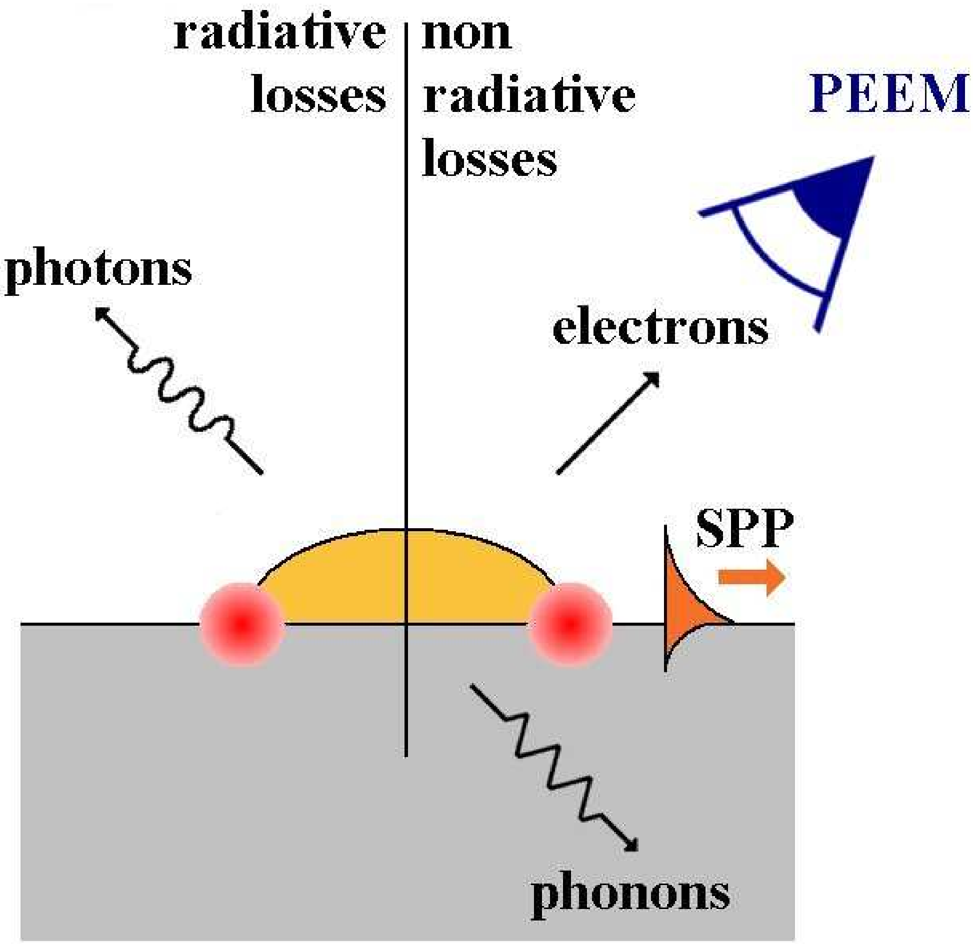
Photoemission electron microscopy, a tool for plasmonics



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Groupe de NanoPhotonique

What is Plasmonics?

➢ "***A way to confine electromagnetic fields over dimensions on the order or smaller than the wavelength $\lambda_{h\nu}$***"

S. Maier in Plasmonics: Fundamentals and Applications (2007) Springer

➢ Interaction processes between electromagnetic radiation and conduction electrons at metallic interfaces

➢ Plasmonics promises :

(i) high spatial integration $\lambda_{h\nu}$ /10 ~ 60 nm (visible)

(ii) high working frequencies $\omega \sim 10^{15}$ Hz = 10^6 GHz (visible)

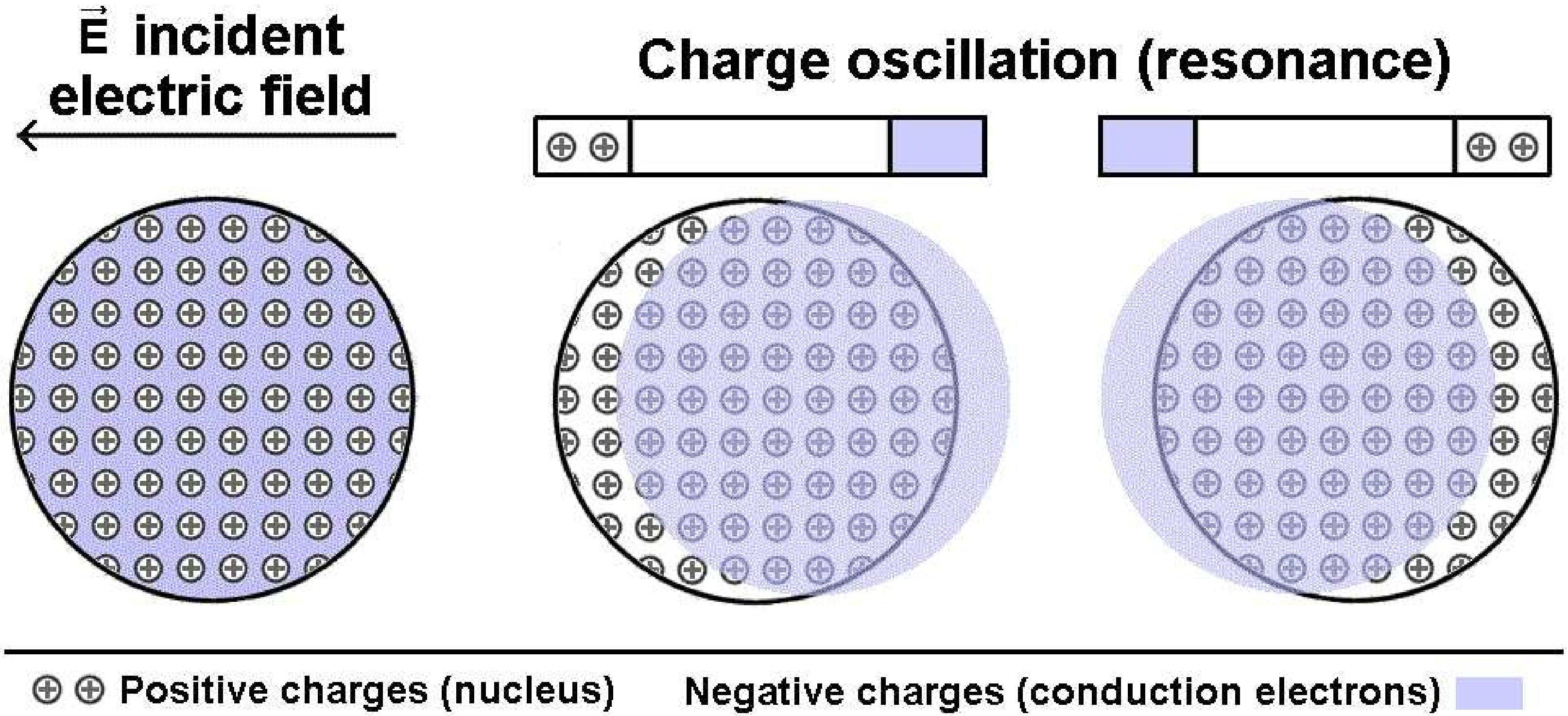
➢ Basic ingredients

(i) Localised surface plasmons LSP (object)

(ii) Surface plasmons-polaritons SPP (interface)

Optics of nano-objects – Localised surface plasmons LSP

➢ Mie resonances. G. Mie, *Ann. Phys.* Leipzig **25** (1908) 377



Sphere of subwavelength dimension r, r ~ 10..100 nm << $\lambda_{h\nu}$

(i) Charge displacements under field excitation

(ii) Coulomb restoring force

$\Rightarrow$ Plasmon resonance = collective, coherent oscillation of charges

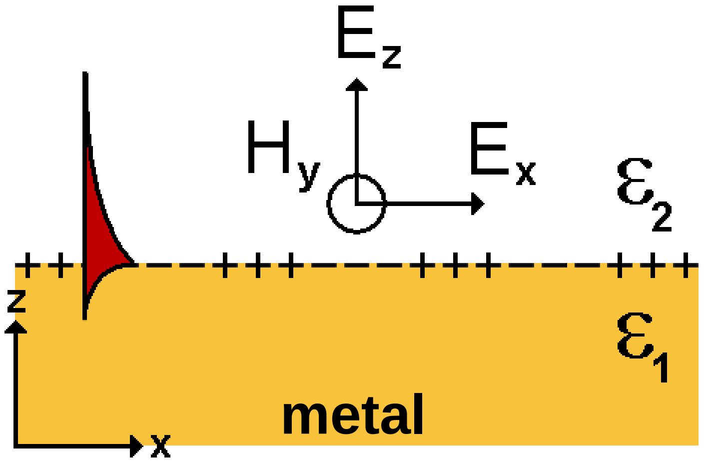
Optics of interface - Surface Plasmon Polariton SPP

➢ Electron charge description

.coherent longitudinal fluctuations of electron charges on a metal boundary (Thomas-Fermi screening length ~ 0.1 nm),

