Surface Plasmon Resonance. Magneto-optical enhancement and other possibilities

Applied Science Department

The College of William and Mary

Plasmonics

Recently surface plasmons have attracted significant attention for a variety of exciting applications (e.g. metamaterials, “cloaking”, etc.)

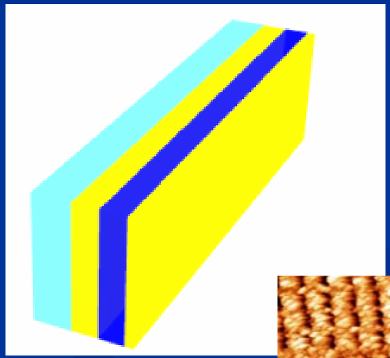
$$k_{SP}=k_0\sqrt{\frac{\varepsilon_d\varepsilon_m}{\varepsilon_d+\varepsilon_m}}$$

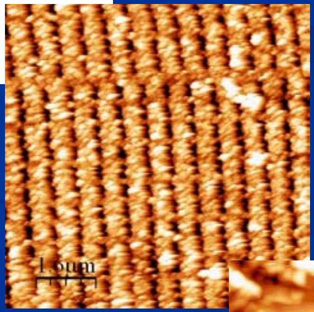
May 2008 - Surface-Plasmon circuitry

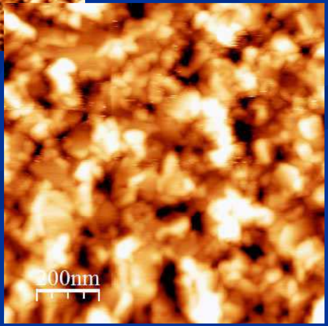
T. W. Ebbesen, C. Genet, S. I. Bozhevolnyi

Outline

- Introduction: Surface Plasmon resonance based sensors
- Magneto-plasmonic sensors
- Au-Co-Au Trilayers
- Gratings
- Au-Co nanocomposites
- What is next?
- Conclusions

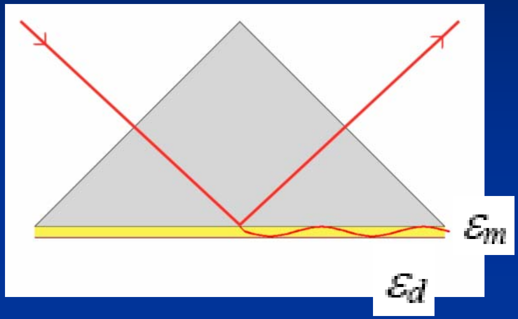






1. Surface plasmon resonance for biosensing

Surface Plasmon Resonance

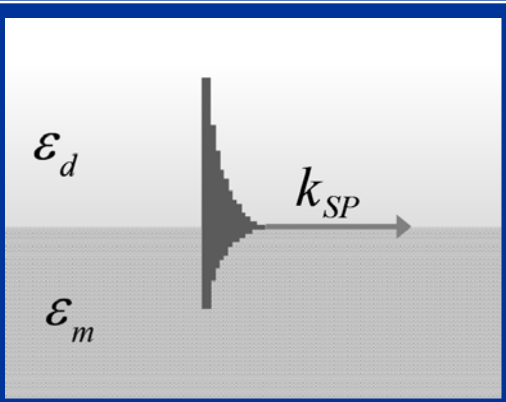


When light strikes a conducting thin film it is possible to excite a surface plasmon polariton i.e. charge oscillations in the metal that lead to evanescent surface electromagnetic waves propagating along a metal/dielectric interface.

For the surface plasmon resonance to be excited, the incident light wave vector must match the surface plasmon resonance momentum. This is possible when:

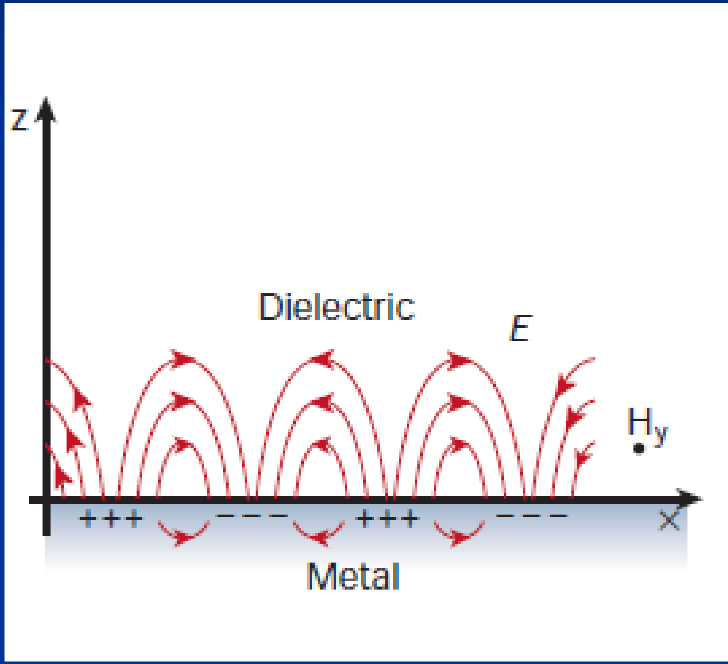
$$\mathrm{Re}[\varepsilon_m] < 0$$

$$\mathrm{Re}[\varepsilon_d] < -\mathrm{Re}[\varepsilon_m]$$

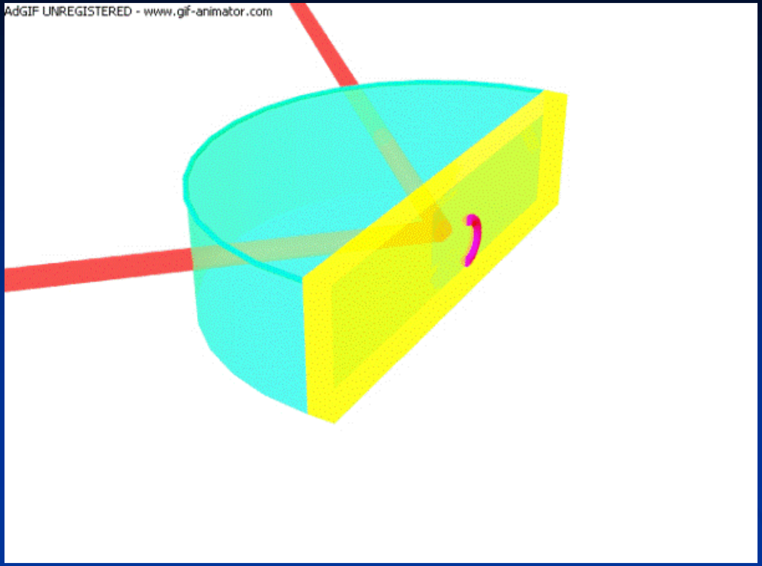


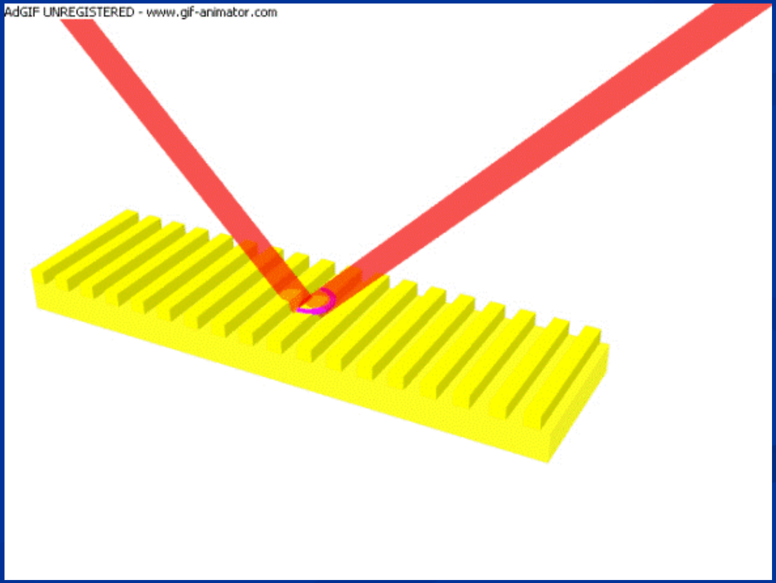
The surface plasmon resonance is highly confined at the interface, and therefore is very sensitive to the dielectric optical properties.

How can SPR be excited?



$$\hbar k_{SP} > \hbar k_0$$



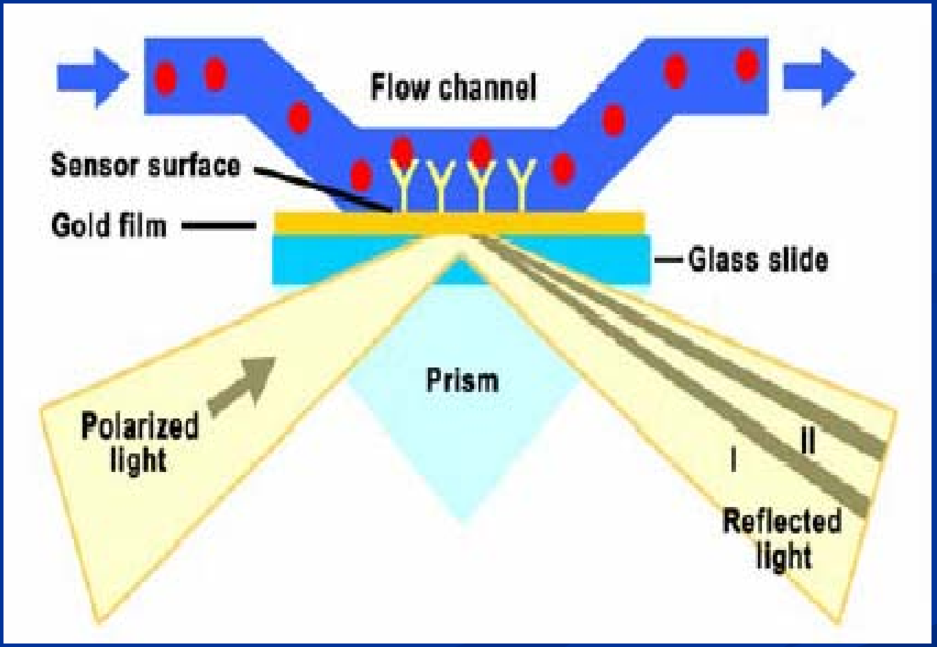


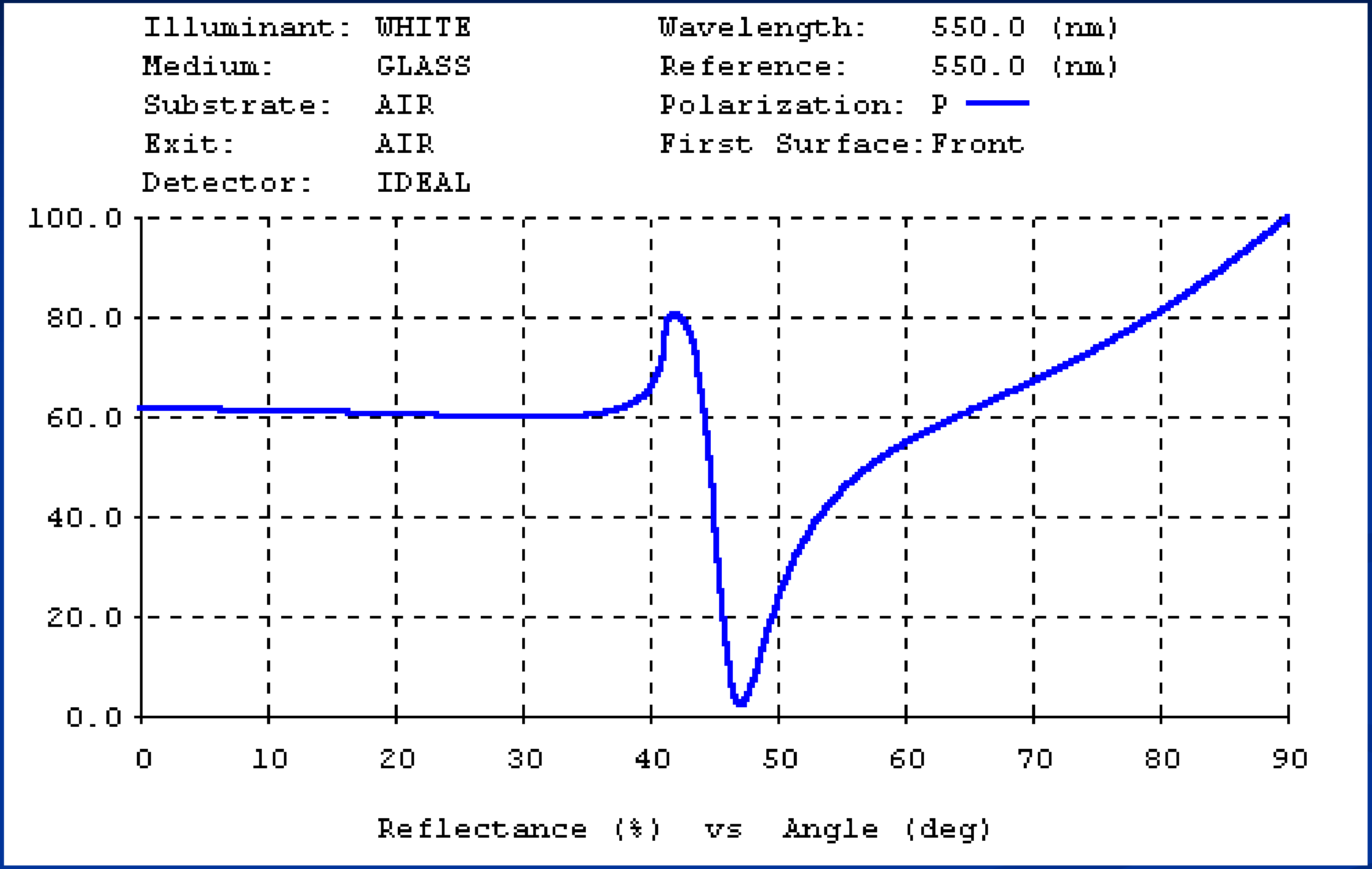
Application: How is SPR used in bio-sensing?

- A glass slide with a thin gold coating is chemically modified to be able to bind to specific bio-agents. The slide is mounted onto a prism.

