Università di Pisa
LM Materials and Nanotechnology - a.a. 2016/17

Spectroscopy of Nanomaterials II sem – part 6

Version 0, Apr 2017
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Plasmonics at the surface: the unconventional optical behavior of metal/dielectric interfaces

OUTLOOK

In the macroscopic world, metals are usually playing no relevant or specific role: they are opaque, reflecting layers, used to produce mirrors, or diffraction gratings, or other conventional systems

On the contrary, in the last few decades there was a strong, and still increasing, revival of interest for metal nanostructure applications in nano-optics and nanophotonics

The key aspect of such an interest is in a subtle interplay between charge oscillations at the metal surface and electromagnetic waves

The related topic is known as **plasmonics**: we will separately discuss plasmonics at a flat interface (here) and at the surface of a localized nanostructure (next lecture)

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Today's menu:
- Mixed appetizers of Maxwell, waves, dielectric constant
  and conductivity
- Main course of surface plasmons, served at a metal/
  dielectric interface (flat)
- Dessert: applications and perspectives
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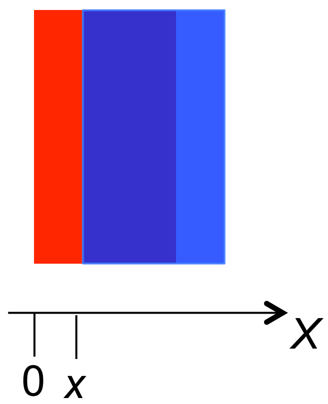
BACKGROUND: BULK PLASMA FREQUENCY



1. Let's consider a metal (bulk) modeled as free positive (red) and negative (blue) charges free to be displaced each other
2. The electric field felt by the negative charge at the position *x* is (from Gauss theorem!):

$$E_x = \frac{\rho S}{\varepsilon_0 S} x$$

with ρ = *ne* the charge density and *S* the cross-section

$$F_x = -e \frac{ne}{\varepsilon_0} x$$

$$a_x = -\frac{ne^2}{m\varepsilon_0} x = -\omega_p^2 x$$

3. The electrons feel a **restoring force**
4. The angular frequency of the so-produced oscillations is called (bulk) **plasma frequency**

$$\omega_p = \sqrt{\frac{ne^2}{m\varepsilon_0}}$$

In classical pictures, the plasma frequency accounts for the restoring force acting on electrons when they are displaced from the (fixed) positive charges

This is a picture valid for the bulk, i.e., for a 3-D system!

For a typical metal, $n \sim 10^{29}$ electrons/m^3
→ $\omega_p \sim 10^{16}$–10^{17} rad/s

Typically, the bulk plasma frequency lies in the UV range (out of our interest)

BACKGROUND: MAXWELL EQUATIONS

$$\begin{cases} \vec{\nabla} \times \vec{H} = \vec{J} + \dfrac{\partial \vec{D}}{\partial t} \\ \vec{\nabla} \times \vec{E} = -\dfrac{\partial \vec{B}}{\partial t} \\ \vec{\nabla} \cdot \vec{B} = 0 \\ \vec{\nabla} \cdot \vec{D} = \rho \end{cases}$$

$$\vec{B} = \mu_0 \vec{H}$$

$$\vec{D} = \varepsilon_0 \vec{E} + \vec{P} = \varepsilon_0 \varepsilon \vec{E} \quad \text{with} \quad \vec{P} = \chi \varepsilon_0 \vec{E} \quad , \quad \varepsilon = 1 - \chi$$

$$\vec{J} = \sigma_c \vec{E}$$

σ_c conductivity

Typically:
ε describes a dielectric
σ_c describes a conductor

Here we introudce a **complex dielectric function** , depending on frequency and accounting for conduction in a metal:

$$\varepsilon = 1 + i \frac{\sigma_c}{\varepsilon_0 \omega}$$

In general, we have complex and frequency dependent dielectric constant and index of refraction

$$\varepsilon = \varepsilon' + i\varepsilon''$$

$$\tilde{n} = \sqrt{\varepsilon} = n + i\kappa$$

A unified approach, based on dielectric constant, is used for both dielectric and metal

DRUDE MODEL FOR THE METAL

Drude model (classical, but its main results are in general agreement with quantum models):

$$\gamma = \frac{1}{\tau_c} = \frac{ne^2}{m\sigma_c} = \frac{\varepsilon_0 \omega_p^2}{\sigma_c}$$

*Electrons in the metal undergo collisions with the lattice, giving rise to **a damping** with rate γ*

Electrons in a metal driven by an oscillating electric field are well described by a damped/driven motion:

$$m\frac{d^2\vec{r}}{dt^2} + \gamma\frac{d\vec{r}}{dt} = -e\vec{E}$$

$$\vec{E} = \vec{E}(t) = \vec{E}_0 \exp(-i\omega t) \rightarrow \vec{r} = \vec{r}(t) = \vec{r}_0 \exp(-i\omega t)$$

$$\rightarrow -\omega^2 m\vec{r}_0 - i\omega\gamma m\vec{r}_0 = -e\vec{E}_0$$

$$\rightarrow \vec{r}_0 = \vec{E}_0 \frac{e}{m\omega^2 + i\omega\gamma m}$$

The polarization field can be written as:

$$\vec{P} = -ne\vec{r} = -\frac{ne^2}{m\omega^2 + i\omega\gamma m}\vec{E} = -\varepsilon_0 \frac{\omega_p^2}{\omega^2 + i\gamma\omega}\vec{E}$$

Drude model leads to a freqeuncy dependent, complex dielectric constant describing the metal

$$\chi = \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \rightarrow \varepsilon = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}$$

APPROXIMATE DRUDE

In a metal (e.g., gold, silver): $\gamma < 10^{14}$ s^{-1} $\omega_p > 10^{16}$ rad/s

In optics (for our purposes): $\omega \sim 10^{15}$ rad/s

$$\Rightarrow \quad \gamma\omega << \omega^2 \qquad \omega_p^2 >> \omega^2$$

$$\Downarrow$$

Approximate Drude foresees a negative and real dielectric constant for a model in the optical range of frequencies

$$\varepsilon \approx 1 - \frac{\omega_p^2}{\omega^2}$$

Notes:

1. The real part of the dielectric constant is **always** negative

2. **Very important:** the occurrence of other processes, in particular **interband transitions** involving conduction band electrons at an energy below the Fermi level is here completely neglected. Such transitions leads to frequency dependent absorption processes eventually falling in the visible range (e.g., close to 350–400 nm for silver, around 500 nm for gold) producing an additional contribution to the imaginary part of the dielectric constant

DISPERSION RELATION

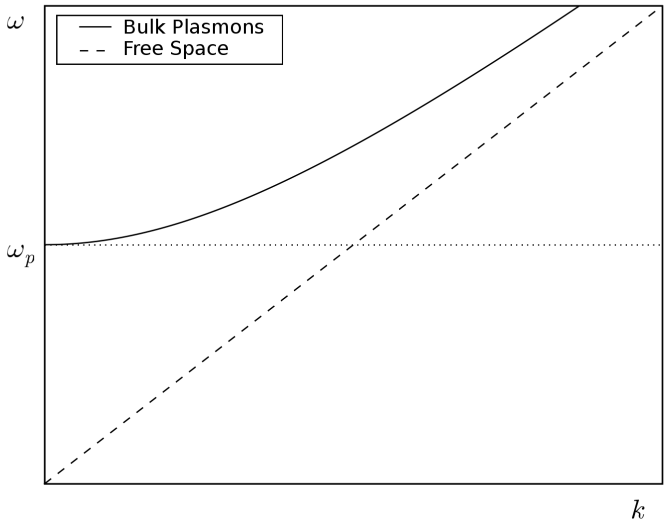
The dispersion relation provides with the link between angular frequency ω and wavenumber *k*