➢ Field description

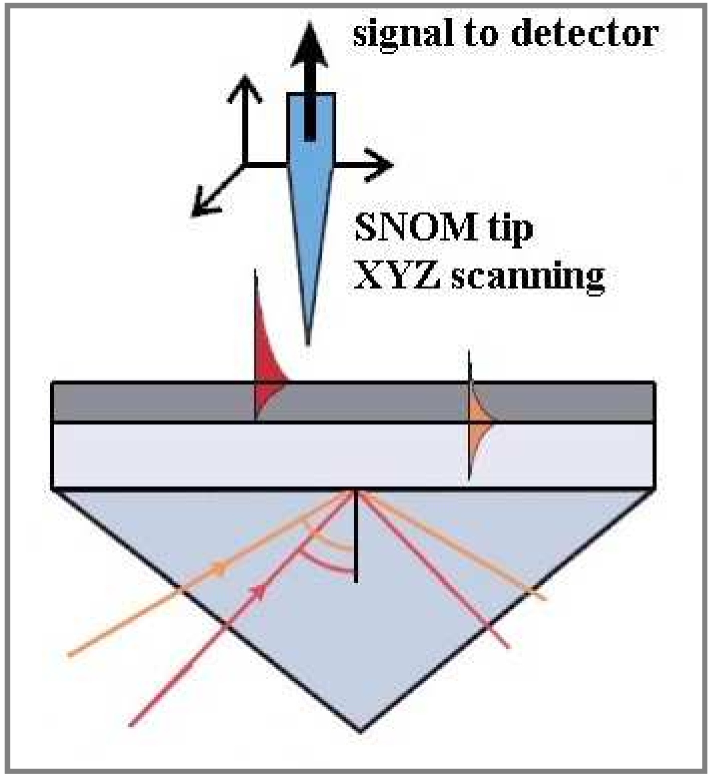
- Propagative wave K_x along the surface plane direction Ox,
- Evanescent wave K_z along the surface normal Oz (Au-vacuum interface, photon excitation 800 nm, skin length λ_{skin} ~ 30 nm metal side, 650 nm vacuum side)



$$E_{SPP}(x,z) = E_0 \exp(ik_x x - k_z |z|)$$

H. Raether Surface Plasmons (1988) Springer

Mapping the evanescent field at the nanometre
SNOM - scanning near-field optical microscopy (1984…)



➢ **Basic principle**

.scanning probe microscopy (SPM)

.introduction of a tip (glass fibre, metal …) in the near field of the object to be studied

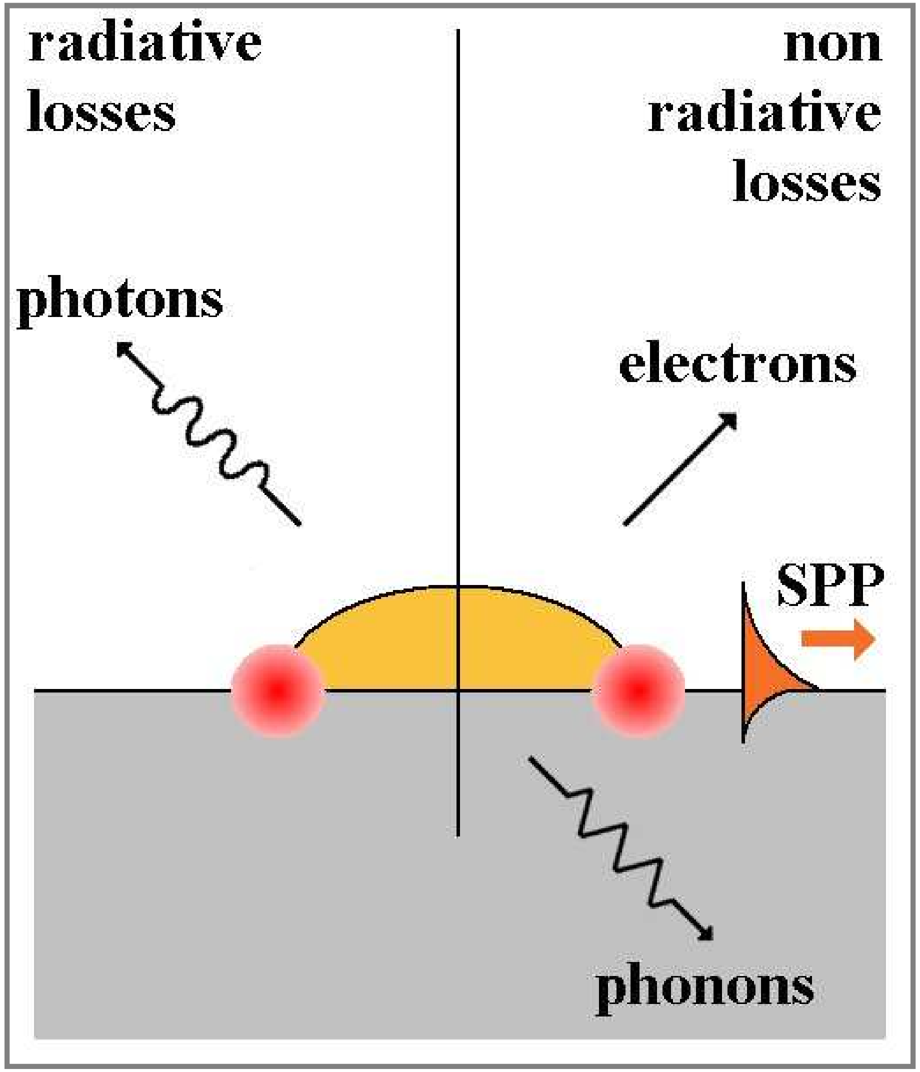
.routine resolution 50 - 100 nm

.many variants

➢ Perturbation of the evanescent field due to LSP excitation and lightning-rod effect at the tip-surface junction,

➢ Low reproducibility of tips.

Mapping the evanescent field at the nanometre
plasmon decay channels



➢ **Plasmon decay channels**

.**free-space radiative** losses (scattering, luminescence),

.**non radiative** losses
Ohm losses (phonons),
secondary SPP excitation,
electron emission,
…

➢ **Mapping the near–field through electron emission.**

Mapping the evanescent field at the nanometre
plasmon decay channels

- **Non radiative losses vs radiative losses for nanoparticles**
  Sphere in vacuum (quasi-static approximation)

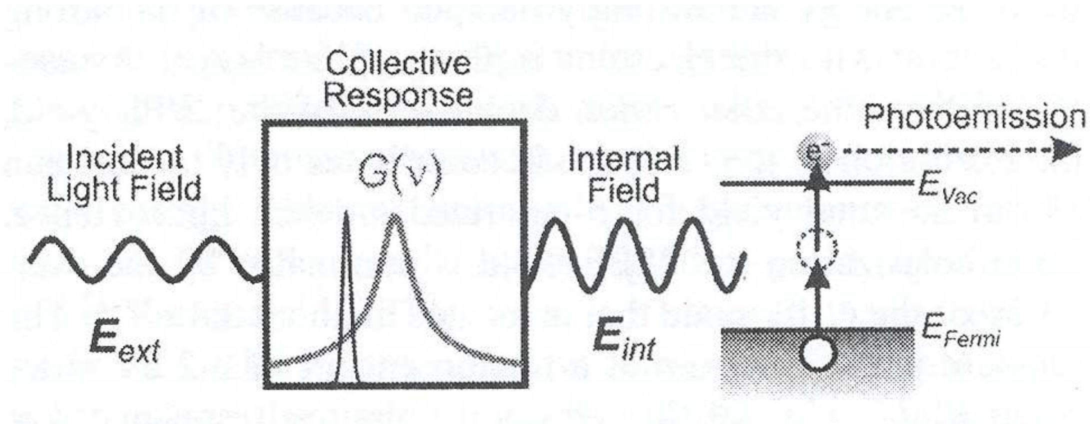
$$\frac{\text{Non radiative losses}}{\text{Radiatives losses}} = \frac{\text{Absorption}}{\text{Diffusion}} = \frac{9}{16\pi^3}\left(\frac{\lambda_{h\nu}}{r}\right)^3 \frac{(\varepsilon_1 - \varepsilon_s)^2 + \varepsilon_2^2}{(\varepsilon_1 + 2\varepsilon_s)^2 + \varepsilon_2^2}$$

Sphere radius r, r << $\lambda_{h\nu}$ [nm]
$\lambda_{h\nu}$ excitation photon wavelength [nm]
$\varepsilon = (\varepsilon_1, \varepsilon_1)$ metal dielectric cste, ε_m medium dielectric cste

N.A. Au sphere r = 25 nm in vacuum under excitation at $\lambda_{h\nu}$ = 800 nm (at resonance).

$$\frac{\text{Non radiatives losses (all channels)}}{\text{Radiatives losses}} = \frac{\text{Absorption}}{\text{Diffusion}} = \frac{3}{2}$$

Photoemission electron microscopy, a tool for plasmonics – Basic principle



(i) Electron collective response (plasmon)

$$E_{\text{int.}}(\nu) = G(\nu).E_{ext.}(\nu),\ G_{Sphère} = \frac{3\varepsilon_m}{\varepsilon + 2\varepsilon_m}$$

$E_{int.}$ Internal electric field [V/m]
G Response function of the many electron system
$E_{ext.}$ Incident light electric field [V/m]

(ii) Non linear photoemission process

$$n.h\nu > \Phi_{Metal}$$

n order of non linearity,
hν photon energy [eV],
Φ_{Metal} metal work function [eV]

M. Merschdorf *et al. Phys. Review B* **70** (2004) 193401

Photoemission electron microscopy, a tool for plasmonics – Basic principle

➢ The non linear photoemission process is proportional to the $2n^{th}$ power of the internal electric field E_{int}

$$I_{e^-} \propto (\vec{p}.\vec{E}_{\text{int.}})^{2n} \propto (\vec{p}.G\vec{E}_{ext.})^{2n}$$

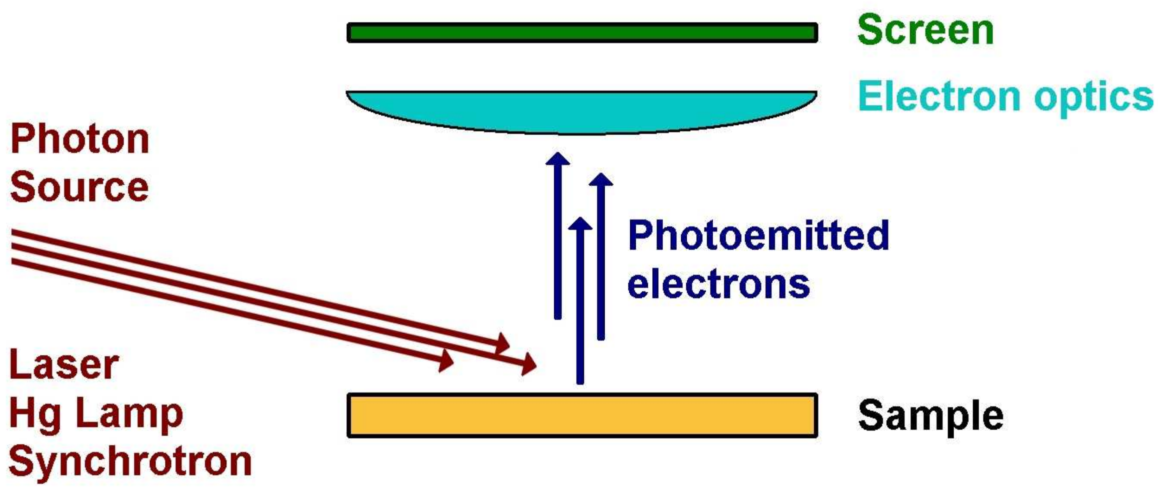
p electron momentum [kg.m/s],
E_{int} internal electric field [V/m],

n non linearity order
$E_{ext.}$ incident light electric field [V/m]

For large objects $\geq \lambda_{h\nu}$, the internal electric field of the plasmon excitation $\vec{E}_{\text{int.}}^{SPP}(r,t)$ (group velocity v_{SPP}) interfere with a 2nd component linked to the incident light field $\vec{E}_{\text{int.}}^{h\nu}(r,t)$ (group velocity c).

