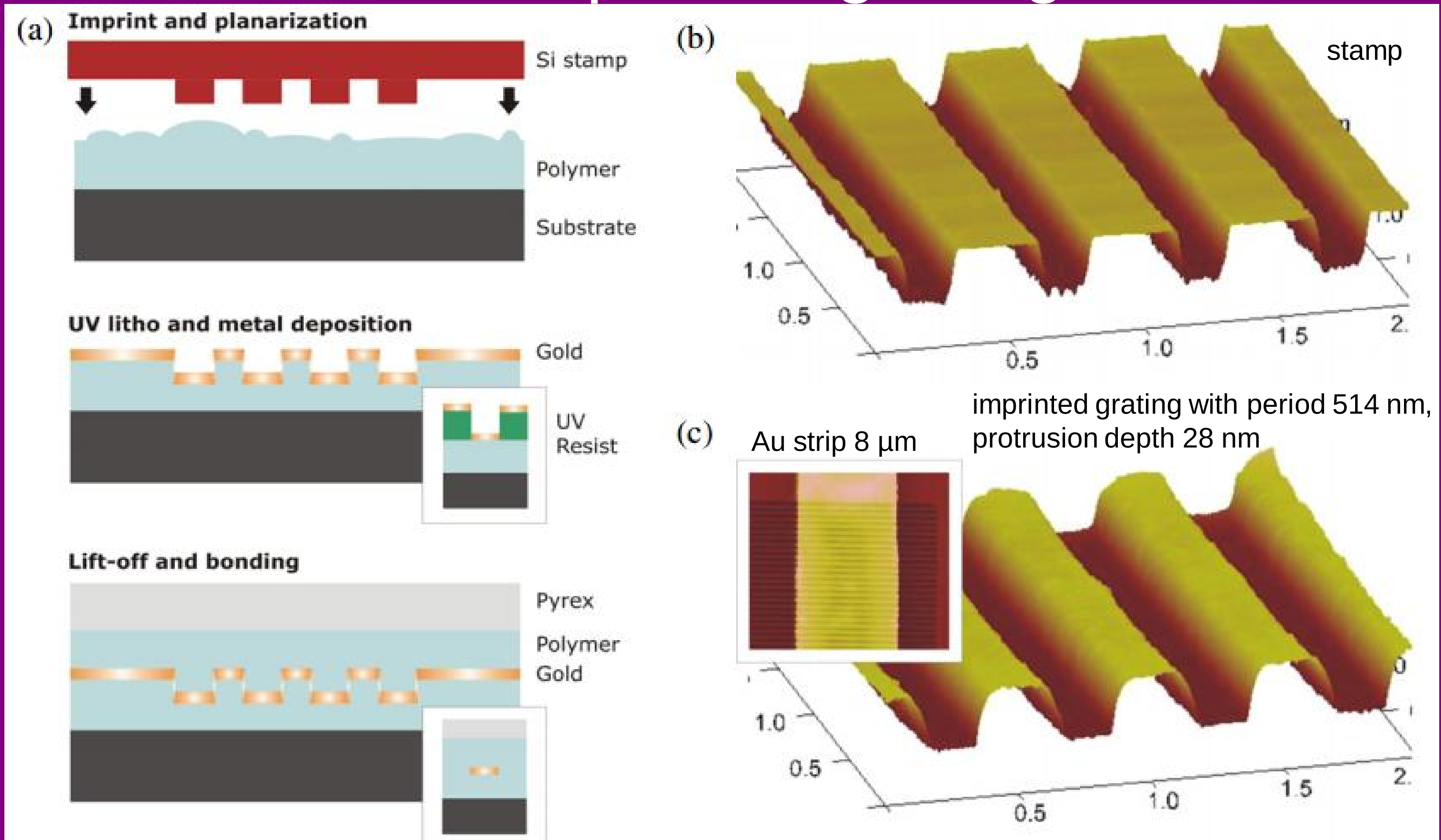
J. Opt. A: Pure Appl. Opt.11(2009) 114001 (11pp)

Metal V-grooves by nanoimprint



J. Opt. A: Pure Appl. Opt.11(2009) 114001 (11pp)

Long-range plasmonic waveguide with nanoimprinted gratings



J. Opt. A: Pure Appl. Opt.11(2009) 114001 (11pp)

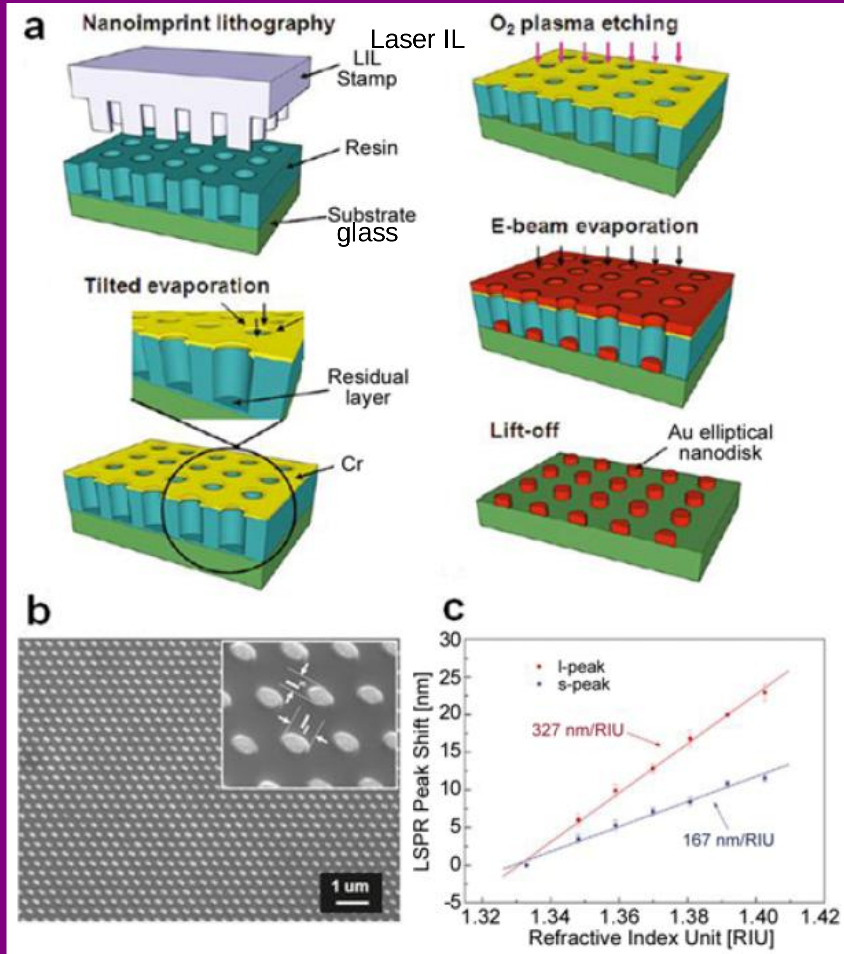
Nanoimprint

- Beyond the limitations set by light diffraction or beam scattering
- Replication in more than two levels, i.e. creating pattern with complicate profile (lithography gives only rectangles)
- Wafer scale processing
- Can be applied only to the planar surface without relief

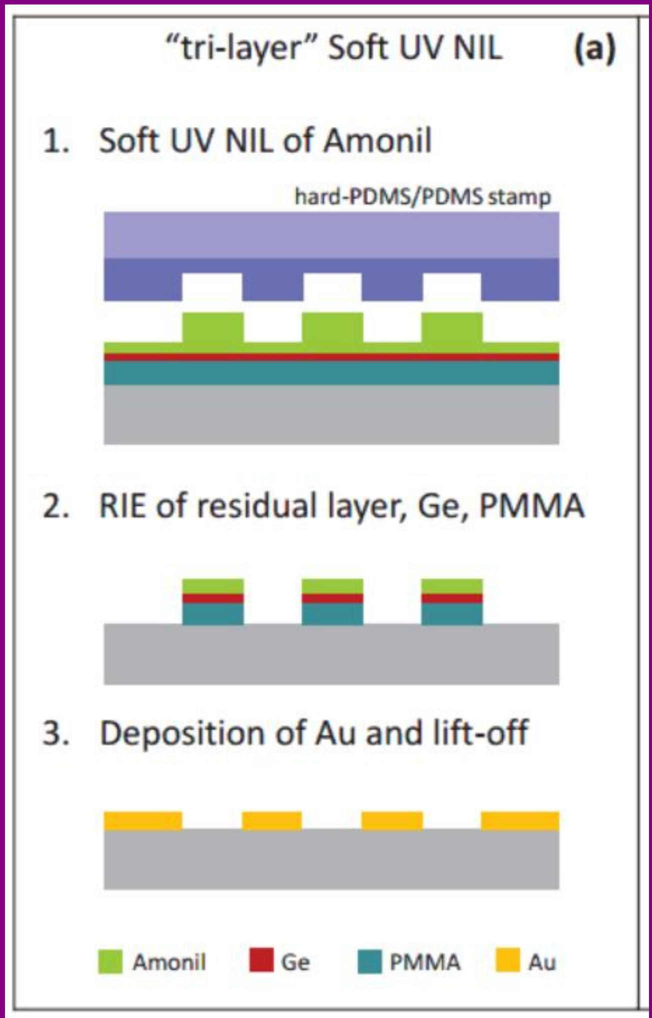
Nanoimprint

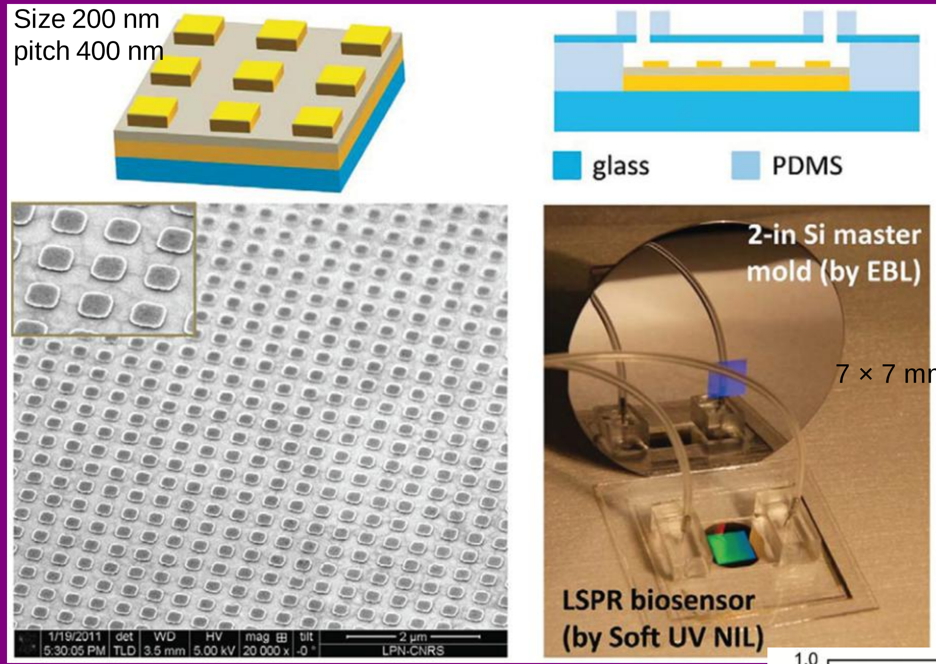
Nano, 5, 2011, 897

- Thermal NIL
- Whole wafer stamp
- Tilted evaporation of Cr is needed to avoid round upper edges of polymer after etching
- Ti 1nm/Au 20nm



Plasmonic nanocavities

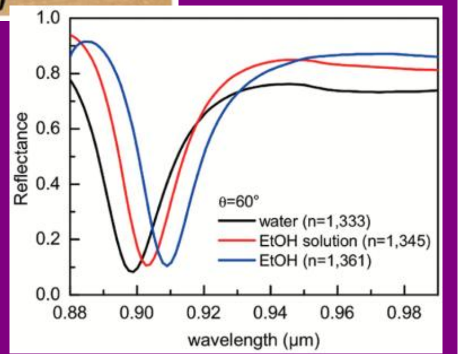




Glass substrate, large surface < 1cm2, Au/dielectric/Au islands.

Ge -10 nm thick to improve the selectivity Amonil/PMMA.

Amonil (NIL resist) is not soluble in solvents

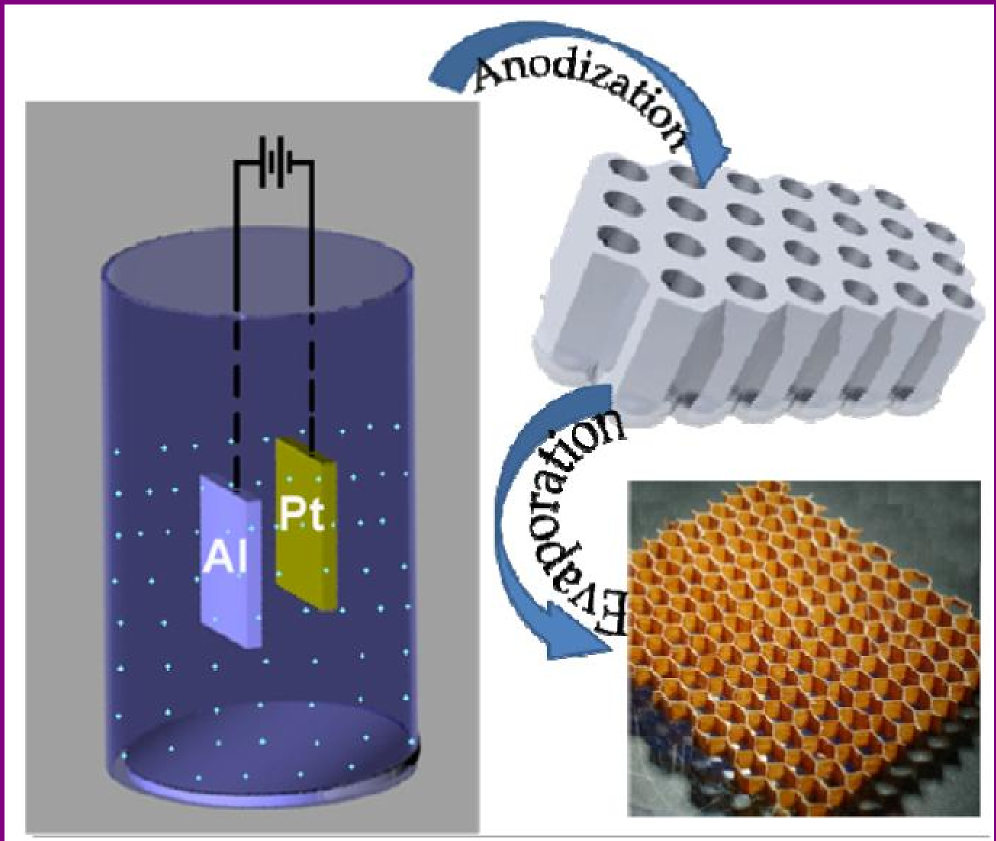


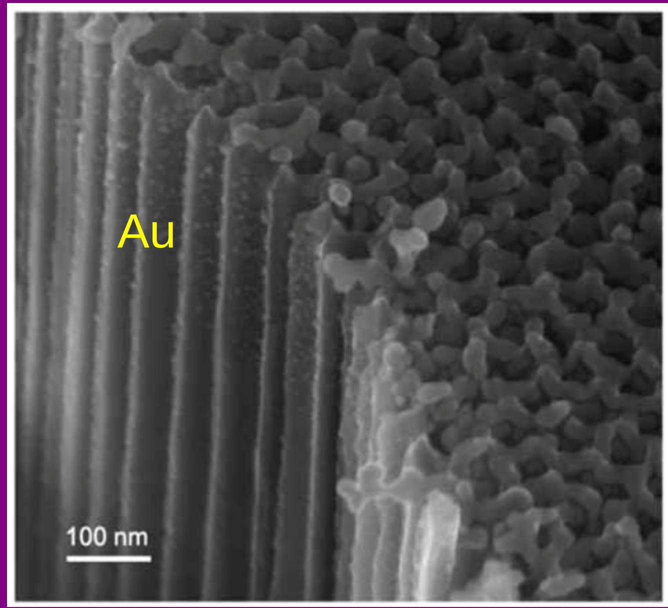
A. Cattoni et al., Nanoletters, 2011, pp. 3557-3563

Template assisted lithography

- Porous anodic Al_2O_3
- Nanosphere lithography (NSL)
- Colloidal lithography
- Shadow mask (stencil)
- Template stripping