In a non-dispersive dielectric (e.g., the vacuum) it is described by a straight line with slope c/n

$$\omega = \frac{kc}{n} = \frac{kc}{\sqrt{\varepsilon}} \approx \frac{kc}{\sqrt{1-\frac{\omega_p^2}{\omega^2}}}$$

$$\rightarrow \omega = \sqrt{\omega_p^2 + k^2c^2}$$

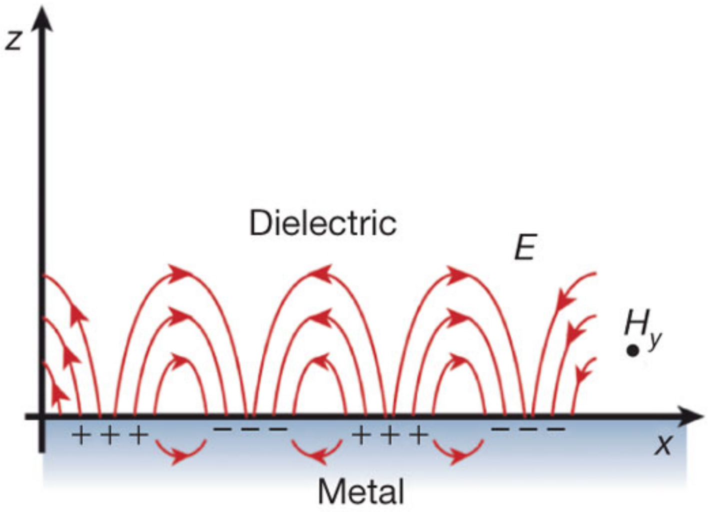
Dispersion relation *ω* vs *k*



Bulk plasmon oscillations show a dispersion always above the dispersion in a dielectric

No much interest for such bulk processes!

PLANE INTERFACE (2-D SYSTEM)



At a metal/dielectric interface (plane) we can assume mutual charge displacement for the **surface** charge

Such a mutual charge displacement may be produced by any physical cause, for instance a localized impact with an energetic particle (see, e.g., the wavelets on a liquid interface)

We now look at a surface charge displacement, i.e., a moduletion of surface charge along one direction belonging to the interface plane, “associated” with an e.m. wave

In other words, we search a suitable solution for the e.m. wave equation $\nabla^2 \vec{E} - \frac{\varepsilon}{c^2}\frac{\partial^2 \vec{E}}{\partial t^2} = 0$

*This solution is called **plasmon polariton***

Note: the solution we are looking for propagates along *x* and the electric field has non-zero components along *x* → *longitudinal e.m. waves!*

SURFACE PLASMON POLARITONS (SPPs) I

We assume sinusoidal (harmonic) behavior:

$$\vec{E}(t) \propto \vec{E}\exp(-i\omega t)$$

$$\rightarrow \nabla^2\vec{E} + \frac{\varepsilon^2}{c^2}\omega^2\vec{E} = 0$$

$$\rightarrow \nabla^2\vec{E} + k_0^2\varepsilon^2\vec{E} = 0 \quad \text{with} \quad k_0^2 = \frac{\omega^2}{c^2}$$

We look for propagation along *x* :

$$\vec{E}(x) \propto \vec{E}\exp(i\beta x)$$

$$\rightarrow -\beta^2\vec{E} + \frac{\partial^2\vec{E}}{\partial z^2} + k_0^2\varepsilon^2\vec{E} = 0$$

$$\rightarrow \frac{\partial^2\vec{E}}{\partial z^2} + (k_0^2\varepsilon^2 - \beta^2)\vec{E} = 0$$

Maxwell equations for the rotors
(***m*** **and** ***d*** **stands for metal and dielectric**)

$$\begin{cases} \vec{\nabla}\times\vec{H}_{m,d} = \varepsilon_0\varepsilon_{m,d}\dfrac{\partial\vec{E}_{m,d}}{\partial t} \\ \vec{\nabla}\times\vec{E}_{m,d} = -\mu_0\dfrac{\partial\vec{H}_{m,d}}{\partial t} \end{cases}$$

We consider only solutions with $E_x \neq 0$ → E_x , E_z , H_y $\neq 0$ (they are called **TM, or p-polarized**, waves) and we assume an **evanescent character** as a function of *z:*

$$\vec{E}(z) \propto \vec{E}\exp(-\kappa_{m,d}\,|z|)$$

Calculating the rotor of *H* in the two media and duly accounting for the absolute value in |*z*|*:*

$$-\kappa_d H_{yd} = -i\omega\varepsilon_0\varepsilon_d E_{xd}$$

$$+\kappa_m H_{ym} = -i\omega\varepsilon_0\varepsilon_m E_{xm}$$

Calculating the rotor of *E* in the two media and duly accounting for $\beta_d = \beta_m = \beta$ *:*

$$-\kappa_d E_{xd} - i\beta E_{zd} = i\omega\mu_0 H_{yd}$$

$$+\kappa_m E_{xm} - i\beta E_{zm} = i\omega\mu_0 H_{ym}$$

SURFACE PLASMON POLARITONS (SPPs) II

Finally, we can put all together and write **continuity equations** for the tangential components of the fields at the interface, i.e., for $z = 0$.

We found:

$$\frac{\kappa_d}{\kappa_m} = -\frac{\varepsilon_d}{\varepsilon_m}$$

and:

$$\beta = \frac{2\pi}{\lambda}\sqrt{\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}}$$

Since β is the wavenumber of the surface plasmon polariton, this is the new **dispersion relation** obtained for a plasmon oscillation at the (plane) interface

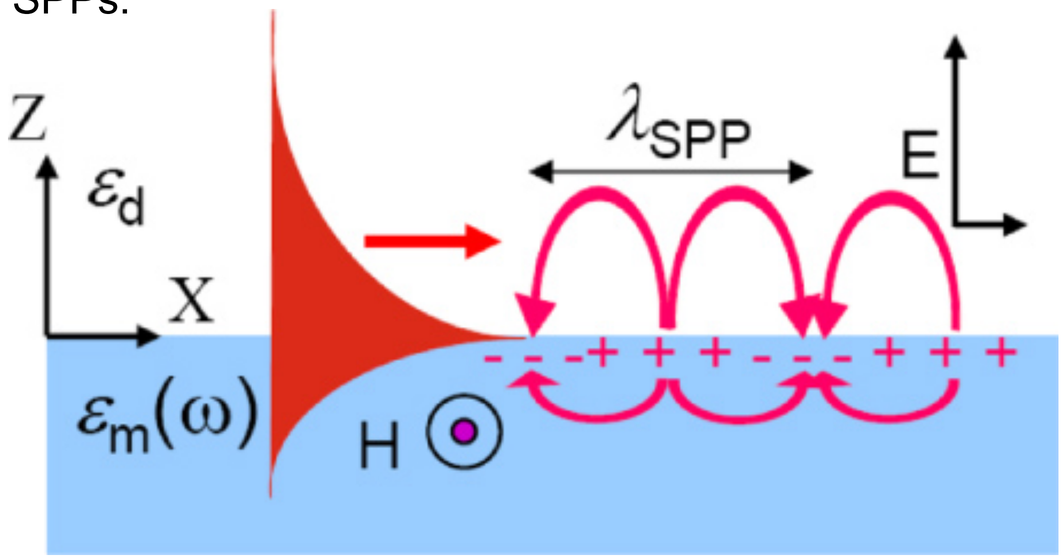
Mathematics shows that it is possible to find a solution of the wave equation accounting for all desired features:

- Longitudinal character (very strange, compared with conventional e.m. waves!)
- Propagating along the interface
- With an evanescent, i.e., exponential decreasing, character along the direction orthogonal to the interface
- *In agreement with the assumed surface charge modulation at the interface*

Mathematics brings a new dispersion relation, dependent on ω (being ε_m dependent on ω), and specific for SPPs