➢ For large objects $\geq \lambda_{h\nu}$, observation of beating interference patterns between ($\vec{E}_{\text{int.}}^{SPP}(r,t)$, $\vec{E}_{\text{int.}}^{h\nu}(r,t)$)

PEEM – photoemission electron microscopy
Instrumentation



➢ **Basic principle. Mapping of the photoemitted electron distribution in two dimensions**

.standard electron optics (magnetic lenses)

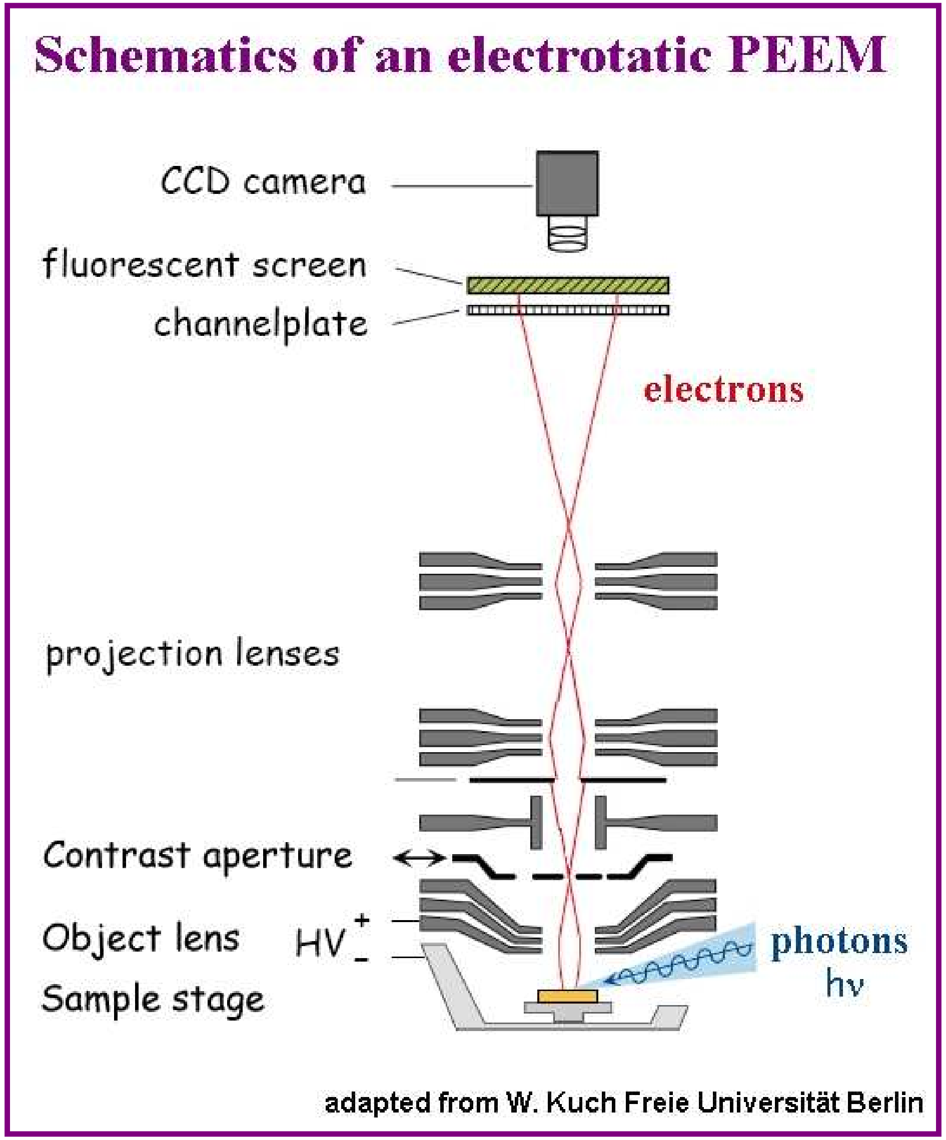
.full field microscopy, ***no physical tip in the vicinity of the measuring volume (≠ SNOM)***

.image contrast: working function Φ (small hν), photoemission lines (important hν)

.lateral resolution (16\84 criteria) 25 - 50 nm

E. Brüche, Z. Phys. **86** (1933) 448, J. Pohl, Zeitschr. f. techn. Physik **12** (1934) 579

PEEM – photoemission electron microscopy (1962…)



- **Basic principle.** mapping of the photoemitted electron distribution in two dimensions.

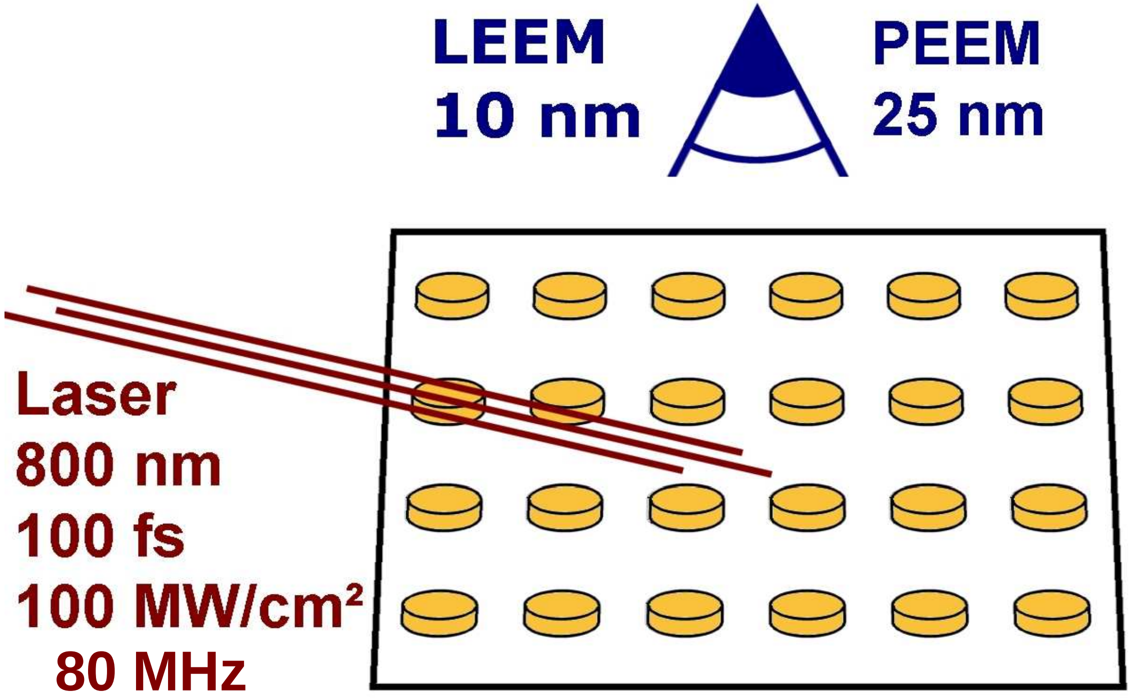
.cathode lens (sample is part of the objective lens)
.high electrostatic voltage 1-10 MV/m

E. Bauer *Rep. Prog. Phys.* **57** (1994) 895

.ultimate resolution ~ electron mean free path (1 nm), in practice limited by **optical aberrations**: chromatic, spherical…
.lateral resolution (16\84) 25-50 nm
.AC resolution (16\84) < 3 nm

Imaging restrictions
.conductive sample
.low roughness

Mapping the evanescent field at the nanometre
LEEM\PEEM imaging mode – Instrument (CEA Saclay)



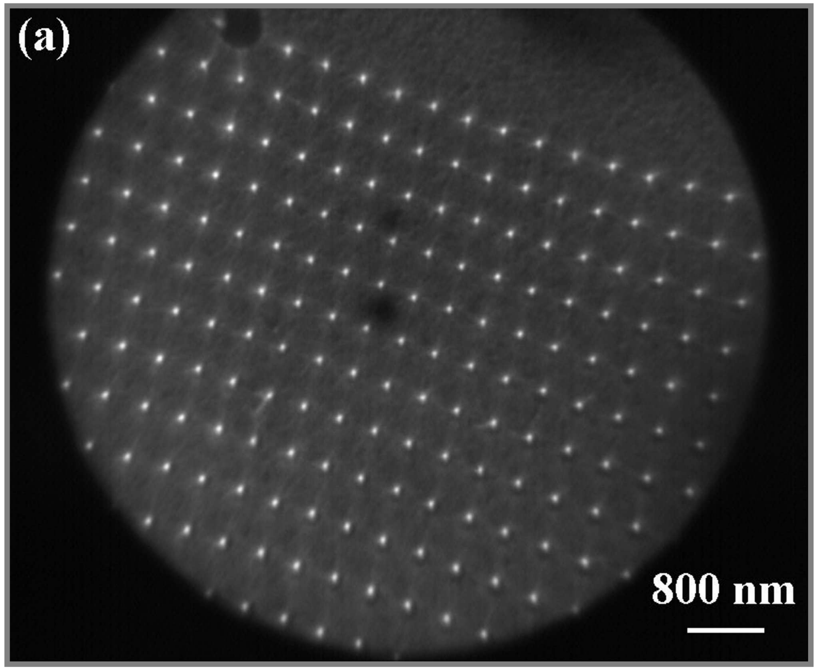
- Conductive sample (no charging effect) of low roughness