APA - anodized porous Al



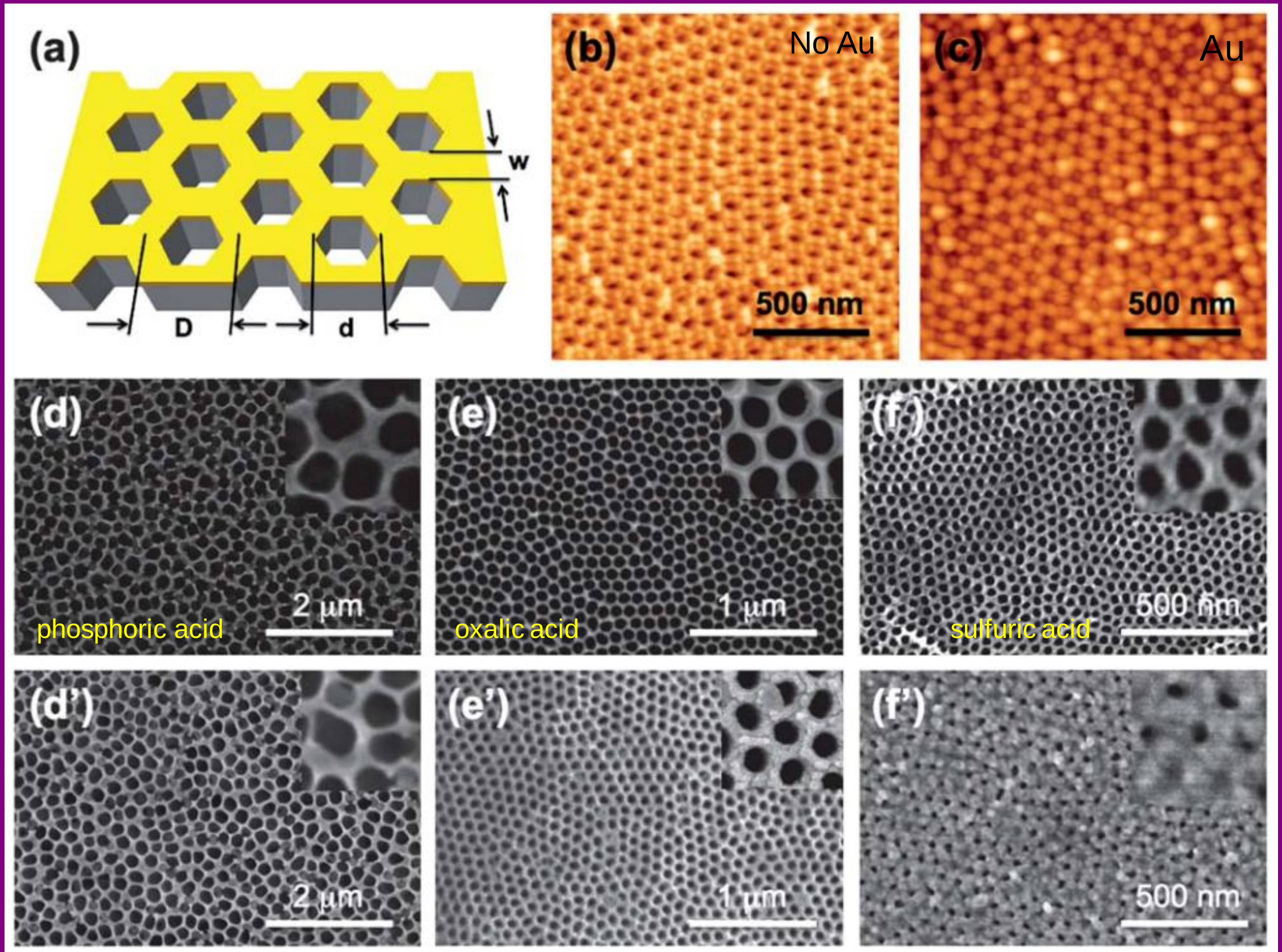


Al foil 250 μm thick
Pre-forming 1h
Wet etching Al_2O_3 40 min
Anodization 12 h
Cleaning and widening 45 min
Al_2O_3 thickness is 50-80 μm

APA covered by Au

Analyst, 2012, 137, 1785–1792

AFM



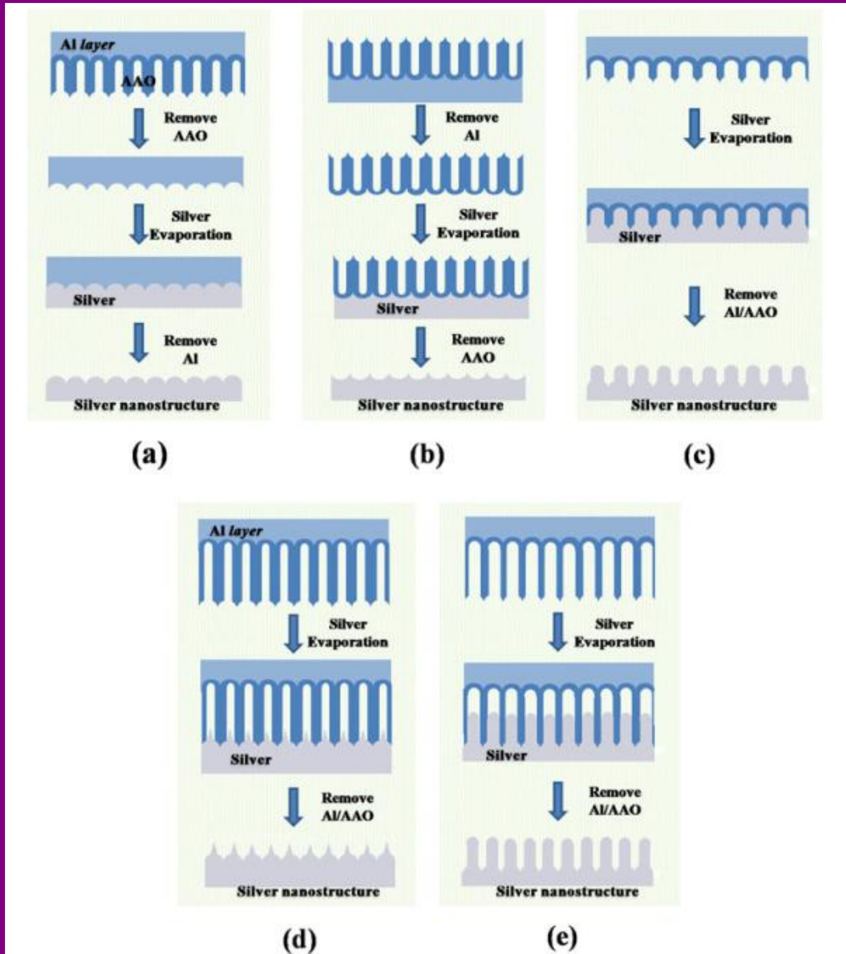
250 μm thick Al foil
Pre-forming 1h
Wet etching Al_2O_3 40 min
Anodization 12 h
Cleaning and widening 45 min
Al_2O_3 is 50-80 μm thick

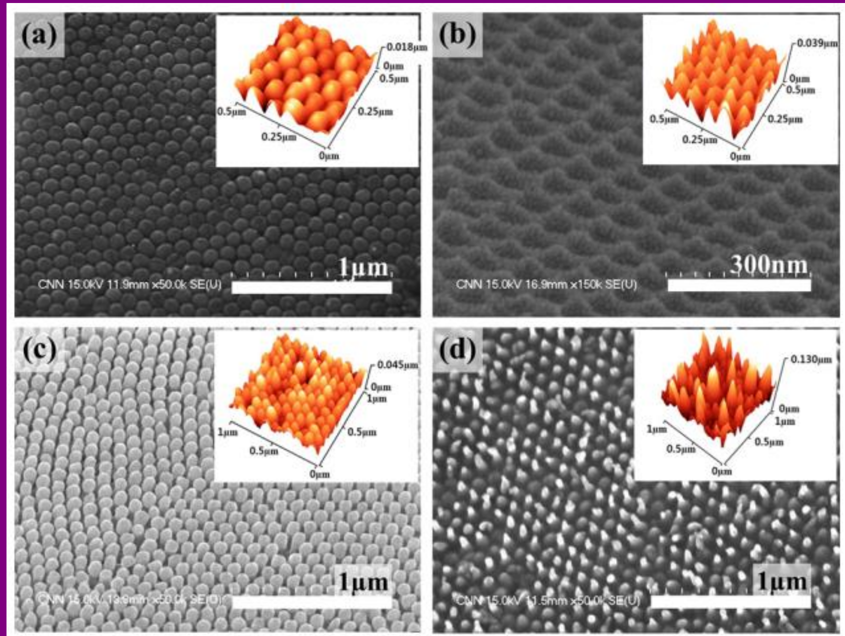
← No Au

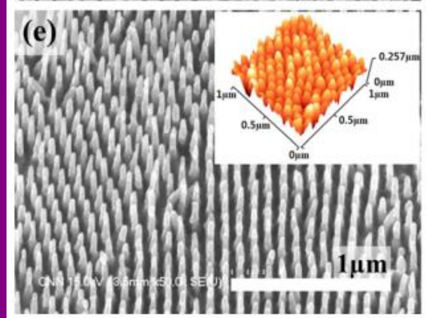
← Au 25 nm, evaporated with rotation

Anodized Al oxide (AAO)

Cha et al. Nanoscale Research Letters 2012, 7:292

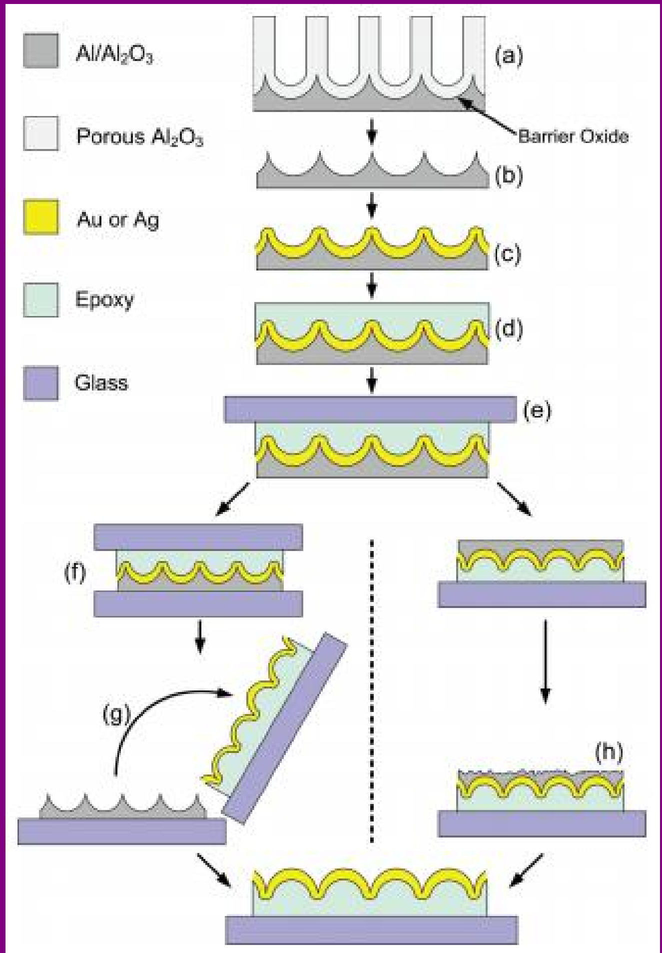






Template 40-80nmx50-100µm
Membrane dissolved in NaOH 24 h
Si/Ag

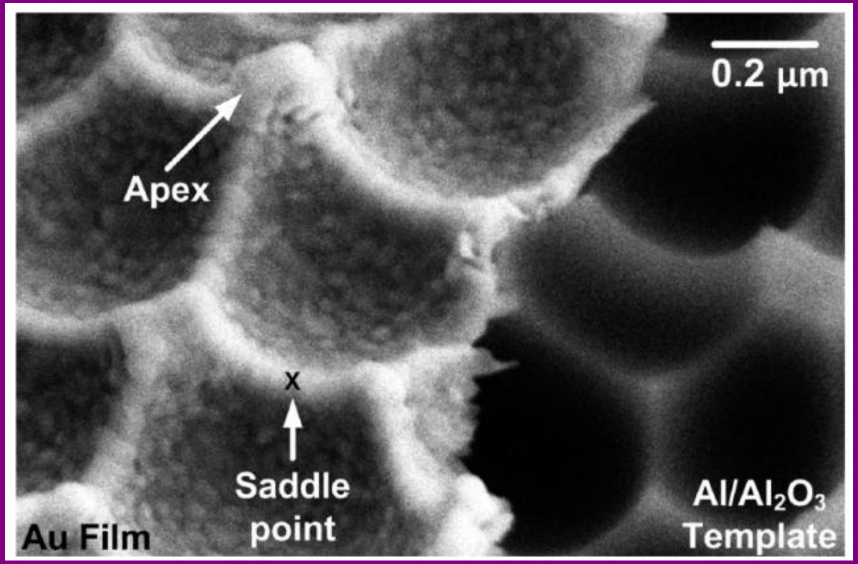
Hemispherical nanostructures



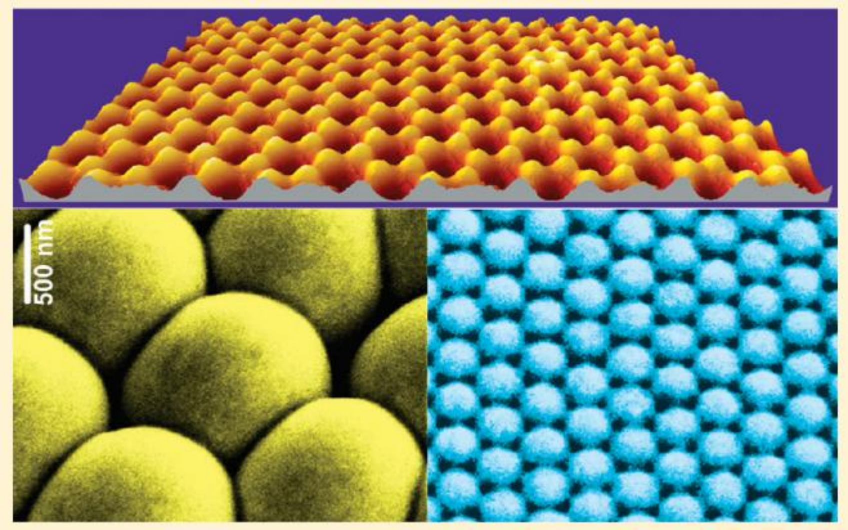
- Fabricating hemispherical shell nanostructures by stripping (left route) and selective Al etching (right route). Sample 1 × 1 cm2
- (a) Preparation and anodization of Al substrate (1 mm).
- (b) Removal of the porous Al_2O_3layer.
- (c) Deposition of a ~0.3 μm thick metal film.
- (d) Addition of Epoxy resin layer.
- (e) Attachment of microscope slide and curing of the Epoxy resin.
- (f) Anchoring the Al side of the template to microscope slide to avoid bending during stripping
- (g) stripping of the nanostructured Au film.
- (h) Selective Al etching as an alternative to stripping.