SUMMARY OF SPP PROPERTIES

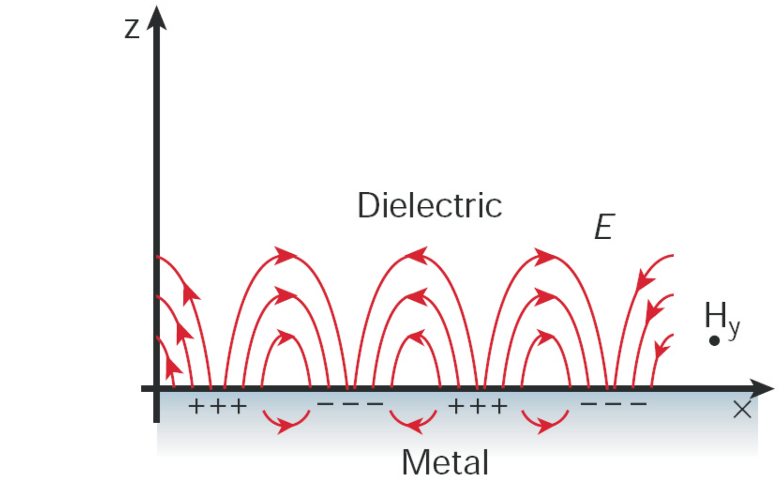
Summarizing, for SPPs:

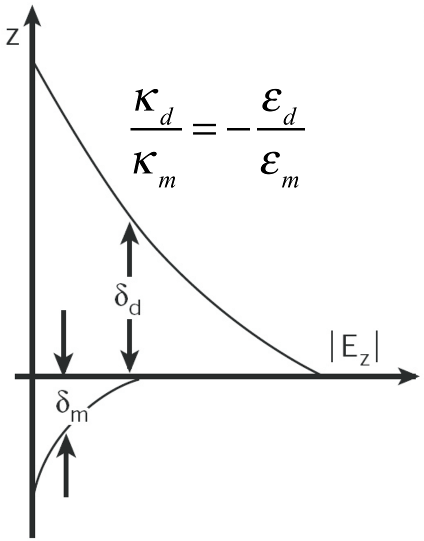


1. An oscillation of the surface charge at the metal/dielectric interface which can be interpreted as a **longitudinal e.m. wave** (TM, or p-polarized)
2. Along *z* (orthogonal to the interface) the electric field gets an **evanescent character**

e.m. energy gets confined (along *z*) in a sub-wavelength size within the metal, depending on κ_m

EVANESCENT CHARACTER OF SPPs





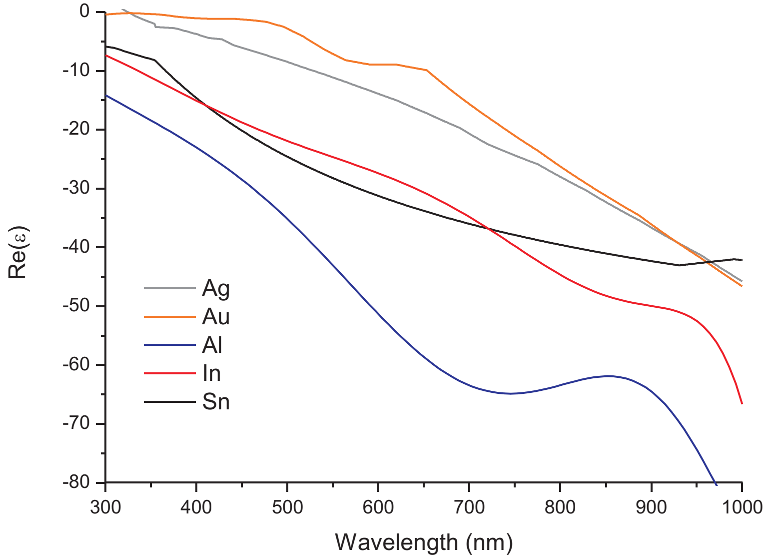
$$E_{d,m}(z) \propto \exp\left(-\kappa_{d,m}|z|\right)$$

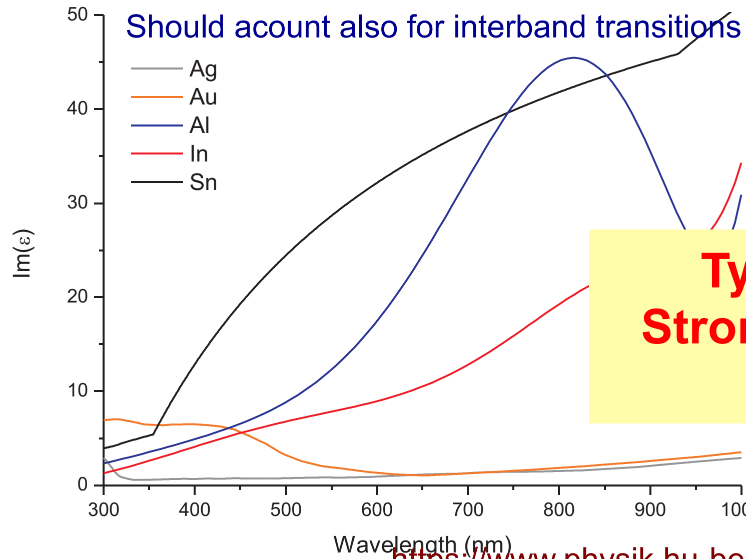
The penetration depth within the metal is

$$\delta_m = \frac{1}{\kappa_m} \approx \frac{2\pi}{\lambda} \mathrm{Im}\{\tilde{n}(\omega)\}$$

with

$$\tilde{n} = \sqrt{\varepsilon' + i\varepsilon''} \;\; ; \; \varepsilon'' = \frac{\omega_p^2 \tau}{\omega\left(1+\omega^2\tau^2\right)}$$





Typically, $\delta_m \ll \lambda$
Strong confinement of e.m. energy

https://www.physik.hu-berlin.de/de/nano/lehre/Gastvorlesung %20Wien/plasmonics

SPP DISPERSION RELATION

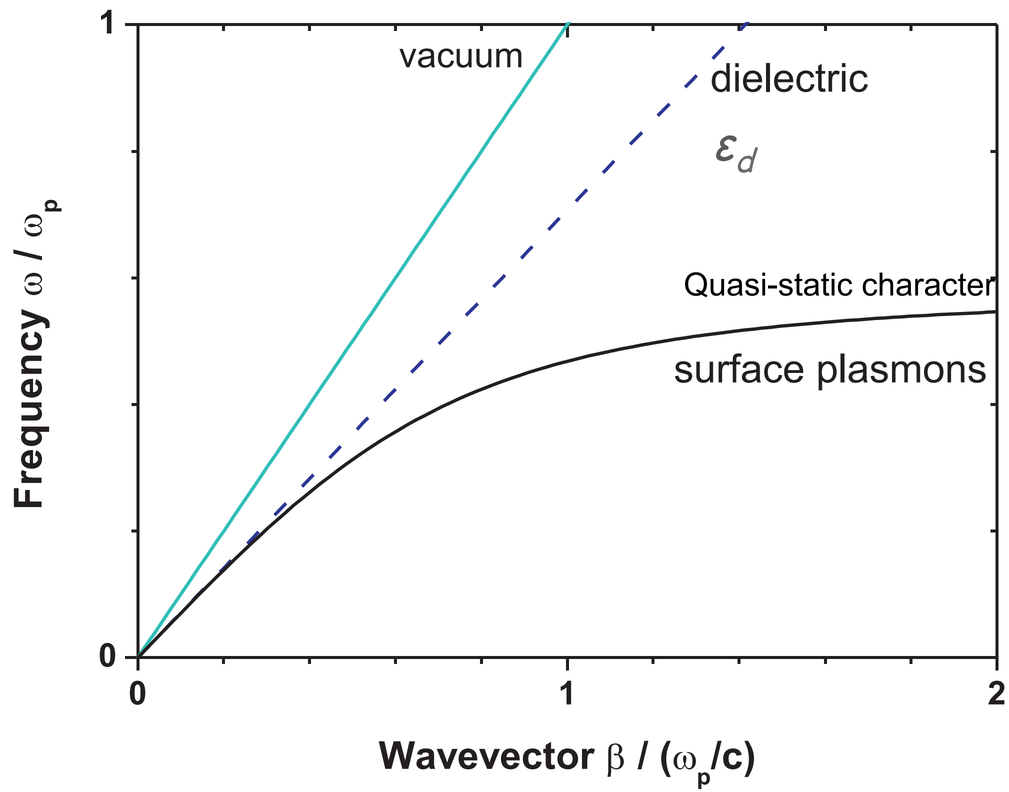
Beavior along the SPP propagation direction (along the interface)

