Plasmonics: Application-oriented fabrication

Part 2. Applications and technological challenges

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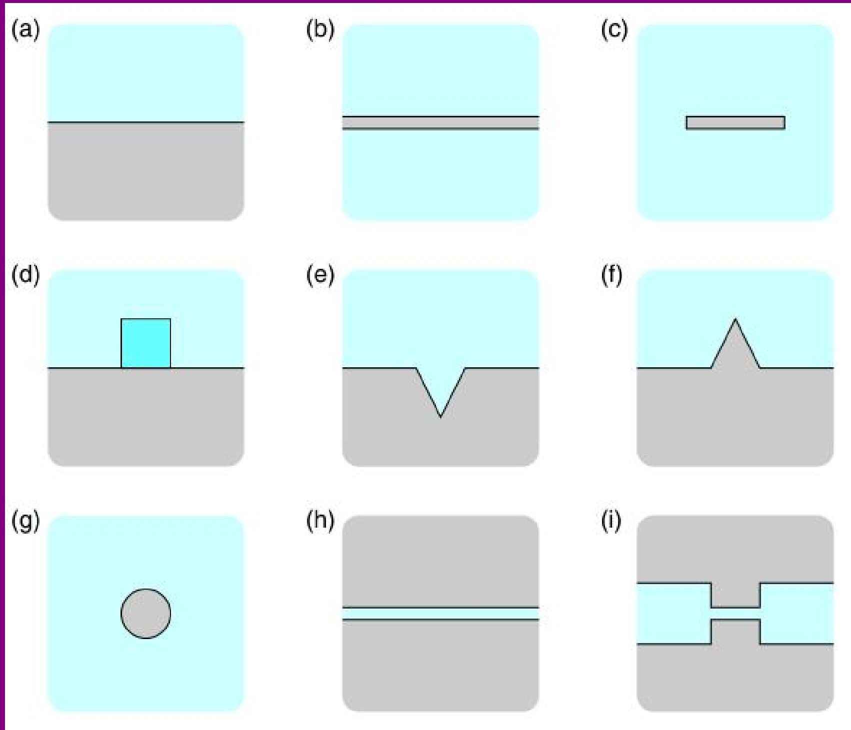
Outline

- Main plasmonic applications and requirements to technology
- Plasmonic device in general
- Ideal nanofabrication process for plasmonics

Cross sections of various plasmonic waveguides

J. Phys. D: Appl. Phys. 45 (2012) 433001



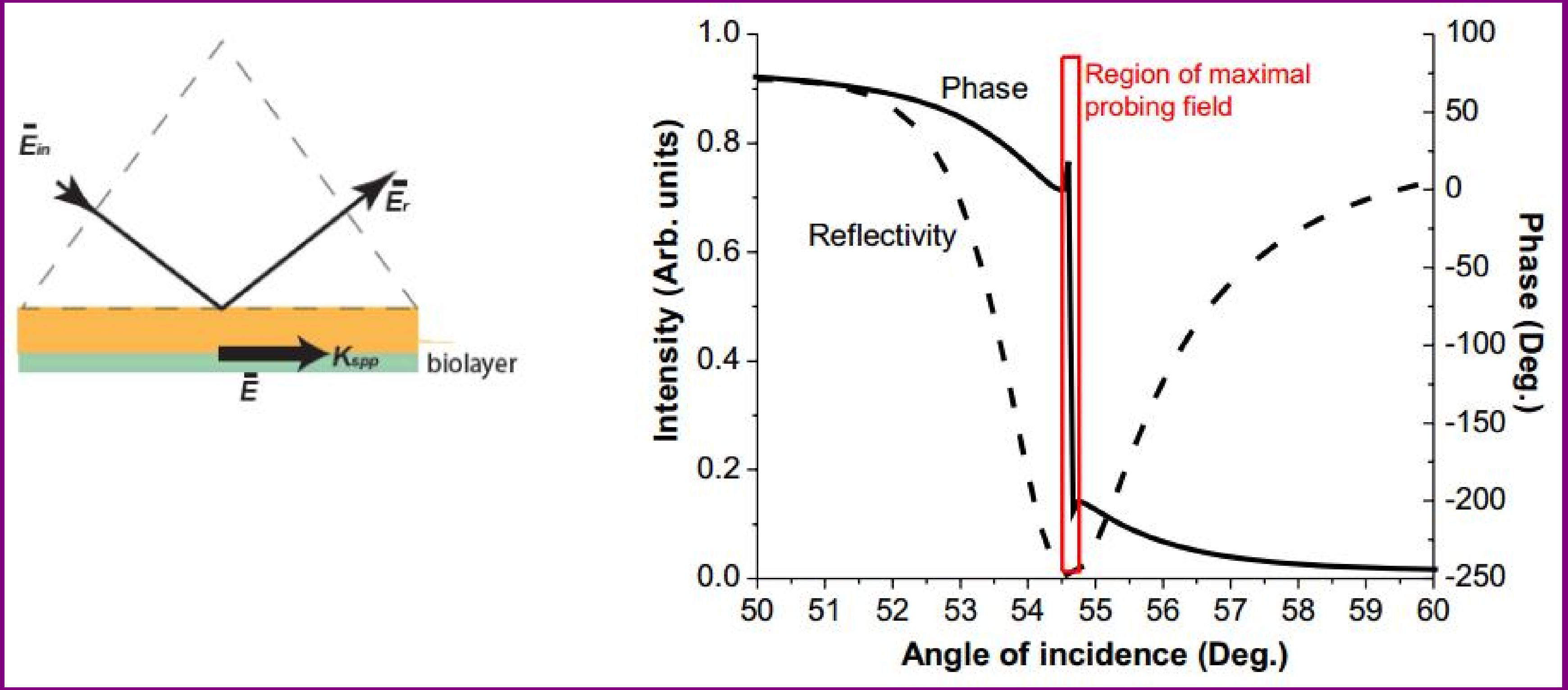
The grey colour indicates metal.

- (a) Plane metal–dielectric interface
- (b) Thin metal film, support the long-range surface plasmons with reduced loss
- (c) Thin metal strip (10 nm x 1 µm) surrounded by a homogeneous medium, propagation loss can be lowered to 0.1 dB cm^{-1}
- (d) Dielectric loaded, the channel width of up to several times the surface plasmon wavelength
- (e,f) V-groove and Λ-wedge with channel and wedge plasmons. 0.6 µm wide and 1 µm deep V-groove in a flat gold substrate provides 100 µm propagation length
- (g) Nanowire, may be also dielectric
- (h) MIM structure
- (i) Chanel-type MIM structure (two opposing metal ridges)

Waveguide fabrication

- Requirements:
  - Regular structures
  - Non-rectangular profile (optional)
  - Metallization of internal surfaces
  - Small chip on a large wafer
  - High volume production
- Methods:
  - Nanoimprint
  - Damascene