Hemispherical

AFM image (1×1μm) of hollows in a template



J. Phys. Chem. C, 2011, 115 (13), pp 5552–5560

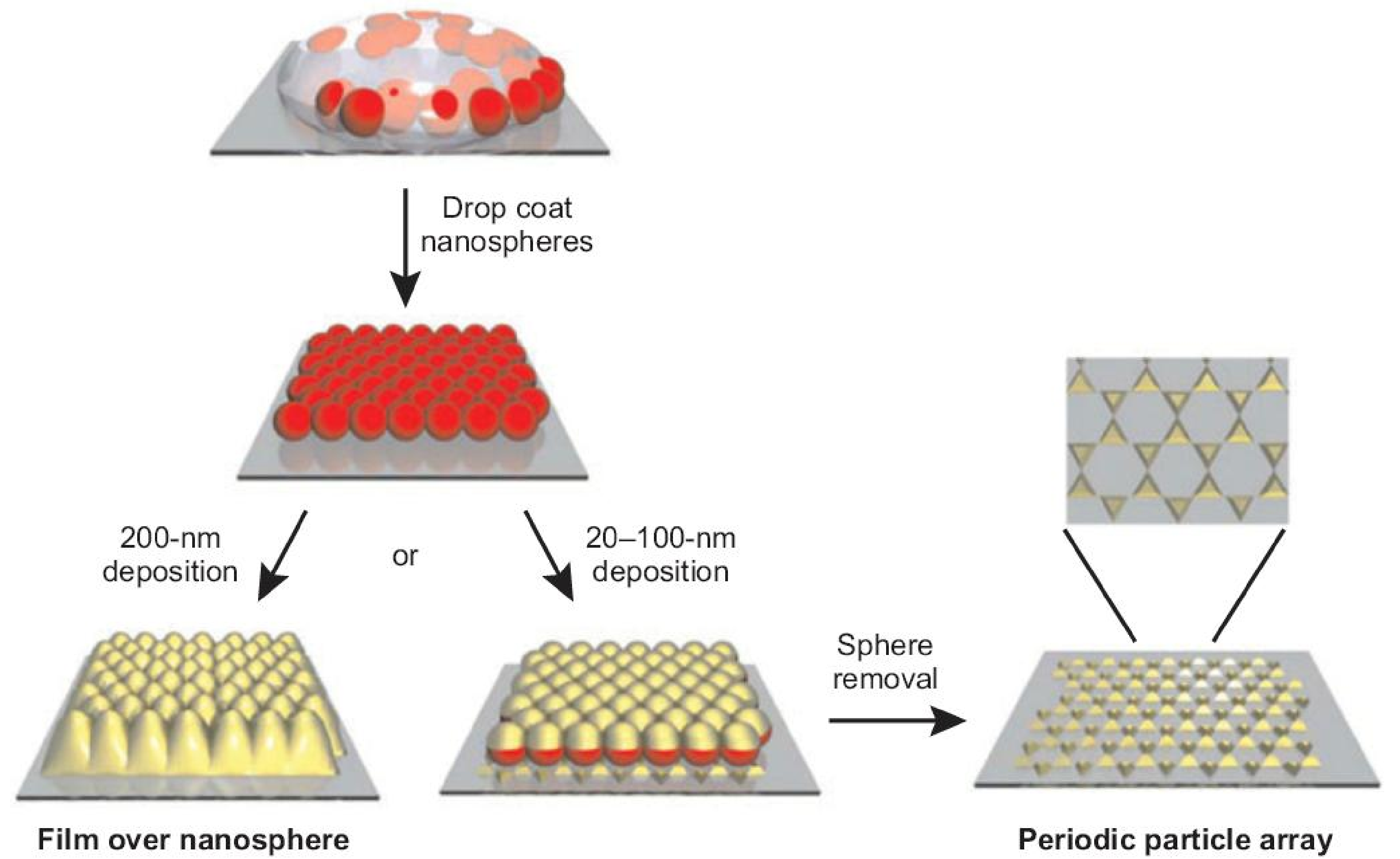


Au hemispherical shells

Anodized Al

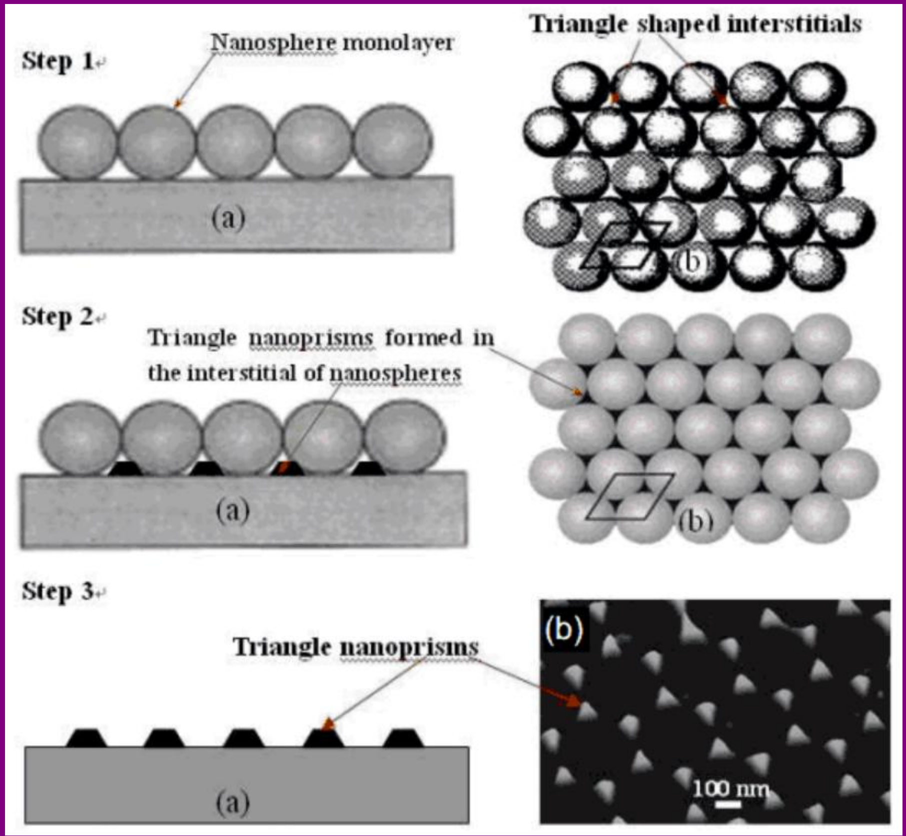
- Wet, very long processing time ~15 h
- Limited ratio size to spacing for pattern
- Simple
- Metal structures on Al_2O_3 membranes can be easily produced

Nanosphere lithography (NSL) I



Stiles P.L. *et all*, Annual Review of Analytical Chemistry, 1, 2008, p.601-26

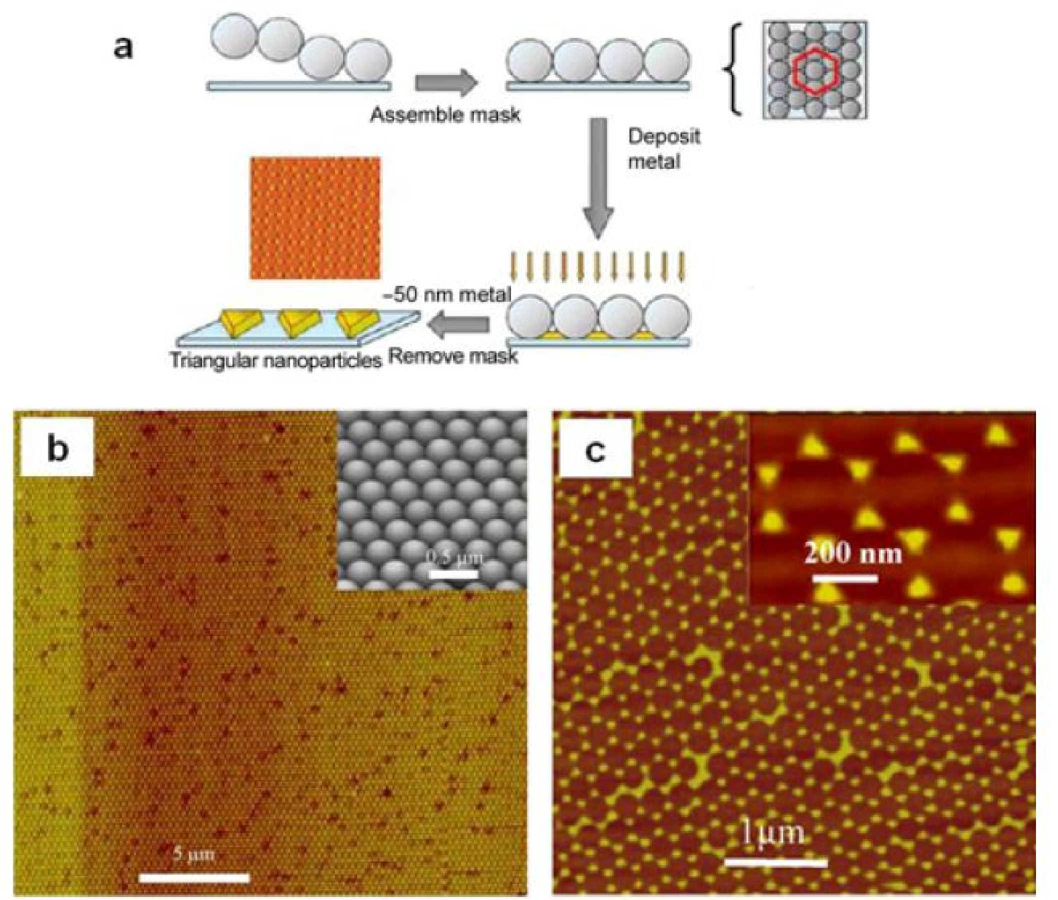
Nanosphere lithography II



- NSL is an inexpensive and versatile hybrid bottom-up procedure.
- Spheres can be applied by dip-coating, drop-coatin or spin on. Problems exist for < 100 nm spheres due to surface roughness.
- Defect-free domains have limited area about 10-100 μm^2 in size.
- Pattern tuning by moving the sample during metal deposition, annealing the latex colloidal mask prior to metal deposition, changing the thickness of the deposited metal, size of the colloidal spheres, number of colloidal layers, or angle of the metal deposition
- Sphere size can be decreased by dry etching after deposition
- Isolated single nanospheres can be prepared by kinetically interrupting particle adsorption at extremely low coverage

Recent Advances in Nanofabrication Techniques and Applications, InTech, 2011, p. 508

Nanosphere lithography III

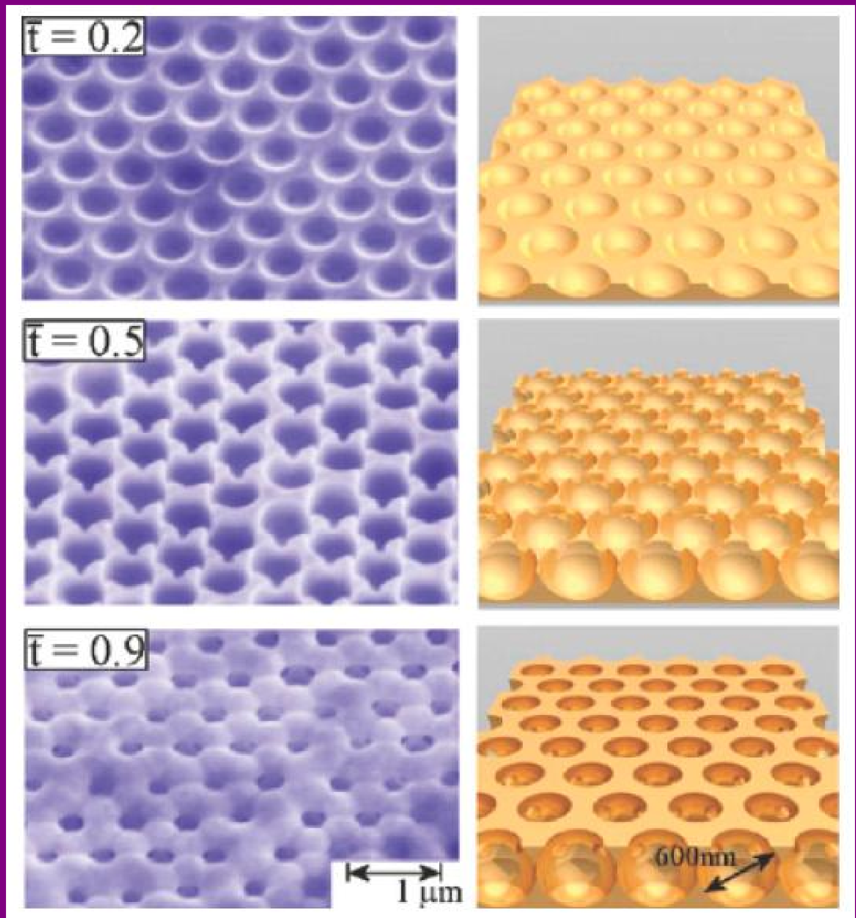


Colloidal crystal mask

Triangular nanoparticles

Periodic spherical voids by NSL

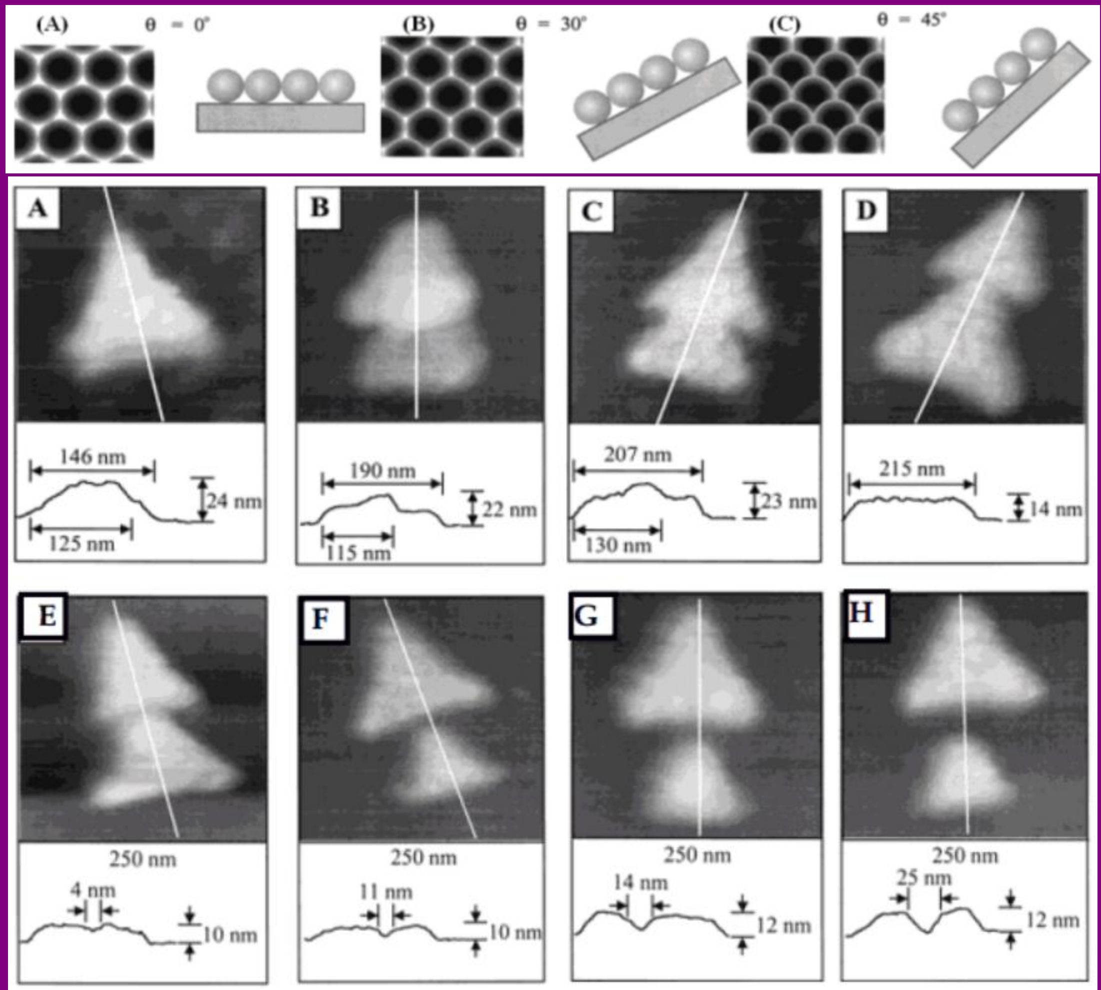
Chem. Rev. 2008, 108, 494−521



- electrochemical deposition of Au through a single-layer self-assembled colloidal template.
- the PS spheres are dissolved in tetrahydrofuran to yield a 'nanovoid array'

SEM images of nanovoid arrays with void diameters of 600 nm at three normalized thicknesses t= 0.2, 0.5, and 0.9 (left), and schematic illustrations of the surface at each thickness (right).

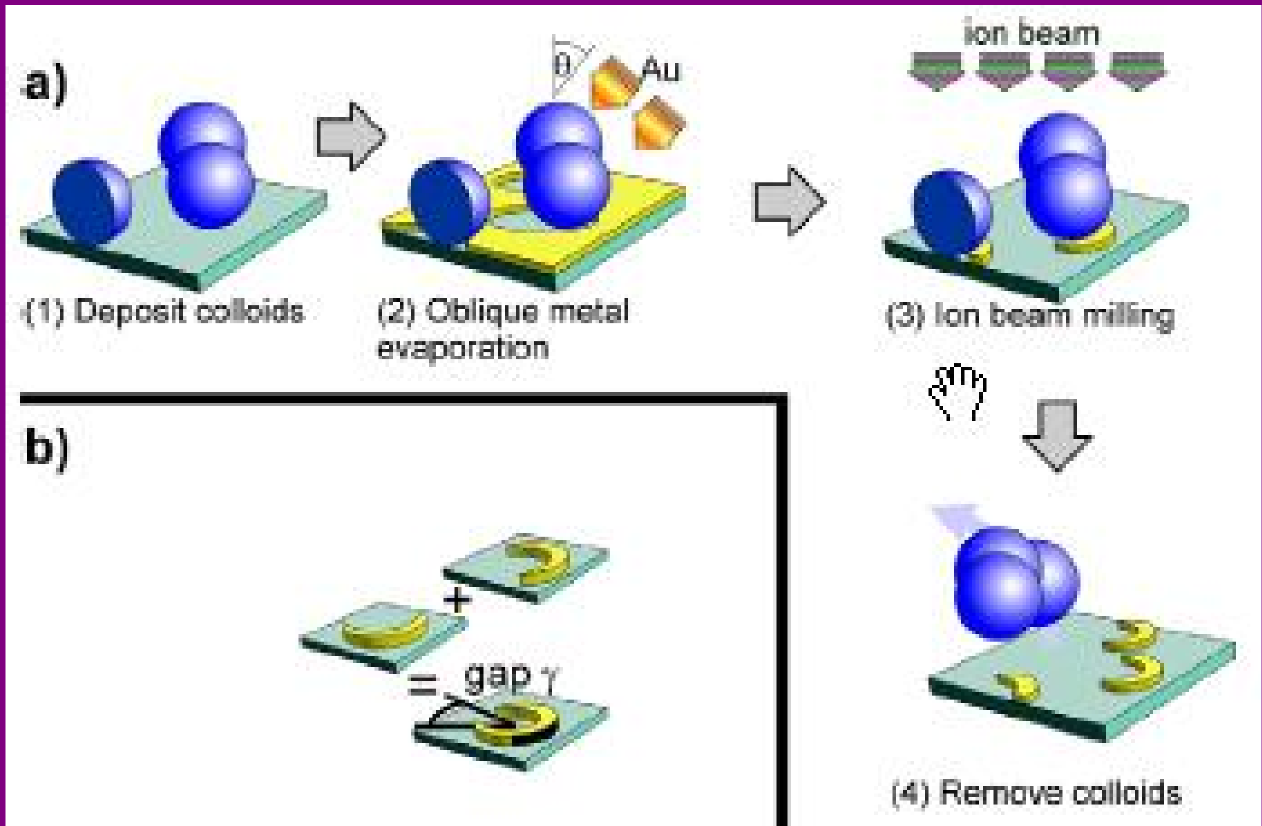
Angle resolved NSL



- Smaller size for the same spheres
- Overlapped and gapped nanostructures by multistep
- AR NSL

Recent Advances in Nanofabrication Techniques and Applications, InTech, 2011, p. 510