$$E_{d,m}(x) \propto \exp(i\beta x)$$

with (Drude model):

$$\varepsilon_m \simeq 1 - \frac{\omega_p^2}{\omega^2}$$

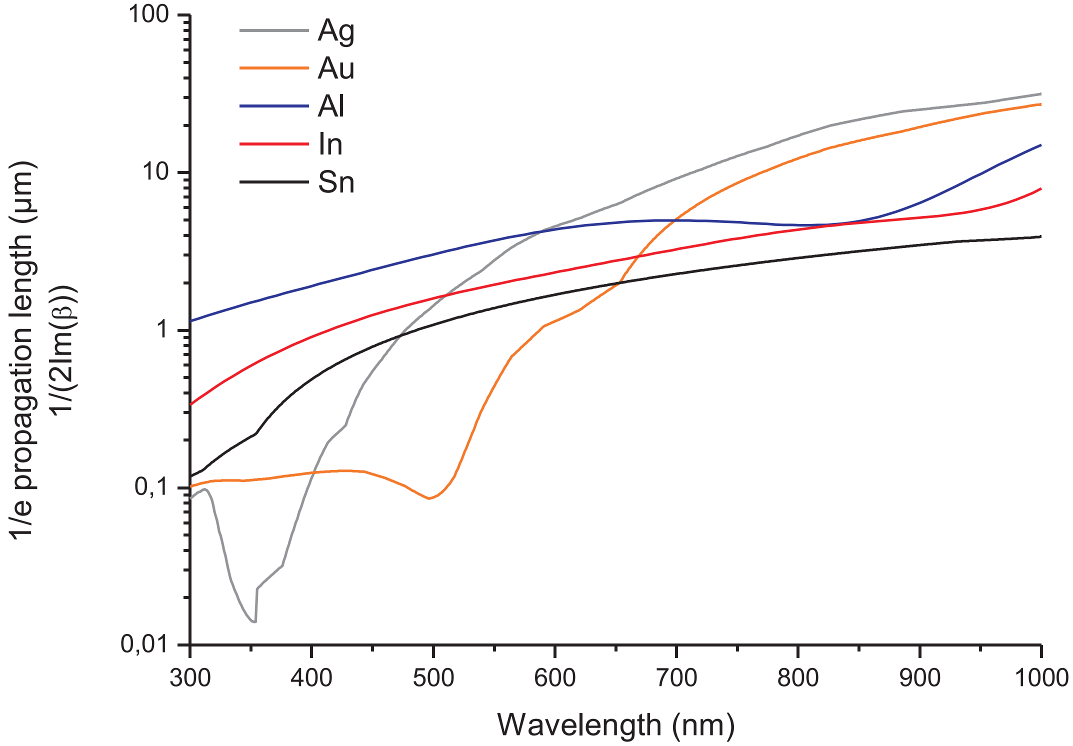
Dispersion relation for SPP: $\beta = \frac{2\pi}{\lambda}\sqrt{\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}} = \frac{2\pi}{\lambda_{SPP}}$



$$\omega_{SPP} \sim \frac{\omega_p}{\sqrt{1+\varepsilon_d}}$$

SPP PROPAGATION LENGTH

Plasmon propagation length (accounts for losses): $$\delta_{SPP} = \frac{1}{2\,\mathrm{Im}\{\beta(\omega)\}}$$



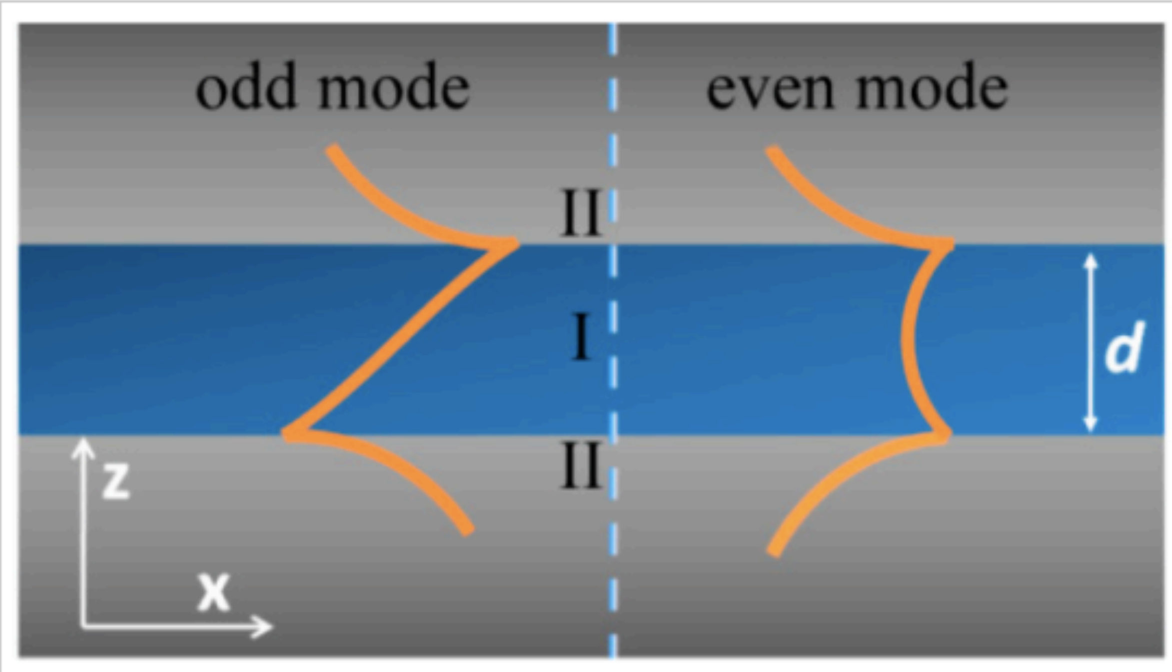
Virtually feasible the realization of SPP-based waveguides (with sub-wavelength thickness and typical propagation length 10-100 µm)

https://www.physik.hu-berlin.de/de/nano/lehre/Gastvorlesung%20Wien/plasmonics

MULTILAYER WAVEGUIDES

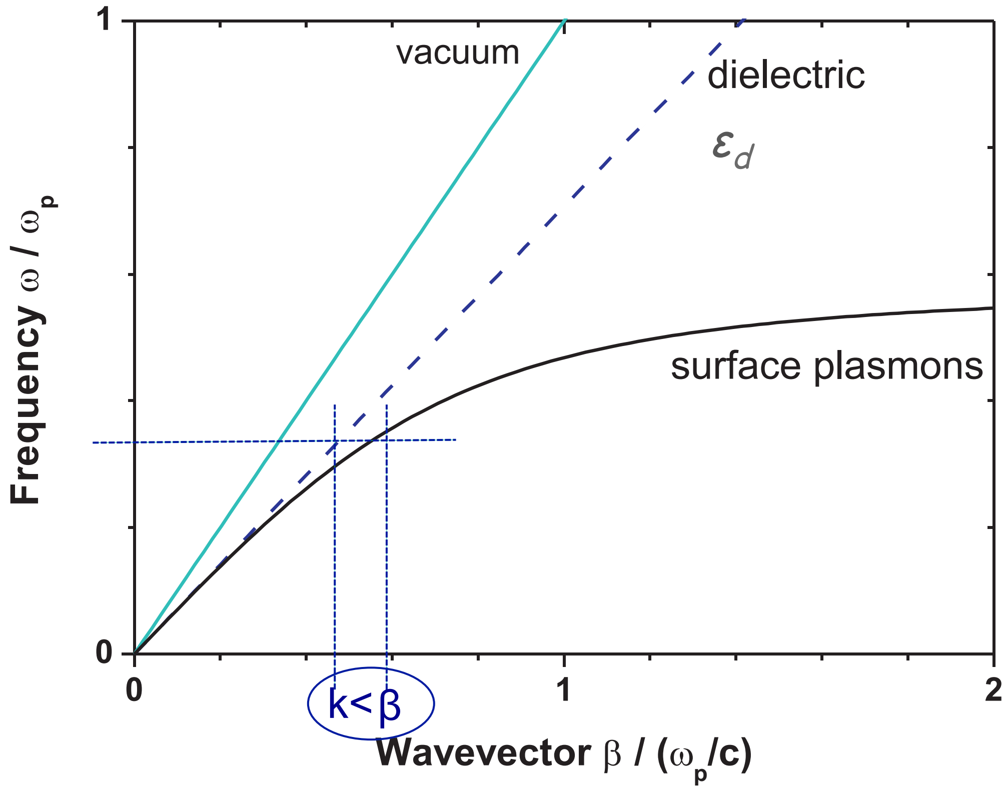
For the sake of completeness: multilayer systems can be realized (e.g., MIM and IMI) featuring stronger field confinement (and improved SPP propagation length)