- LASER source Ti:Al_2O_3, 100 fs, wavelength 720 - 950 nm (IR), incidence angles 0°& 75°/ ⊥

- LEEM \ PEEM III Elmitec, www.elmitec-gmbh.com
  .PEEM field of view 1.5 - 150 µm, lateral resolution (16\84) 25 - 50 nm
  .LEEM field of view 1.5 - 80 µm, lateral resolution (16\84) 10 – 20 nm

Near-field mapping – PEEM

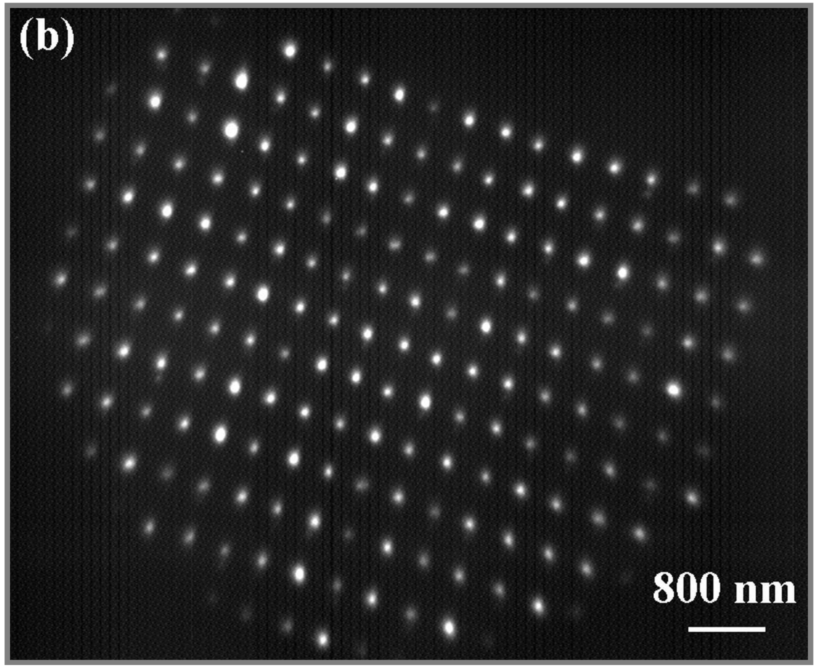
Nano-particles assemblies - LSP



Au disks/ITO ∅120 nm, lattice step 400 nm

- **LEEM picture (topographic imaging mode)**

  Excitation = electrons (LASER off),
  Signal = backscattered electrons.



Au disks/ITO grazing incidence p pol. 150 MW/cm²

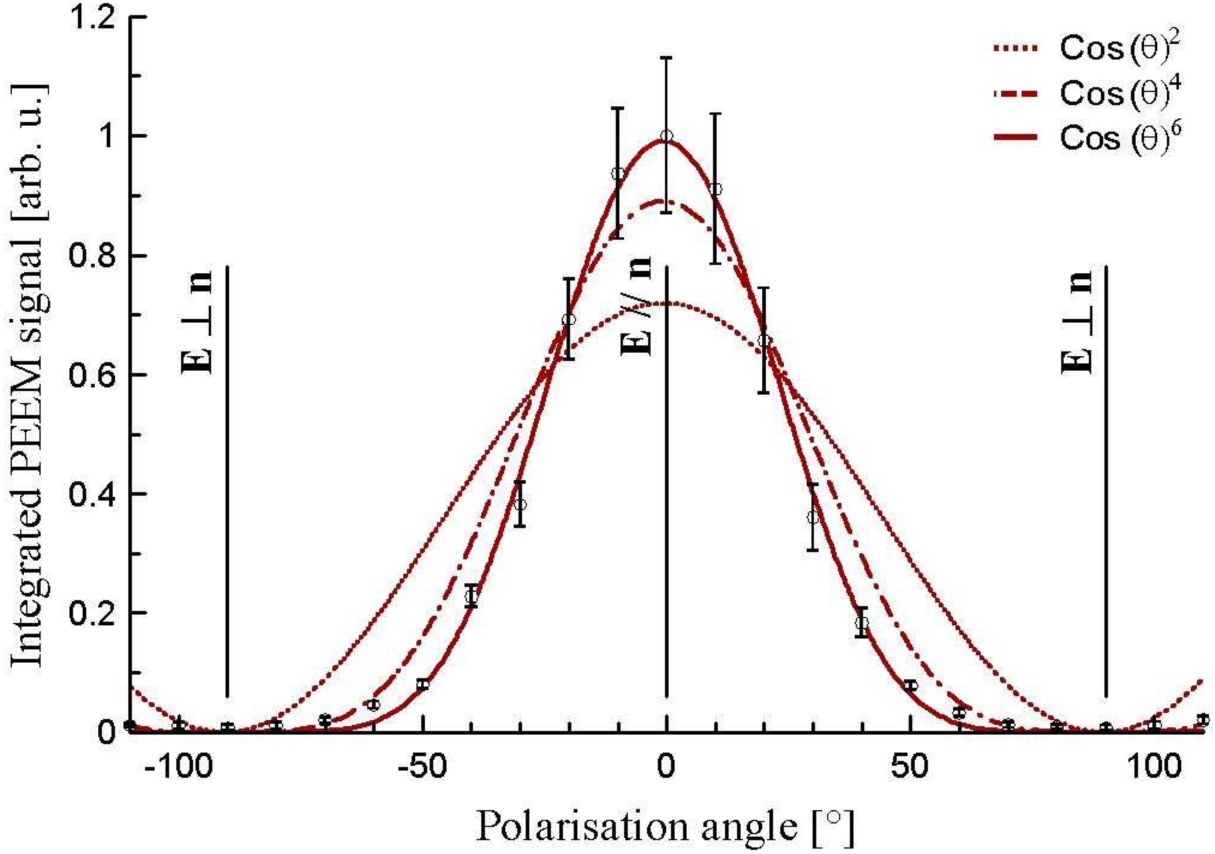
- **PEEM picture under LASER illumination**

  Excitation = 766 nm photons,
  hn (1.62 eV) < F_{Au} (4.6 - 5.1 eV),
  Signal = photoelectrons !

L. Douillard *et al. J. of Appl. Phys.* **101** (2007) 083518

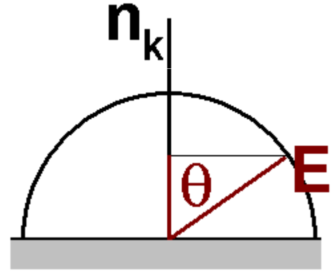
Non linear photoemission – PEEM

Nano-particles assemblies – Off plane polarisation dependence



Au disks/ITO ∅120 nm

grazing incidence 17°
photon 880 nm (1.41 eV)
Power dens. 140 MW/cm²

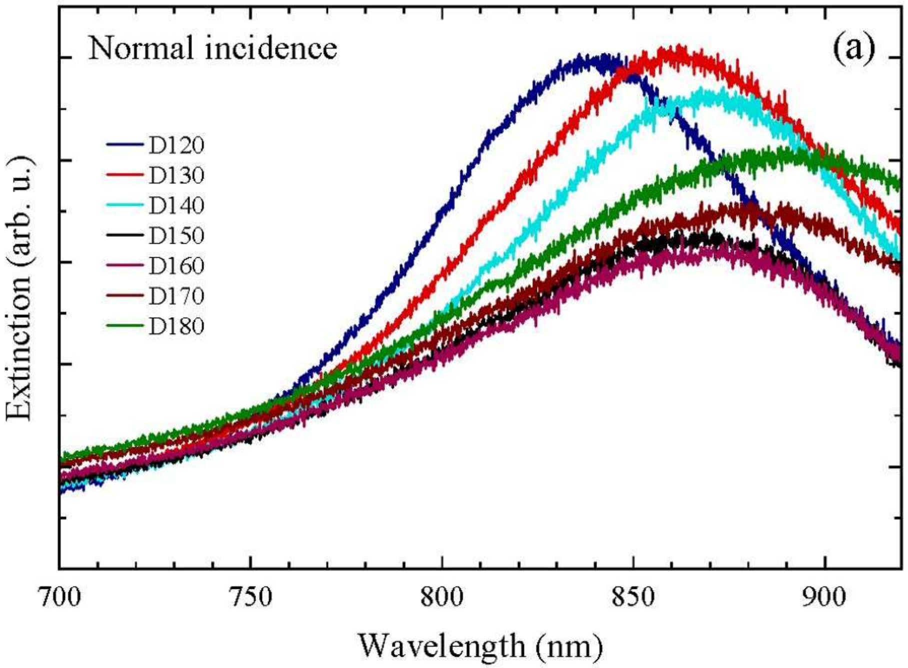


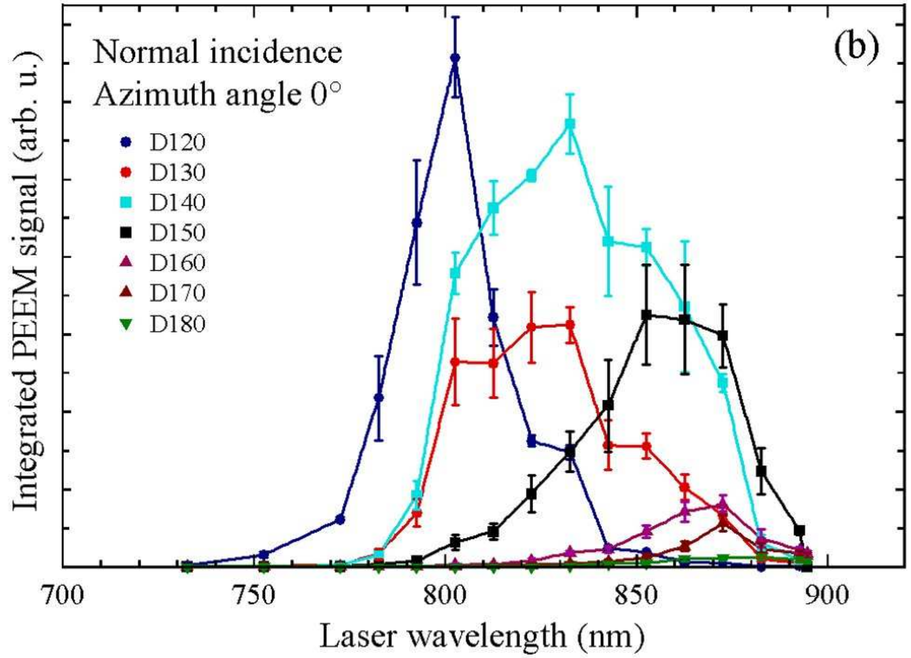
- Dependence of the photoemission yield with the polarisation angle at grzing incidence

  .PEEM integrated signal scales as $\cos(\theta)^6$

  .Three photon photoemission process (3*1.41 eV = 4.23 eV, Φ_{Au} = 4.6 eV)

Extinction spectrometry vs PEEM microscopy
Nano-particles assemblies – LSP resonance wavelengths





➢ **Optical extinction spectra**

.Au disks/ITO ∅ 120 – ∅180 nm
.normal incidence 0°
.transmitted light

➢ **PEEM wavelength dependence under LASER illumination (LSP)**

.Au disks/ITO ∅ 120 – ∅ 180 nm
.normal incidence 0°
.Signal = three photon photoelectrons !