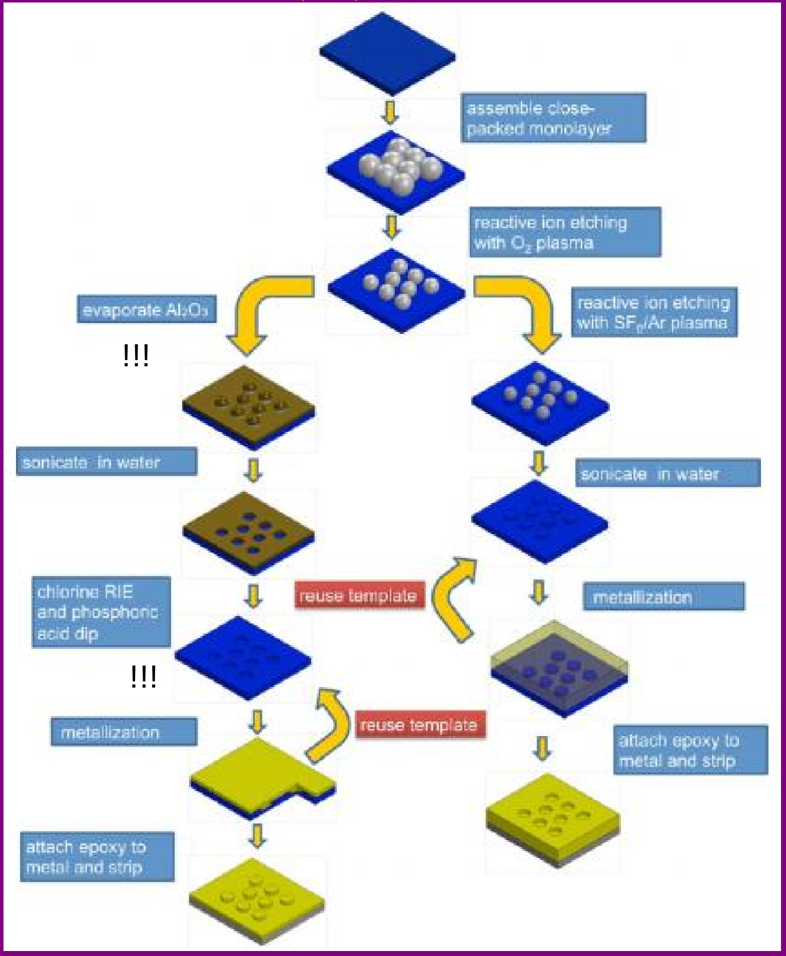
Nanocrescents fabricated by nanosphere lithography



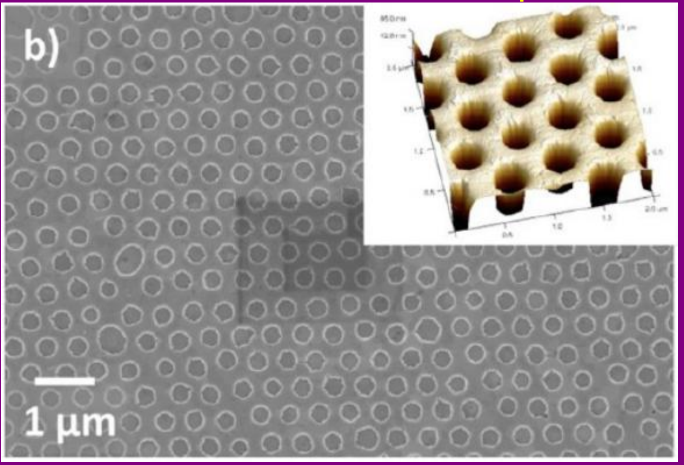
H. Rochholz *et al.*, New Journal of Physics, **9** (2007) 53

Pillars and wells by NSL

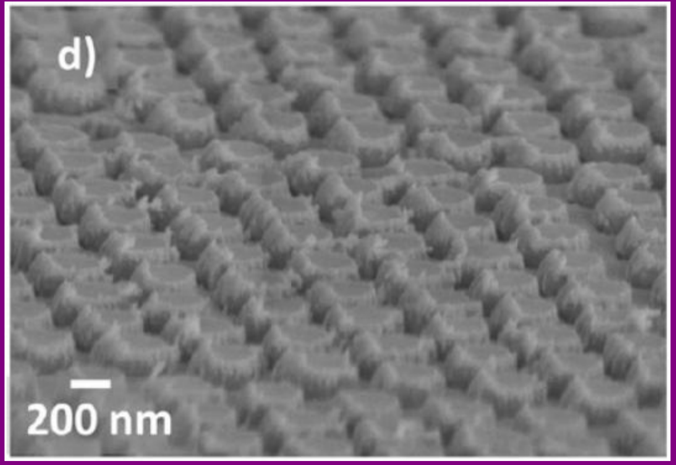
Nano Lett.2013, 13, 2623−2627



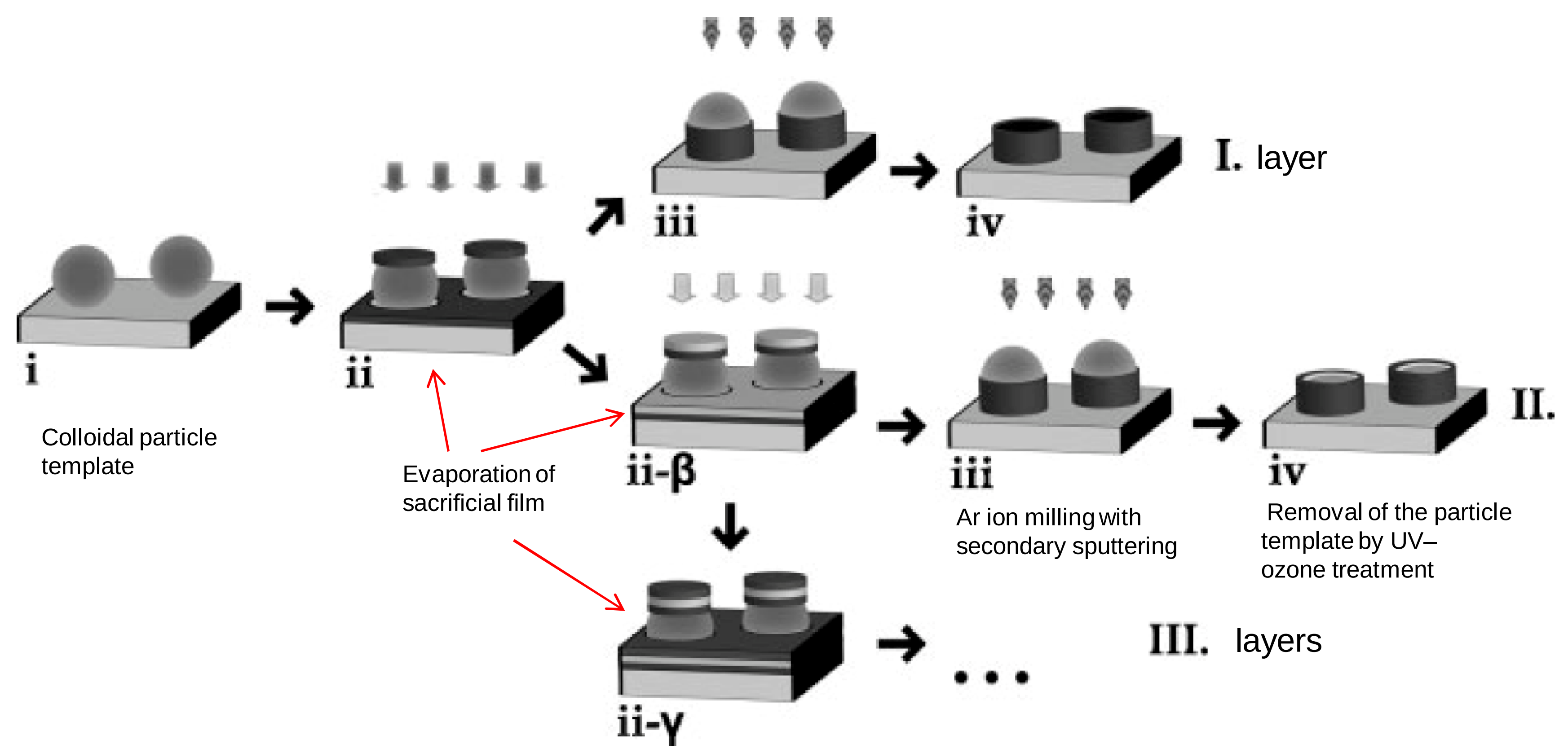
Au nanowells, 70 nm depth



Au nanopillars, 70 nm depth



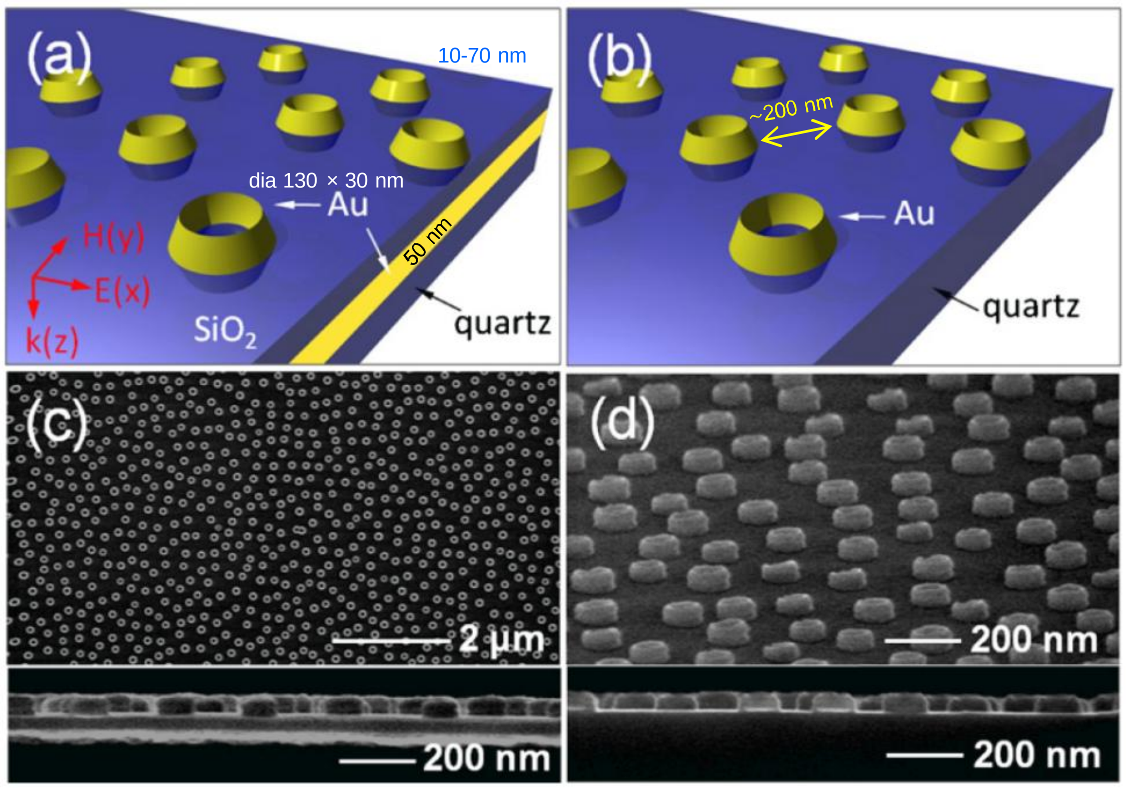
Multilayer rings

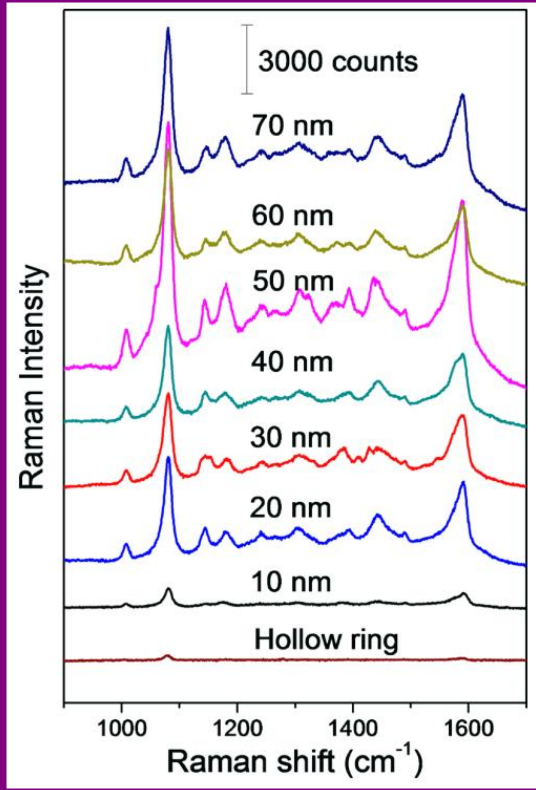


Small 2008, 4, No. 10, 1630–1634

Nanosphere lithography Au-SiO2-Au

100 nm polystyrene spheres   Au is sputtered, Xe^{+} milling, PS spheres are removed by O2 plasma





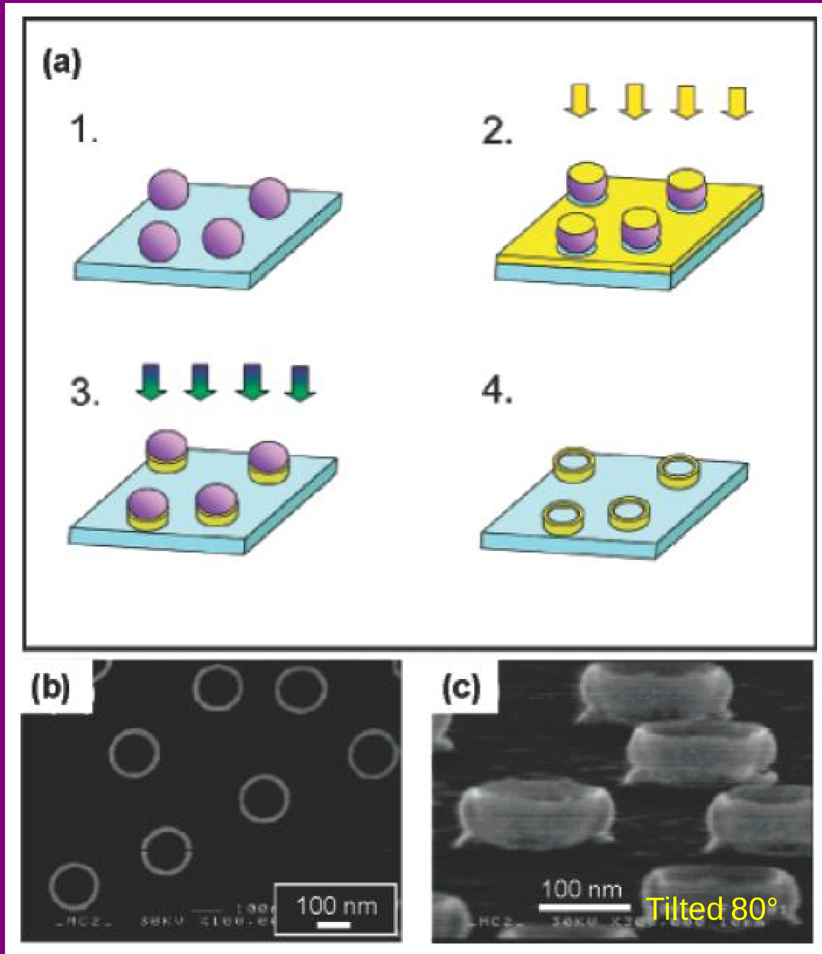
Appl. Phys. Lett. 97, 163106 (2010)

Small area – several cm^2
SiO_2 method is not mentioned
Xe milling and nanosphere limit higth of rings