Figure 2. Schematic structure of metal–insulator–metal or insulator–metal–insulator (MIM or IMI) with *d* the thick core layer. The core layer and claddings are represented by Roman numbers "I" and "II", respectively. The odd and even modes are represented by the orange-colored curve, respectively.



$$\omega_{\pm} = \omega_{SP}\sqrt{1 \pm \exp(-\beta d)}$$

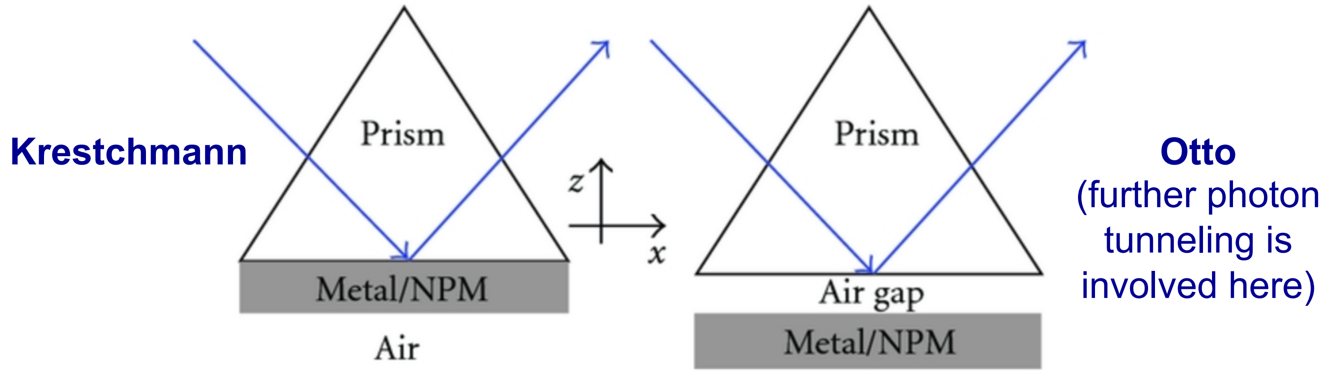
LAUNCHING (COUPLING WITH) SPP



Momentum conservation hampers coupling propagating (transversal) e.m. waves with plasmon polaritons, since, for a given ω , $k < \beta$

→ specific SPP excitation methods must be used

KRETSCHMANN (OTTO) CONFIGURATIONS



At the prism/metal interface total internal reflection occurs

According to Snell law: $$\frac{\sin\theta_{outside}}{\sin\theta_{prism}} = \frac{n_{prism}}{n_{outside}} \simeq \frac{n_{prism}}{n_{air}}$$

Total internal reflection for $$\sin\theta_{outside} = \sin\theta_{prism}\frac{n_{prism}}{n_{outside}} \geq 1 \rightarrow \sin\theta_{prism,crit} \geq \frac{n_{outside}}{n_{prism}}$$

For the momentum (wavevector module) conservation:

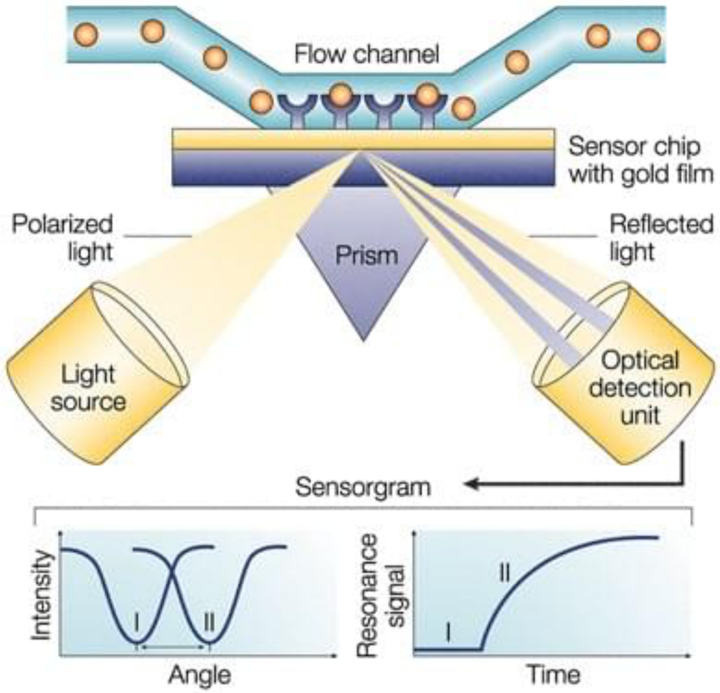
$$\vec{k}_{outside} = k_{outside}\left[\sin(\theta_{outside})\hat{x} + \cos(\theta_{outside})\hat{z}\right] \rightarrow \cos(\theta_{outside}) = \sqrt{1-\sin^2(\theta_{outside})} = i\sqrt{-1+\sin^2(\theta_{outside})}$$

$$\rightarrow k_{outside,z} \ \text{imaginary} \rightarrow \text{evanescent wave}$$

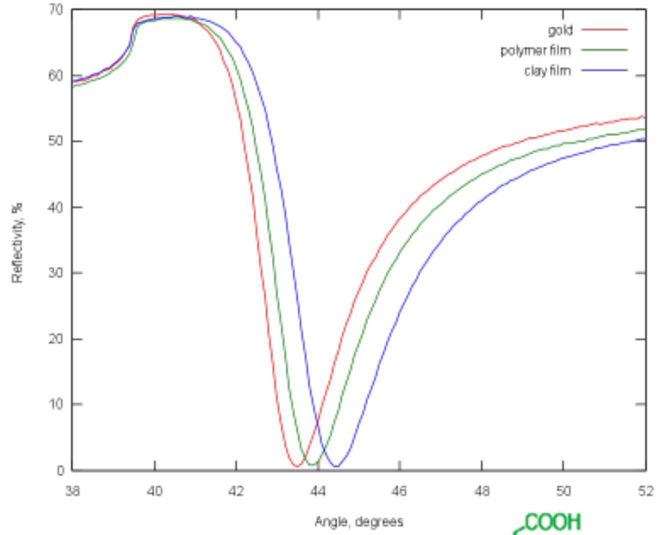
$$k_{outside,x} = \frac{2\pi}{\lambda}\sin\left(\theta_{outside}\right) = \frac{2\pi}{\lambda}\sin\left(\theta_{prism}\right)\frac{n_{prism}}{n_{air}} = \frac{2\pi}{\lambda}\sin\left(\theta_{prism}\right)\sqrt{\varepsilon_{prism}}$$

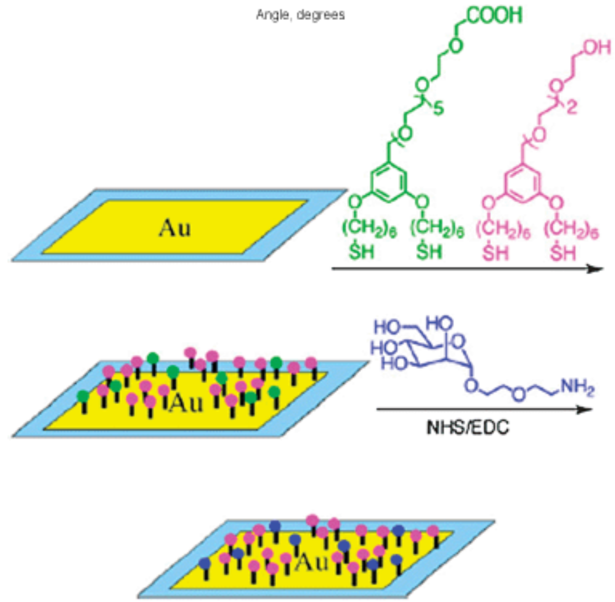
can be equal to $$\beta = \frac{2\pi}{\lambda}\sqrt{\frac{\varepsilon_m \varepsilon_{air}}{\varepsilon_m + \varepsilon_{air}}}$$