- Light passes through the prism and slide, reflects off the gold and passes back through the prism to a detector

- Changes in reflectivity versus angle or wavelength give a signal that is proportional to the volume of bio-agent bound near the Au surface.

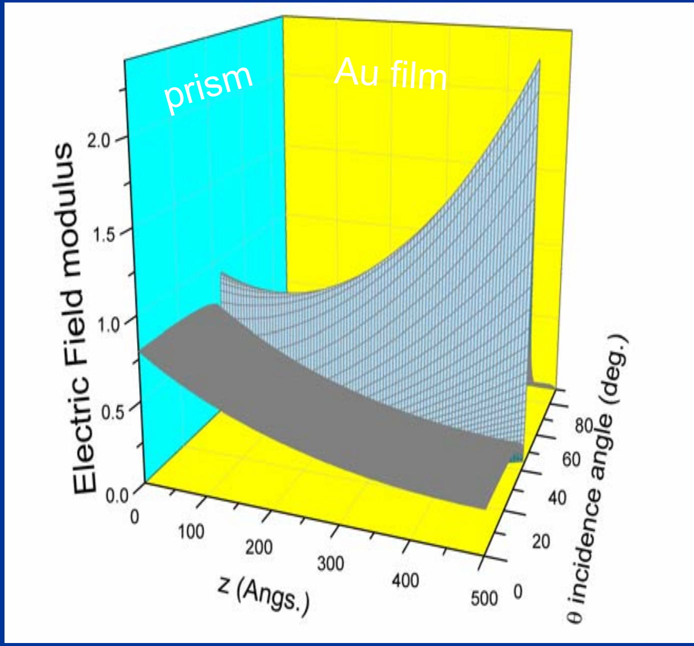


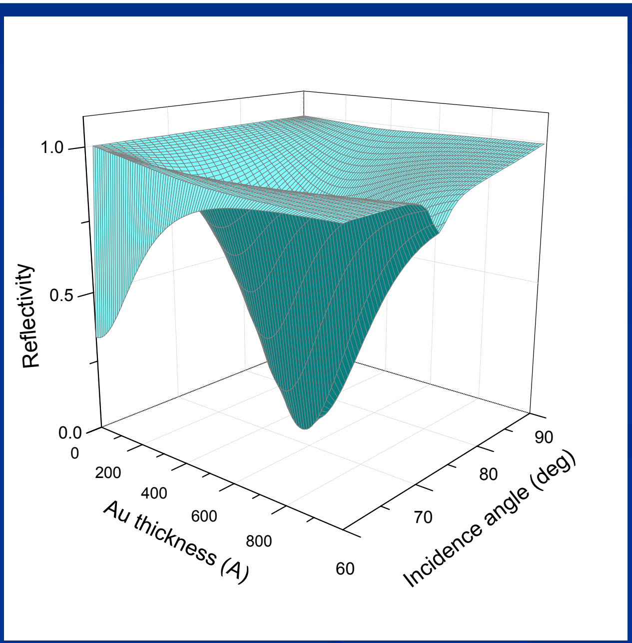

Illuminant: WHITE
Medium: GLASS
Substrate: AIR
Exit: AIR
Detector: IDEAL
Wavelength: 550.0 (nm)
Reference: 550.0 (nm)
Polarization: P
First Surface: Front
100.0
80.0
60.0
40.0
20.0
0.0
0
10
20
30
40
50
60
70
80
90
Reflectance (%) vs Angle (deg)

Fundamentals

When surface plasmon resonance is excited, it radiates light backwards.

The electromagnetic field is highly enhanced at the metal/ dielectric surface interface



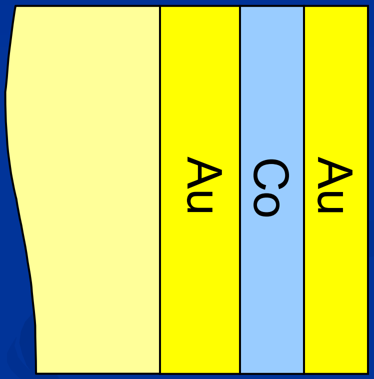


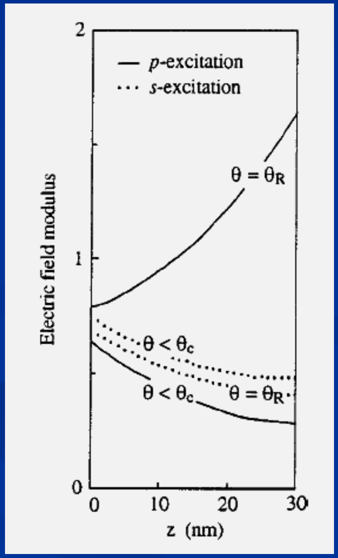
The Au films thickness can be optimized to achieve full extinction in the reflected beam-> this is the optimum excitation condition for surface plasmon resonance

2. Magneto-optical effects and surface plasmon resonance

Fundamentals

Since the electromagnetic field is strongly enhanced inside the Au film when the surface plasmon resonance is excited, the introduction of a magnetic film can cause <u>strong enhancement of its magneto-optical activity.</u>

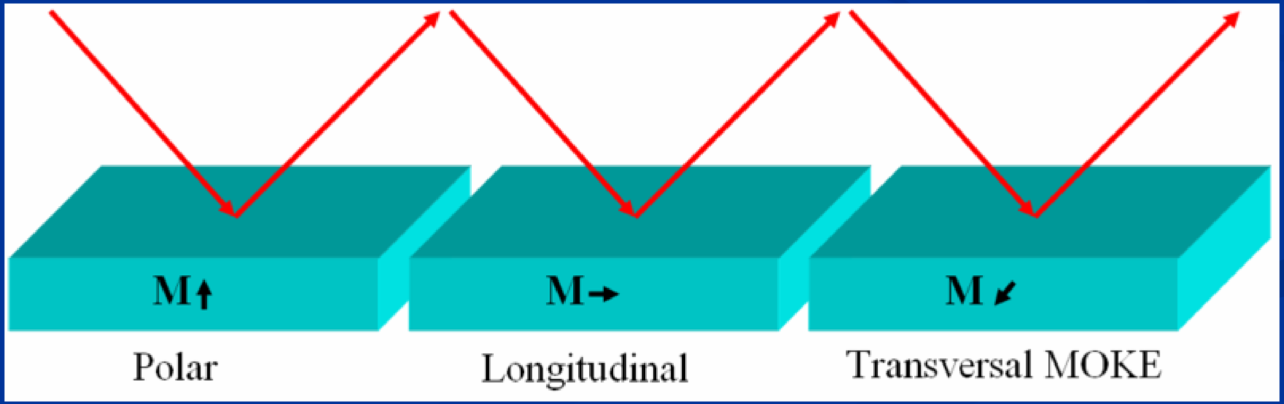




C. Hermann, PRB 63, 235422 (2001)

Magneto-optical Kerr effect

- The light that is reflected from a magnetized surface can change in both polarization and reflectivity.
- This results from the off-diagonal components of the dielectric tensor ε.
- MOKE can be further categorized by the direction of the magnetization vector with respect to the reflecting surface and the plane of incidence.



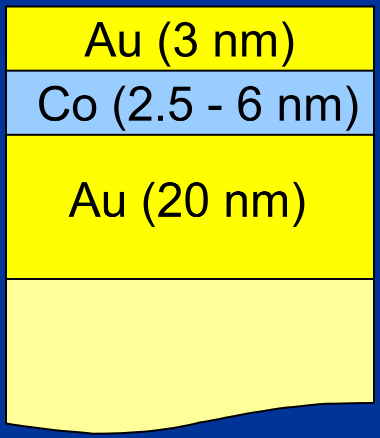
Transverse MOKE

- When the magnetization is perpendicular to the plane of incidence and parallel to the surface it is said to be in the *transverse* configuration.
- In this geometry, the MOKE effect results in a change in reflectivity that is proportional to the component of magnetization that is perpendicular to the plane of incidence and parallel to the surface.
- Further, the surface plasmon is also affected:

$$k_{\parallel} = k_{\parallel}^{0}\left[1 + \frac{2i}{\epsilon^2 - 1}\left(\frac{\epsilon}{1+\epsilon}\right)^{1/2}(q_0 d Q m_y)\right]$$

J. B. González-Díaz et al., PRB **76**, 153402 (2007).

System studied

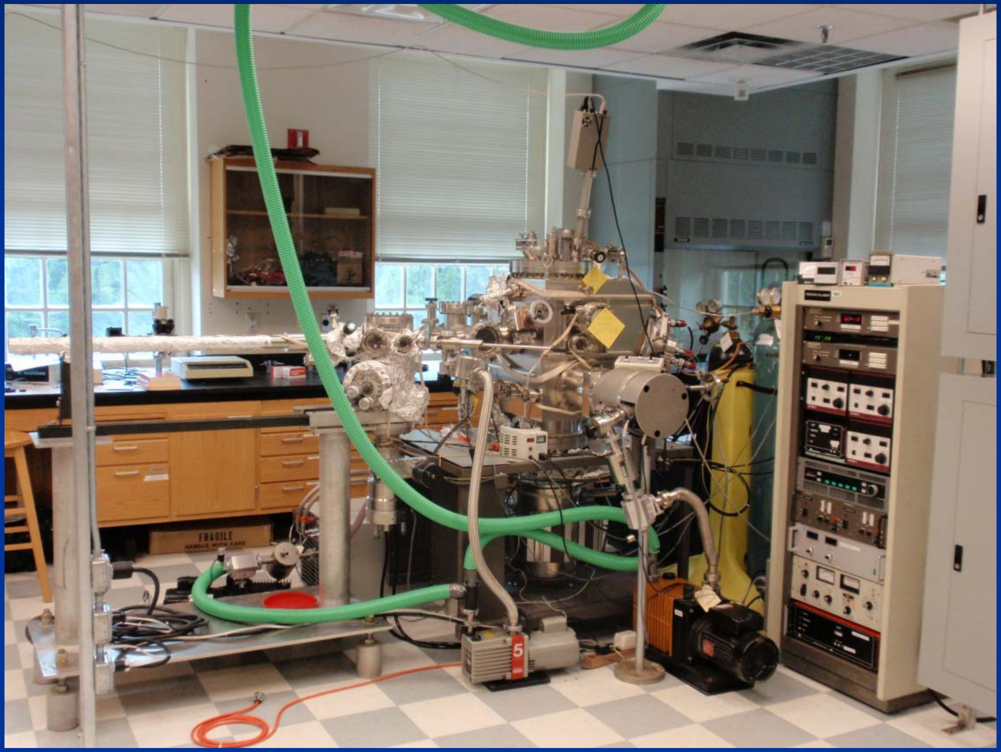


Au-Co-Au tri-layer samples were grown on glass with DC sputtering. Accurate control of the growth rate allowed precise control of the layers thickness. Au and Co thickness were designed to achieve:

- Optimum excitation of the surface plasmon resonance
- Maximum enhancement of the MO activity.

Preparation

Preparation: sputtering deposition



Sputtering System

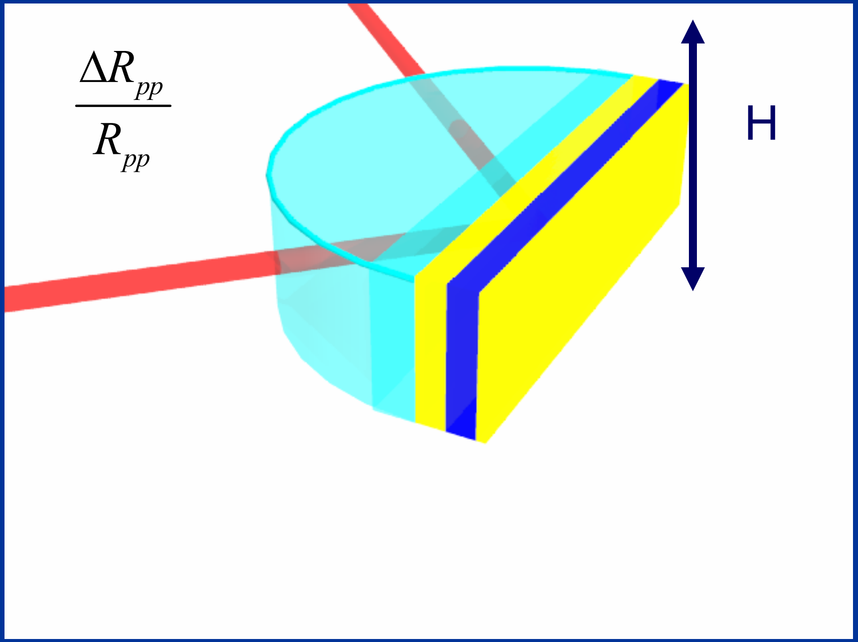
- Base pressure 10^{-9} Torr (UHV).
- Rheed, Quadrupole in-situ.
- Substrate temperature:RT-700°C.
- 6 magnetron sputtering guns
- Gas: Ar, etc...