SPP sensor

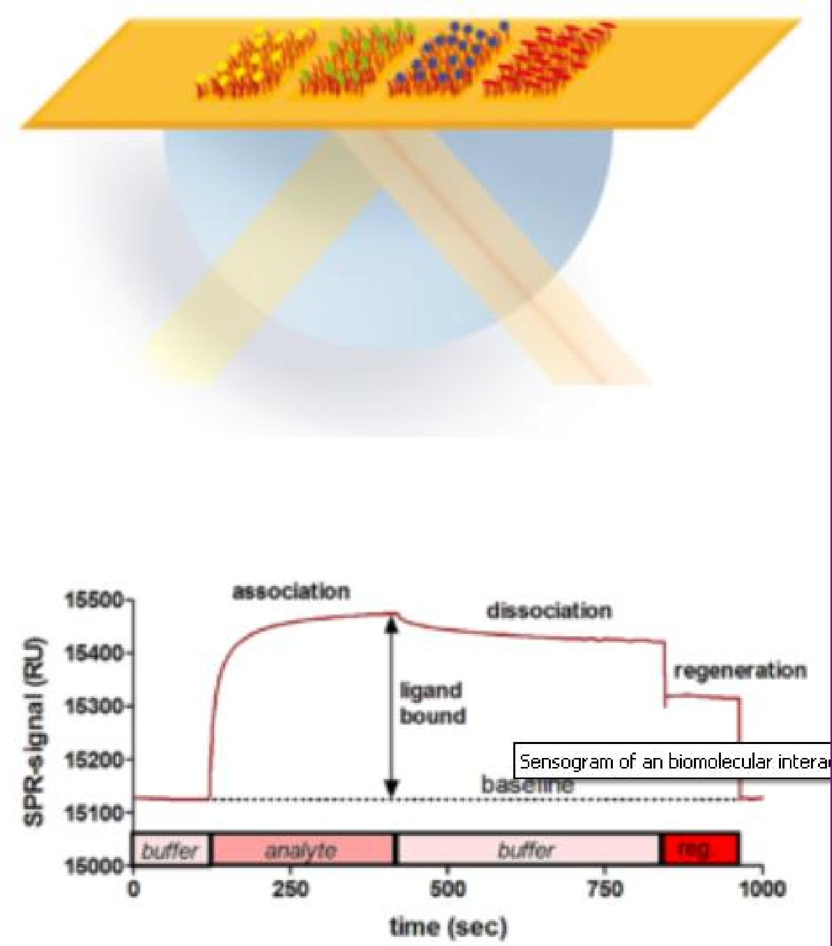


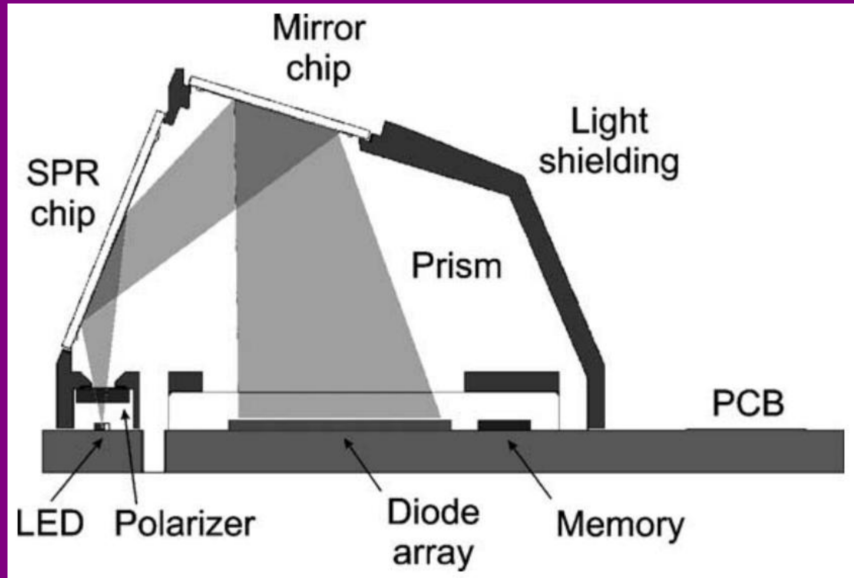
Ann. Phys. (Berlin) 524, No. 11, 637–662 (2012) / DOI 10.1002/andp.201200203

Industry SPP sensors

Biacore

SPR shift with RI variation

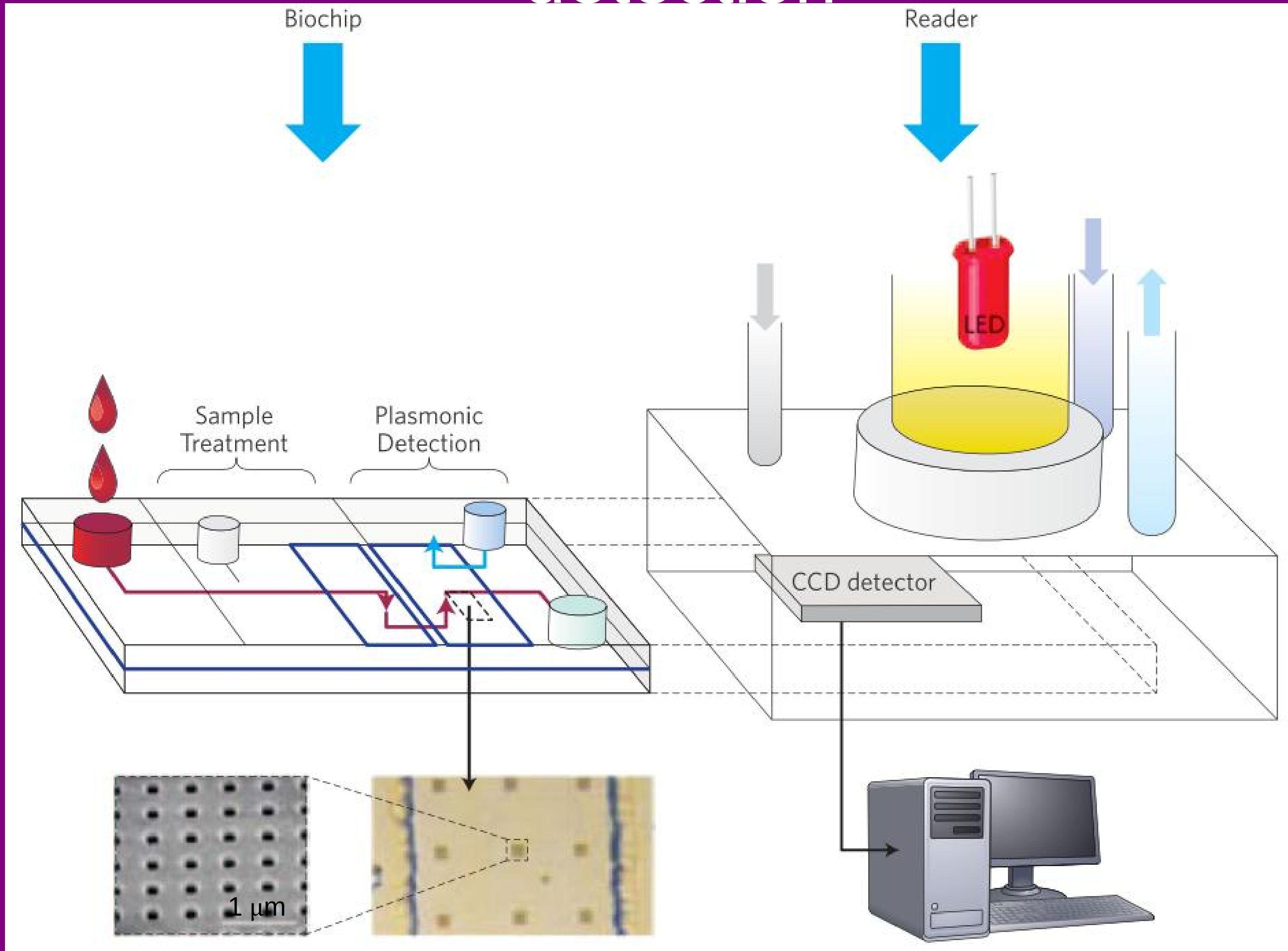




Texas Instrument, 5cm × 0:7cm × 3 cm, angle scan, 830 nm

T.M. Chinowsky et al. / Sensors and Actuators B 91 (2003) 266–274

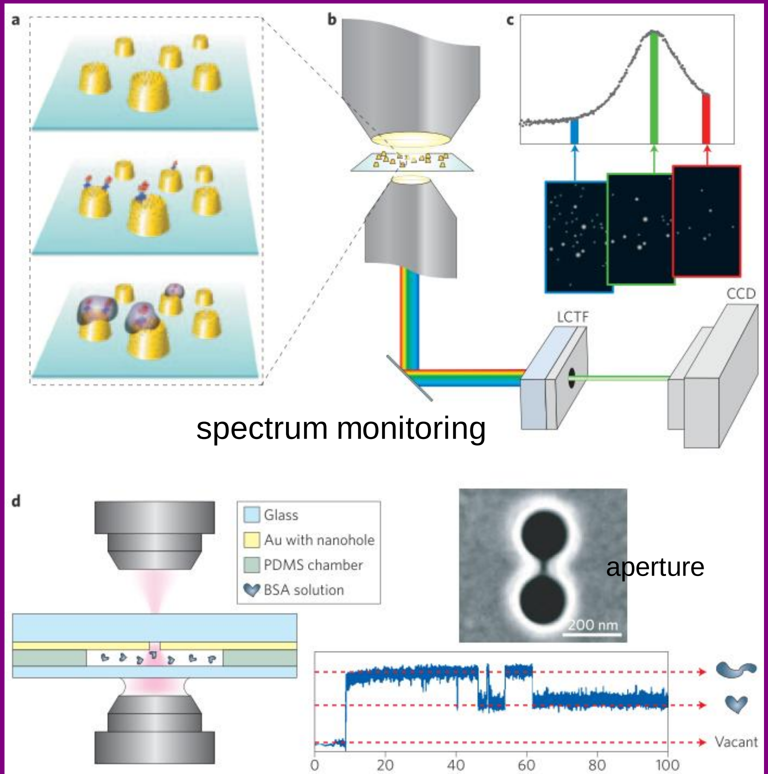
Biosensor with plasmonics-enabled detection