4-aminothiophenol (4-ATP), laser 785 nm,
50 times increase for 50nm SiO2

Colloidal lithography

Phys. Rev. . Lett. 2003, 90, 057401

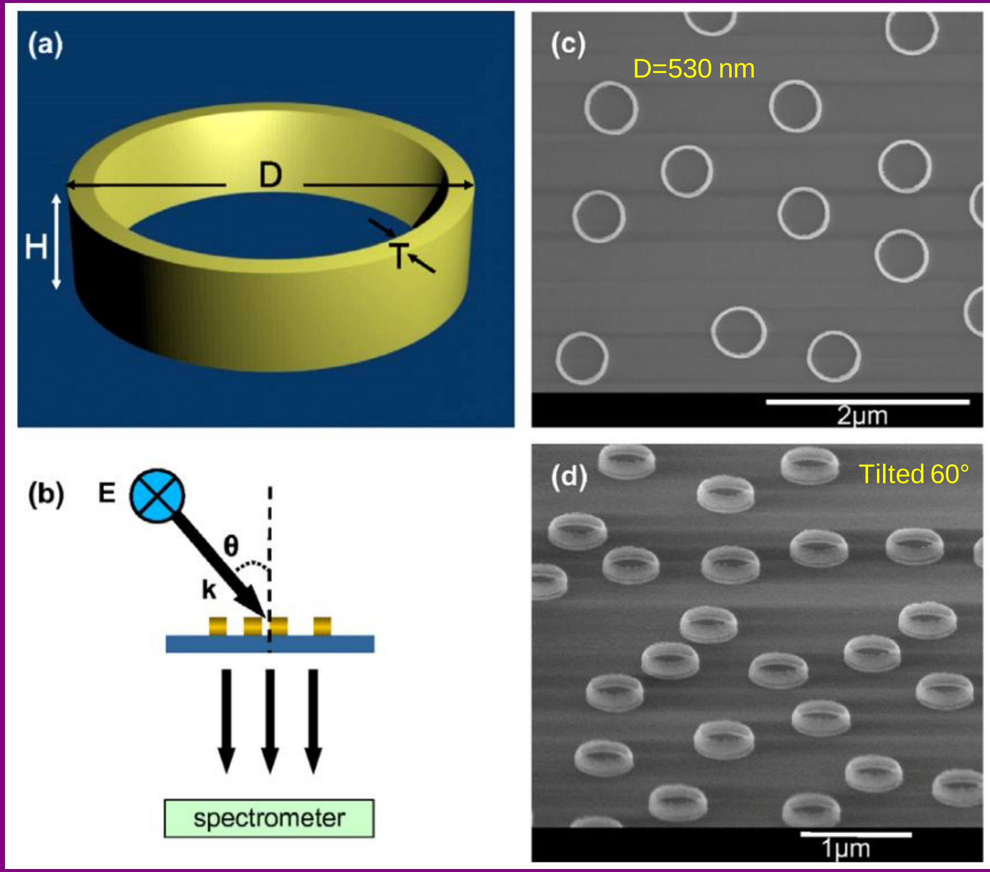


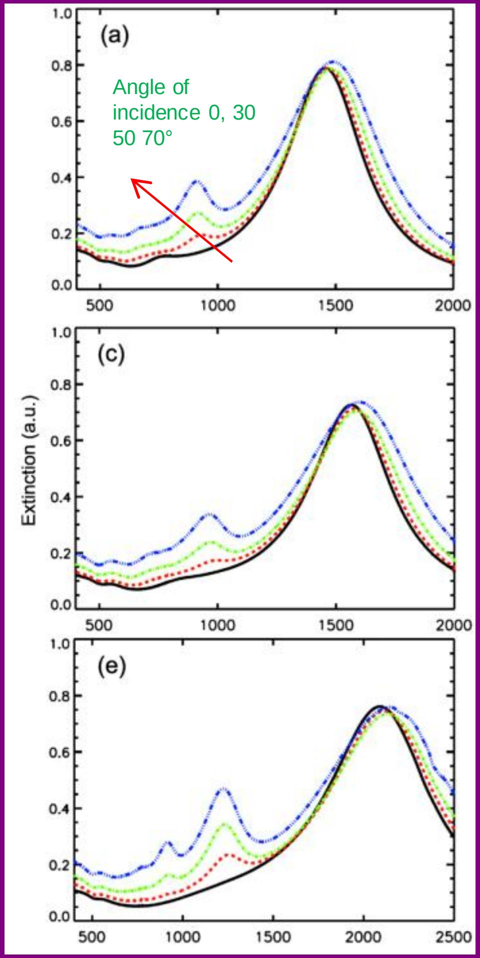
- Colloidal lithography involves adsorbing polystyrene (PS) particles onto a substrate via electrostatic self-assembly (by adjusting the electrolyte concentration of the colloidal solution).
- The main difference between colloidal lithography and NSL is that the colloidal spheres do not form an hexagonally close pack monolayer on the substrate
- Nanoring fabrication:
  - (1) Polystyrene colloidal particles
  - (2) A 20-40 nm thick Au film is evaporated at normal incidence
  - (3) Argon-ion beam etching
  - (4) UV-ozone treatment

Colloidal lithography

T= 20-40 nm, D=315-530 nm, H=120-170 nm

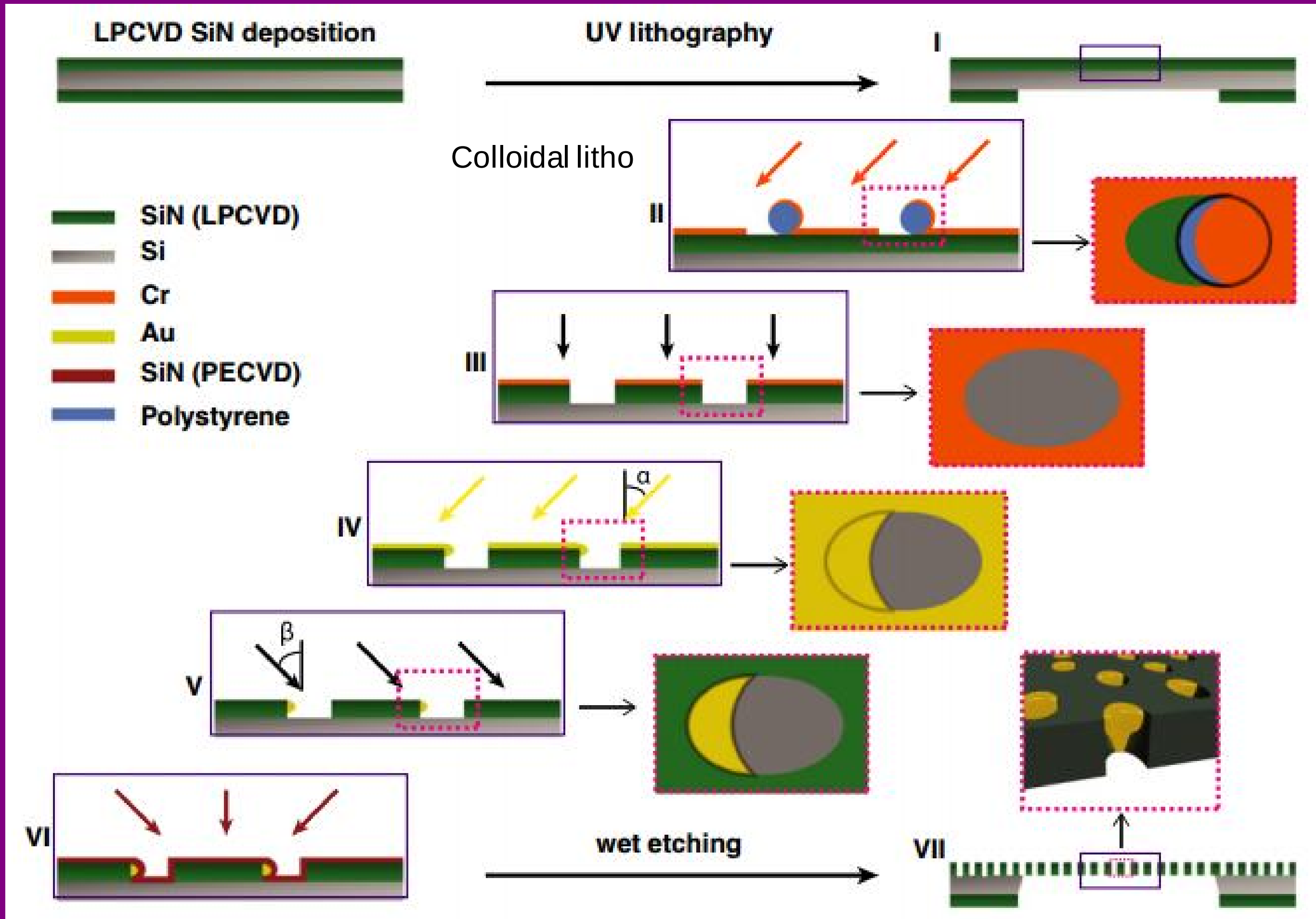
Different geometries





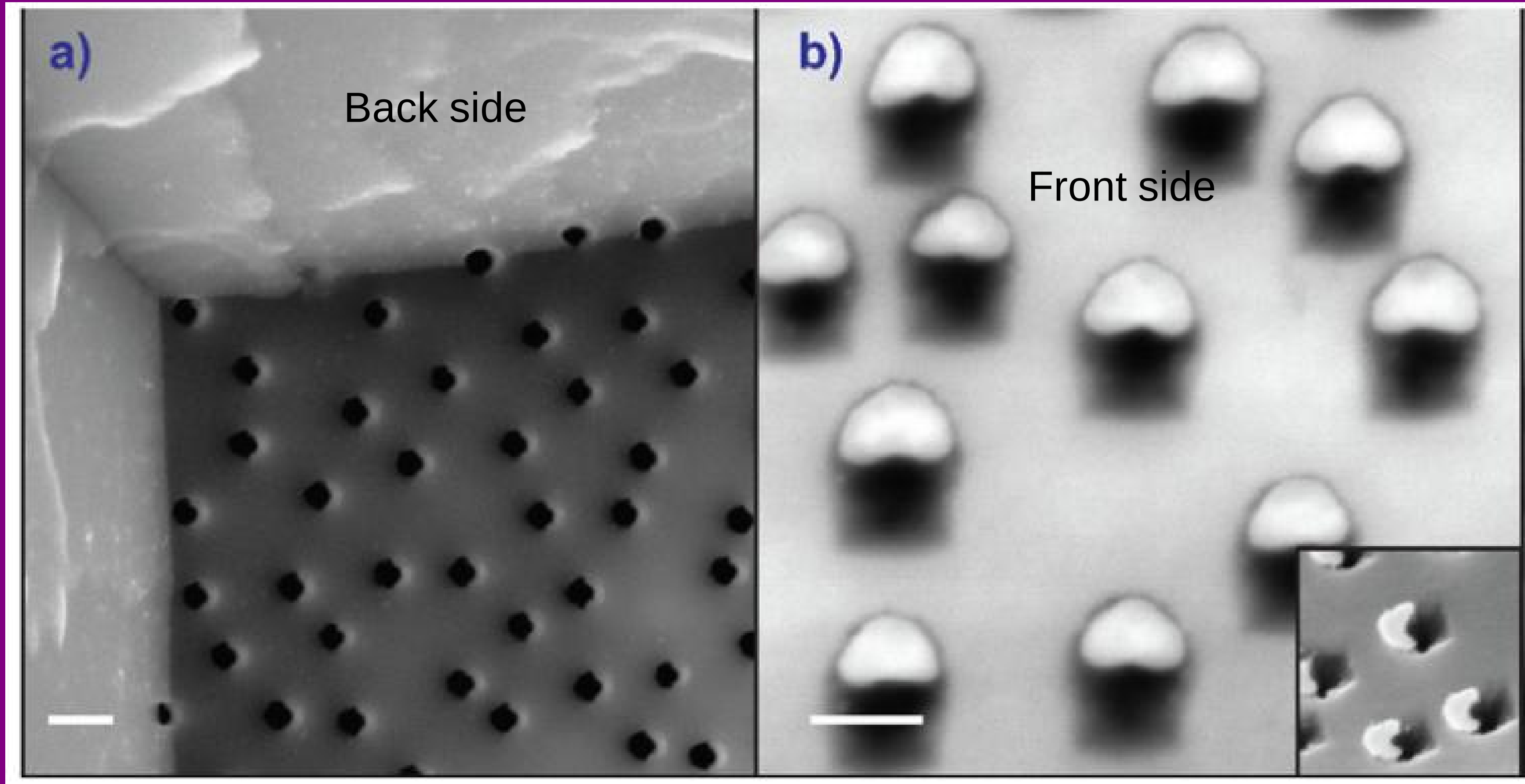
F. Hao et al. / Chemical Physics Letters 458 (2008) 262–266

Arrays of nanopores containing plasmonic particles



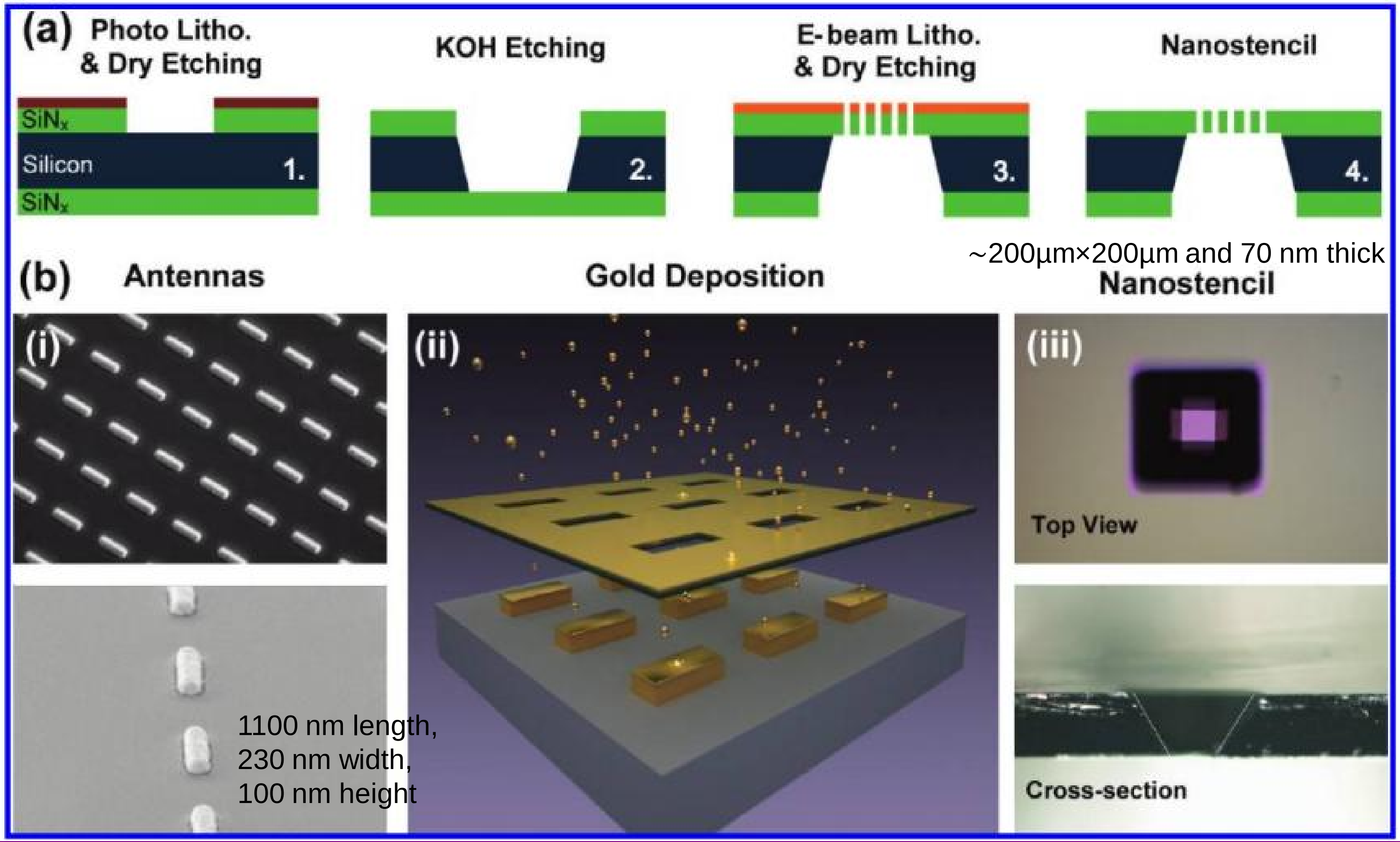
Nanotechnology 23 (2012) 415304 (7pp)

Membranes with plasmonic pore particles



Nanotechnology 23 (2012) 415304 (7pp)

Shadow mask



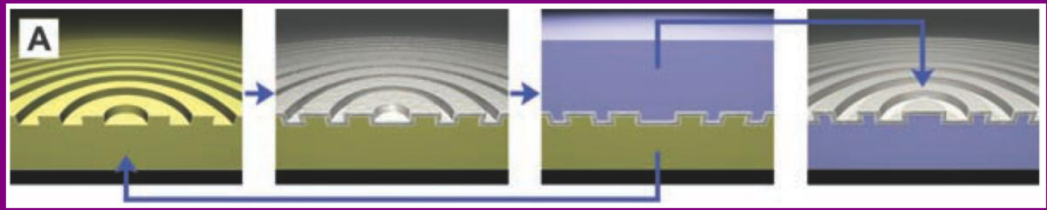
Nano Lett., 2010, 10 (7), pp 2511–2518

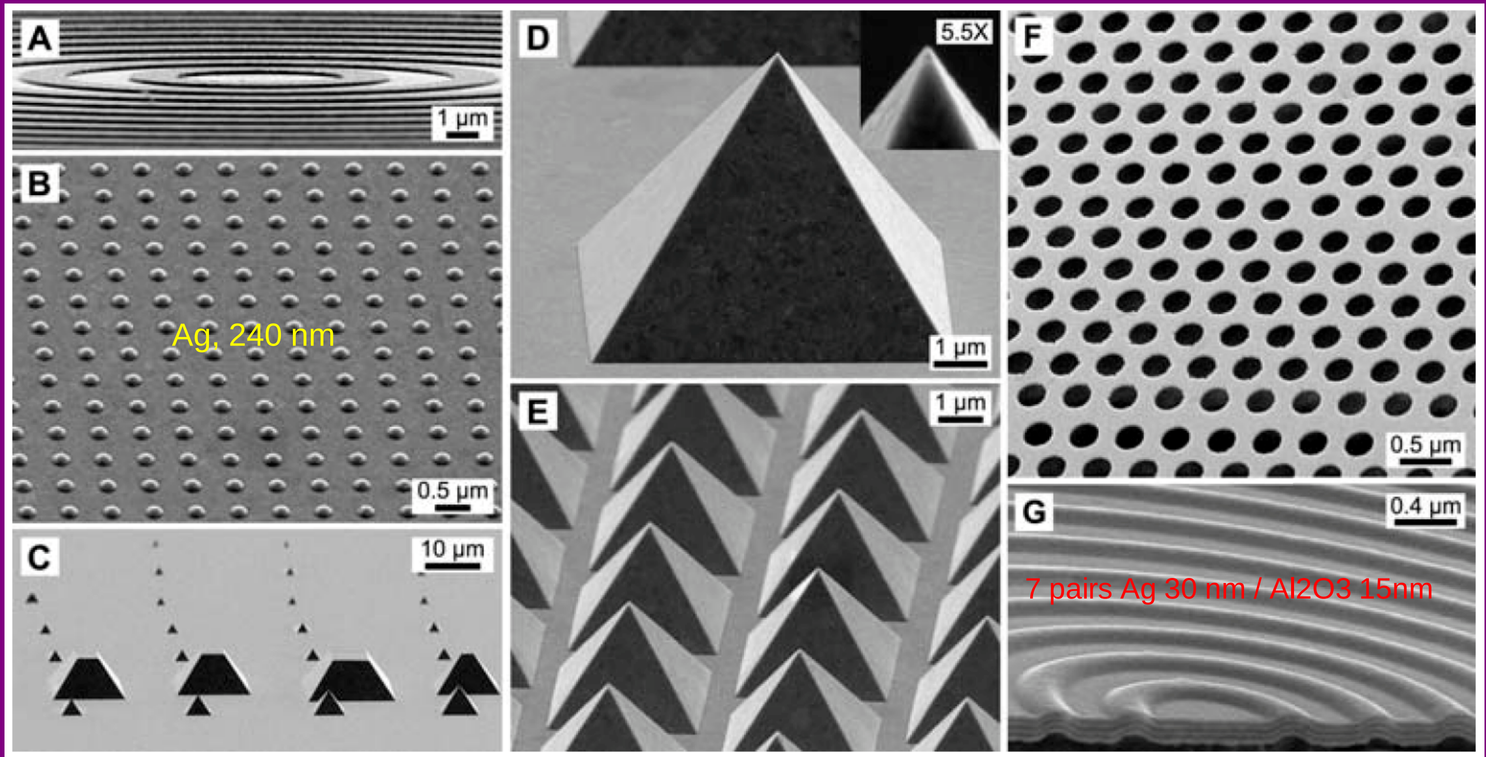
Shadow mask

- Contact gap - 15% size enlargement, rounded corners, transition area
- Reusing for multiple times
- Any substrate material
- Several masks can be used consequently
- Several deposition angles for controllable pattern shifting
- Alignment problems for multilayers