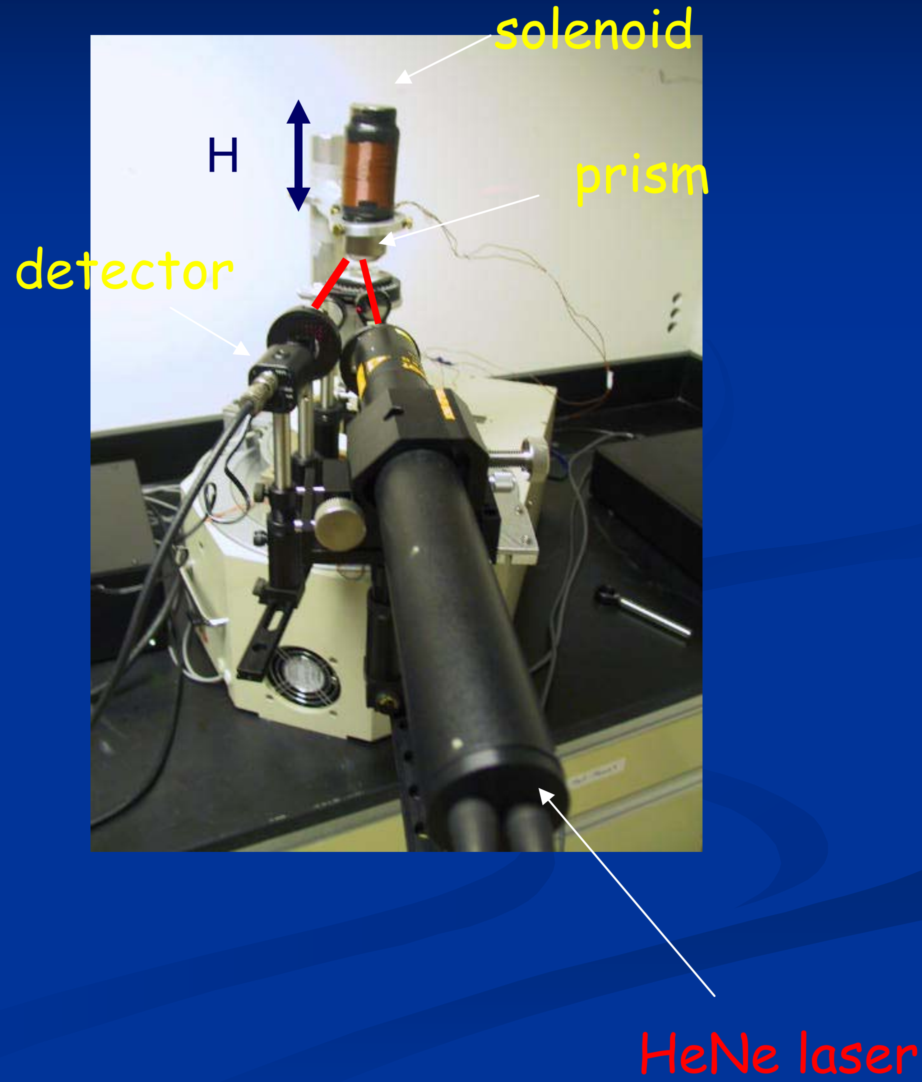
Deposition rates ($P_{Ar}=5.10^{-3}$ Torr)

- Au→0.32 Å/s
- Co→0.066 Å/s
- Cr→0.13 Å/s
- Ni→0.12 Å/s
- Ag→1.03 Å/s

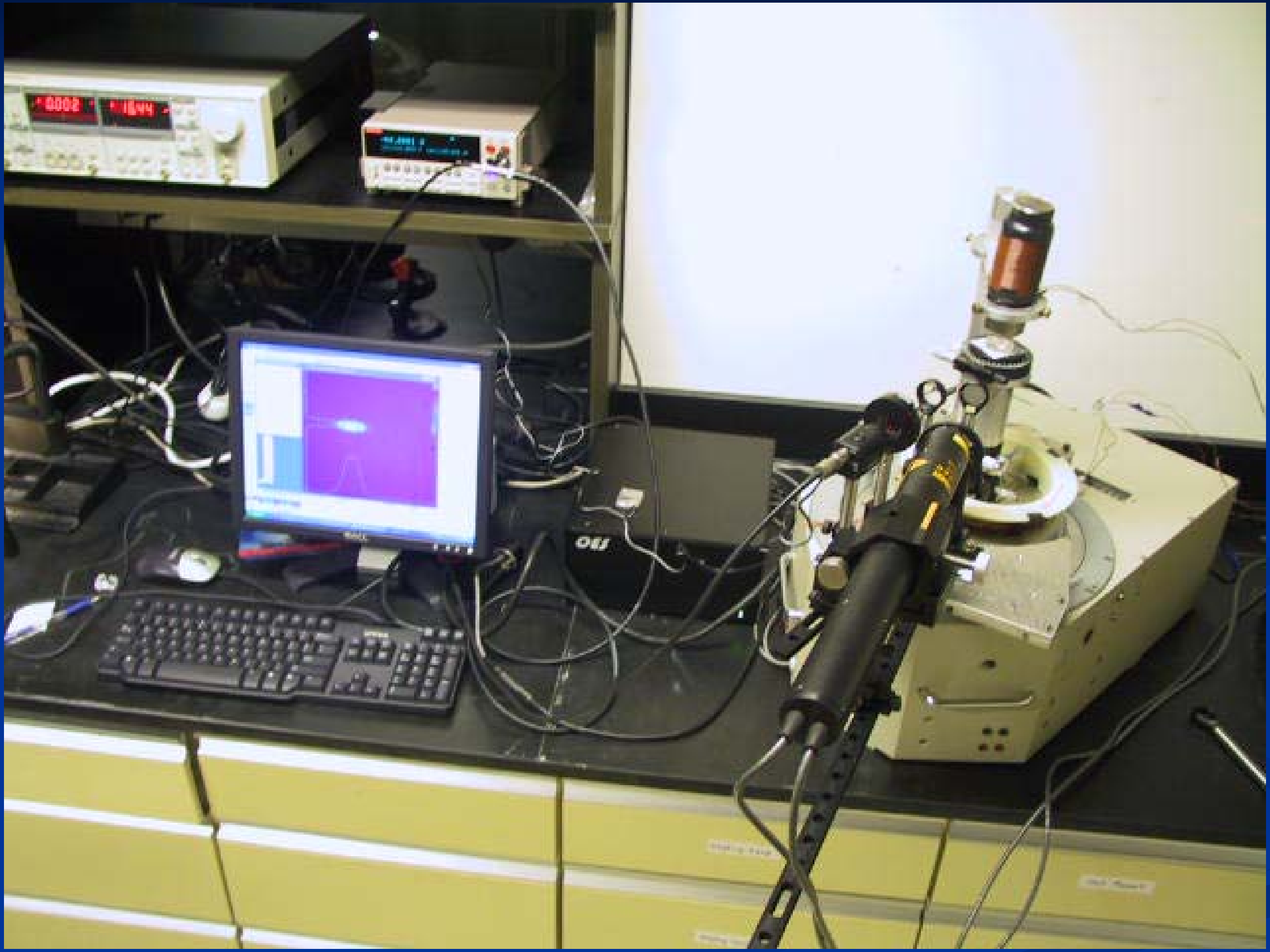
High purity and thickness control!

Characterization

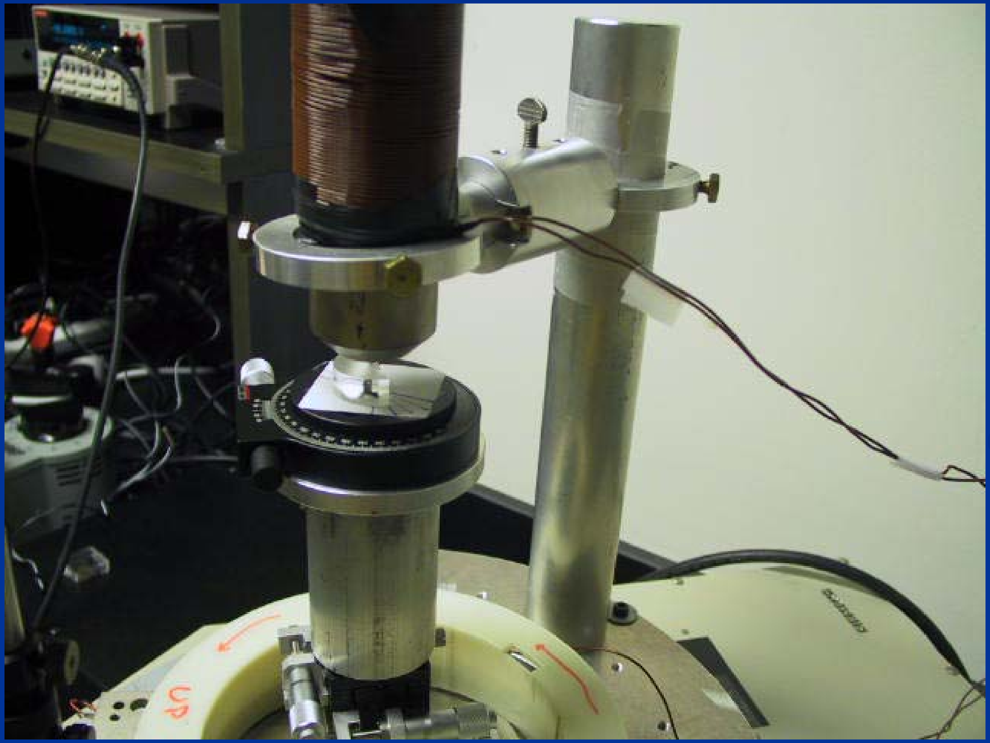


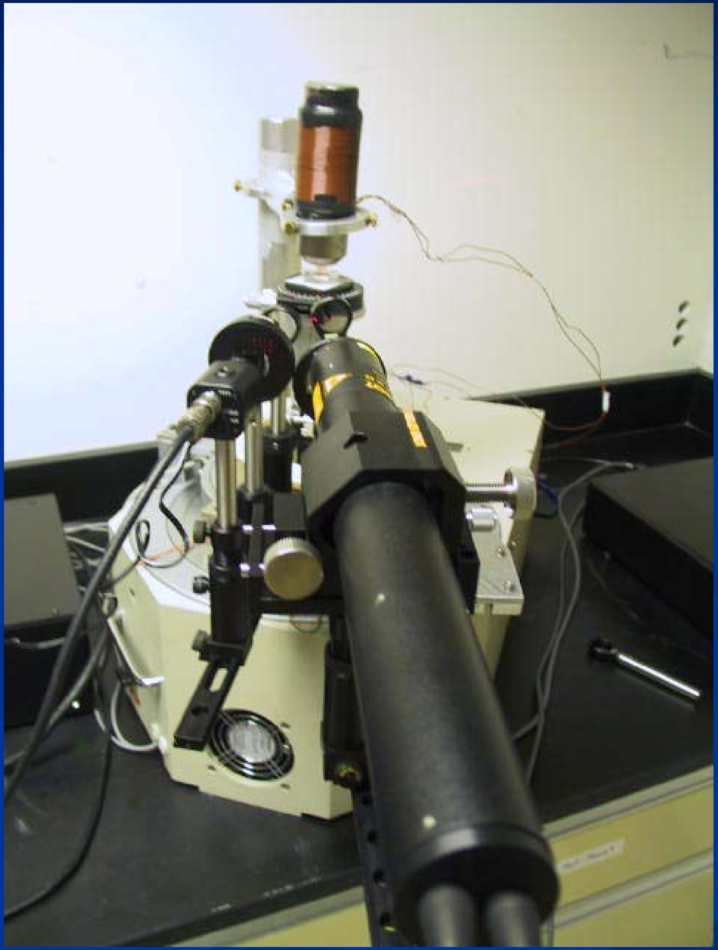


Custom SPR station



Custom SPR station

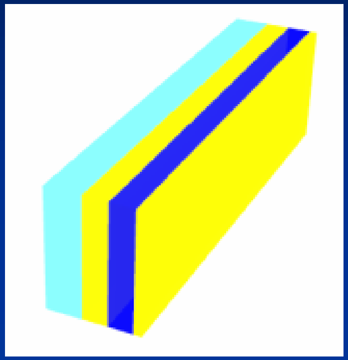


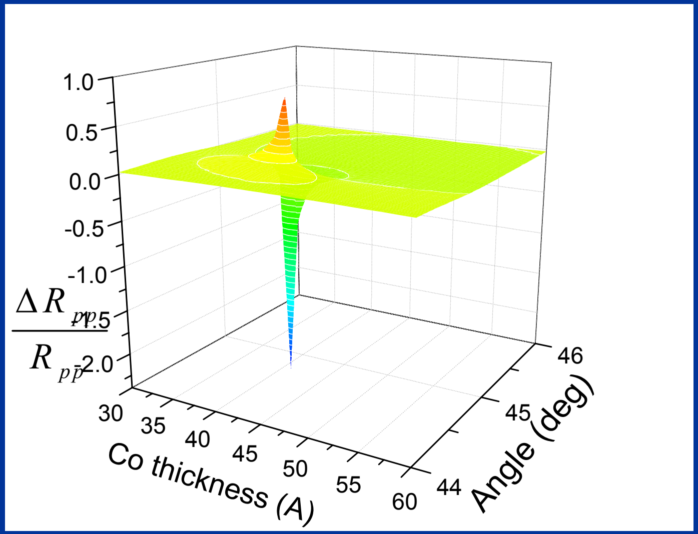


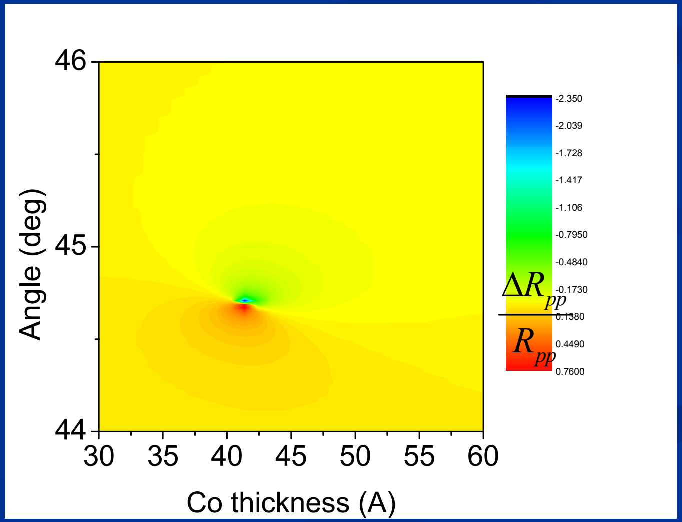
Au-Co-Au

Au (3 nm)