L. Douillard *et al. J. of Appl. Phys.* **101** (2007) 083518

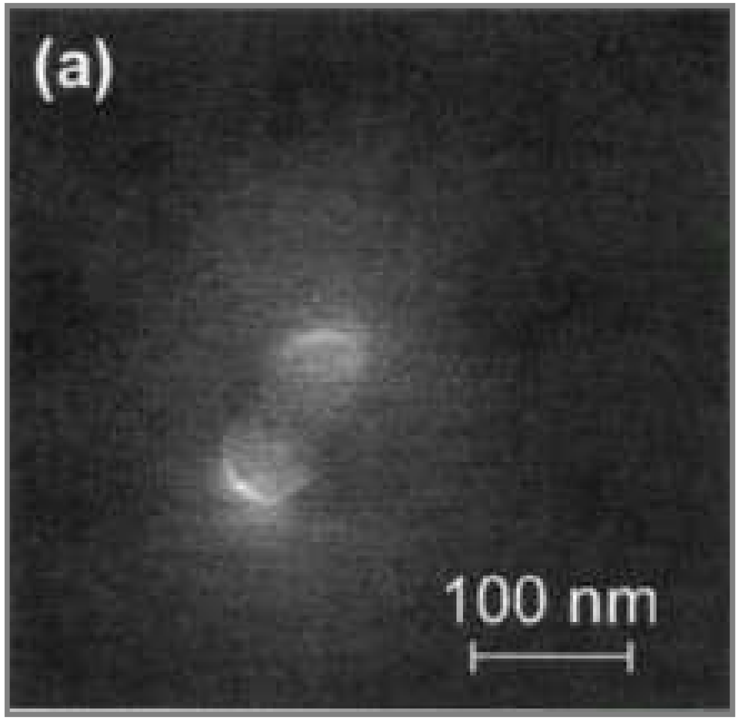
Photoemission electron microscopy, a tool for plasmonics

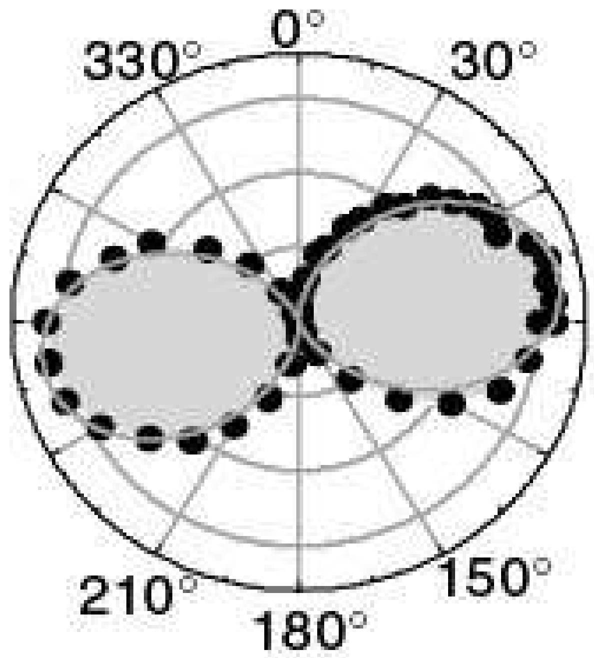
- **Mapping of the near-optical field at the nanometre**

- **Dynamics of surface plasmons-polaritons (nanometre, femtoseconde)**

- **Manipulation of the near-field through LASER pulse shaping (coherent scheme)**

Near-field mapping of single objects – Photoluminescence
Nanoantenna – dipolar mode





➢ Near-field photoluminescence imaging of an elliptic rod
rod = dimer of Au spheres, ∅ 40 nm.

A. Bouhelier *et al. Appl. Phys. Lett.* **83** (2003) 5041

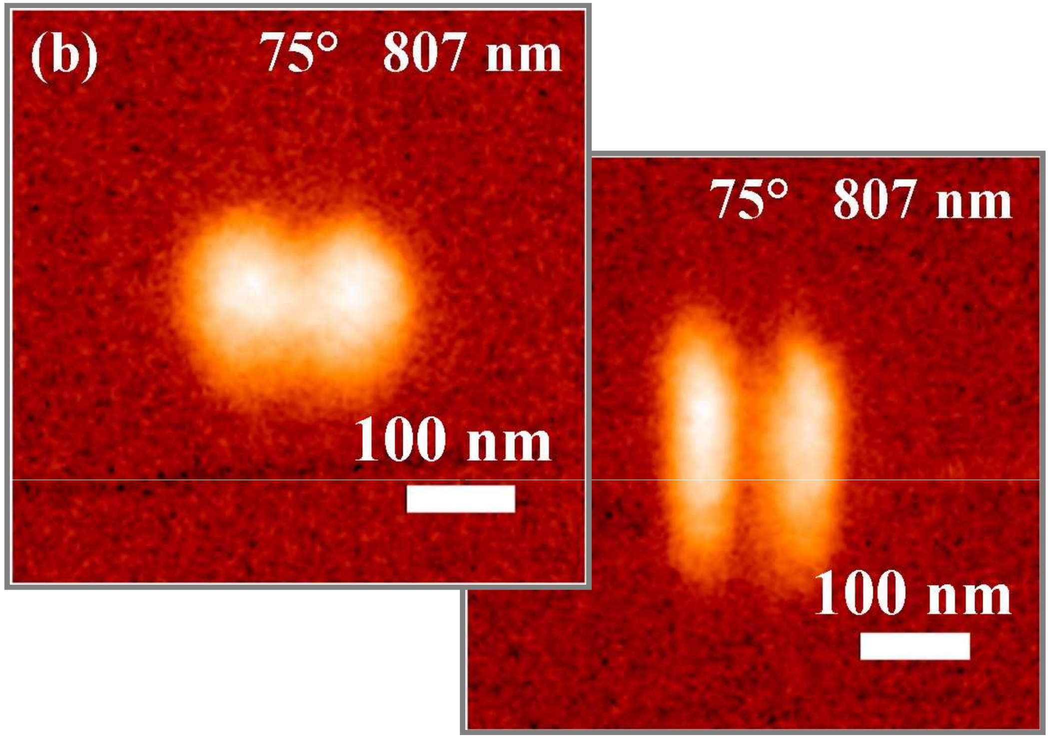
➢ Polar diagram of the light intensity scattered by one single monocrystalline Au rod (100 x 20 x 20 nm^3).

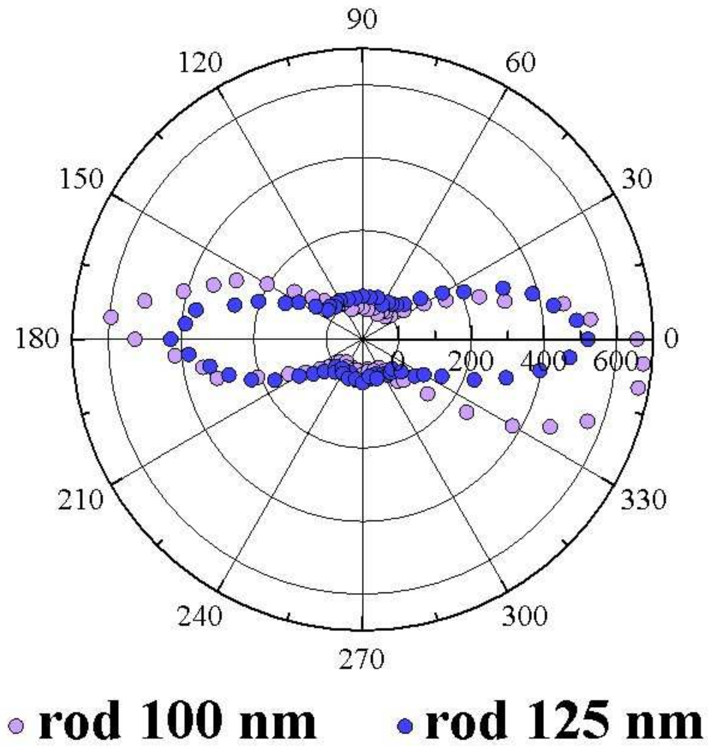
➢ **dipolar emission** - dark field microscopy.