SURFACE PLASMON RESONANCE SPECTROSCOPY



Nature Reviews | Drug Discovery





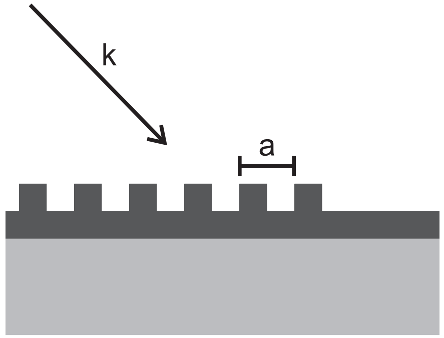
Coupling with SPP depends on the angle and implies a decrease of the total internal reflected signal

Modification of the surface through, e.g., adsorption of particles, modify the dielectric constant, hence the resonance angle

Functionalization of gold through thiol groups

OTHER COUPLING METHODS

Coupling of SPP can be accomplished also by using a **grating** directly inscribed on the noble metal film

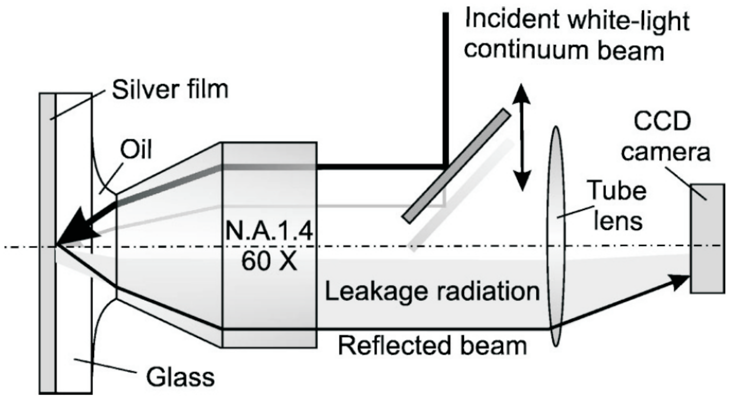


Because of grating diffraction

$$k_x = \frac{2\pi}{\lambda}\sin\theta \pm m\frac{2\pi}{a} \quad \text{, with } m \text{ integer}$$

can be equal to $\beta = \frac{2\pi}{\lambda}\sqrt{\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}}$

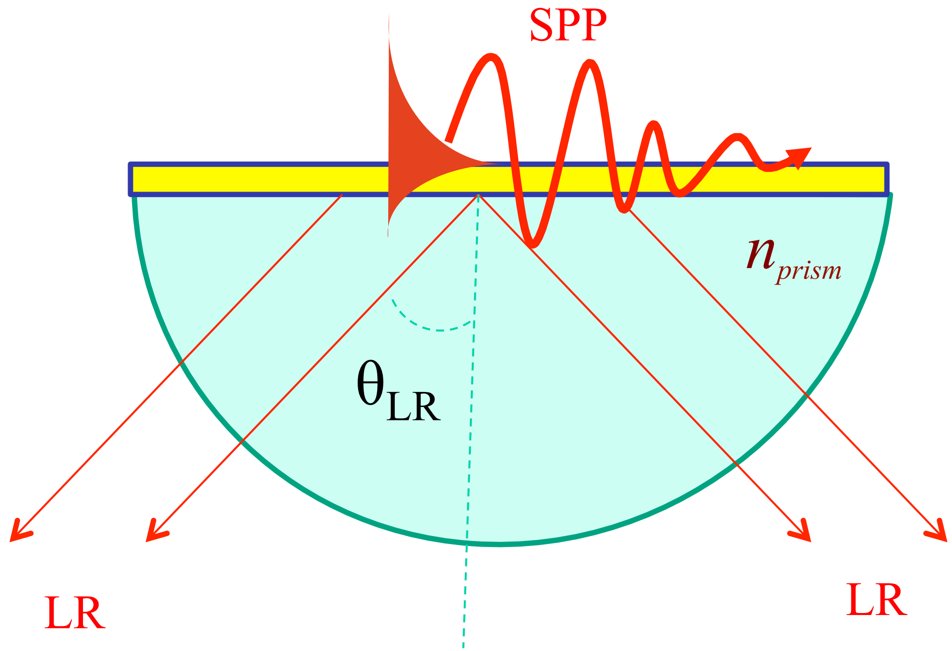
Or by using a very large NA objective (NA≥1.4, called **TIRF objectives**)



Or by using a **near-field** (we will see more on optical near-fields in the future)

VISUALIZATION OF SPPs

In SPP propagation, the e.m. energy is mostly confined within the metal: the evanescent field at the surface cannot be collected by conventional optics (made for propagating waves!)



Leakage spectroscopy:
the evanescent wave turns back to propagating radiation through interaction with a medium

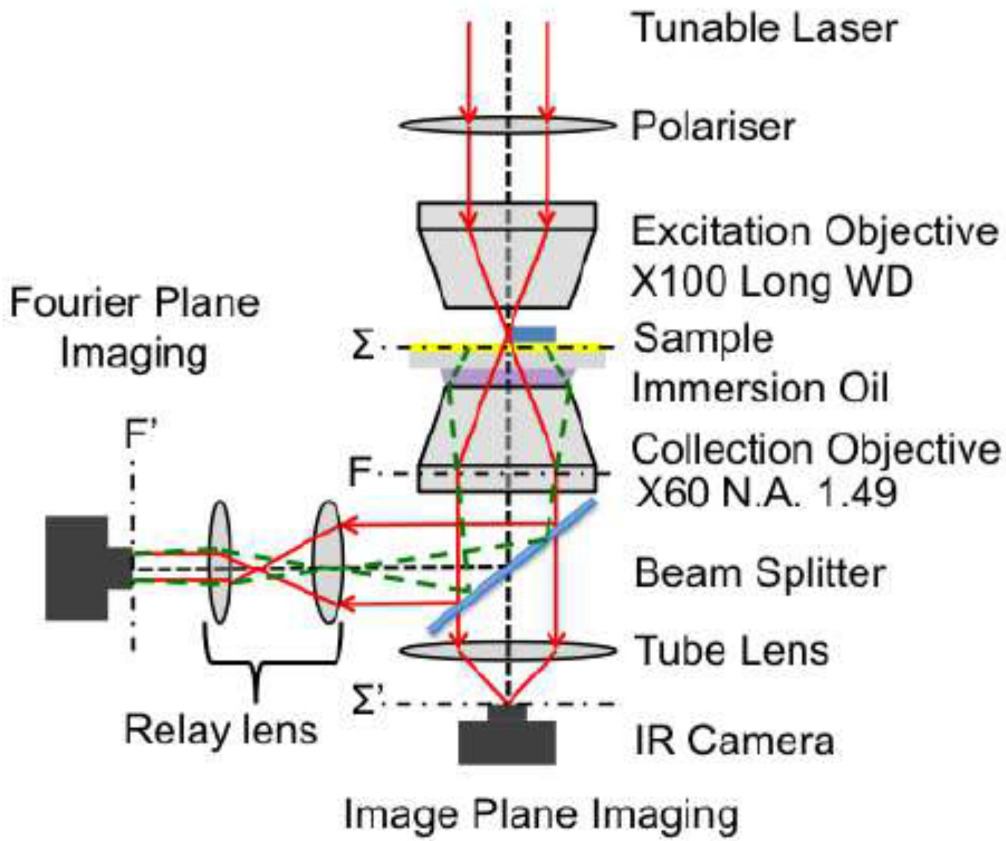
Process similar to a **photon tunneling** (we will see more on that in the future)