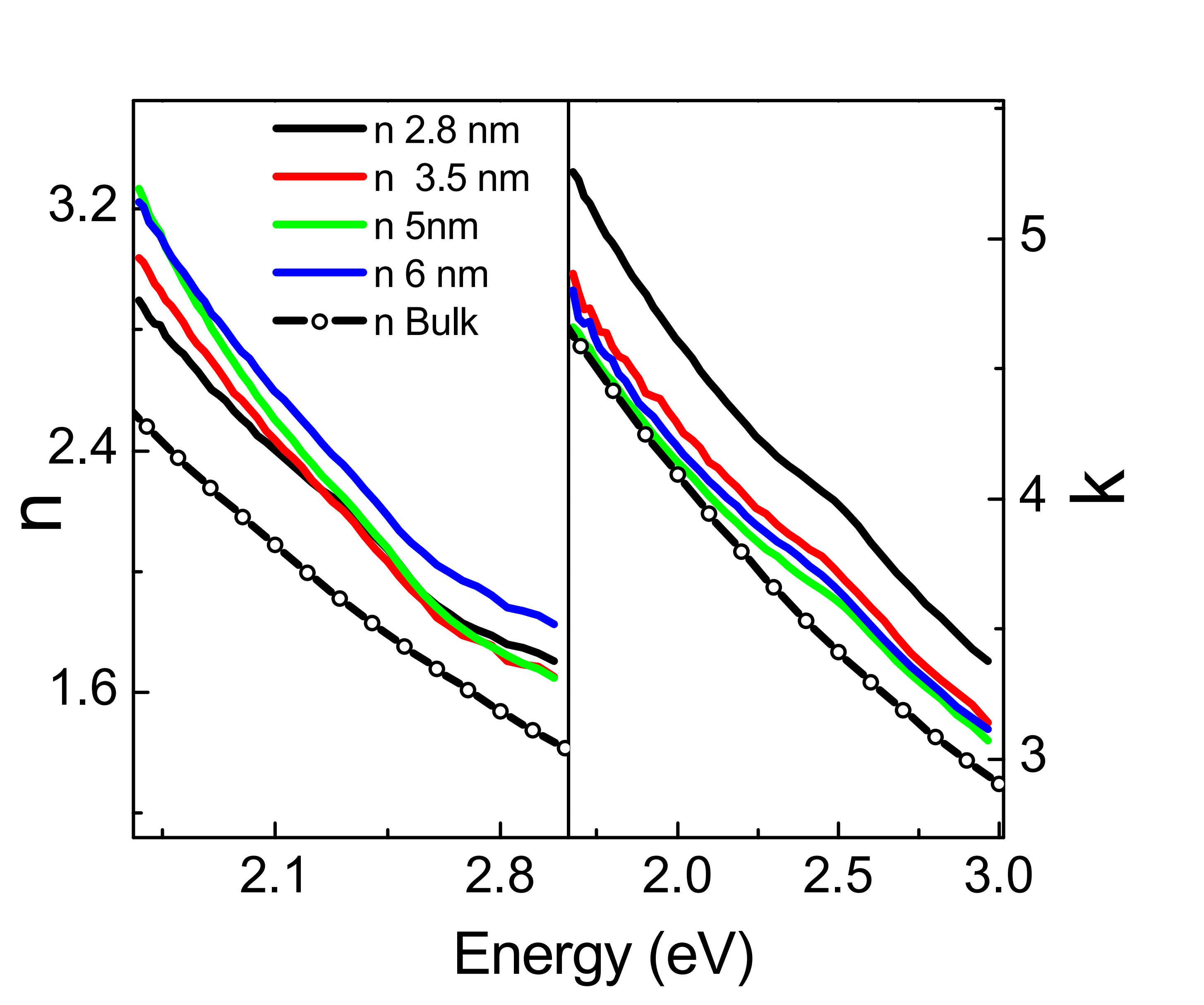
Co (2-10 nm)





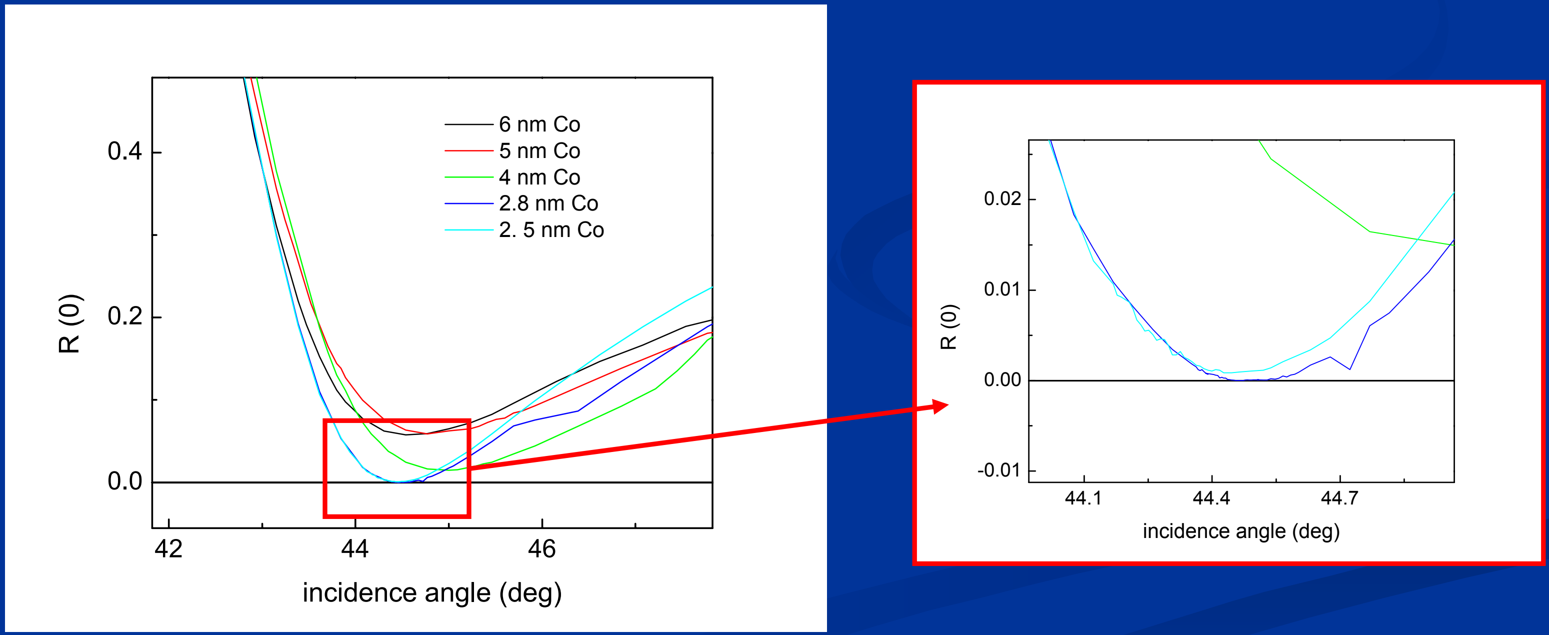


Deviation of the optical constants from bulk values



Results (I)

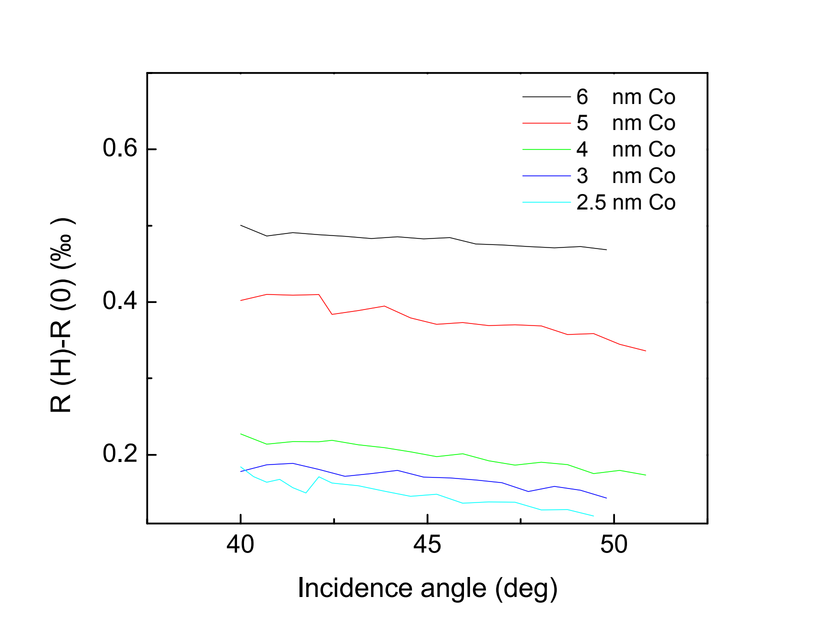
The thickness of all the metallic layers was designed to achieve full extinction of the reflected intensity.



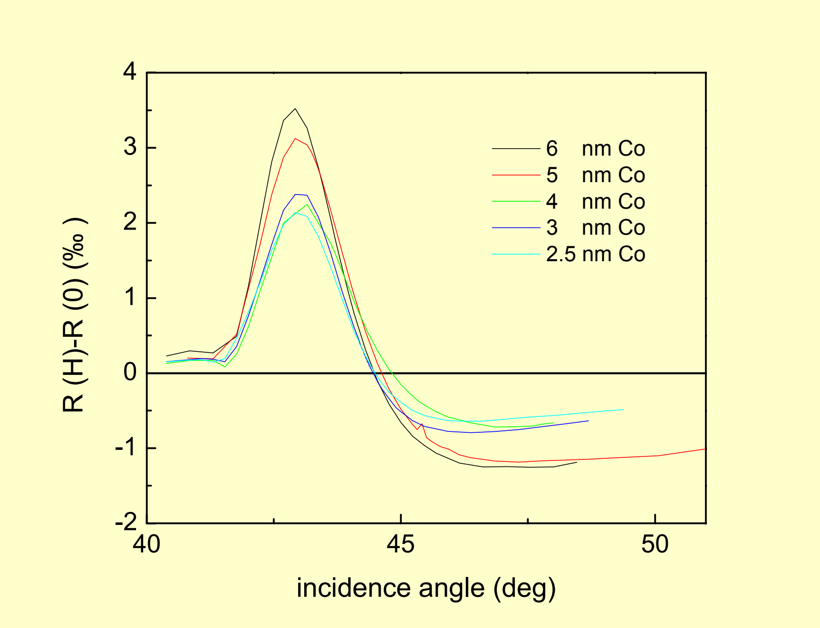
Results (II)

Transverse Kerr magneto-optical signal

With no prism (i.e. the Au surface plasmon is not excited)



With prism (plasmon excited)

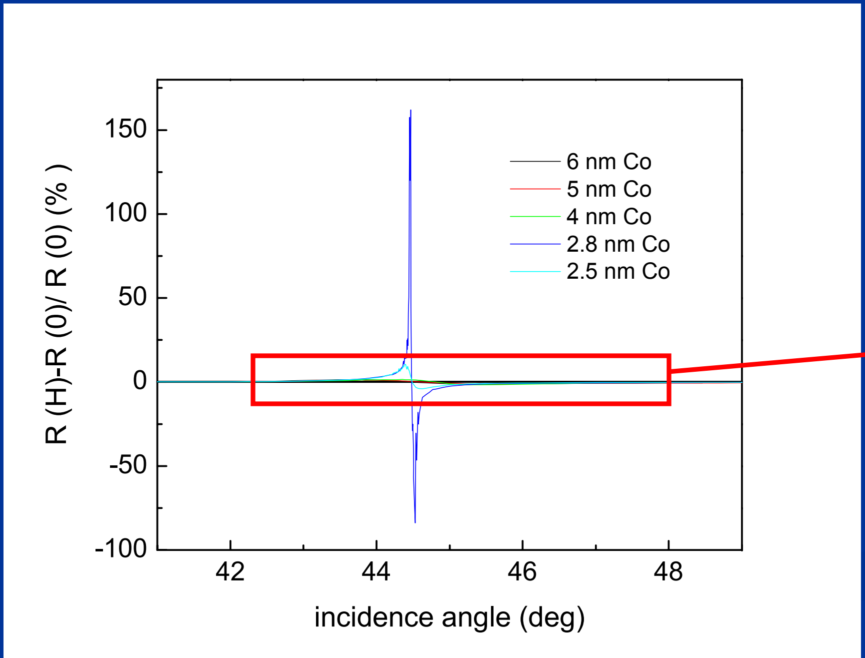


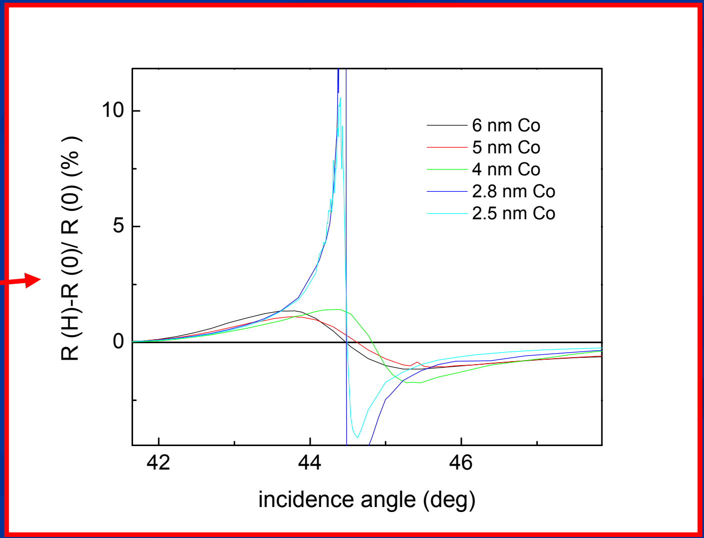
The measured signals are normalized with respect to the incident excitation. When the surface plasmon is excited we observe ~ one order magnitude enhancement in the transverse magneto-optical Kerr signal.