G. Brolo, NATURE PHOTONICS | VOL 6 | NOVEMBER 2012 | p.709

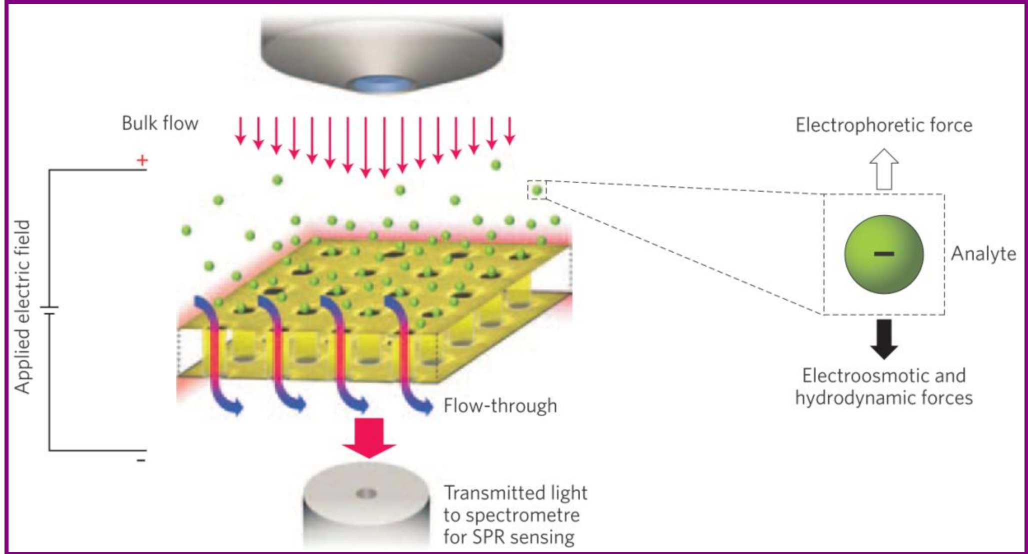
Plasmonic biosensor detection

Plasmonic single-molecule detection



intensity monitoring

Combination of electric field- and pressure-driven flow



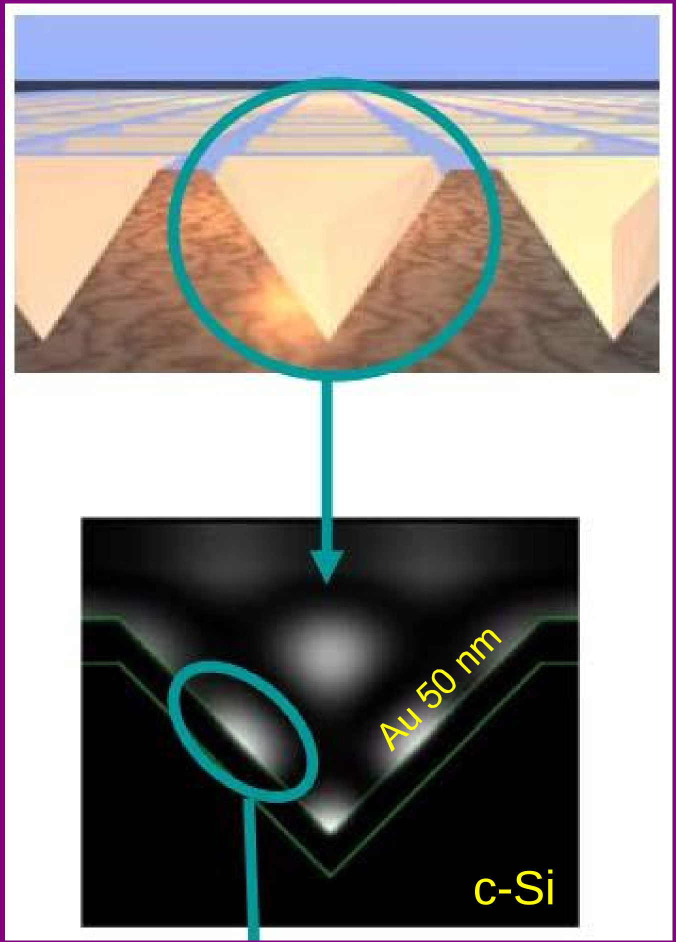
G. Brolo, NATURE PHOTONICS | VOL 6 | NOVEMBER 2012 | p.709

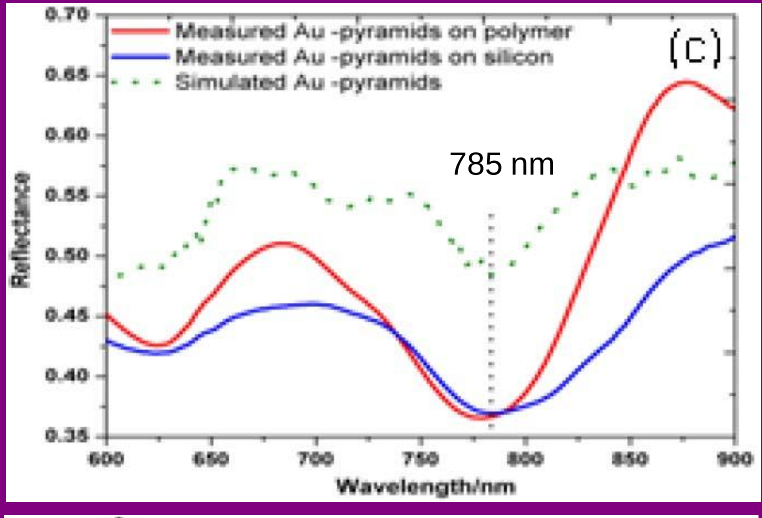
Biosensor and SERS substrate fabrication

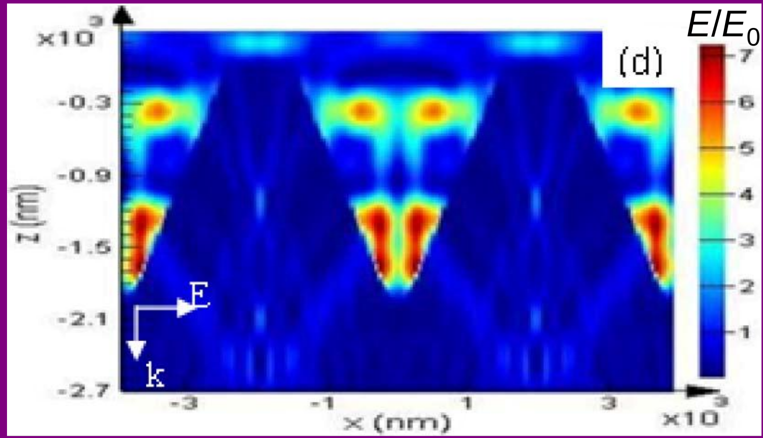
- Requirements:
  - Regular and irregular structures
  - Broad range – from thin film to nanostructures
  - Small chip on a large wafer
  - High volume production
- Methods:
  - Nanoimprint
  - NSL
  - Template based
  - Self-organized films

Commersial SERS substrate (Klarite)

Very high enhancements are 'sacrificed' in favor of homogeneity and reproducibility