C. Sönnichen *et al. PRL* **88** (2002) 77402

Near-field mapping of single objects – PEEM

Nanoantenna – dipolar mode





➢ PEEM imaging of one single polycrystalline Au rod (100 x 35 x 30 nm^3)

lateral resolutions 40 & 21 nm

photon wavelength $\lambda_{h\nu}$= 807 nm

excitation field // rod axis

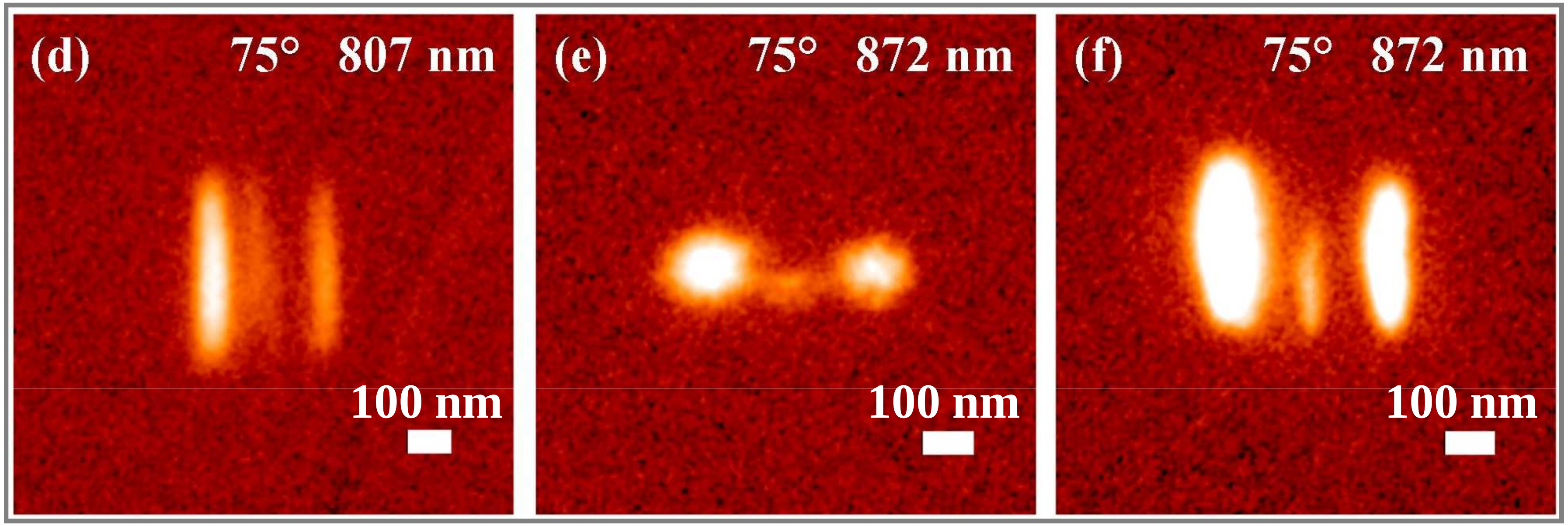
➢ Polar diagram of the photoelectron yield of one single rod

➢ **Dipolar emission**

m = 1 ⇔ L = ½ * λ_{SPP}

L. Douillard *et al. Nano Lett.* **8** (2008) 935

Near-field mapping of single objects – PEEM
Nanoantenna – quadrupolar mode

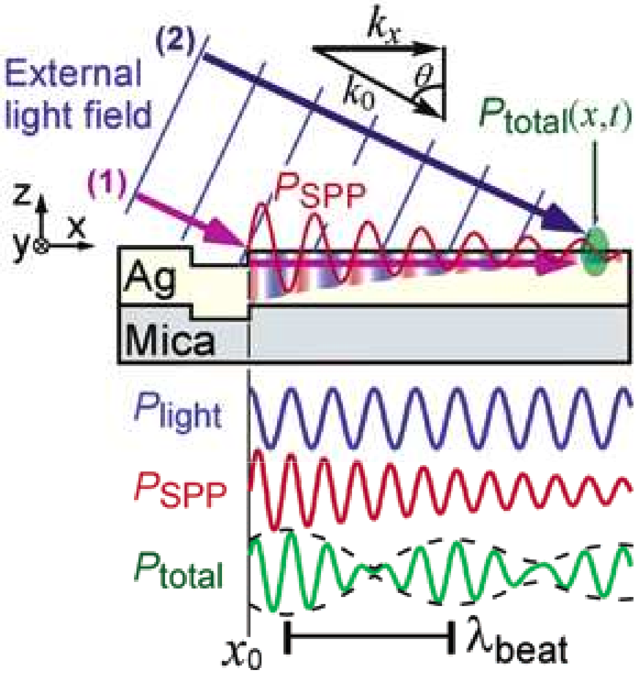


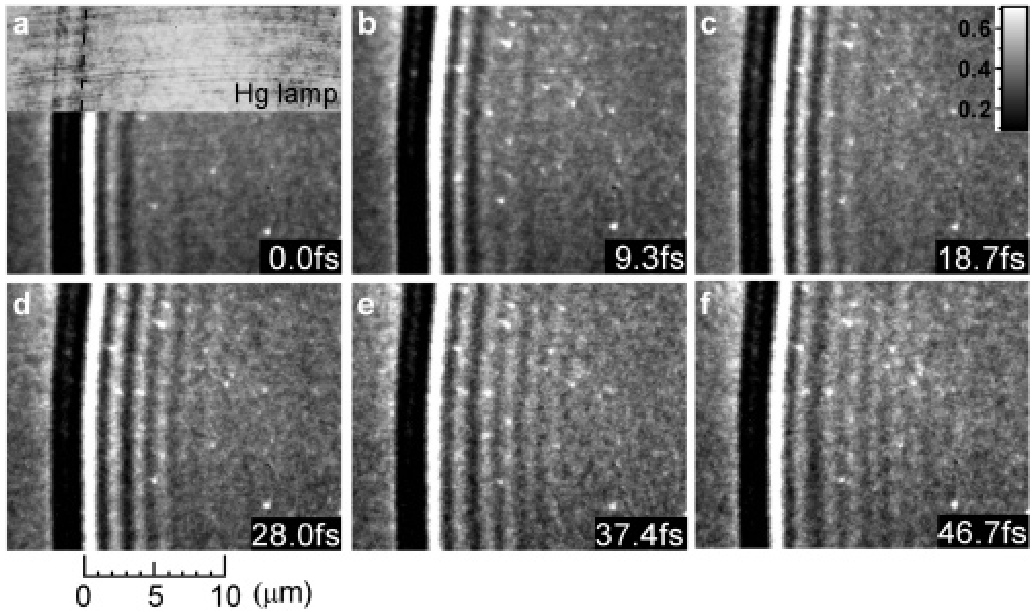
- PEEM imaging of single polycrystalline Au rods.
  dimensions (d) 250 x 35 x 30 nm^3, (e, f) 325 x 35 x 30 nm^3
  lateral resolutions 40 & 21 nm
  excitation field // rod axis

- Quadrupolar mode m = 2 ⇔ $L = \lambda_{SPP}$

L. Douillard *et al. Nano Lett.* **8** (2008) 935

Propagation of surface plasmons-polaritons – PEEM
Ag/vacuum interface





(i) Ag/vac. interface (ii) Excitation 400 nm@100 mW, 10 fs, incidence 65? ⊥, pol. p (iii) PEEM focus GmbH

➢ **Surface plasmon polariton propagation excited at step edge ($\vec{k}$ conservation) – beating interference pattern**

Pump probe experiment

Two photon photoemission process 2*3.1 = 6.2 eV > Φ_{Ag}= 4.2 eV

Resolutions temporal ≈ 1 fs, spatial ≈ 10 nm

A. Kubo *et al. Nano Lett.* **7** (2007) 470

Surface plasmons-polaritons propagation– SNOM
Monocrystalline nanowire

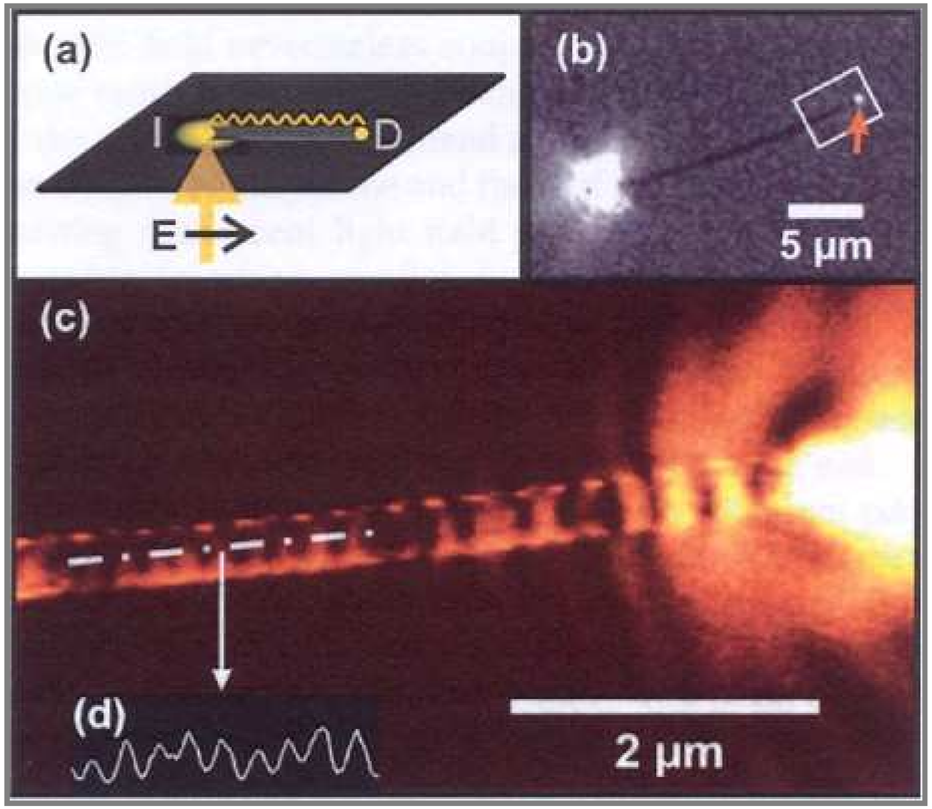


Figure captions

Monocrystalline Ag nanowire under LASER excitation (length 18.6 µm, diameter 120 nm).