Results (III)

Combining the enhancement of the MO effect and the extinction of the reflected beam, a remarkable enhancement of the relative field-dependent variation of the reflectivity is obtained

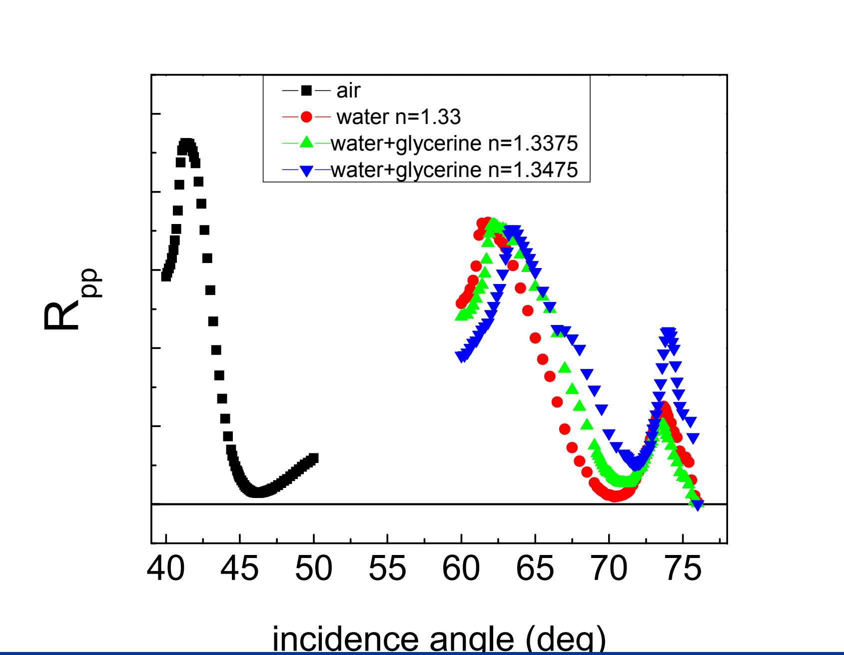
$$\frac{\Delta R_{pp}}{R_{pp}} = \frac{R_{pp}(M_s) - R_{pp}(0)}{R_{pp}(0)}$$

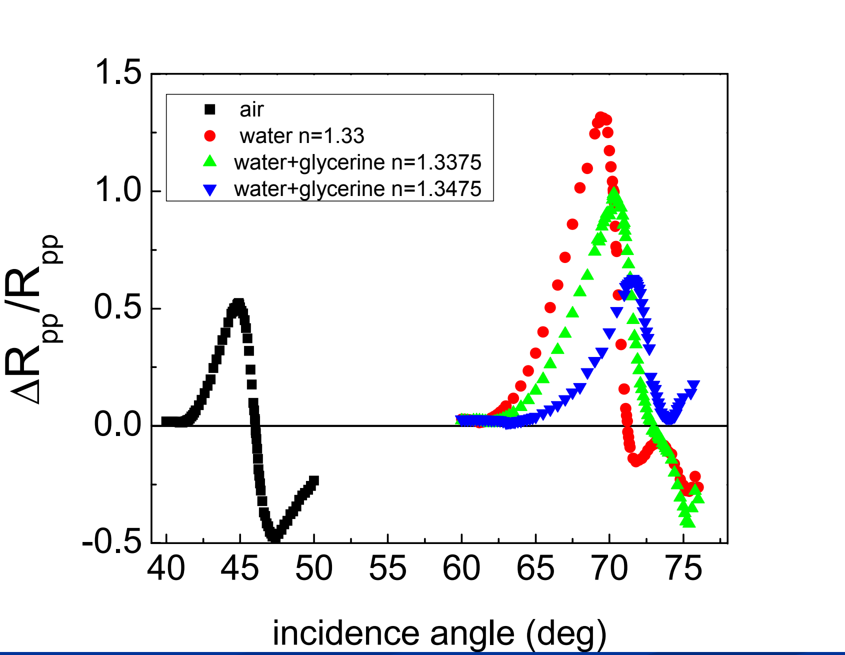




Measurements in water solutions

- Reflectivity (R)
- Field-dependent ΔR/R





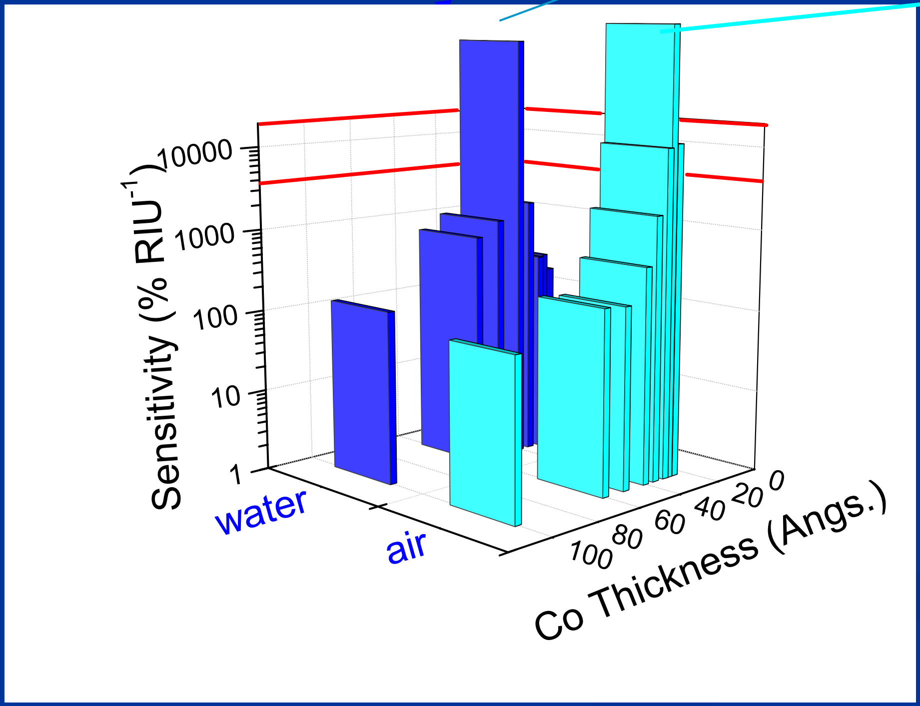
Angle shift

Sensitivity: Typical metric to compare sensors

$$Sensitivity = \frac{\partial\left(\frac{\Delta R_{pp}}{R_{pp}}\right)}{\partial n_d} = \% \cdot RIU^{-1}$$

170,800 % RIU^{-1} in water

280,000 % RIU^{-1} in air



MO-SPR (Cr-Co-Cr-Au) →19,100 % RIU^{-1}

B. Sepúlveda et al. Opt. Letters 31, 1085 (2006).

SPR →3,900 % RIU^{-1}

J. Homola et al. Sens. and Act. 54, 3 (1999).

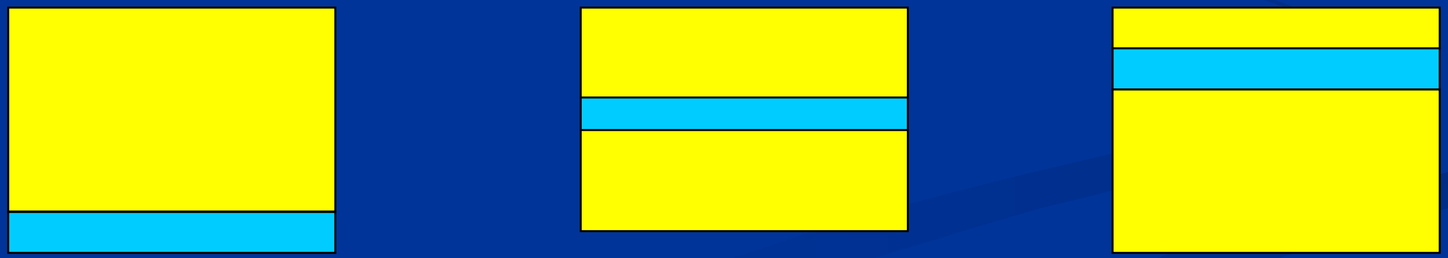
The Physics: Plasmon Excitation, Electric Field depth dependence and Magneto-optical enhancement

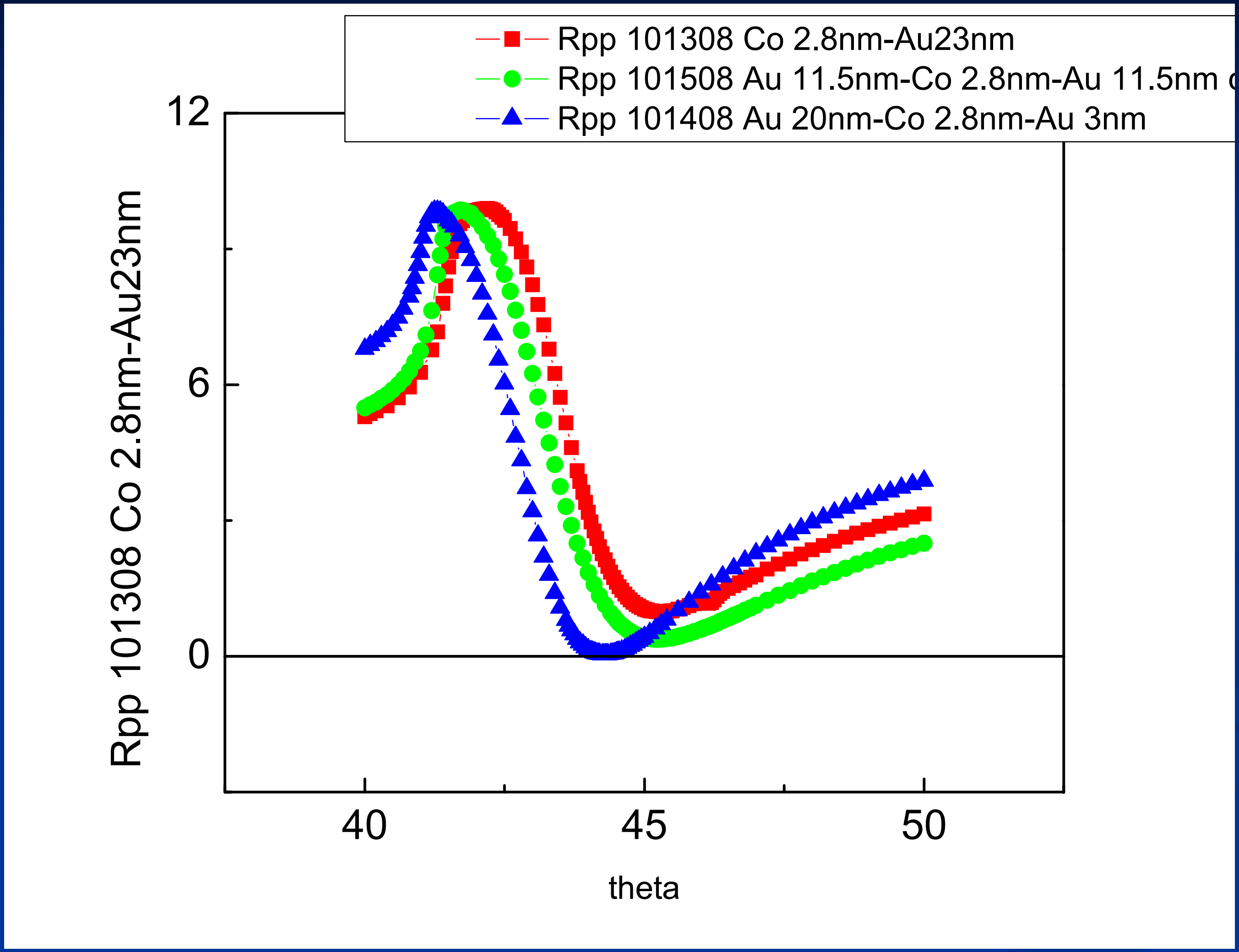
Grown 3 samples with the Co film placed in three different positions

Co (2.8 nm)-Au (23 nm)

Au(11.5 nm)-Co (2.8 nm)-Au (11.5 nm)

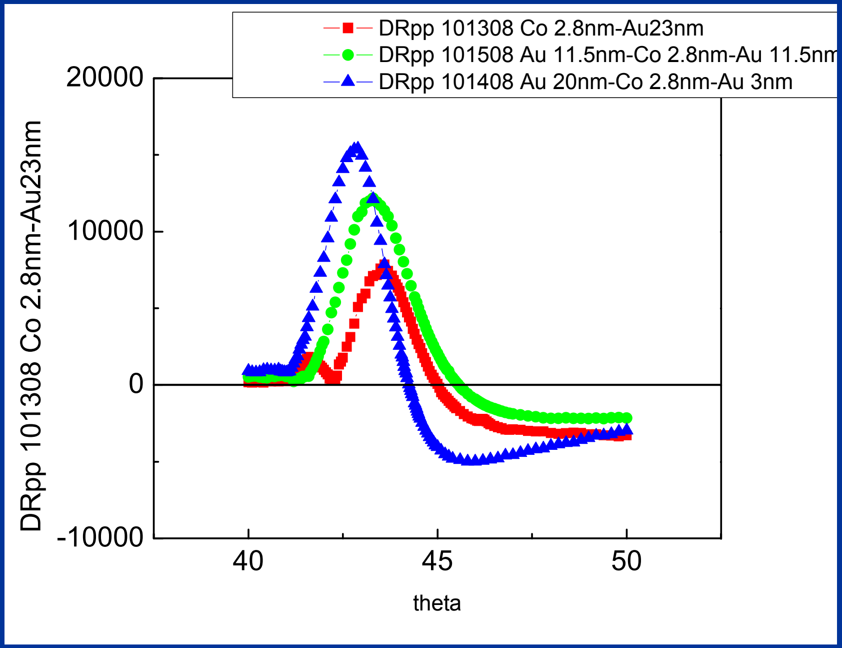
Au(20 nm)-Co (2.8 nm)-Au (3 nm)



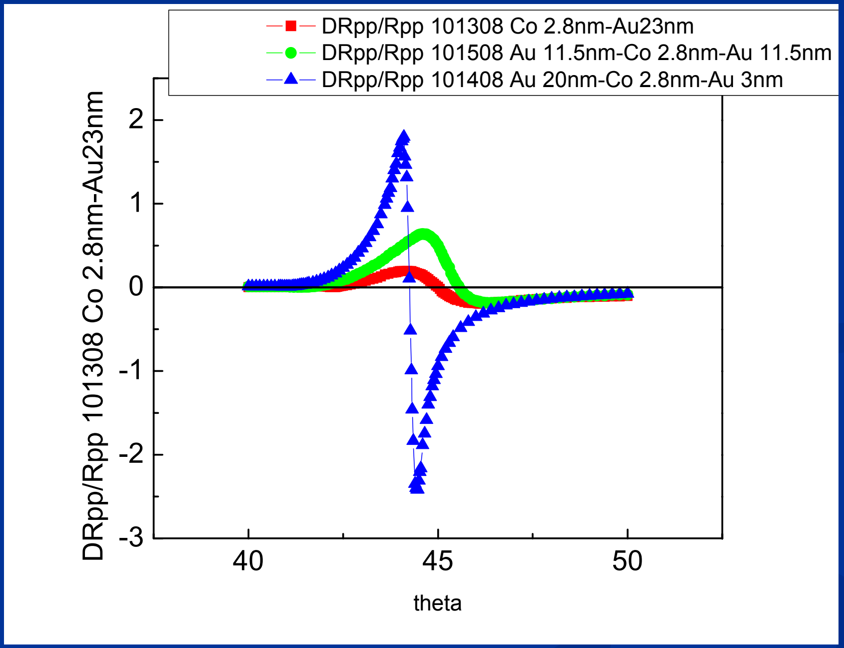


Reflectivity. We note that the position of the minimum changes because the conditions to excite the plasmon have changed.