Due to boundary conditions and conservation of the in-plane wave-vector along the different interfaces, SPPs leak through the thin gold film **into the glass substrate**

Leaked radiation is "re-emitted" at a **specific angle θ_{LR}**

$$\sin\theta_{LR} = \frac{\mathrm{Re}\{\beta\}}{|k_{LR}|} = \frac{\mathrm{Re}\{\beta\}}{n_{prism} 2\pi / \lambda}$$

LEAKAGE SPECTROSCOPY



Collection of leaked radiation requires extremely large NA objectives (e.g., NA = 1.49, which is the maximum achievable)

Such objectives are called **TIRF** objectives

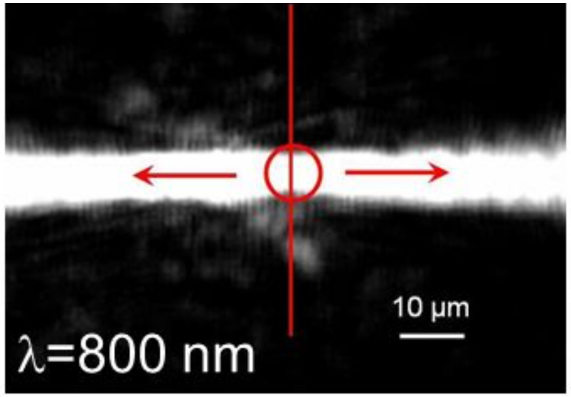
Discrimination between light scattered from the plasmon system and the leaked radiation requires a specific setup, similar to dark-field microscopy:

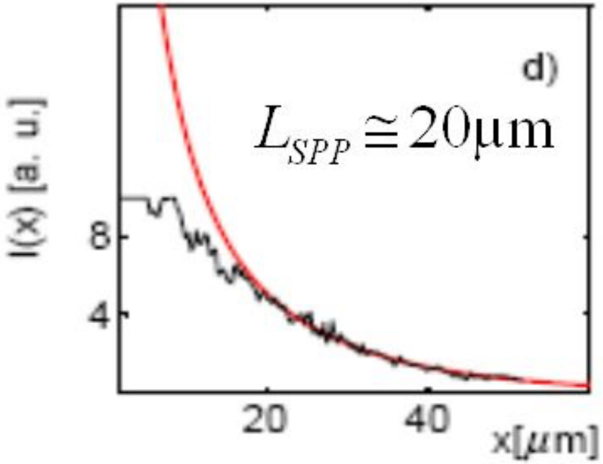
- The image is made of the *back focal plane* of the objective
- This is called Fourier plane
- In such a way, the peripheral re-emitted radiation, i.e., the leaked radiation, is collected
- **The image taken by the camera brings information on θ_{LR}**

Leakage spectroscopy requires a specific setup to collect at the leakage angle, and enables characterizing the SPP

LEAKAGE SPECTROSCOPY EXAMPLES

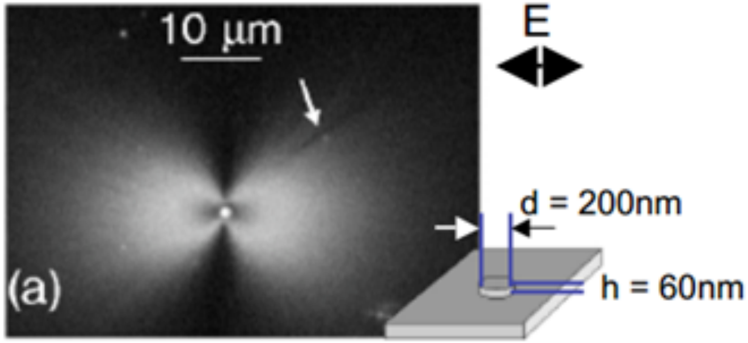
Leakage spectroscopy of SPP on 50 nm Au film and analysis of the SPP propagation length

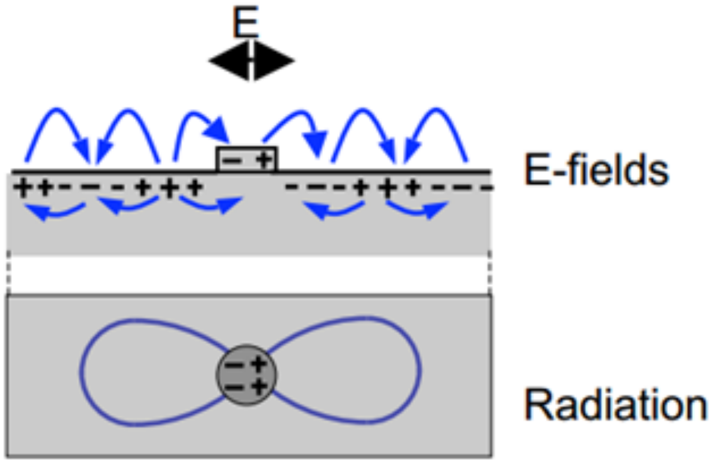




Stepanov et al., Optics Letters **30**, 1524 (2005).
Hohenau et al., Optics Letters **30** ,893 (2005).

Leakage spectroscopy of localized plasmon resonances (we will more in the future) from an Au disc

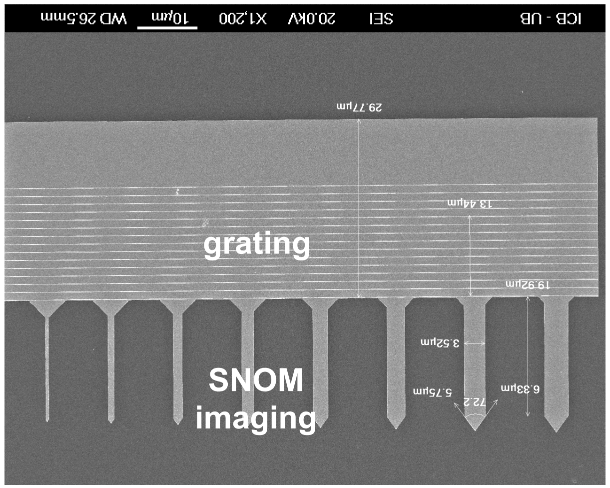


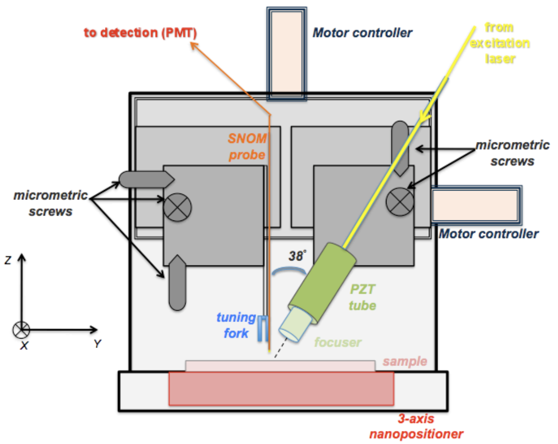


A dipolar pattern is observed since, for the selected excitation, a surface charge dipole is formed at the Au disc

ANALYSIS OF SPPs BY NEAR-FIELD (SNOM)

Scanning Near-field Optical Microscopy (SNOM) is able to **directly** convert the evanescent field at the metal/dielectric interface into an “ordinary” wave (we will see more in the future)





Gold on silicon thin film (30-40 nm thick) with lithographed structures consisting in “fingers” terminated with a tapered region (different taper angle and width)