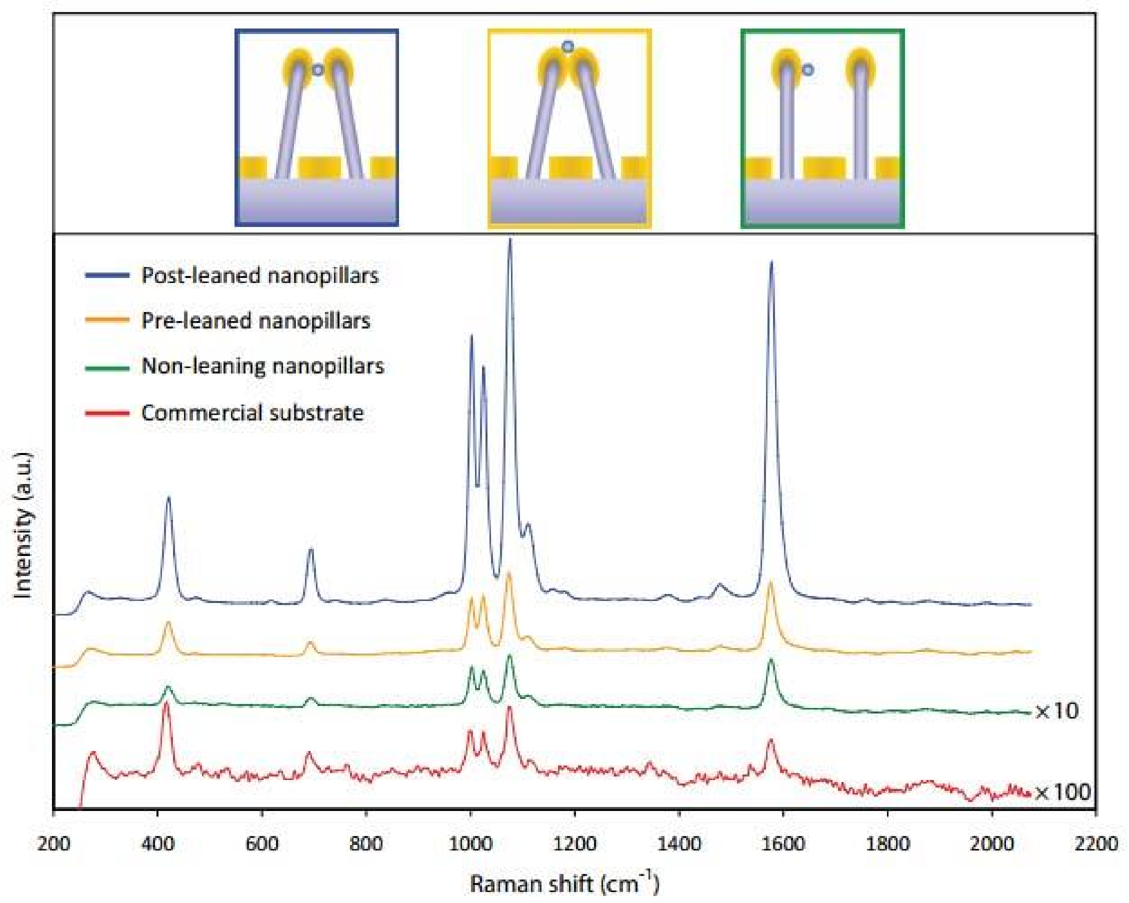


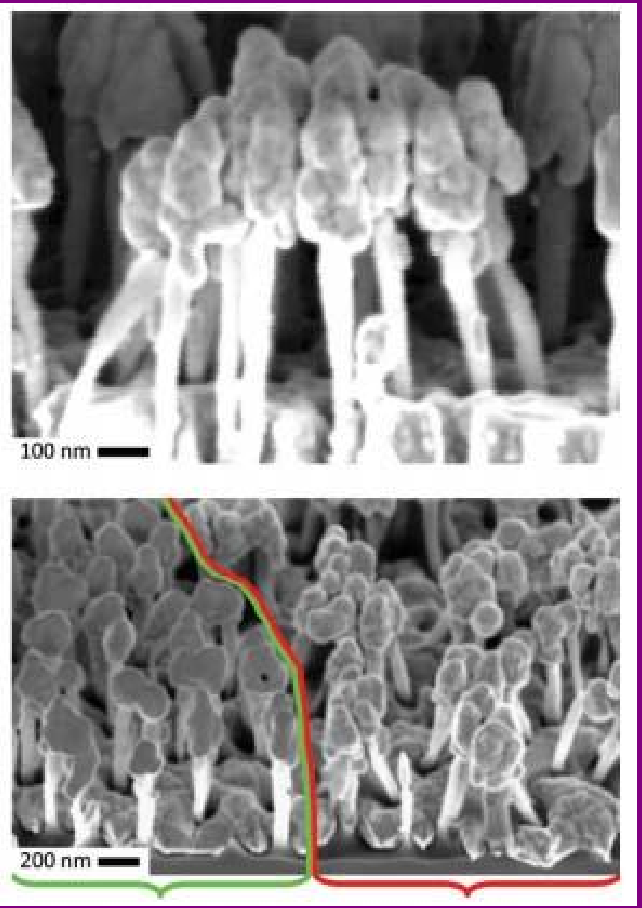


www.d3technologies.co.uk - www.renishawdiagnostics.com/en/klarite-sers-substrates

ZHIDA XU, Master Thesis, University of Illinois at Urbana-Champaign, 2011

Leaning Si pillars





M.S. Schmidt et al., Adv. Mater. 2012, 24, OP11–OP18

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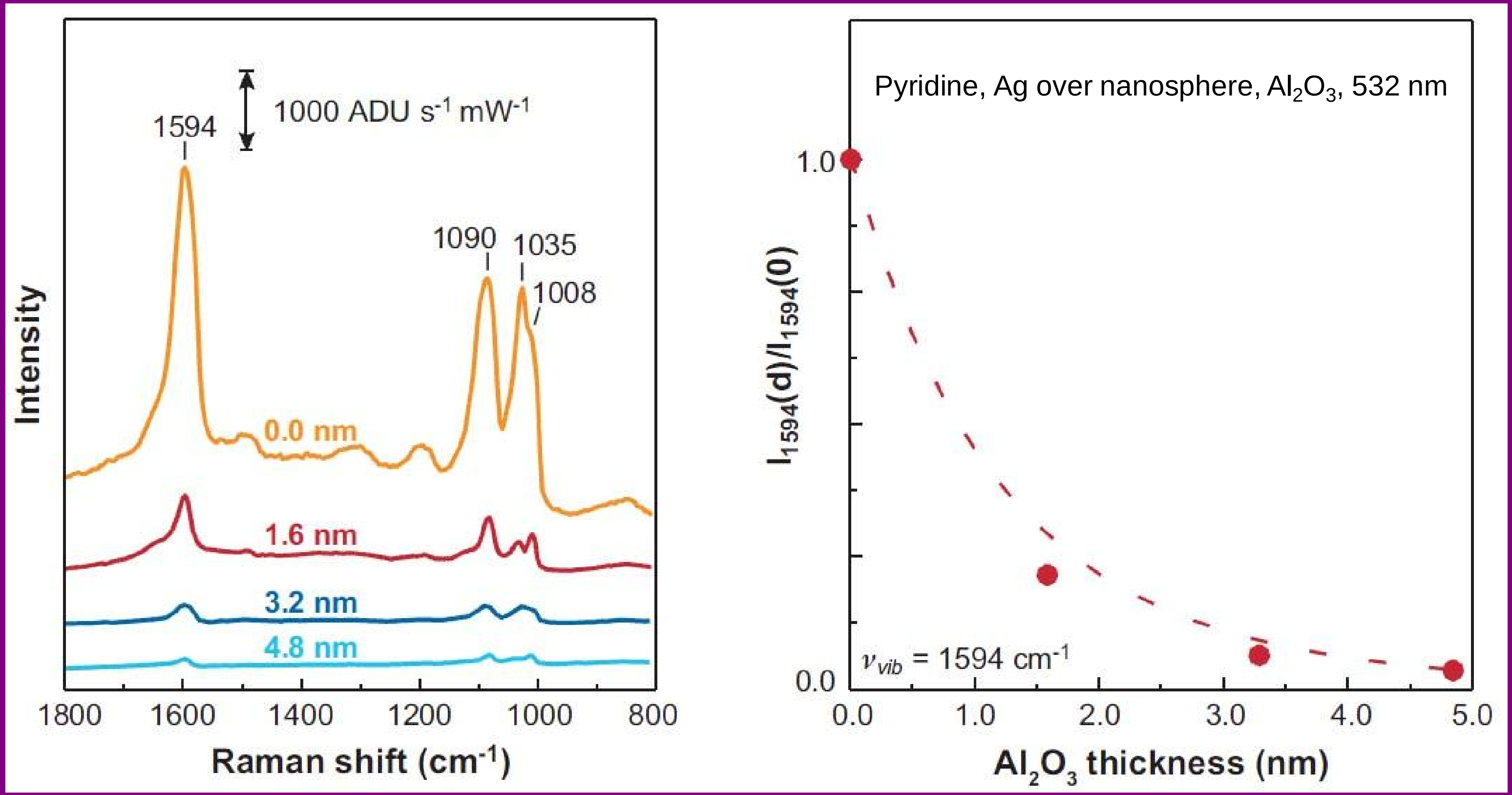
SERS, distance dependence