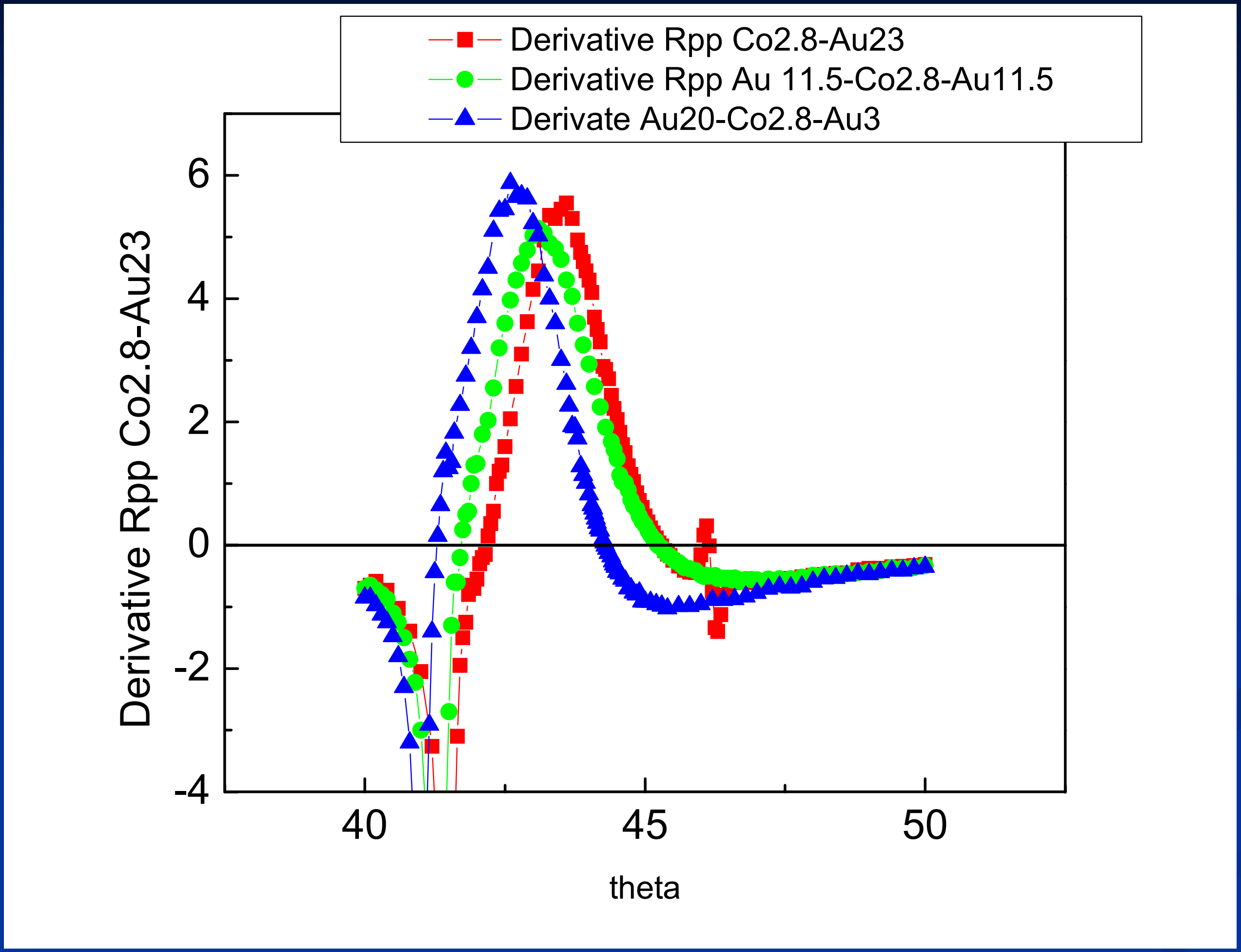
Experimental magneto-optical data



ΔR_{pp}

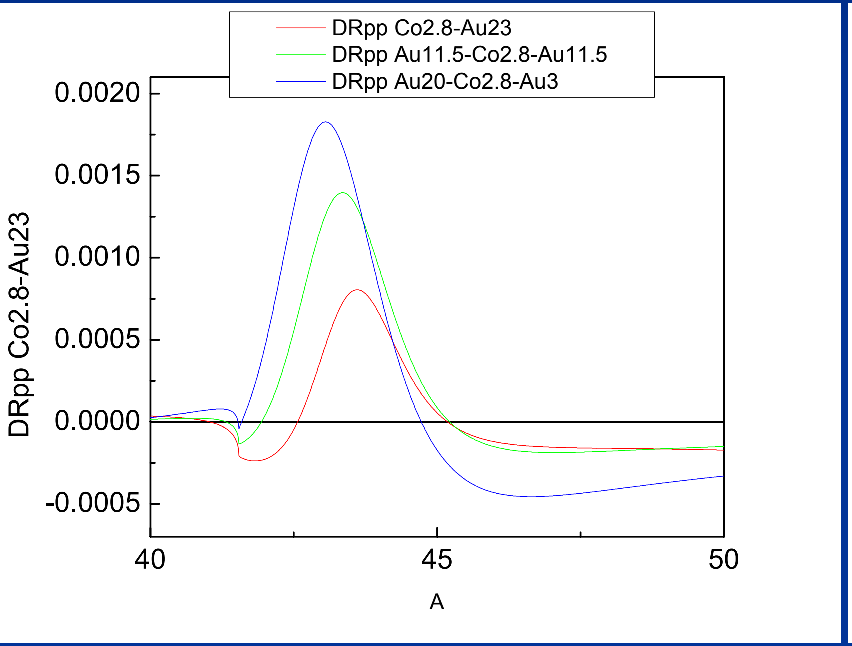


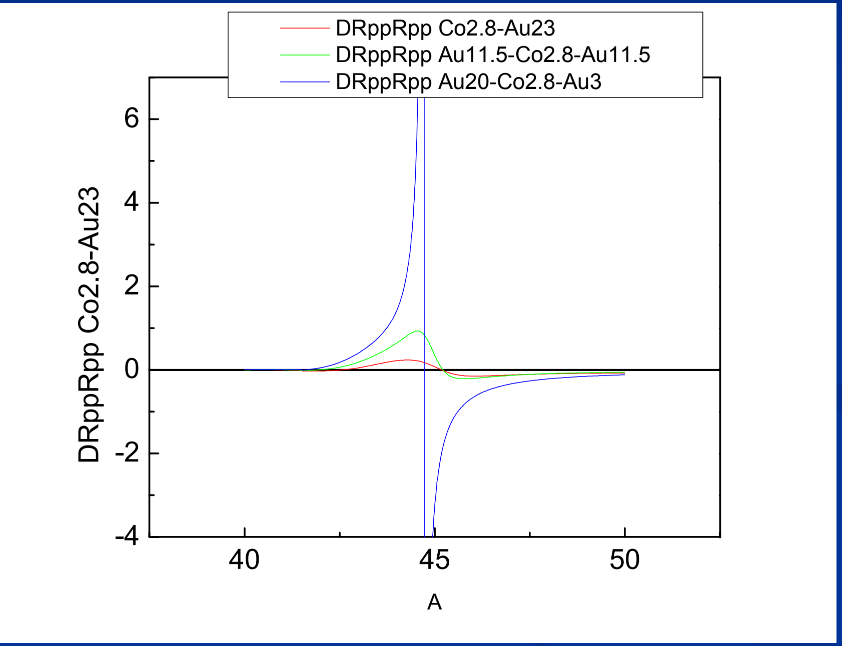
$\Delta R_{pp}/R_{pp}$



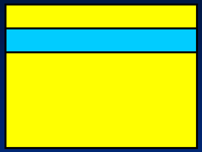
The derivative of R_{pp}: does not evolve in the same manner as the experimental ΔR_{pp} -> the changes observed in ΔR_{pp}, i.e. the magneto-optical response, are not related to modification of the plasmon excitation in the samples.

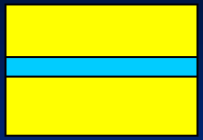
Simulations (transfer matrix formalism)