Template stripping, ultrasmooth surface

Prashant Nagpal et al., Science, 325, 594 (2009)





Holes 265 nm, Ag 30 nm
Ag was deposited on Si
with pits (NSL)

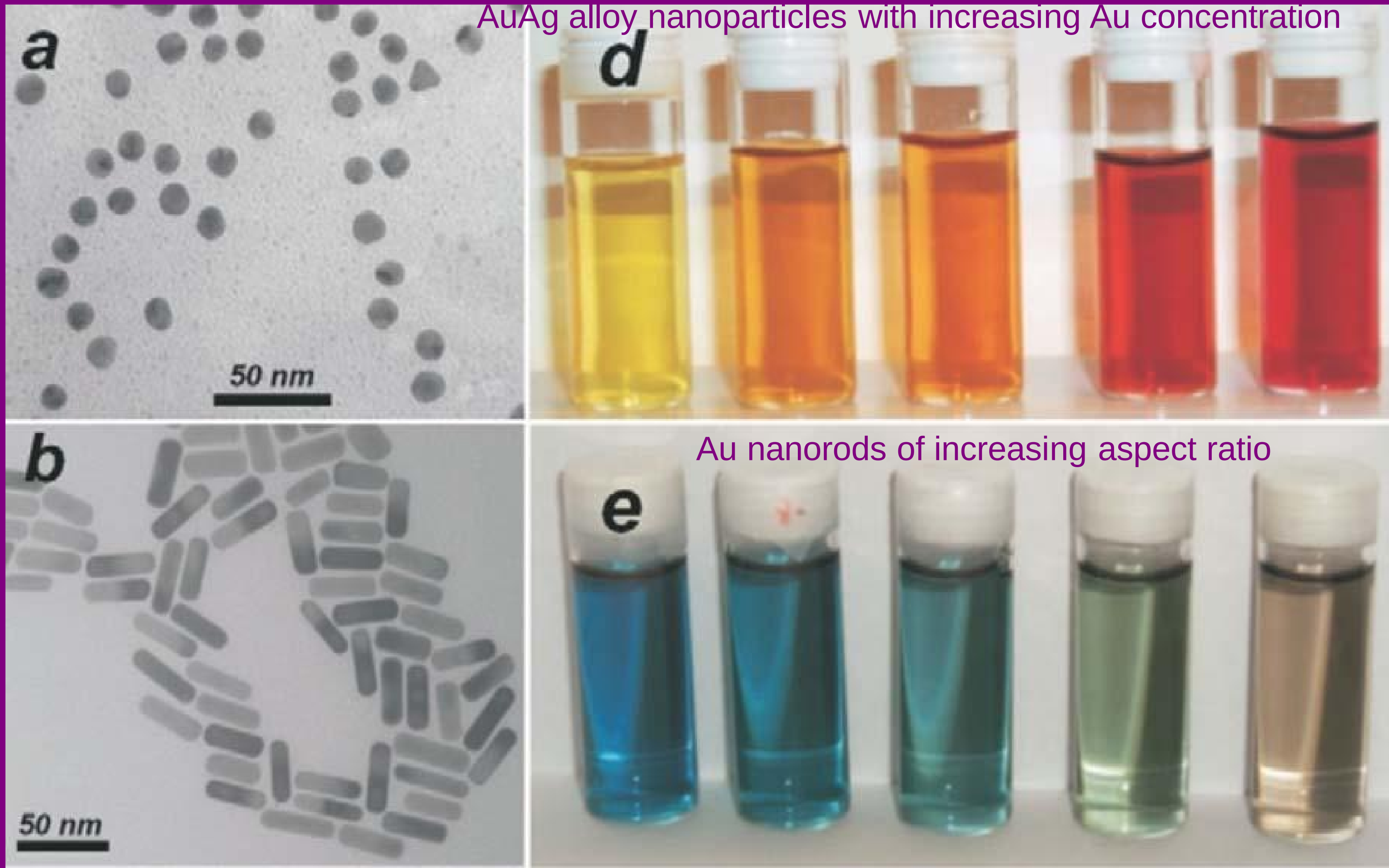
Template stripping

- Small samples, i.e. limited area
- Inclined walls, already vertical sidewals create problem for stripping
- Limited size, does not work below 100 nm
- Smooth surface
- Template can be used several times

Solution-Phase Syntheses

- Mainly Au, Ag or Cu nanoparticles (diameter10 – 80 nm) in water
- Produced by:
  - Chemical reduction. Process depends on:
    - Kind of metal
    - Reducing reagent AgNO3, K(AuCl4)
    - Temperature (boiling 1 h)
    - Stabilizing agents
    - Metal ion concentration
  - Laser ablation
  - Photoreduction
- The best SERS is provided by highly aggregated colloids
- Cube, triangle, nanorod shapes of particle

Material and size effect in plasmon resonance



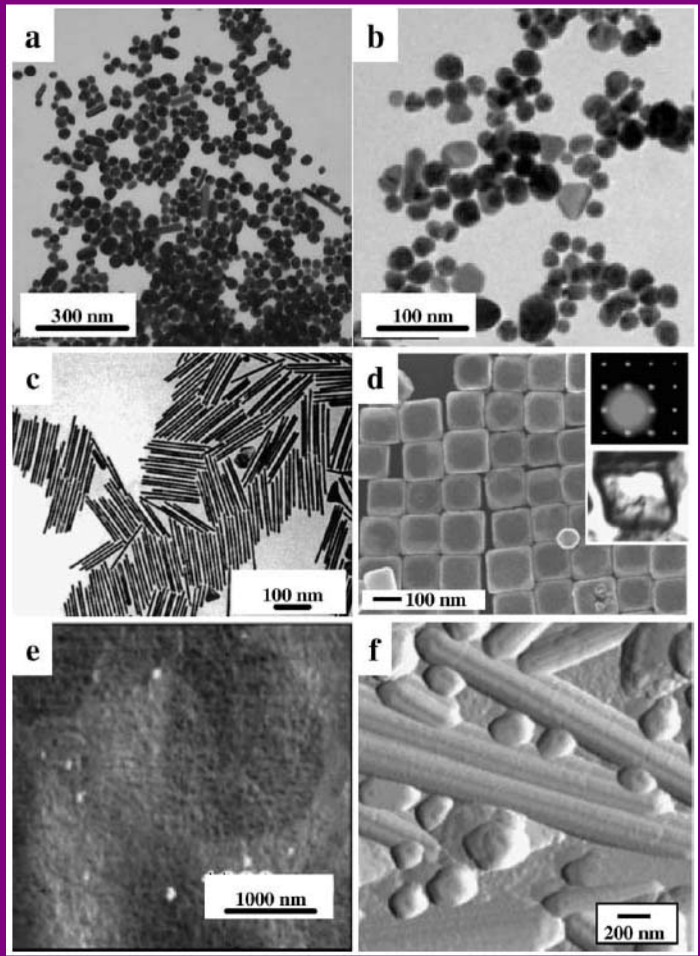
Materials Today, Feb 2004, p. 26-31

Solution-Phase Syntheses

- Bottom-up solution-phase synthesis is a versatile approach to forming NPs that allows control over their size, shape, composition, and structure (e.g., solid or shell).
- Generally involves the reduction of metal salts in a solution containing an appropriate stabilizer to control the growth and suppress the aggregation of the NPs.
- Reduction of the metal salt can be carried out electrochemically, photochemically, sonochemically, or using chemical reductants such as citrate, hydrides, alcohols, hydrogen, hydroxylamine, or hydrazine.
- These particles have facets and should be more correctly called 'quasi-spheres'

Colloids images

TEM of Ag citrate colloid
λ_{max}= 406 nm



TEM of Au borohydride colloid,
Au particles 20-70 nm,
λ_{max}= 535 nm

TEM of Au nanorods,
λ_{max}= 525 nm and 885 nm

TEM of Au nanosquares

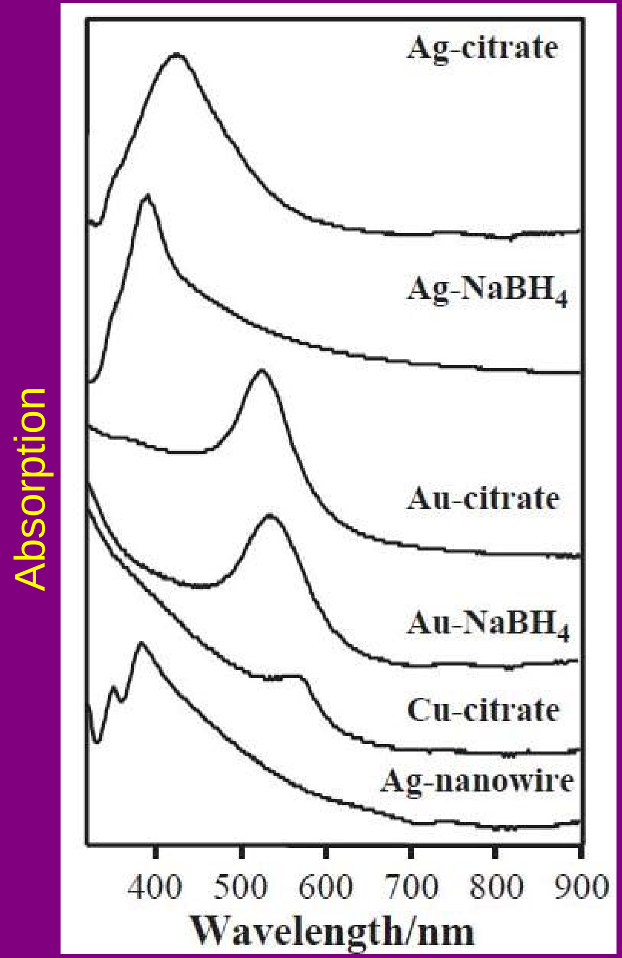
AFM of Au nanospheres embedded in film of biopoymer chitosan (inert organic matrix)

AFM of Ag nanowires in dendrimer matrix

R.F. Aroca et al. / Advances in Colloid and Interface Science 116 (2005) 45–61

SPR of colloids

Observed effects are due to particle size, concentration, aspect ratio.

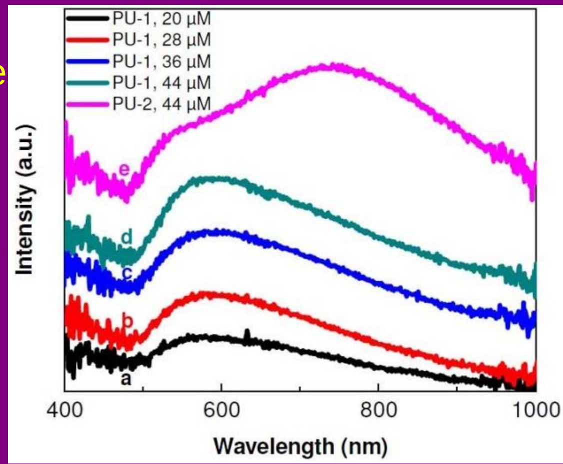


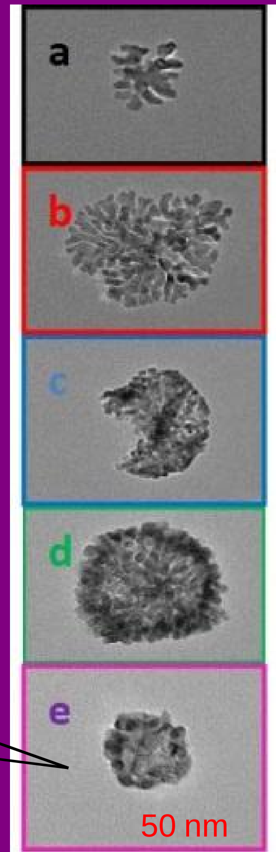
Partical surface charge determs stability, adsorbivity, electrokinetic properties

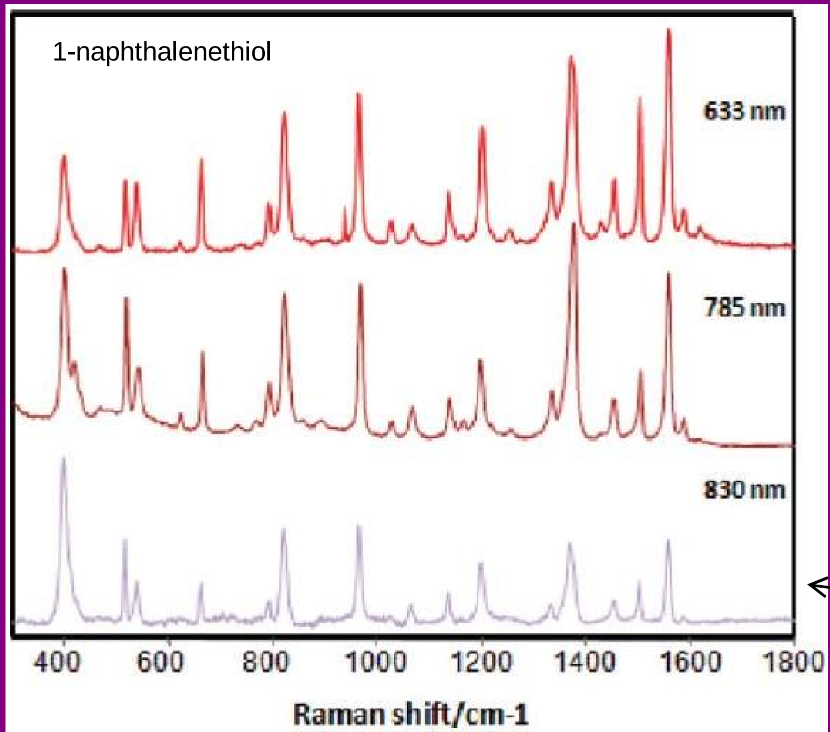
R.F. Aroca et al. / Advances in Colloid and Interface Science 116 (2005) 45–61