$$I_{SERS} = \left(\frac{a+r}{a}\right)^{-10}$$

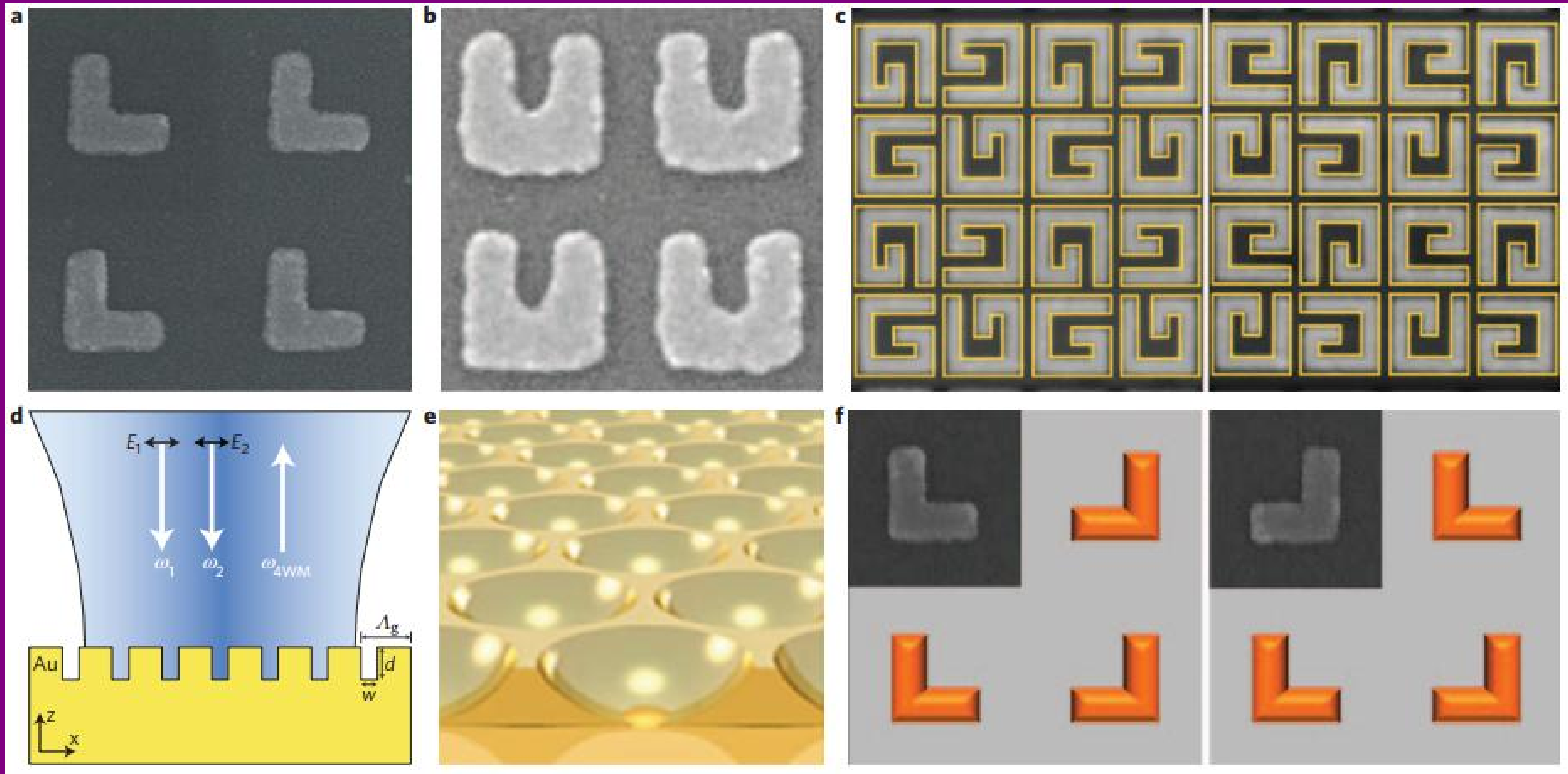


Stiles P.L. *et all*, Annual Review of Analytical Chemistry, 1, 2008, p.601-26

Nonlinear plasmonics

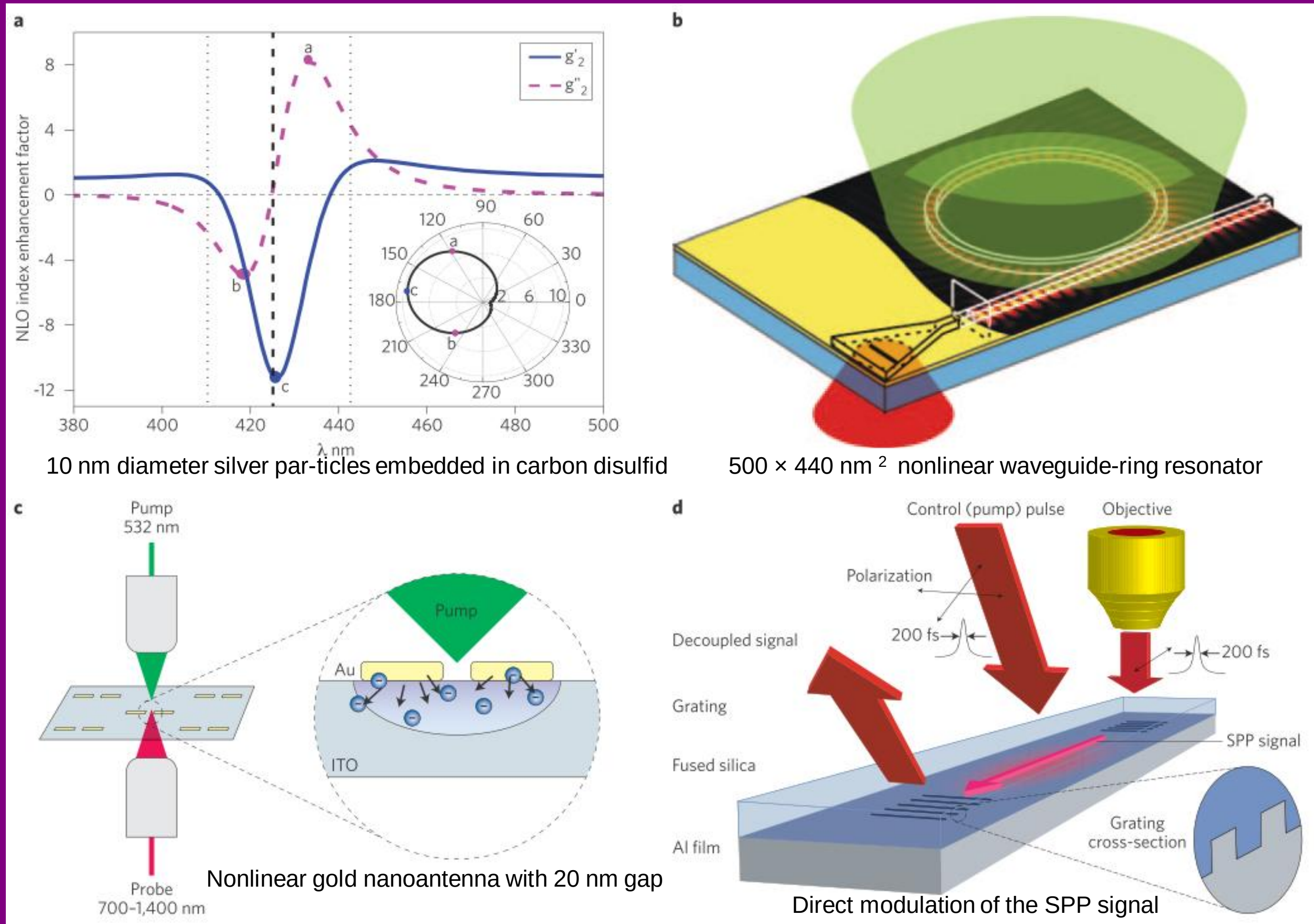
- Nonlinear optical effects arise when electronic motion in a strong electromagnetic field cannot be considered harmonic. For applications, the most important effects occur at second (SHG) and third harmonics.
- Two ways to enhance nonlinear effects:
  - plasmonic structures provide field enhancement near the metal–dielectric interface (intrinsic and extrinsic response)
  - plasmonic excitation parameters (SPP wavevector and the LSP resonance frequency) are very sensitive to the refractive indices of the metal and the surrounding dielectric, which are nonlinearly changed.
- Centrosymmetry is detrimental to second-order response even in the presence of local-field enhancement
- Nonlinear effects are utilized with reduced power
- Scale down nonlinear component in size
- The response time is ultrafast (femtosecond timescale)

Structured metal surfaces for nonlinear plasmonics



A. Zayats, NATURE PHOTONICS| VOL 6 | NOVEMBER 2012 | p.737

Plasmonic systems for enhancing nonlinear optical Kerr effect



10 nm diameter silver par-ticles embedded in carbon disulfid

500 × 440 nm ^{2} nonlinear waveguide-ring resonator

Nonlinear gold nanoantenna with 20 nm gap

Direct modulation of the SPP signal

A. Zayats, NATURE PHOTONICS| VOL 6 | NOVEMBER 2012 | p.737

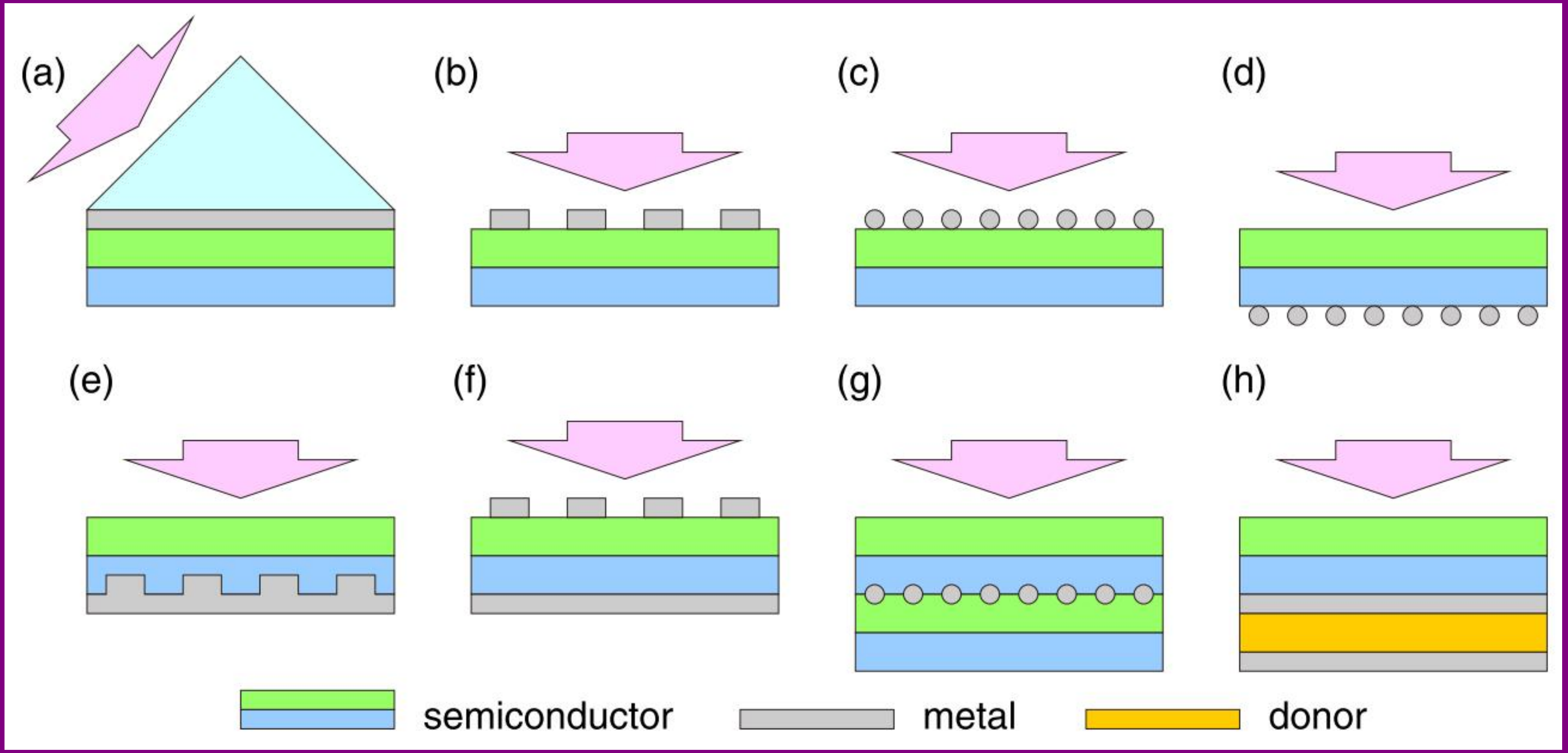
Nonlinear plasmonic fabrication

- Requirements:
  - Regular asymmetrical structures
  - Small substrates
  - Low volume production
- Methods:
  - EBL
  - FIB
  - Nanoimprint
  - NSL