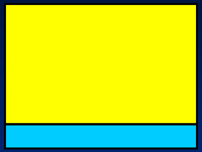


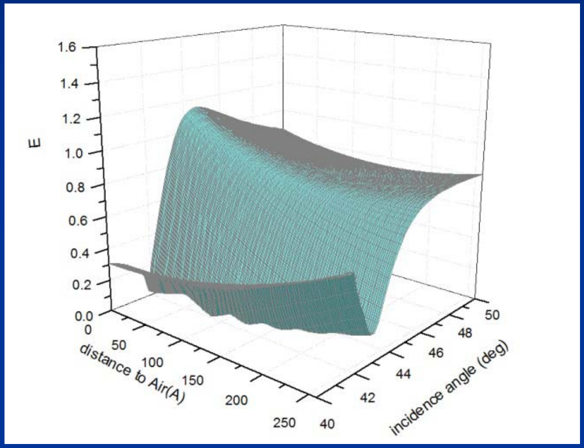


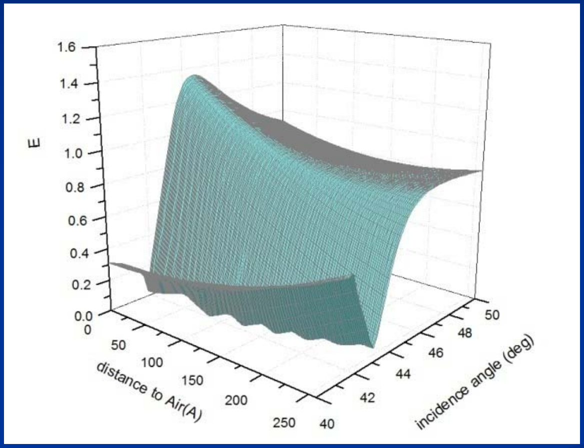
Electric Field

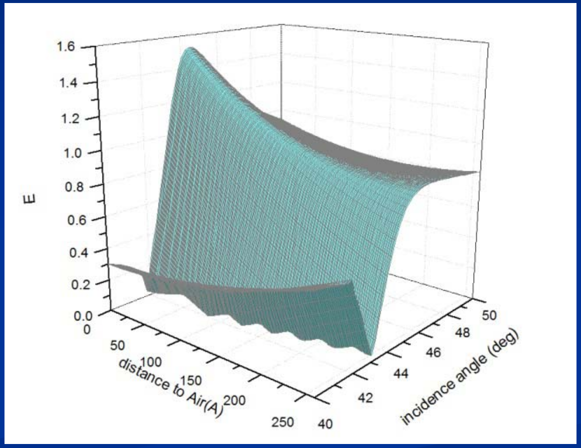


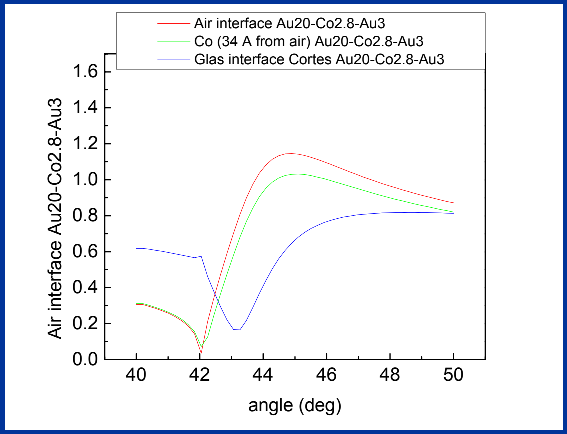


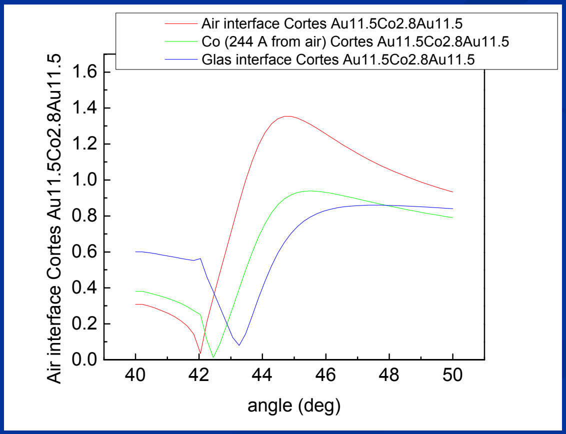


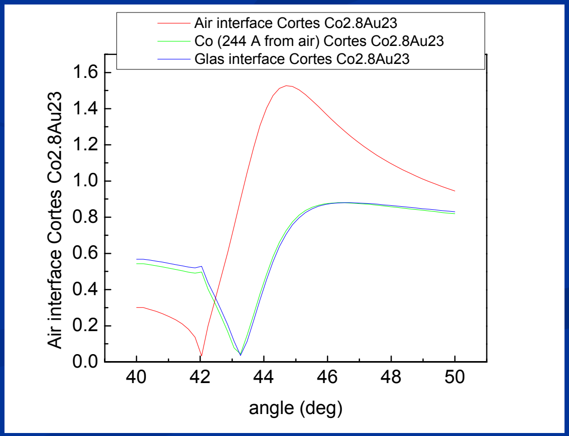




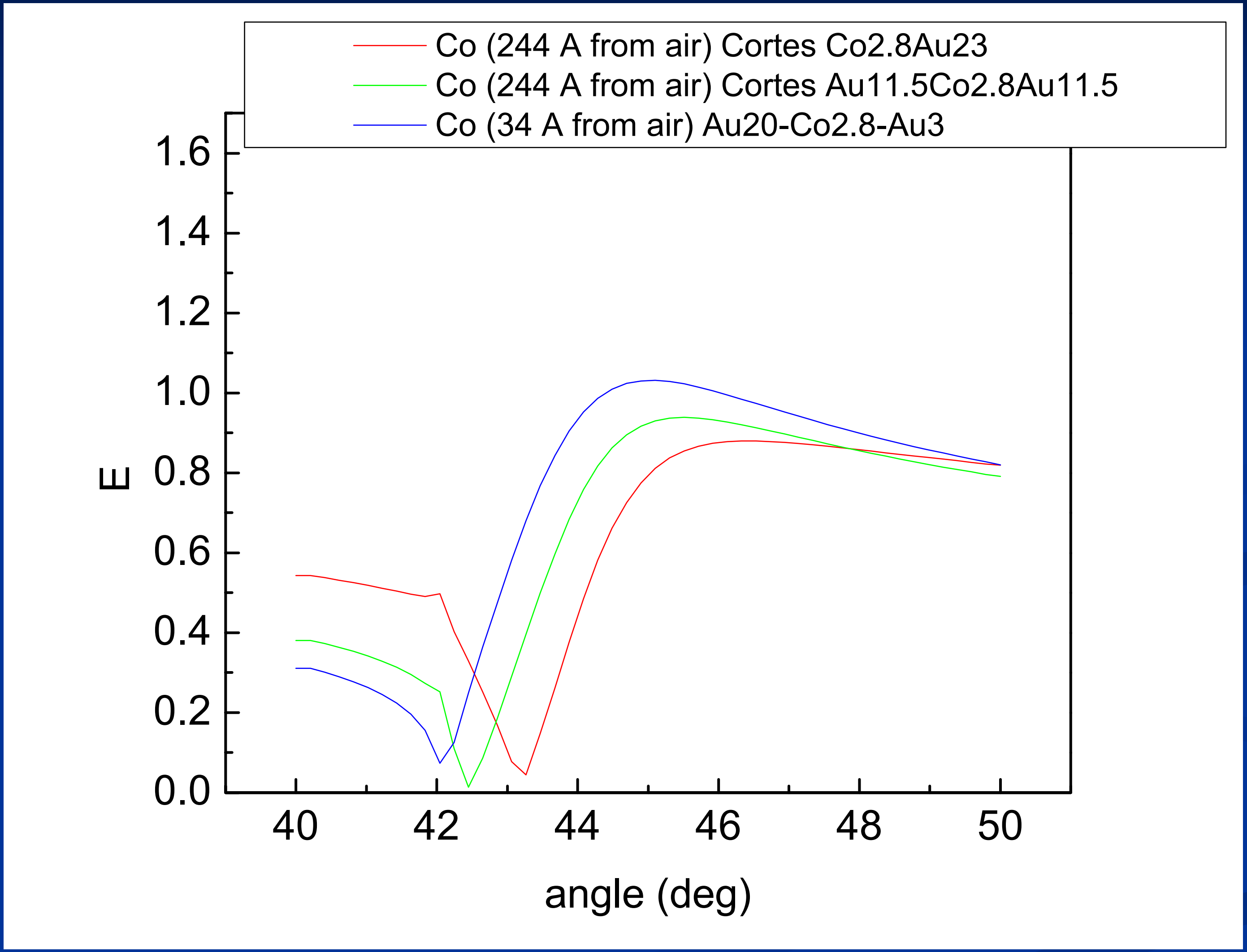






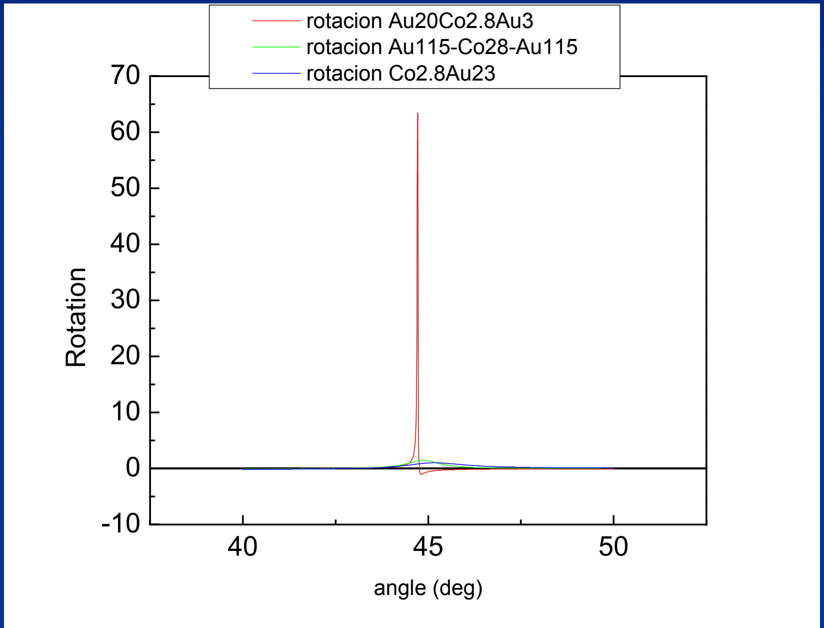


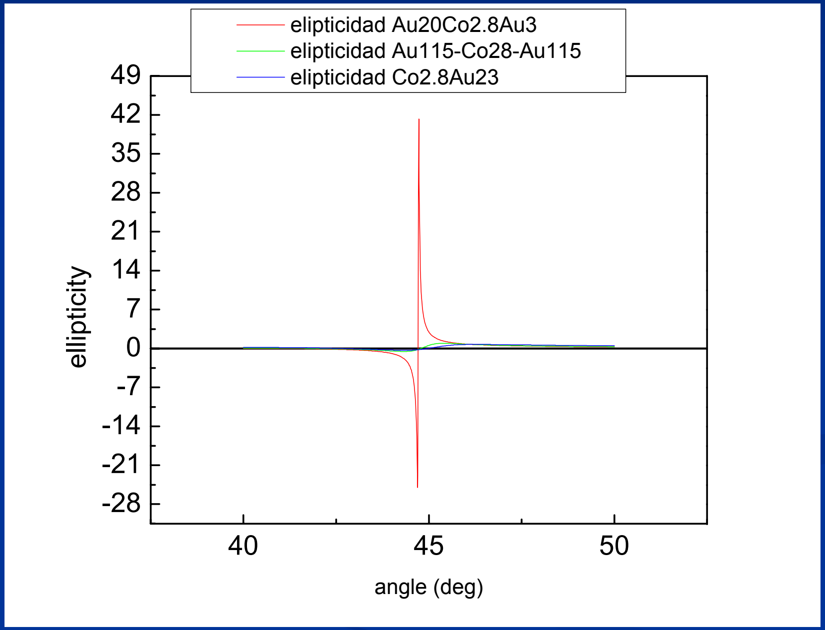
Electromagnetic field in the middle of the Co film in the 3 samples



Thus, the field enhancement due to SPP excitation enhances also the MOKE

Simulations polar

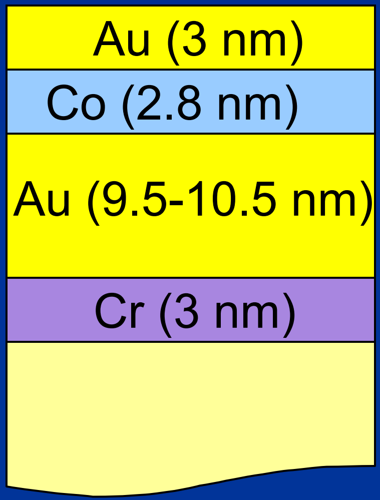




Our simulations also indicate dramatic enhancement of the polar Kerr rotation and ellipticity. We will investigate this experimentally.

Adhesion issues: Cr-Au-Co-Au

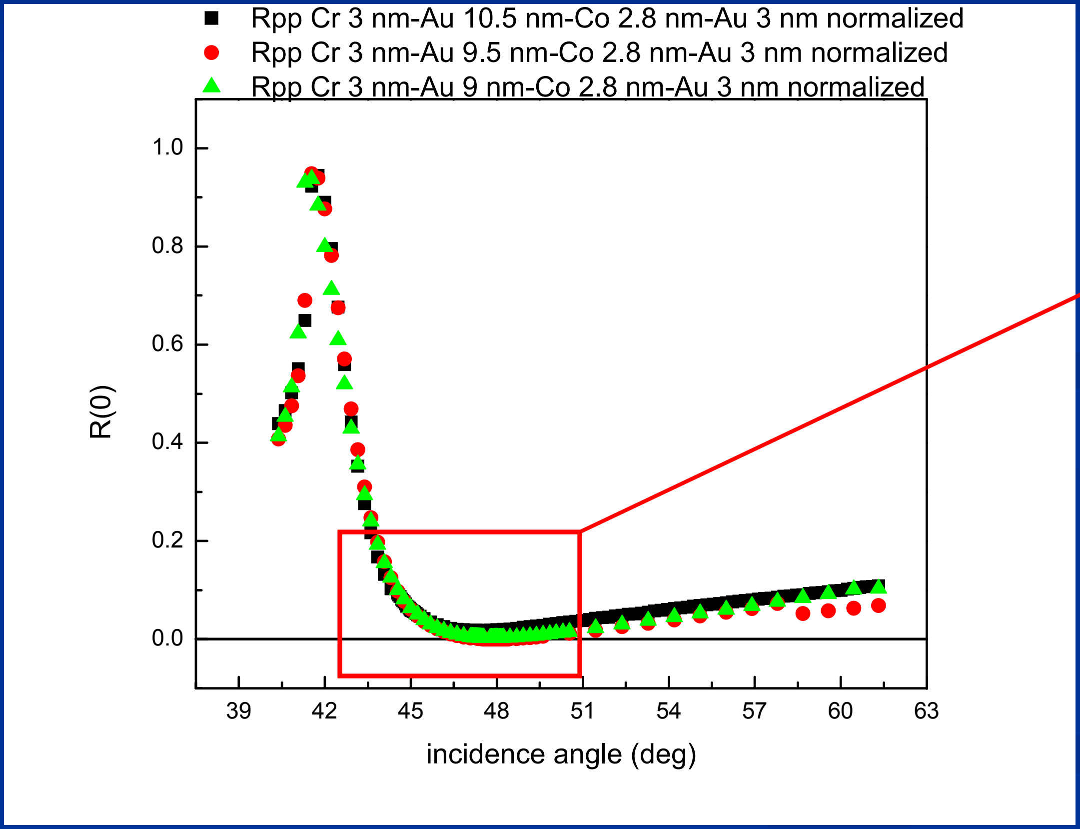
In order to explore the material for a possible bio-sensing application there are additional concerns.

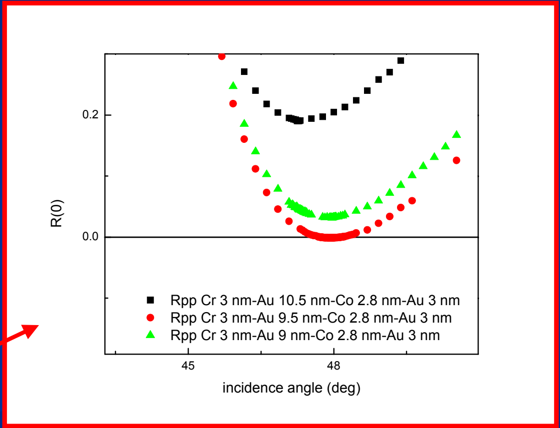


- Adhesion of Au on glass is poor. Tri-layers are degraded when exposed to a water flux.
- Cr has been extensively used to improve the adhesion of Au on glass, but it is a highly absorptive metal and therefore it broadens the surface plasmon resonance peak.
- At present time the common belief has been that the introduction of Cr layers decreases the sensitivity of these kind of sensors.
- We have demonstrated that this is not true.

Results: Cr-Au-Co-Au

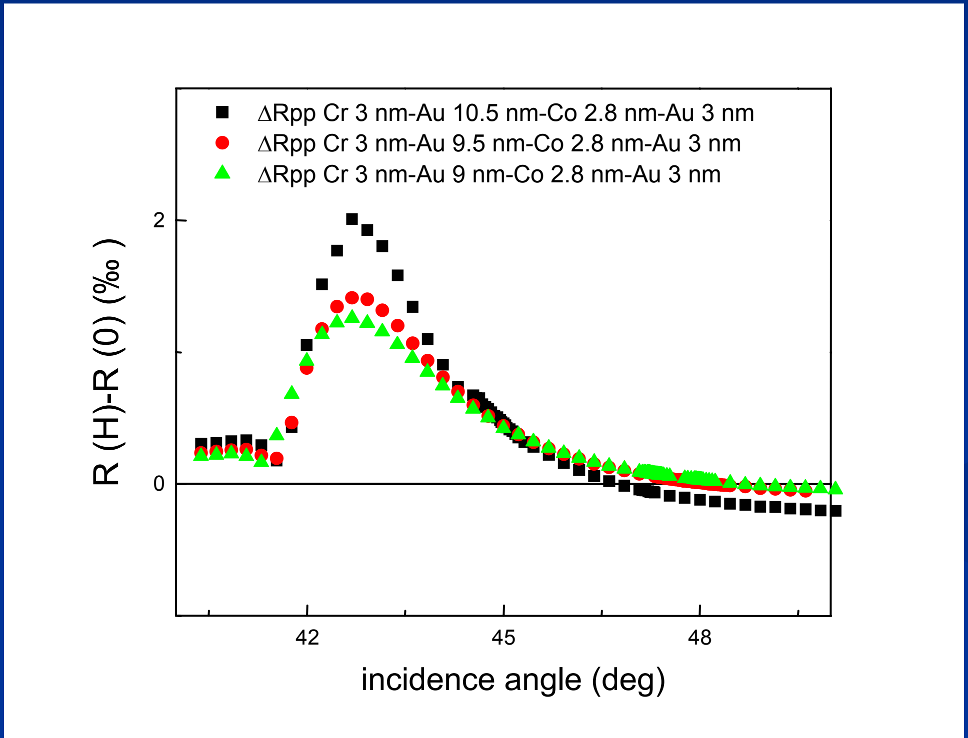
The thickness of the layers was once more designed to achieve the full extinction of the reflected intensity