(a) Excitation scheme,
(b) topographic image,
(c) SNOM image of selected area (b),
(d) profile of the SNOM signal along the nanowire axis

➢ **Surface plasmon polariton propagation along a nanowire.**

H. Ditlbacher *et al. Phys. Rev. Lett.* **95** (2005) 257403

Surface plasmons-polaritons propagation – PEEM
polycrystalline nanowire (EBL)

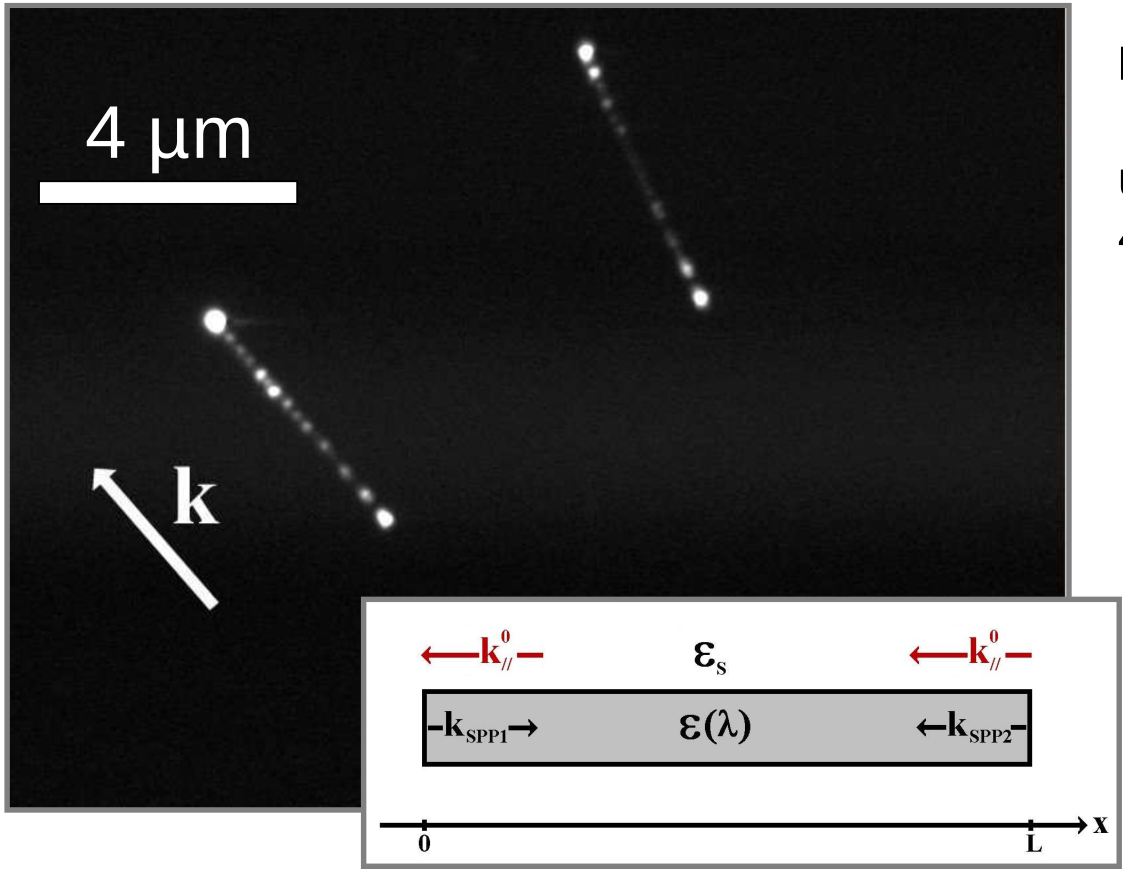


Figure caption
Au polycrystalline nanowire under LASER excitation (Length 4 µm, diameter 30 nm).

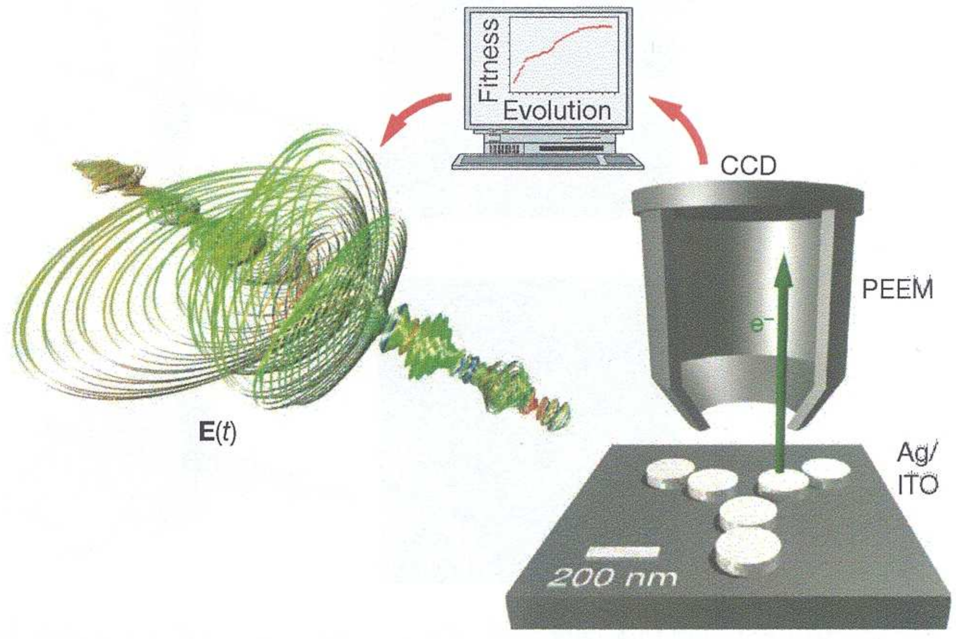
hν wavelength $\lambda_{h\nu}$= 800 nm,
grazing incidence 15°,
p polarisation,
power density ~ 150 MW/cm²

Imagerie PEEM grand champ basse résolution

➢ **Surface plasmon polariton propagating along one single Au wire**. Plasmon polariton wavelength λ_{SPP} = 335 nm, attenuation length L_{SPP} = 3300 nm.

L. Douillard *et al. Nano Lett.* **8** (2008) 935

Manipulation of near-field at the nanometer – PEEM
Nano-objects – Ag disks



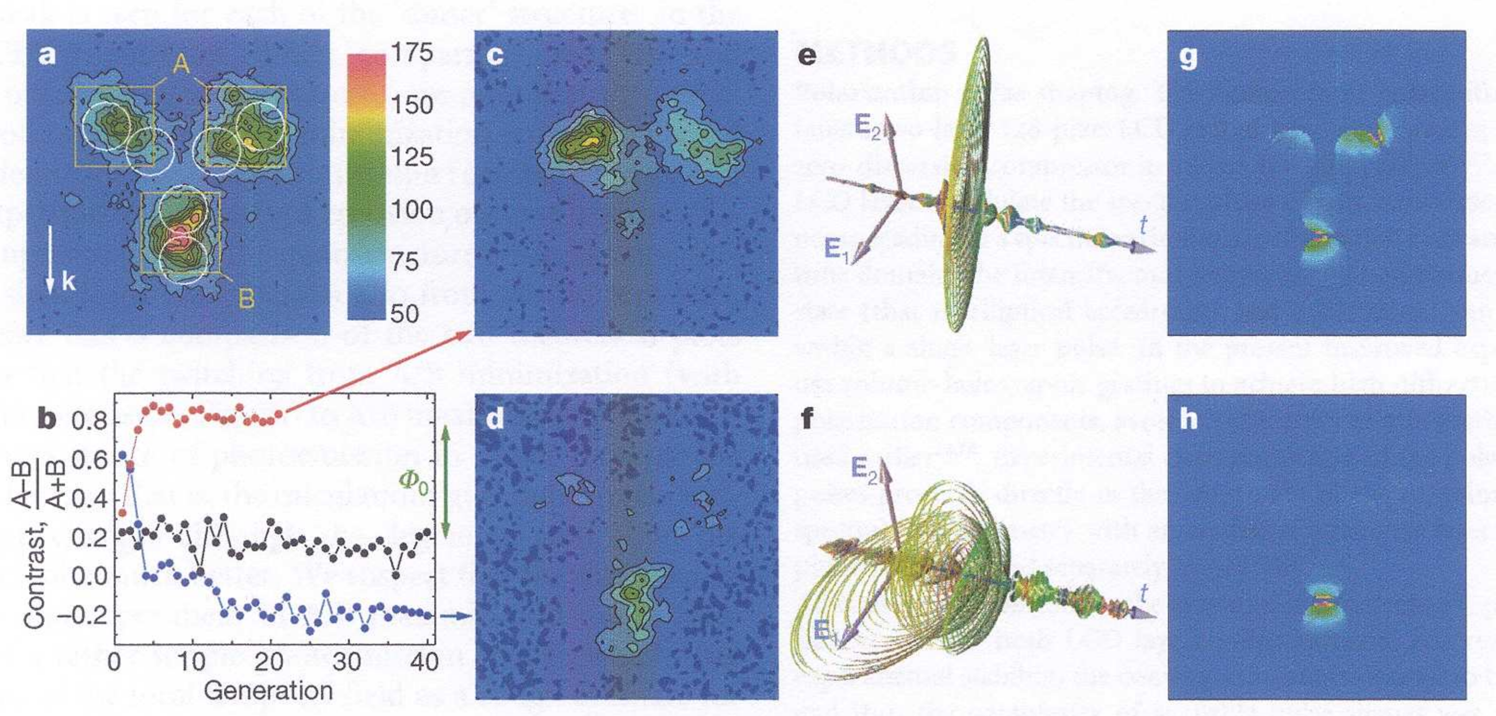
➢ **Manipulation of near-optical field at subwavelength scale through polarisation pulse shaping**

Adaptive polarisation shaping of femtosecond laser pulses

Mapping of the near field of a star like shape (Ag disks / ITO) by two photon photoemission process, subwavelength resolution ≈ 50 nm

M. Aeschlimann *et al. Nature* **446** (2007) 301

Manipulation of near-field at the nanometer – PEEM
Nano-objects – Ag disks



(a) Reference p polarisation, incidence 65°, $\lambda_{h\nu}$ = 790 nm FoV (1.13 µm)²