SPR and photovoltaics

- Enhancement of the local field
- Enlargement of the scattereing cross-section by LPR
- Confinment using MIM modes
- Coupling of the incident light to waveguide modes

Plasmonic solar cells



J. Phys. D: Appl. Phys. 45 (2012) 433001

Plasmonic solar cell fabrication

- Requirements:
  - Regular and random arrays
  - Large area substrates
  - Multilayer structure
  - High volume production
  - Rough (non-flat) surface above pn-junctions and metallization
- Methods:
  - NSL
  - Shadow (stencil) mask
  - Self-organizing films

Chip area and volume of production

- Chip area, based on functional properties:
  - SERS – small area, small to large volume
  - Metamaterials – large area, small to large volume
  - Waveguides – small area, large volume
  - Solar cells – large area, large volume
  - Sensors – small area, large volume
  - Non linear plasmonics – small area, small volume

Plasmonic device in general

- Combination of metal and dielectric parts
- Critical dimensions are 20 – 150 nm
- Metal thickness is 50 – 200 nm
- Metal part separation is 2 – 200 nm
- Multilayer design (optional)
- Non rectangular shape (spheres, rods, groovs, rings)
- Large area devices
- Integrated part of more complicate devices

Fabrication problems of plasmonics

- No dry etching methods, but Al in Cl_2
- Large area is totally covered by small structires with critical dimensions. Compare to CMOS – channnel area is the small fraction of total area
- Ag and Au are killers of electronic properties of semiconductors. They have large diffusion coefficients in volume and on the surface
- High temperature processing is limited by 500 C
- Smooth metal surface is required (optional)

Main steps of plasmonic nanofabrication

- Formation of the functional layer
- Patterning
- Transfer the pattern into the functional layer
- Formation of interlayer dielectric
- Planarization

Formation of metal layer

- Physical vapour deposition (PVD)
  - e-beam evaporation
  - sputtering
  - pulsed laser deposition
  - ion beam sputtering
- Electroplating, limited number of metals, roughness
- Atomic layer depostion (ALD): Ru, Pt, Au, Ag. Good conformality, bad metal quality

Patterning

- Optical lithography
  - Contact mask, limited by 1μm resolution
  - Stepper, 22 nm with phase shift mask and double patterning lithography
- Scanning beam lithography
  - Electron beam lithography (EBL)
  - Focused ion beam (FIB)
- Shadow mask (stencil)
- Self-organized masks

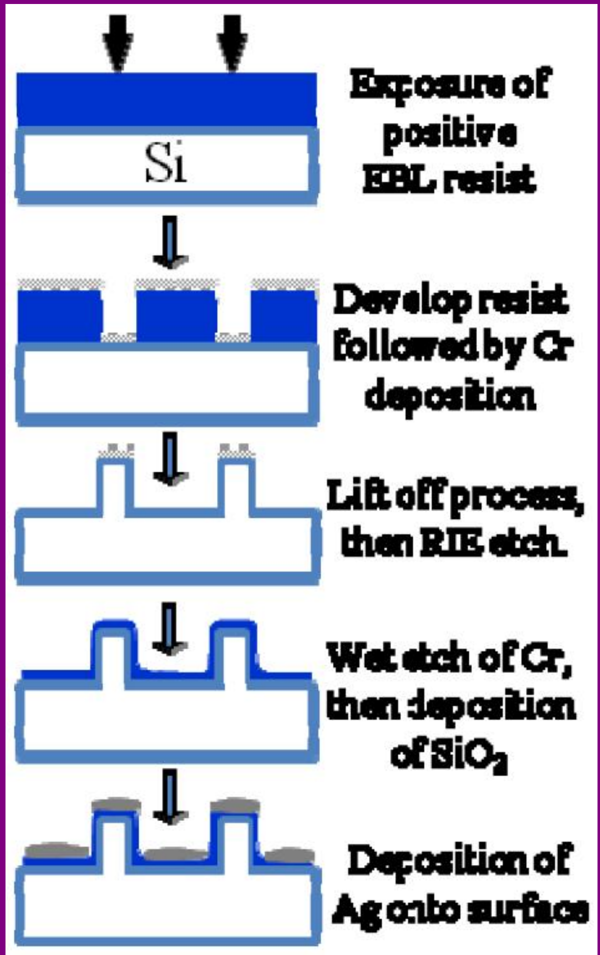
Pattern transfer

- Etching
  - Wet
  - Dry
- Lift-off (reverse pattern)
- Selective deposition (growth)
- Chemical mechanical polishing (CMP)

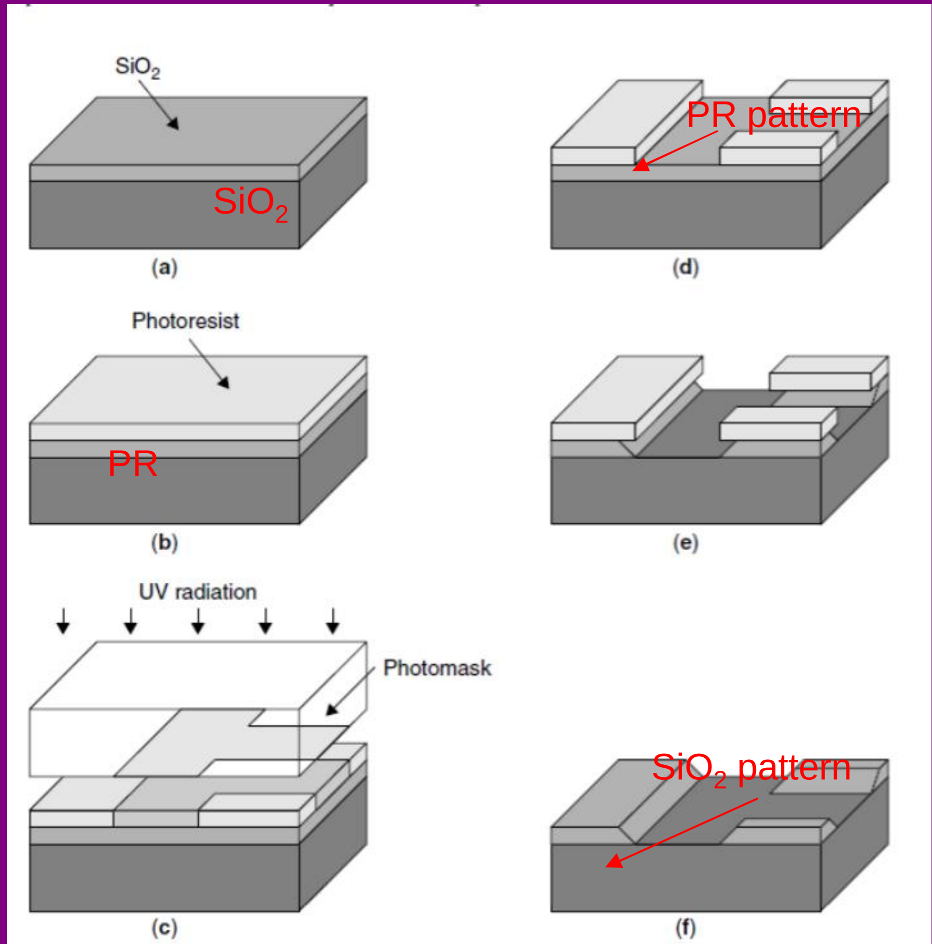
Scanning beam lithography

- Scanning beam lithographies are capable of precise control over the size, shape, and spacing of metallic nano-structures
- Low throuhput
- EBL can be used to attain sub-20 nm resolution using specialized resists such as hydrogen silsesquioxane (HSQ) or NaCl crystals
- FIB is a related technique that uses a focused beam of ions (typically Ga+) to perform both additive and subtractive patterning by physical or chemically assisted processes. These include:
  - FIB milling,
  - ion-assisted etching,
  - FIB-induced deposition
- FIB is capable of forming patterns with ~10 nm resolution using either PMMA or inorganic resists.