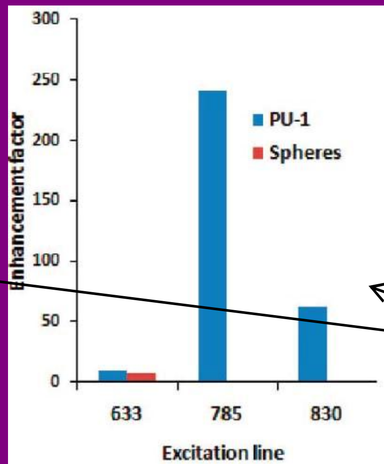
Gold Lace Nanoshells

PU means amphiphilic polyurethane template







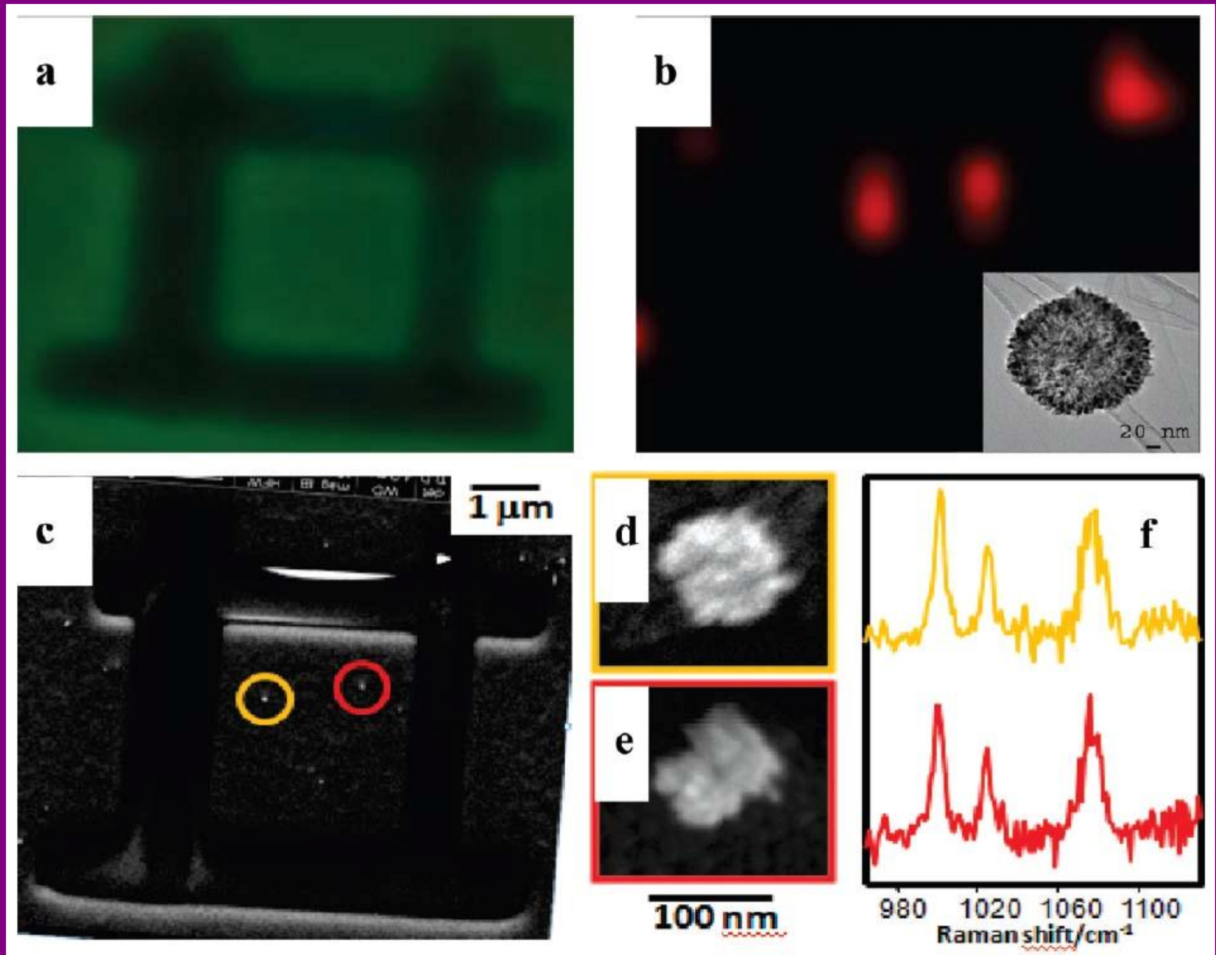


M. Yang et al., SERS-Active Gold Lace Nanoshells with Built-in Hotspots, *Nano Lett.* 2010, *10*, 4013-–4019

Images of single lace nanopartilce

Optical

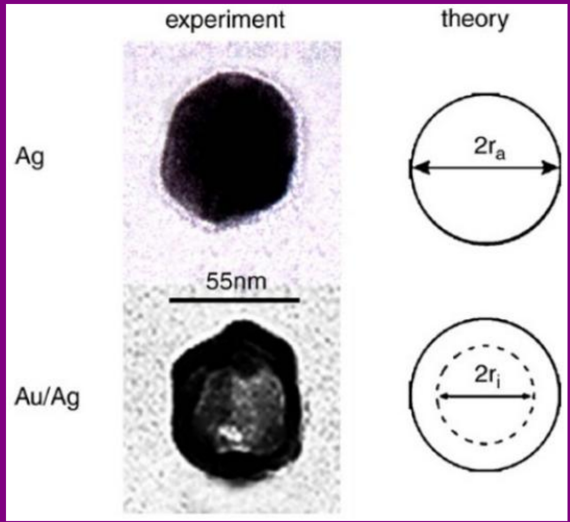
Raman



SEM

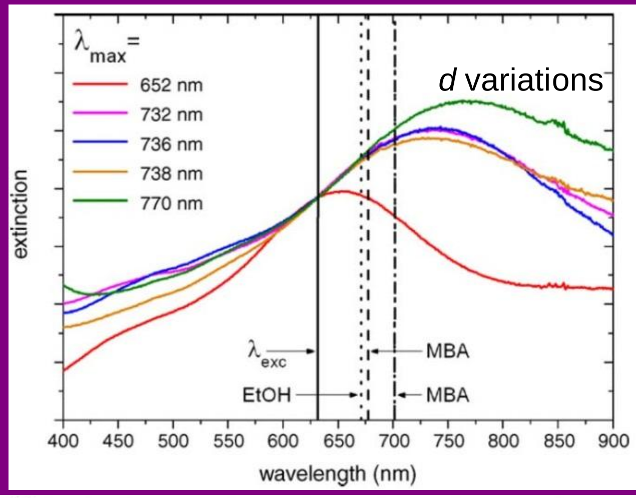
M. Yang et al., SERS-Active Gold Lace Nanoshells with Built-in Hotspots, *Nano Lett.* 2010, *10*, 4013-–4019

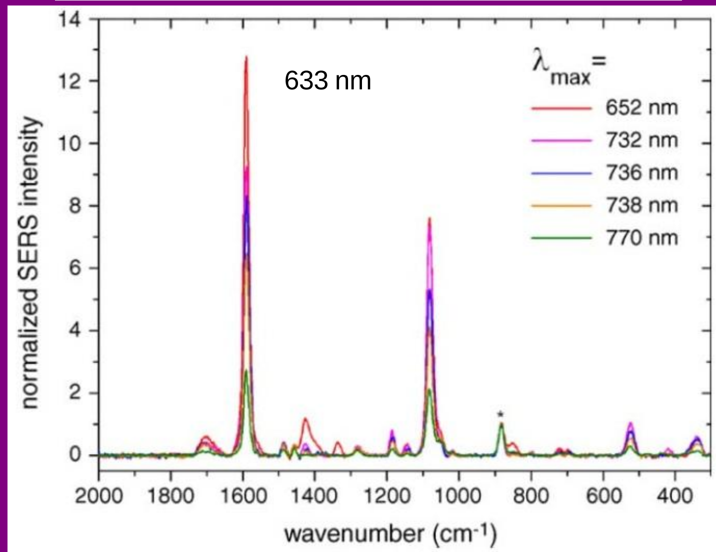
Nanoshells



$d = (r_a - r_i)$

4-mercaptobenzoic acid (MBA)





- additional degree of tunability of SPR by changing the thickness *d* of shells
- more uniform signal (less fluctuations)

M. Gellner et al. / Vibrational Spectroscopy 50 (2009) 43–47

Metal nanostructured films

Prepared by different methods:

electrochemistry methods
physical vapor deposition (PVD) and annealing
oblique angle deposition
glanced angle deposition (GLAD)

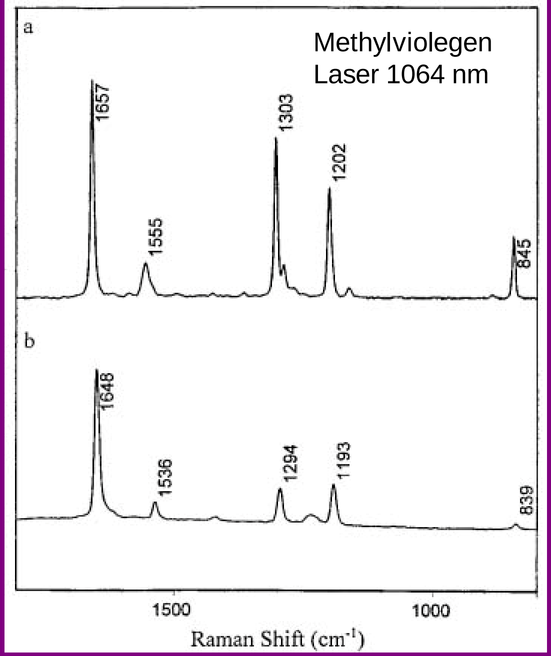
- Applicability to any substrate
- High purity
- Structure can be controlled by deposition rate (0.5 A/s), substrate roughness, temperature, mass thickness (6 nm), post annealing
- Cold-deposited (-100 ºC) Ag (pore, voids, cavities)

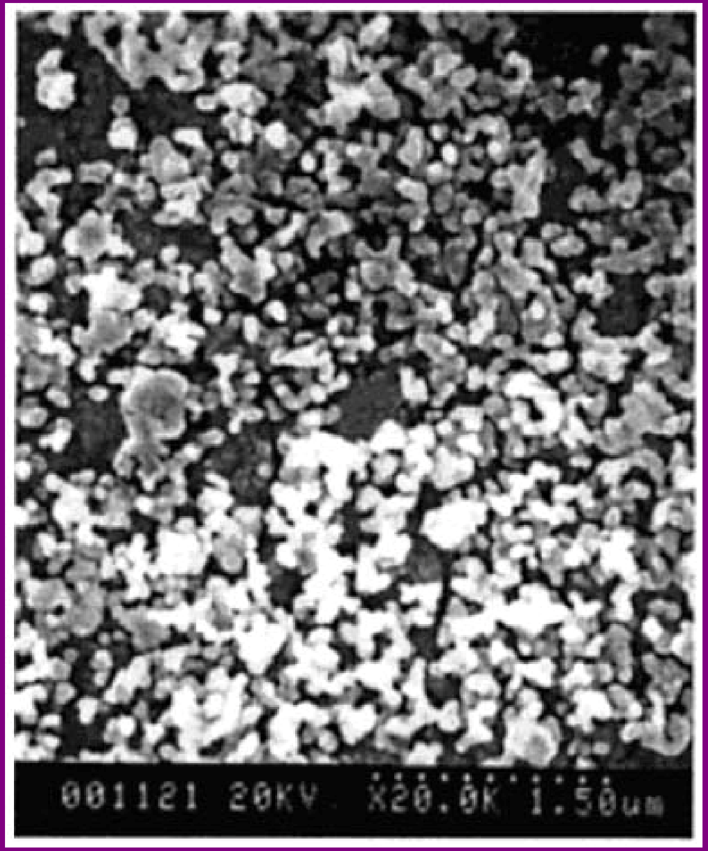
Metal electrodes

- Surface protrusions 25-500 nm
- Ag in KCl electrolyte
- Oxidation-reduction cycles