{Pulse shaping (e); (c, exp.); (g, theory)}; {Pulse shaping (f); (d, exp.); (h, theory)}

➢ **Manipulation of near-optical field at subwavelength scale through polarisation pulse shaping**

M. Aeschlimann *et al. Nature* **446** (2007) 301

Photoemission electron microscopy, a tool for plasmonics - Conclusion

- **PEEM** = An alternative tool to SNOM variantes for plasmonics

Full field microscopy	High electrostatic field
No probing tip	Electron reservoir
High resolution 20 nm	Conducting substrate

- **Mapping of the near-optical field at the nanometre**

- **Dynamics of surface plasmons-polaritons (nanometre, femtoseconde)**

- **Manipulation of the near-field through LASER pulse shaping (coherent scheme)**

Photoemission electron microscopy, a tool for plasmonics - Conclusion

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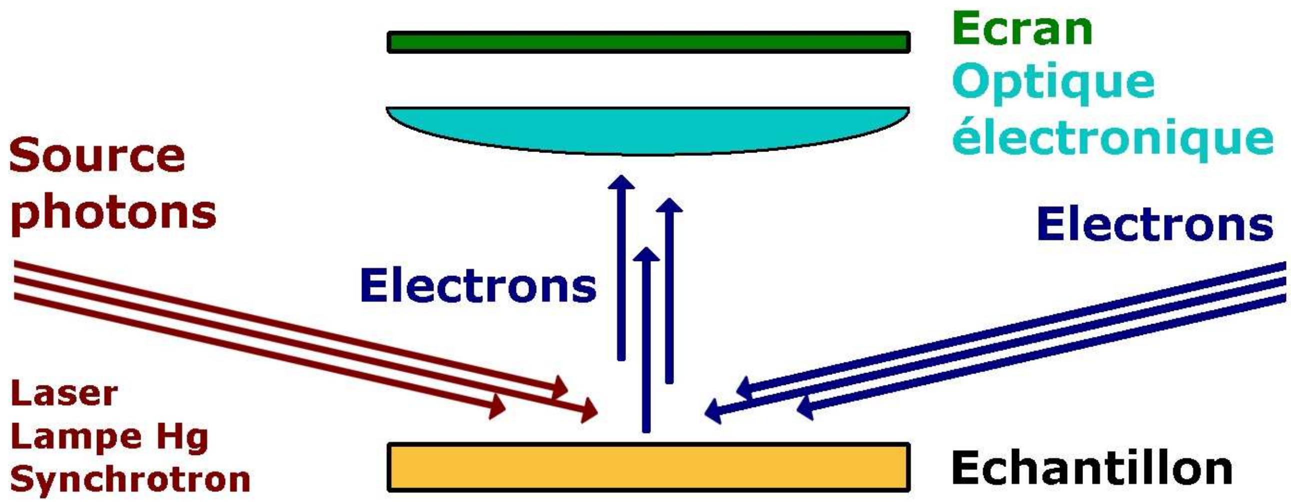
http://www-lnio.utt.fr/

Laboratoire Charles Fabry (J.-J. Greffet),
Institut d'Optique *Graduate School* (LCFIO)
F-91127 Palaiseau, France
http://www.institutoptique.fr/

LEEM – low energy electron microscopy
Instrumentation



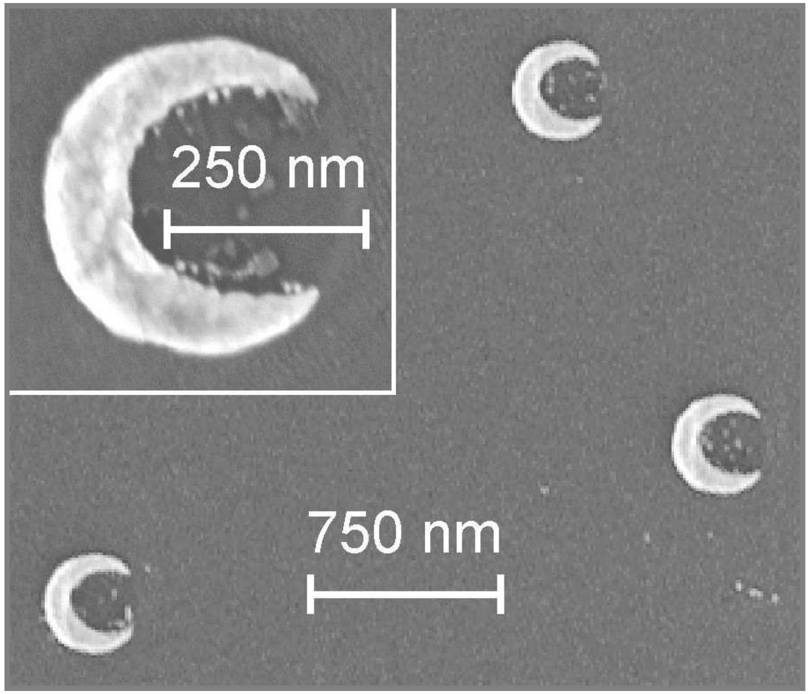
➢ **Principe. Imagerie via électrons rétrodiffractés à basse énergie, LEEM = TF(LEED)**

.sonde topographique
.microscopie plein champ
.aucune sonde physique dans l'espace de mesure (≠ SNOM)

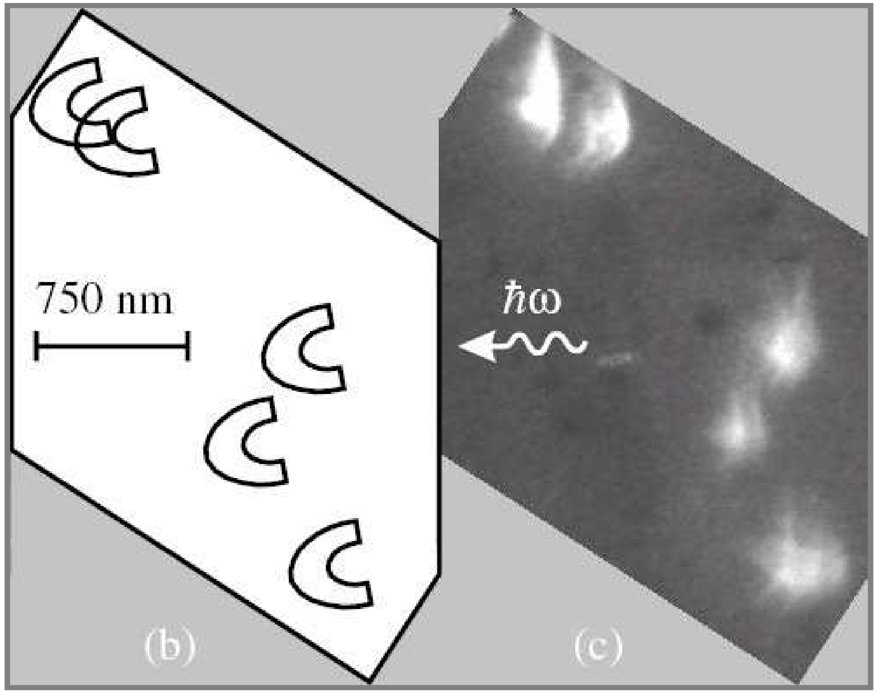
.contraste par différences de réflectivité e^-, interférences (chemins optiques e^-)…
.résolution latérale (16\84) 10 nm (< 3 nm sur instruments AC)
.sensibilité de surface ~ libre parcours moyen inélastique

W. Telieps, E. Bauer *Appl. Phys.* A **44** (1987) 55

Mapping the evanescent field at the nanometre
Individual nano-objects



SEM image **Ag crescents/SiOx,** height 50 nm



Ag crescents/SiOx photon 400 nm, 200 fs

- Enhanced electron emission between the tips of the silver crescents,
- Map of the near field right at the metal surface (electron reservoir).

M. Cinchetti *et al. Phys. Rev. Lett.* **95** (2005) 47601

Microscopie de photoémission d'électrons, un outil pour la plasmonique - Bibliographie

➢ Cartographie du champ proche optique aux échelles nanométriques

« The spatial distribution of non linear-effects in multi-photon photoemission from metallic adsorbates on Si(111) » O. Schmidt, G. Fecher, Y. Hwu, G. Schönhense *Surf. Sci.* **482** (2001) 687

« Photoemission electron microscopy as a tool for the investigation of optical near fields » M. Cinchetti, A. Gloskovskii, S. Nepjiko, G. Schönhense *Phys. Rev. Lett.* **95** (2005) 047601

« *In Situ* monitoring of surface plasmons in single-crystalline Ag-nanowires » L. Chelaru, F. Meyer zu Heringdorf *Surf. Sci.* **601** (2007) 4541

« Short range plasmon resonators probed by photoemission electron microscopy » L. Douillard, F. Charra, Z. Korczak, R. Bachelot, S. Kostcheev, G. Lerondel, P.-M. Adam, P. Royer *Nanoletters* **8** (2008) 935

Microscopie de photoémission d'électrons, un outil pour la plasmonique - Bibliographie

Dynamique de plasmons-polaritons (nanomètre, femtoseconde)

« Femtosecond imaging of surface plasmon dynamics in a nanostructured silver film » A. Kubo, K. Onda, H. Petek, Z. Sun, Y. Jung, H. Koo Kim *Nanoletters* **5** (2005) 1123

« Femtosecond microscopy of surface plasmon polariton wave packet evolution at the silver/vacuum interface » A. Kubo, N. Pontius, H. Petek *Nanoletters* **7** (2007) 470

Microscopie de photoémission d'électrons, un outil pour la plasmonique - Bibliographie

➢ Manipulation du champ proche optique par mise en forme d'impulsions

« Adaptative subwavelength control of nano-optical fields » M. Aeschlimann, M. Bauer, D. Bayer, T. Brixner, F. Javier Garcia de Abajo, W. Pfeiffer, M. Rohmer, C. Spindler, F. Steeb *Nature* **446** (2007) 301

« Attosecond nanoplasmonic-field microscope » M. Stockman, M. Kling, U. Kleineberg, F. Krausz *Nature Photonics* **1** (2007) 539