Optical lithography



Lift-off



Direct etching

Lift-off vs. direct etching II

- Lift-off:
  - resist layer should be at least twice as thick as the lift-off thickness (metal), i.e. limited aspect ratio of metal structures
  - vertical mask sidewalls or overhanging structures
  - easy to remove mask, high chemical activity
  - functional layer is deposited on residues that left after mask fabrication
  - patterned layer particles are left in the solvent and redeposit on the sample
  - rough edge of the pattern, due to film destroying
- Direct etching:
  - mask thickness is not connected with etched layer thickness. It depends on etching chemistry
  - shape of mask sidewalls is not critical
  - functional layer is deposited on clean or prepared surface
- Result:
  - direct etching provides smaller critical dimensions, higher reproducibility and better areal uniformity

Formation of interlayer dielectric

- Chemical vapour deposition (CVD)
- Atomic layer deposition (CVD)
- Electrochemistry
- Spin-on
- Oxidation

Planarization

- Etchback

- Chemical mechanical polishing

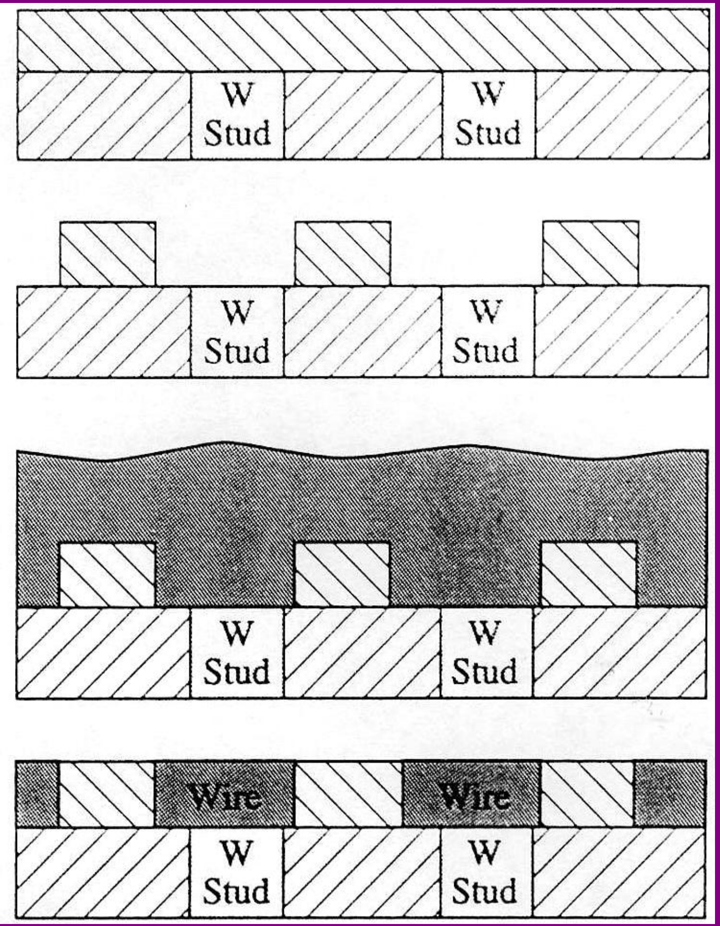
Damascene process – solution for plasmonics

Oxide deposition

Wire lithography, RIE of oxide

Metal stack depostion

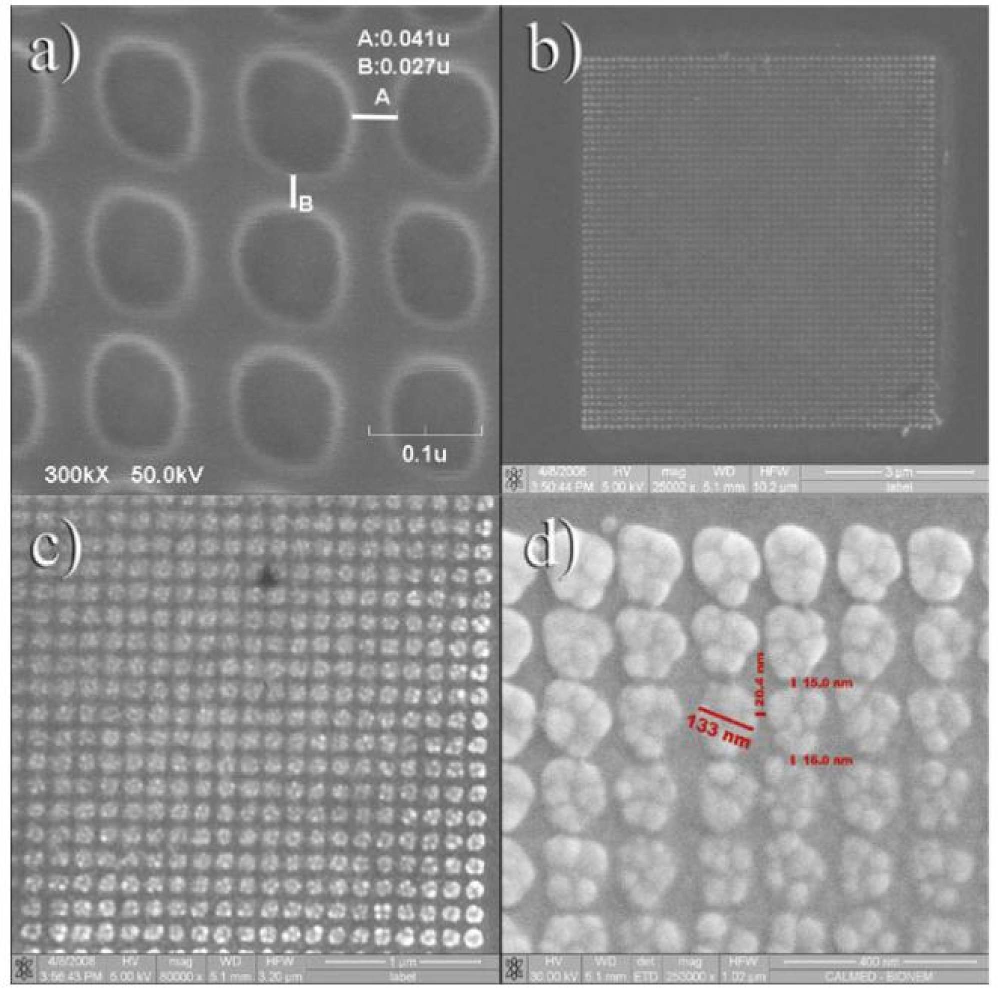
Chemical mechanical polishing (CMP)



Damascene process features

- Bottom seed layer:
  - PR mask with metal pattern
  - selective electroplating
  - PR mask removing (Ag corrosion)
  - seed layer removing (problem, because structure thickness and seed layer are similar; for dry removing pattern deteriorates, for wet – stop time and pattern deteriorate; ALD thin seed layer – change plasmonic properties)
- Top seed layer:
  - SiO_2 mask
  - blank electroplating
  - CMP of metal
  - SiO_2 remove – works!
- Space between metal parts about twice of CD! Impossible produce small dimers
- ALD – bad metal quality

Selective gold electroplating

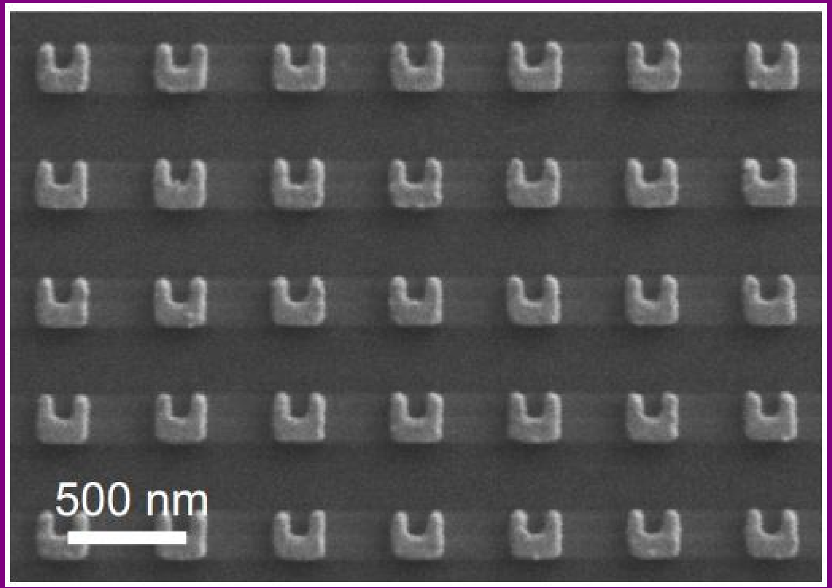


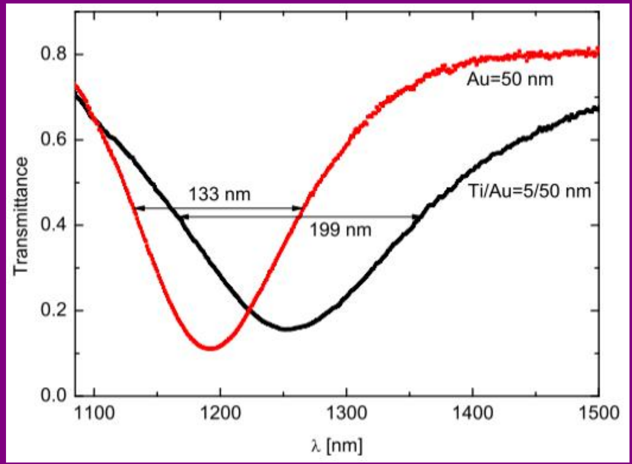
Substrate Si/Cr 10nm/ Au 20nm
EBL pattern on 100 nm thick resist
Au thick 80 nm by electroplating
8s at 10mA/cm2