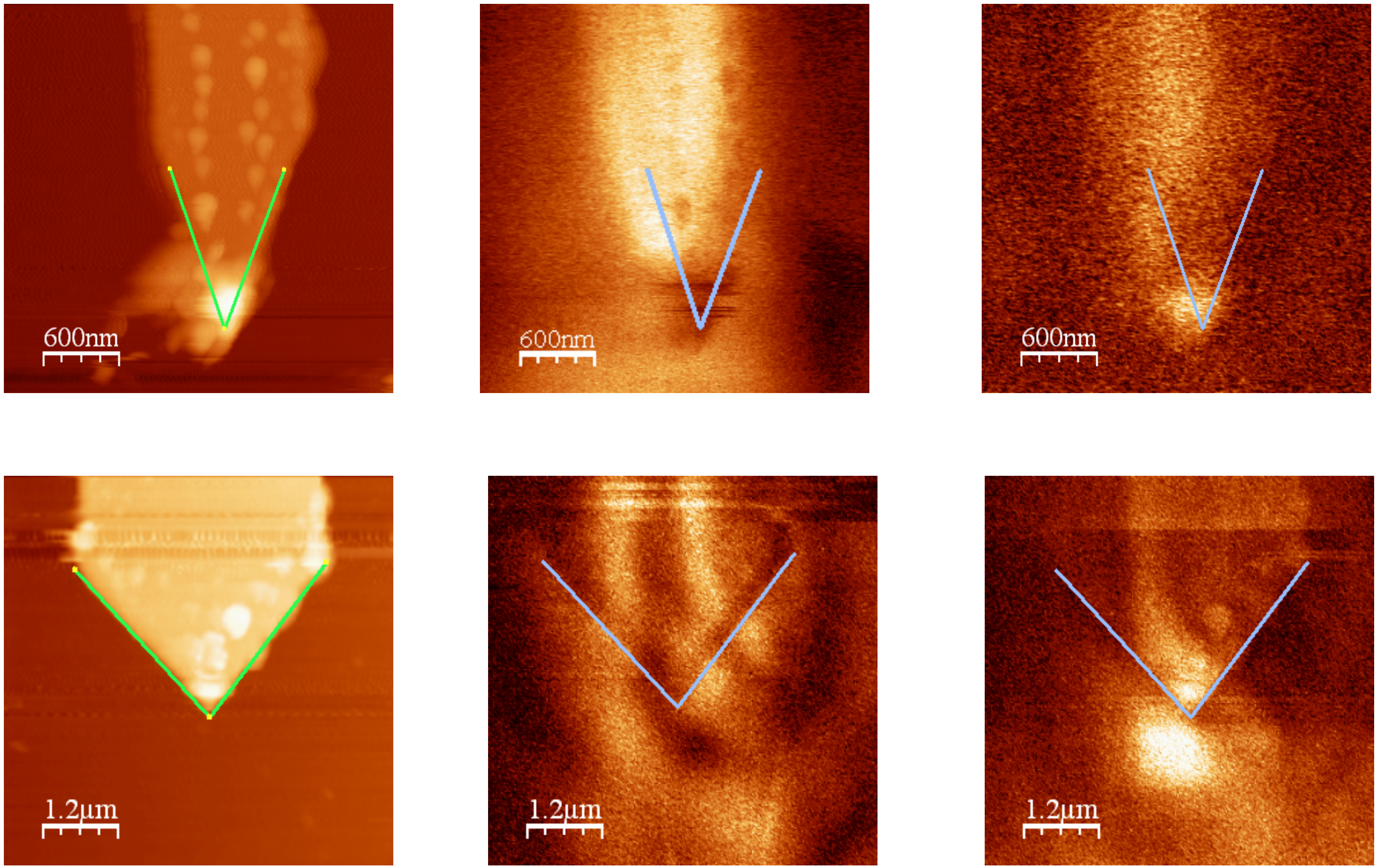
SPP excitation is accomplished by sending light, at a certain angle, onto a diffraction grating inscribed in the film

SNOM imaging is carried out at a 20–25 μm from the excitation spot (sent onto the grating)

SNOM is operated in the **collection mode** (we will see more on that in the future): a phyiscal probe, in close proximity with the surface, converts the evanescent e.m. field associated with the SPP onto a propagating wave guided, through an optical fiber, to a detector

A scan is made and a topography map is simultaneously acquired

EXAMPLES OF SPPs IMAGED BY SNOM I

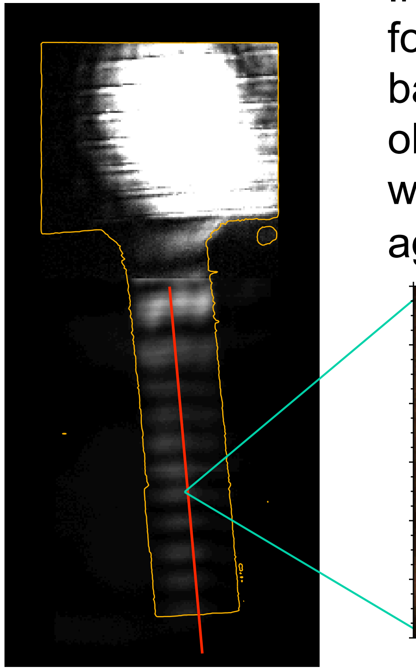


Topography

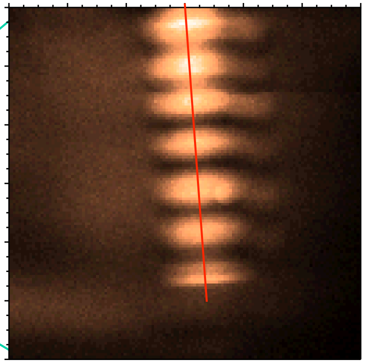
Pol // to the grating (SPP is launched)

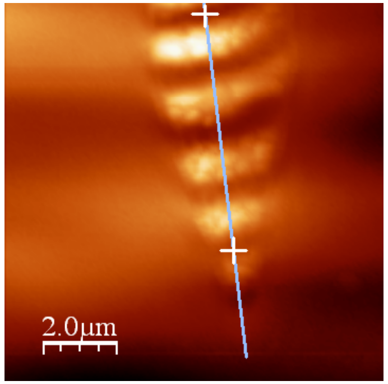
Pol orthogonal to the grating (negligible SPP coupling)

EXAMPLES OF SPPs IMAGED BY SNOM II



Interference between forward propagating and backward reflected SPPs observed: the SPP wavelength $\lambda_{SPP} = 2\pi/\beta$ agrees with expectations





- SPPs are duly launched in the "tapered finger"
- Propagation length and SPP wavelength are in agreement with expactions
- E.m. energy (in the near-field) is found at the taper end

SPPs in lithographed gold films are an efficient method for guiding e.m. radiation (and concentrating it at the taper end) in devices with a sub-wavelength size, at least in the vertical direction

Interfacing macro and nanoworlds is feasible!

CONCLUSIONS

- ✓ Metals, materials very much diffused in optics for conventional purposes (e.g., mirrors, diffraction gratings) can support special excitation modes
- ✓ Surface Plasmon Polaritons are a mixed state of radiation and charge density oscillations which can be interpreted as longitudinal e.m. waves
- ✓ Special features pertain to such longitudinal wave, such as the evanescent character of the field in the vertical direction, that leads to strong confinement of e.m. energy in sub-wavelength size scales
- ✓ SPPs are at the basis of an extremely sensitive spectroscopy
- ✓ SPPs can realize a kind of interface between the macro (conventional propagating waves) and the nano worlds

That's not all, folks!
We will see the unexpected properties of charge oscillations in localized systems, that is in nanoparticles (next lecture)!

FURTHER READING

For a complete textbook on plasmonics:

S.A. Maier, Plasmonics: Fundamentals and Applications, Springer, New York (2007).

For a solid and well-established textbook on the same topic (without much applications!):

H. Raether, Surface Plasmons, Springer-Verlag, Berlin Heidelberg (1988).
Brandon, W.D. Kaplan, Microstructural Characterization of Materials, Wiley, New York (1999).

For a useful and comprhensive analysis, Maier's inspired:

O. Benson, Uni Berlin, Chapter 7 of his Nanophotonics lectures [freely available at https://www.physik.hu-berlin.de/de/nano/lehre/Gastvorlesung%20Wien/plasmonics]

For comprehensive reviews on surface plasmon nanosensors (including also localized resonances):

J. Homola, et al., Sensors and Actuators B 54, 3 (1999).
H.H. Nguyen, et al., Sensors 15, 10481 (2015) https://dx.doi.org/10.3390%2Fs150510481