SERS

bulk Raman



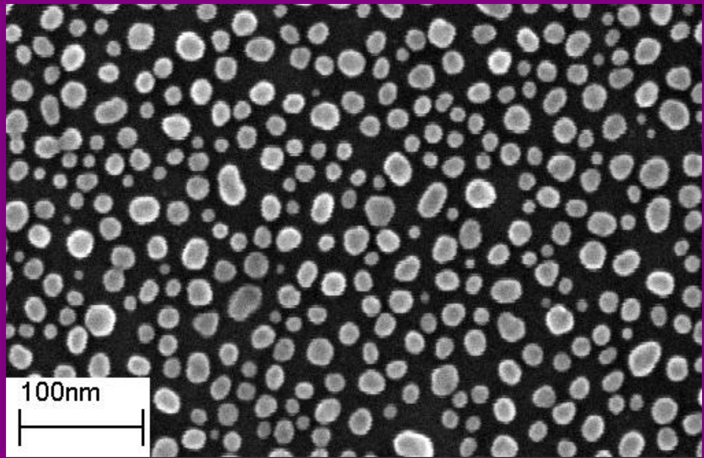


Zheng et al., J. Phys. Chem. B, Vol. 106, No. 5, 2002, p.1019-23

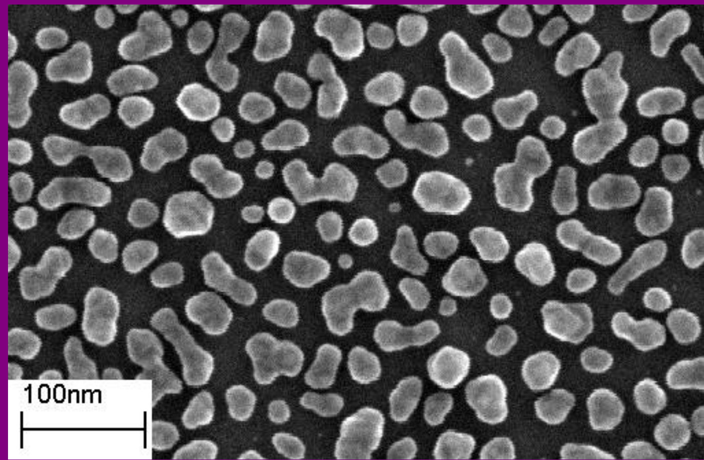
As deposited silver films

Room temperature

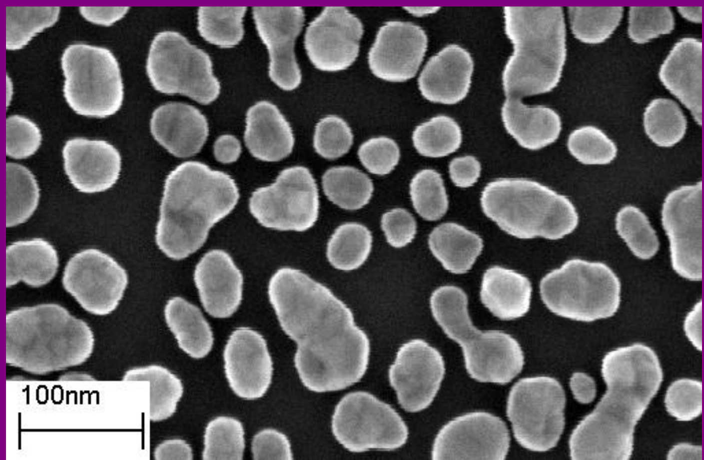
4 nm
0.2 Å/s



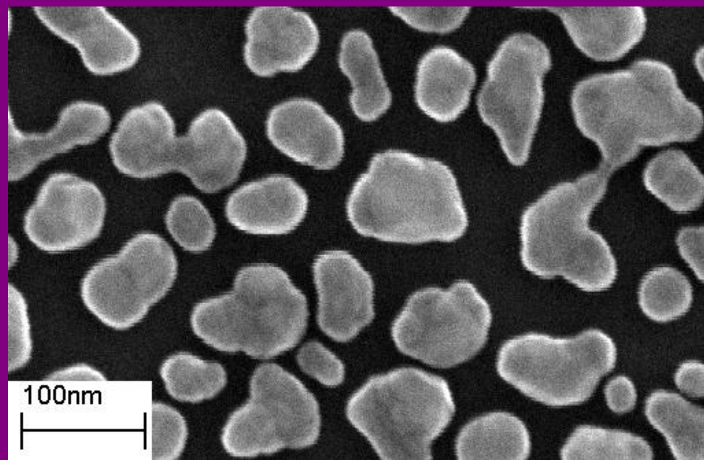
5.5 nm
0.5 Å/s



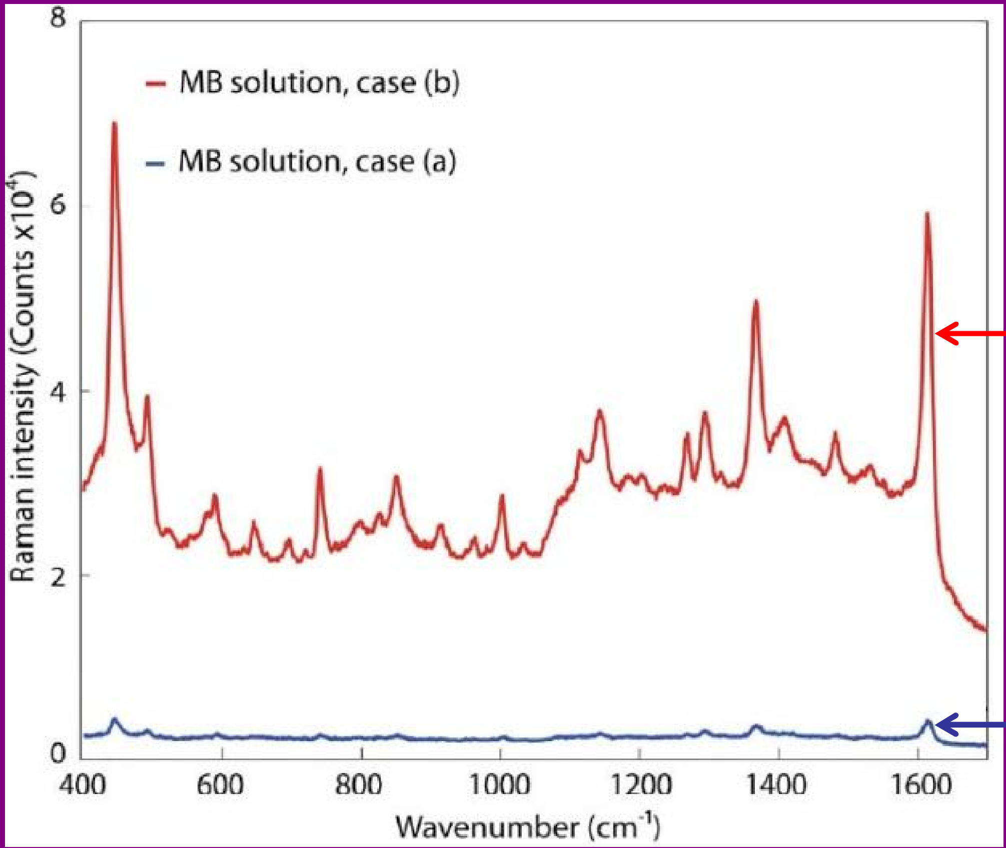
10 nm
2.0 Å/s

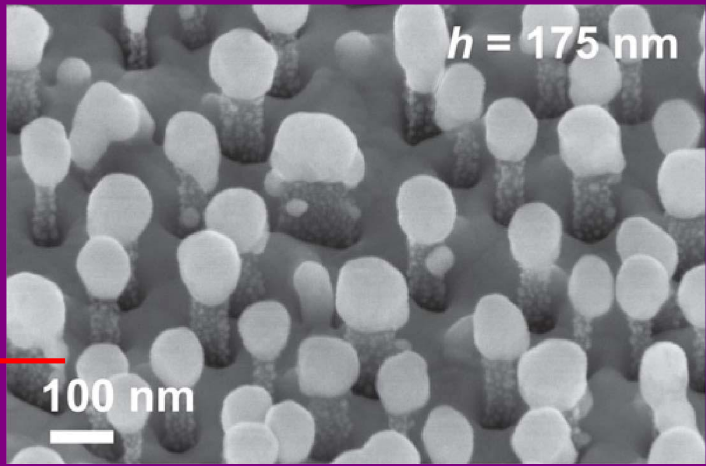


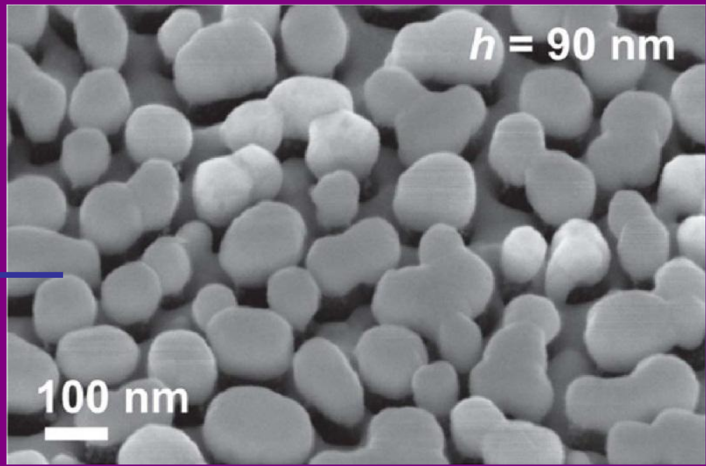
12 nm
0.2 Å/s



Pillars, produced by etching of metal film

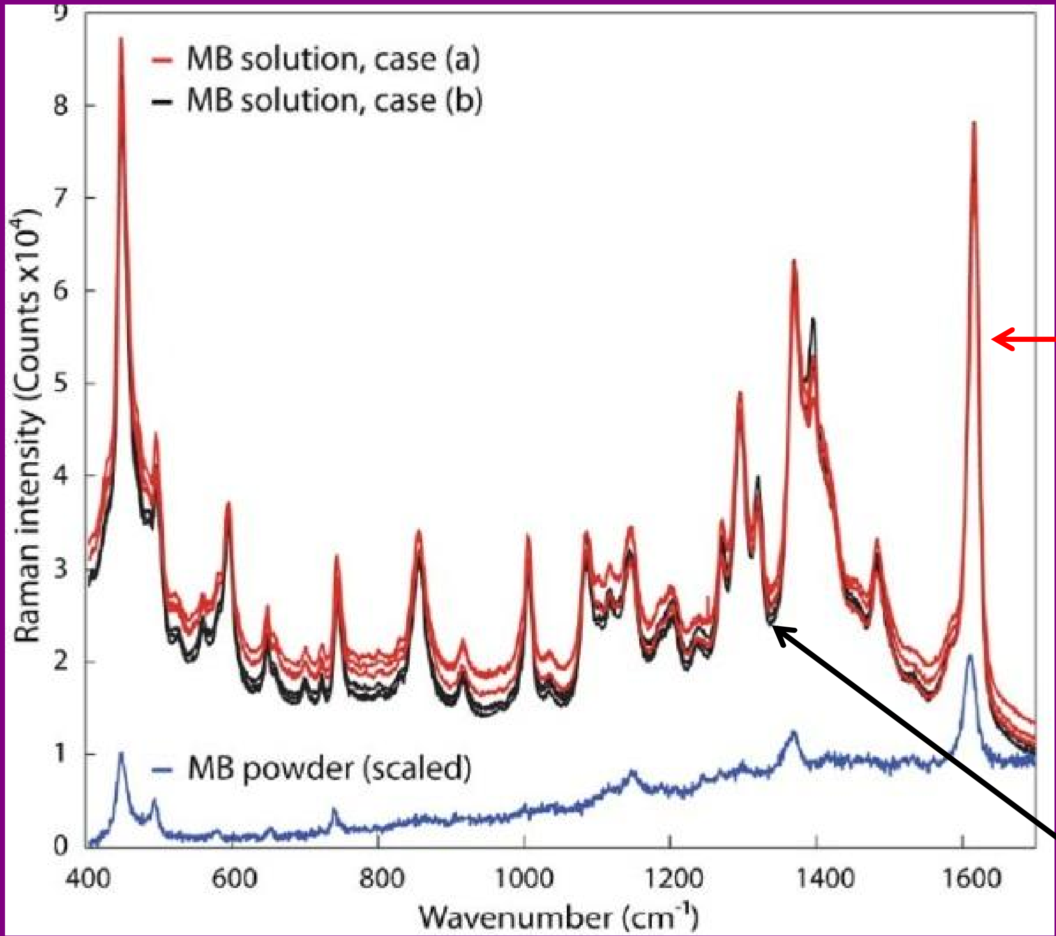


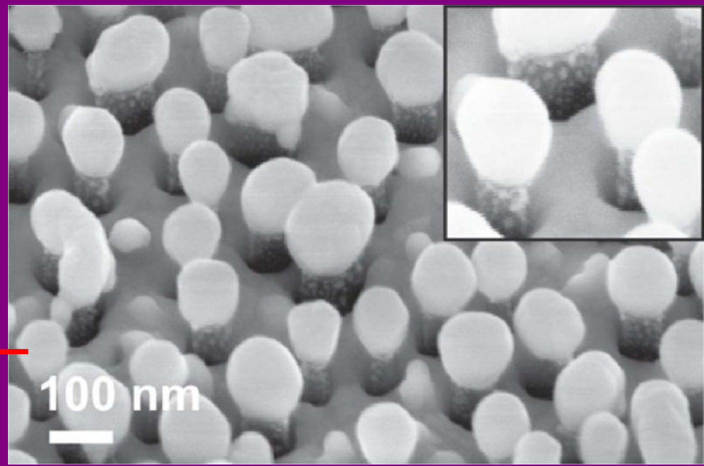


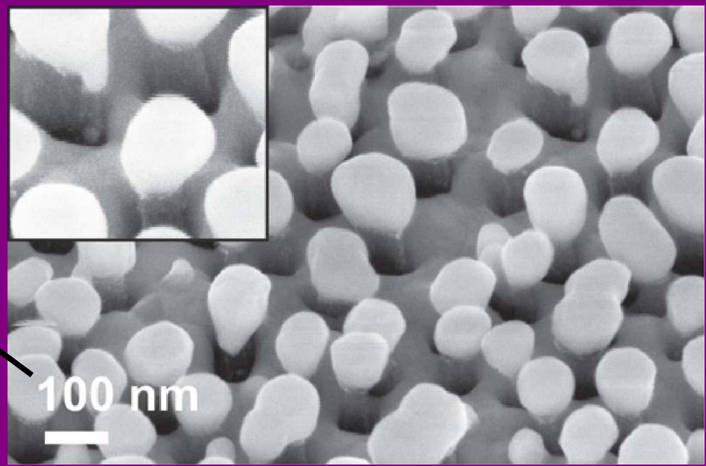


A. Shevchenko et al., Appl. Phys. Lett. 100, 171913 (2012)

Fine structure of deposited metal film

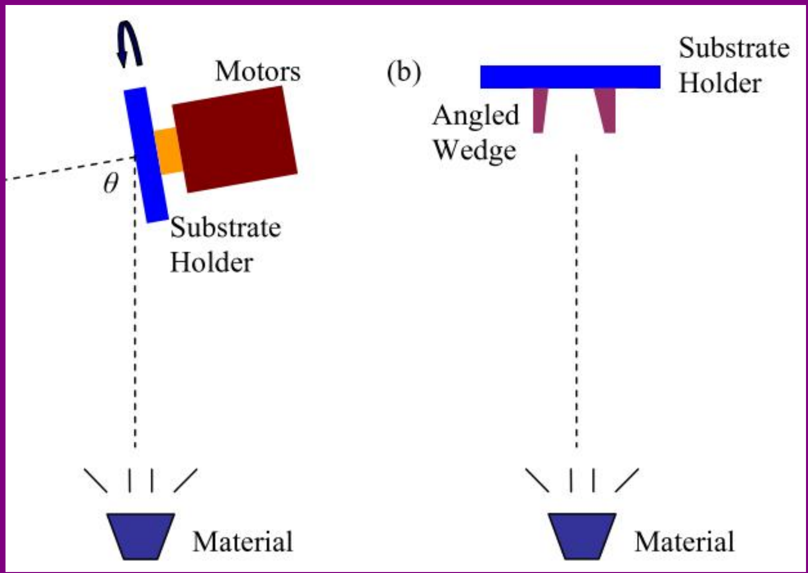




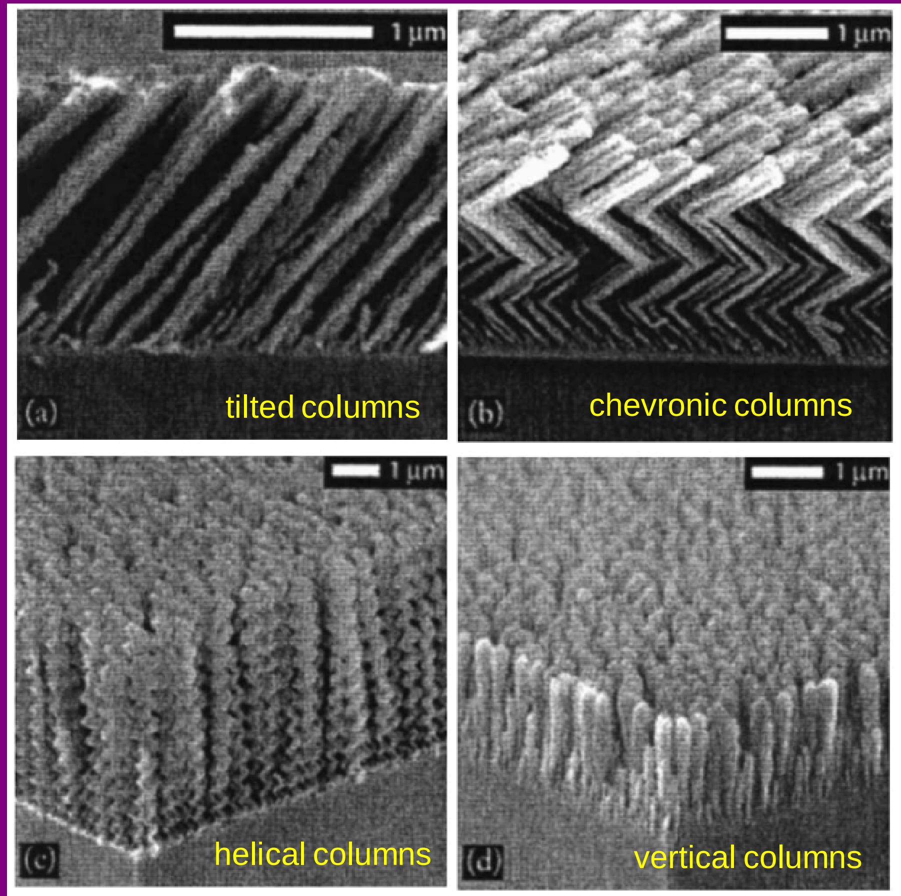


A. Shevchenko et al., Appl. Phys. Lett. 100, 171913 (2012)

Oblique angle deposition

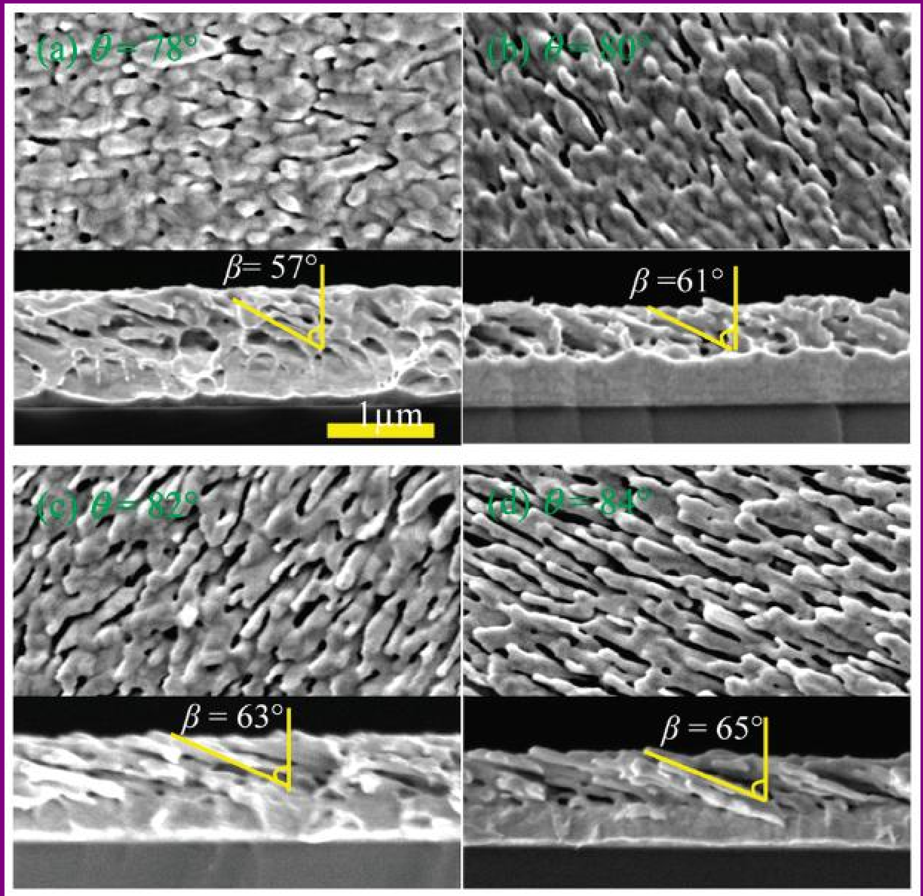


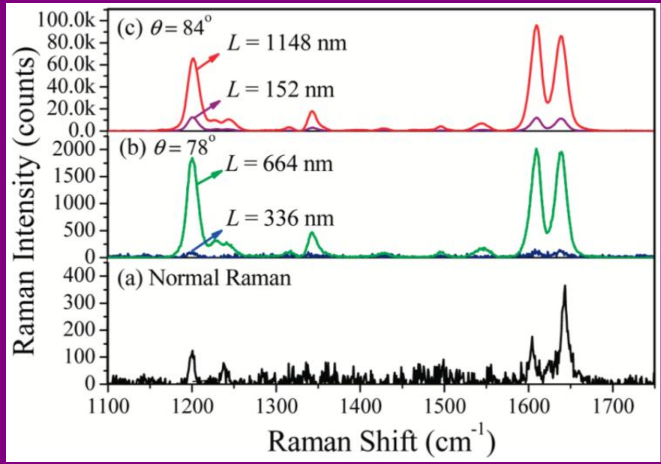
Nanotechnology21(2010) 175303 (9pp)

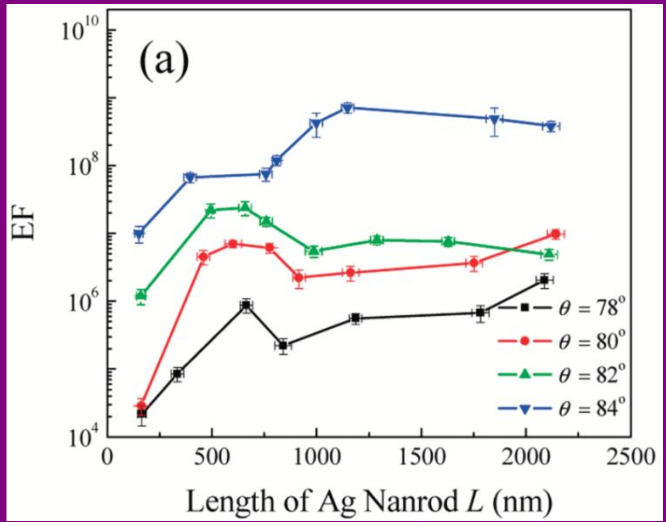


J. Vac. Sci. Technol. A, Vol. 25, No. 5, Sep/Oct 2007

GLAD







J. Phys. Chem. C, Vol. 114, No. 18, 2010, 8177

GLAD features

- Wafer scale, i.e. the whole wafer can be covered by the nanostructures
- No adhesion layer – problems during further processing
- Limited variations of morphology

Comparison of the fabrication methods

Self-organizing

- Limited shapes and sizes
- Only random, not regular arrays of structures
- Normally, bad adhesion of the mask

Nanoimprint

- Template (mold) patterning
- Proximity effects
- Removal of residual layer
- Template wear
- High pressure on the functional layer

Summary

- Plasmonics is rapidly development area of nanophotonics. It promises attractive applications in many fields of science and engineering
- There is no ideal method to fabricate low cost plasmonic devices in reproducible way
- Every plasmonic application has own, most suitable fabrication tehnique and vice versa every nanotechnology method has limited application

Plasmonic future

- Application of new plasmonic materials (graphene, semiconductors). It helps to reduce the losses inherent in the interaction of light with metal, but only in visible range
- Development of the new fabrication techniques