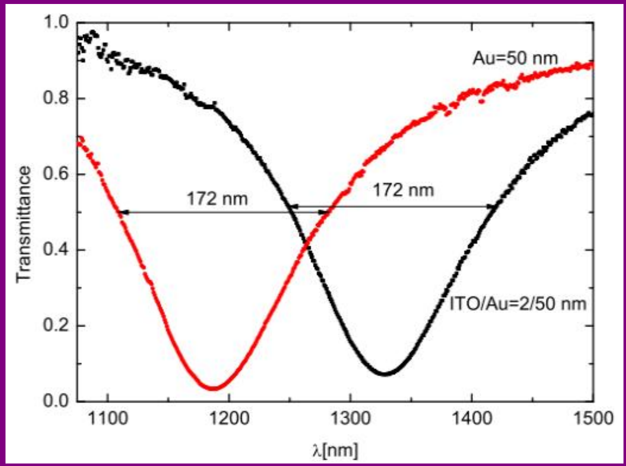
G. Das et al. / Biosensors and Bioelectronics 24 (2009) 1693–1699

Effect of adhesion layer

50 nm thick Au SRRs on a 1 mm thick fused silica substrate.
Side length 200 nm, height=50 nm, period 500 nm



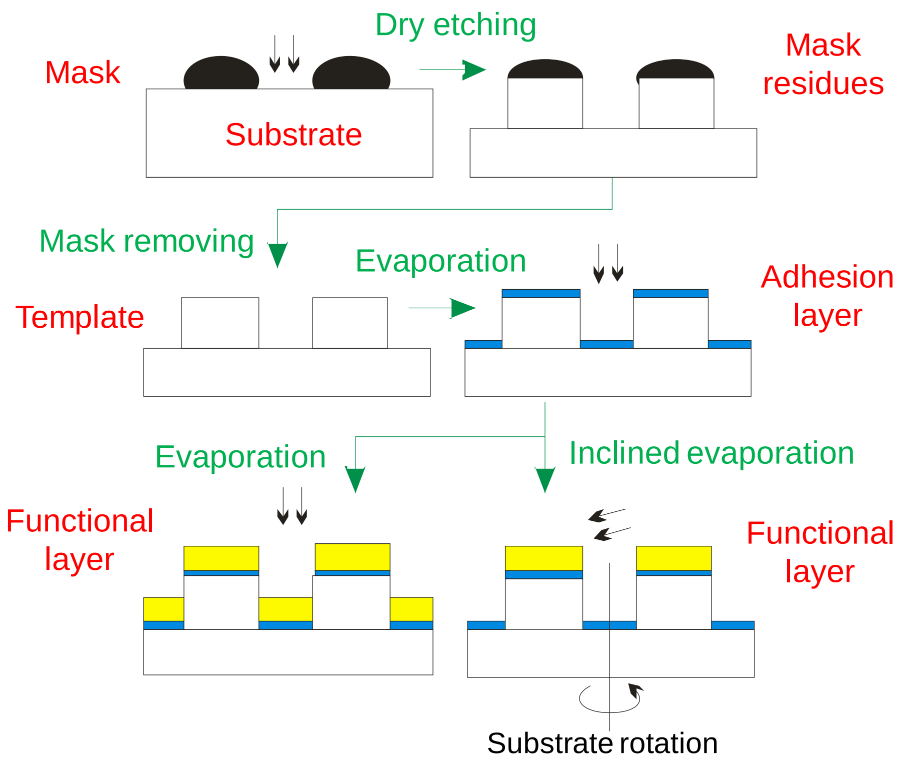




Spin on electron resist (150 nm)
Deposition of 15 nm Al layer to prevent charge accumulation.
EBL, 1.2×1.2 mm^2 area , 100 kV, 200 µC/cm^2 , 2 nA current, 6 nm spotsize
Al iremove and developing
O_2 plasma descum
Deposition of a 2–5 nm adhesion layer, Ti or ITO, and 50 nm Au.
The final lift-off is.

Appl. Phys. Lett.97, 263103 (2010)

Random mask with adhesion layer



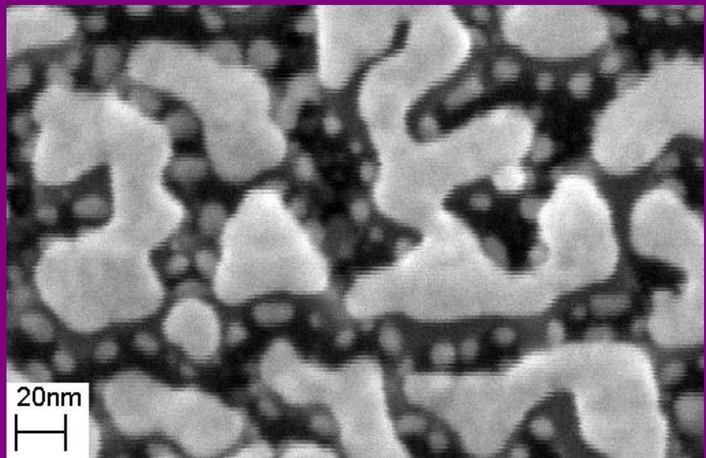
V. Ovchinnikov ,Proceedings of ICQNM 2011, ThinkMind Digital Library, pp. 6-11

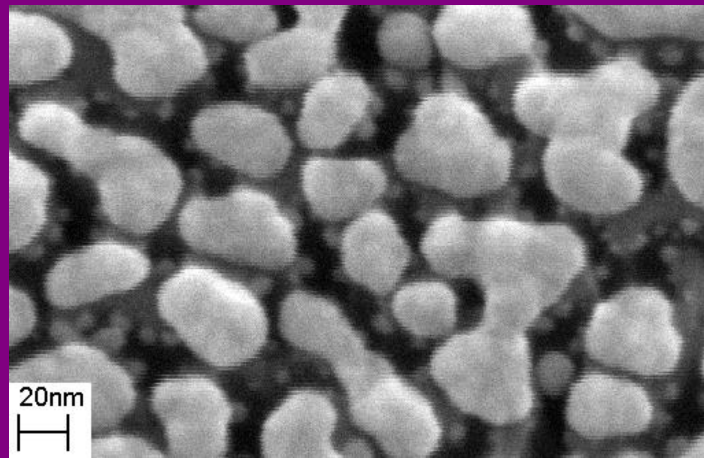
Self-organized metal with adhesion layer

Normal evaporation

Evaporation angle 70º

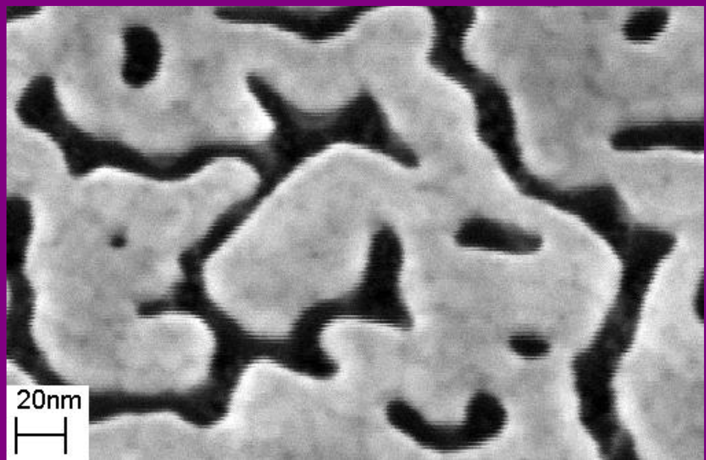
Au=8nm,
tilted 30º

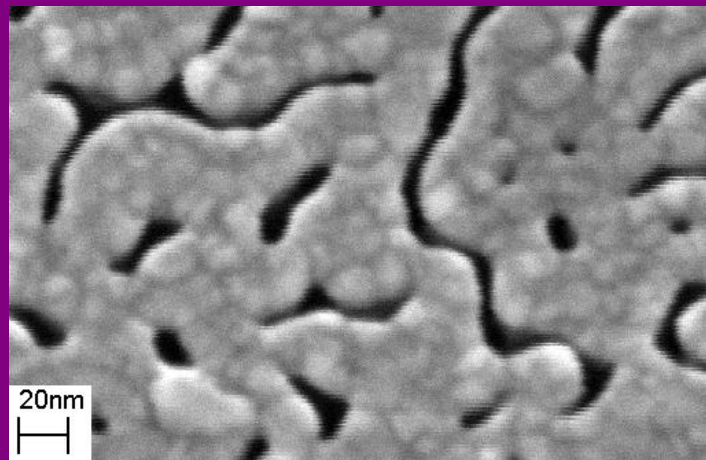




Ag=8nm,
tilted 30º

Ti=1 nm
Au=8nm,
tilted 30º





Ti=1 nm
Ag=8nm,
tilted 30º

Intermediate conclusion II

- Reproducible fabrication of metal nanostructures is still main problem of plasmonics
- Small area samples for research purposes are easily fabricated by beam lithography and lift-off
- Large area samples are mainly limited in design:
  - random arrays for template lithography
  - limited ratio of size to space for interference lithography