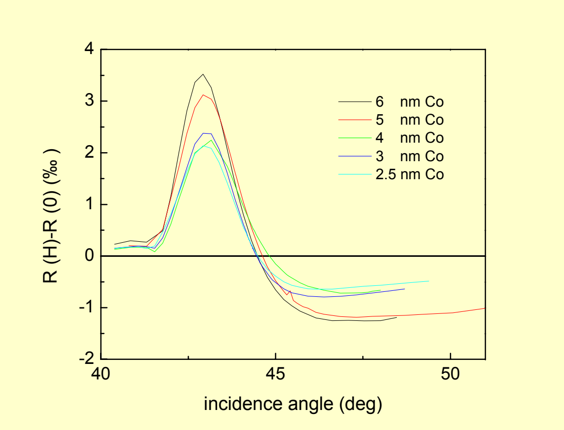




Results: Cr-Au-Co-Au

Transverse Kerr magneto-optical signal



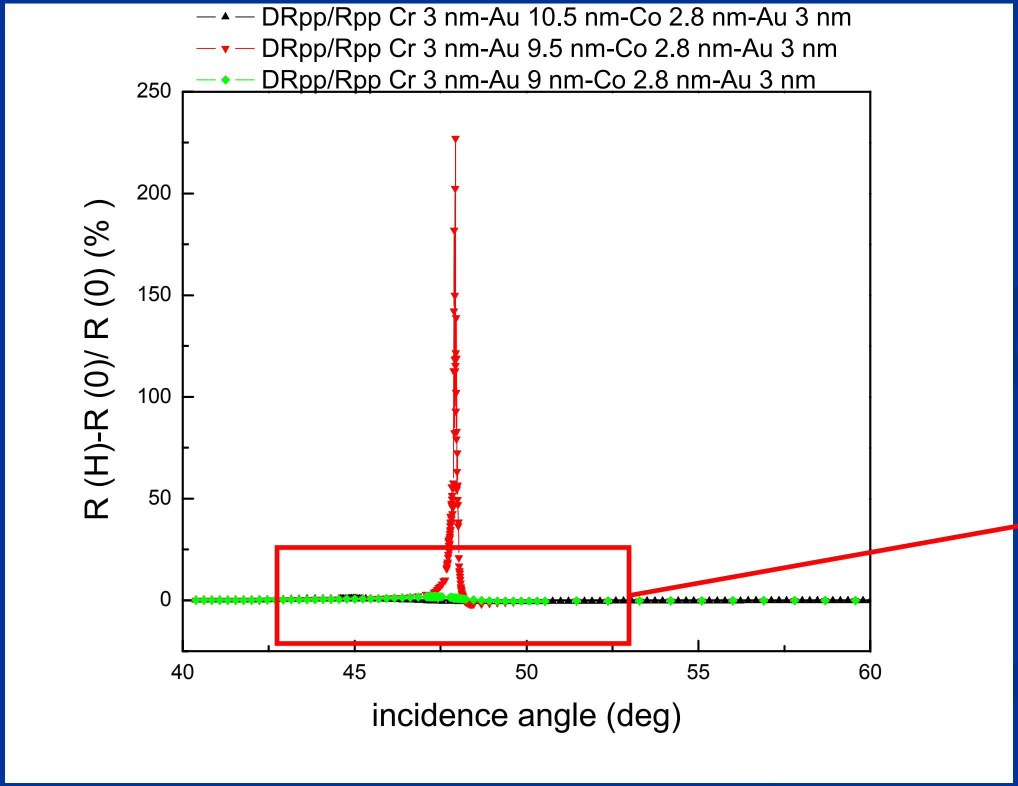


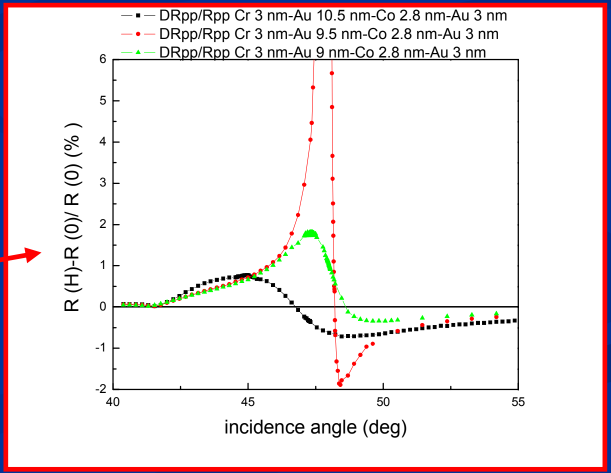
Recall transverse Kerr effect Without Cr buffer layer

- A small decrease in the normalized signal is observed due to increased absorption in the Cr buffer layer

Results: Cr-Au-Co-Au

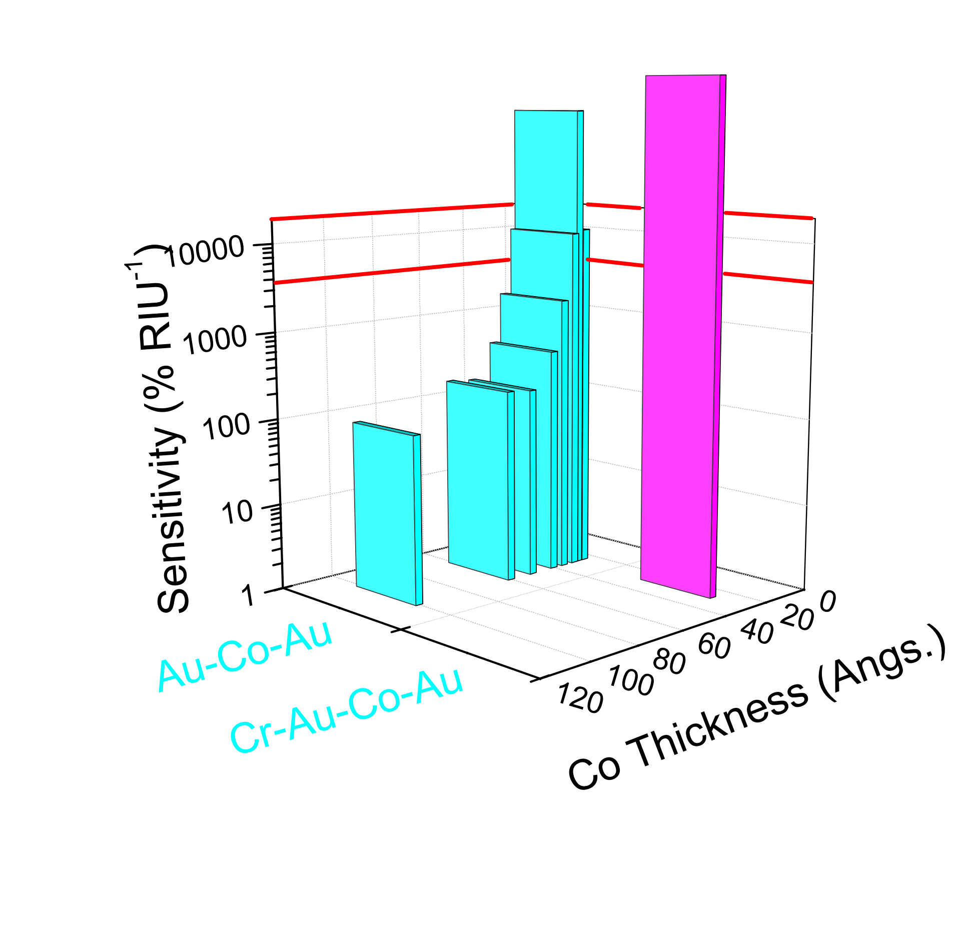
Yet, combining the enhancement of the MO effect and the extinction of the reflected beam, again a remarkable enhancement of the relative variation of the reflectivity is obtained.





Sensitivity

$$Sensitivity = \frac{\partial\left(\frac{\Delta R_{pp}}{R_{pp}}\right)}{\partial n_d} = \% \cdot RIU^{-1}$$



703,000 % RIU^{-1} in air

280,000 % RIU^{-1} in air

SPR → 3,900 % RIU^{-1}

J. Homola et al. Sens. and Act. 54, 3 (1999).

Detection limit

703,000 % RIU^{-1} in air	Δn_{min}=1.42 x10^{-7} RIU
280,000 % RIU^{-1} in air	Δn_{min}=3.57 x 10^{-7} RIU
170,800 % RIU^{-1} in water	Δn_{min}=5.85 x 10^{-7} RIU
MO-SPR (Cr-Co-Cr-Au) →19,100 % RIU^{-1} *B. Sepúlveda et al. Opt. Letters 31, 1085 (2006).*	Δn_{min}= 5 x 10^{-6} RIU
SPR →3,900 % RIU^{-1} *J. Homola et al. Sens. and Act. 54, 3 (1999).*	Δn_{min}= 5 x 10^{-5} RIU

Conclusions

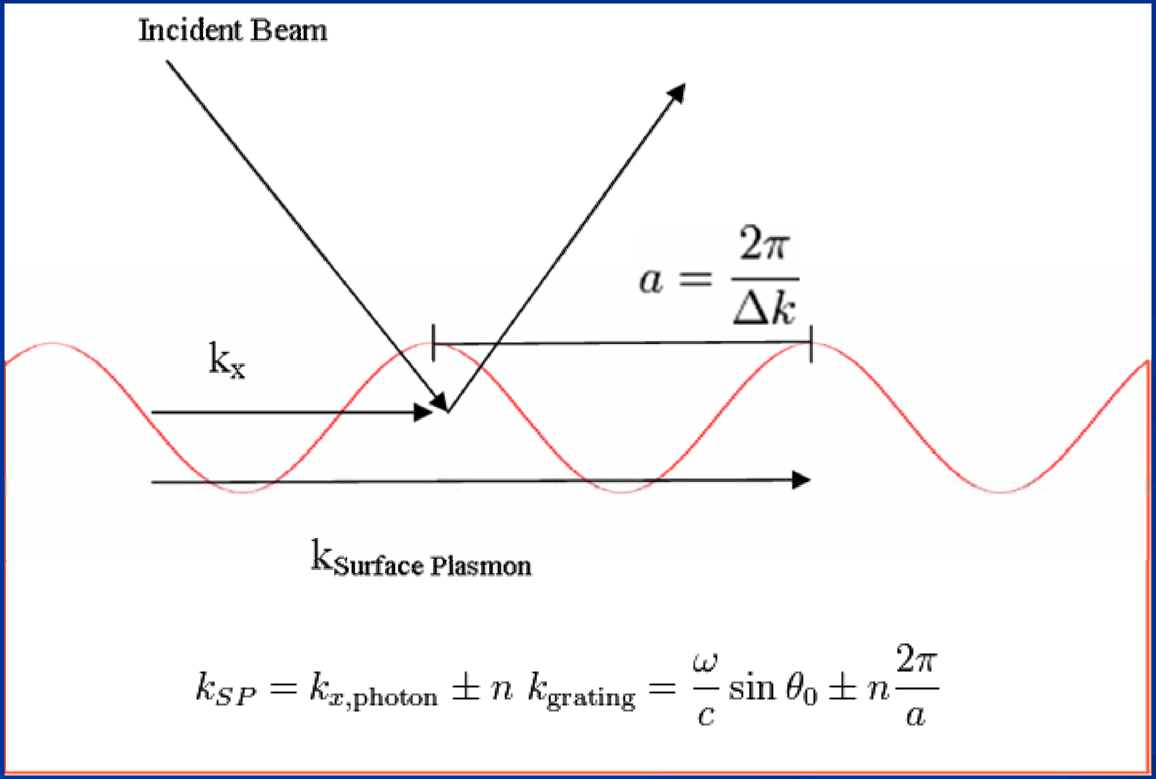
- A large enhancement of the magneto-optical response of Au-Co-Au trilayers with and without Cr buffer layer was obtained when the surface plasmon resonance was excited.
- Layer thickness was designed to achieve maximum extinction of the reflected beam.
- Combining both effects, a remarkable enhancement of the relative change in reflectivity ($\Delta R_{pp}/R_{pp}$) was obtained.
- This feature can significantly improve the detection limit in sensors based on surface plasmon resonance.

WORK IN PROGRESS

- We have achieved field modulated enhanced SPR in trilayered Au-Co-Au samples and also with trilayers grown on a Cr buffer layer. We are now testing these sensors in liquids.

- We are also investigating the use of diffraction gratings nano-patterned on the sensor surface to couple the light to the surface plasmons. This approach can eliminate constrains on the thickness of the films deposited and the kind of substrate used.

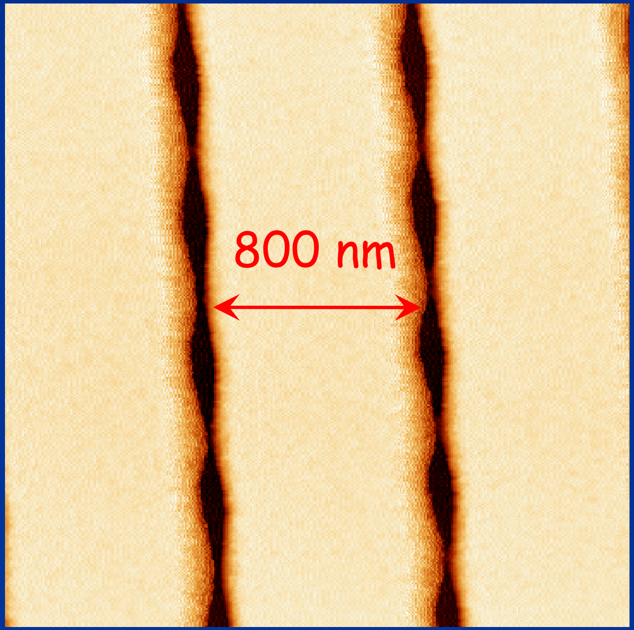
Diffraction gratings and plasmons

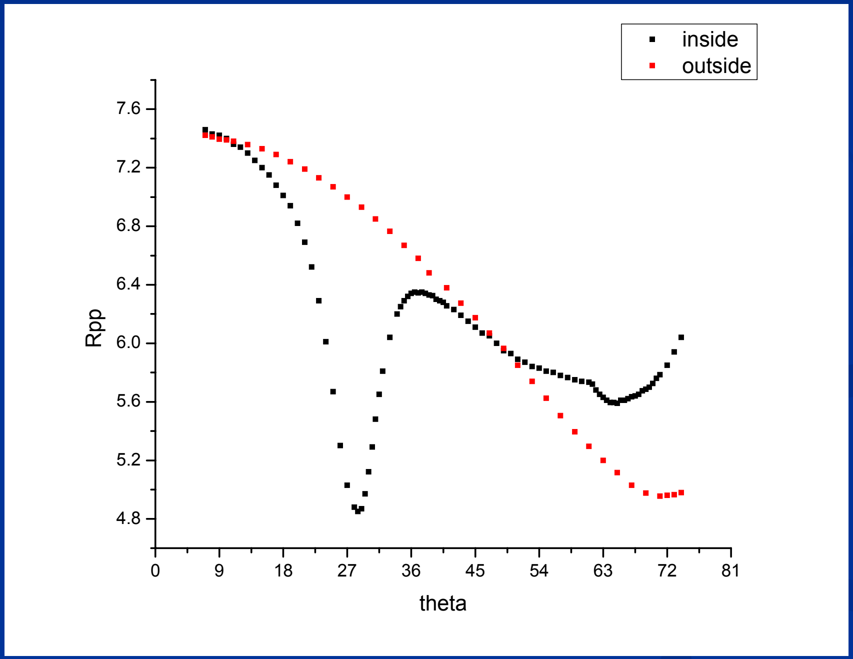


Nano-patterning

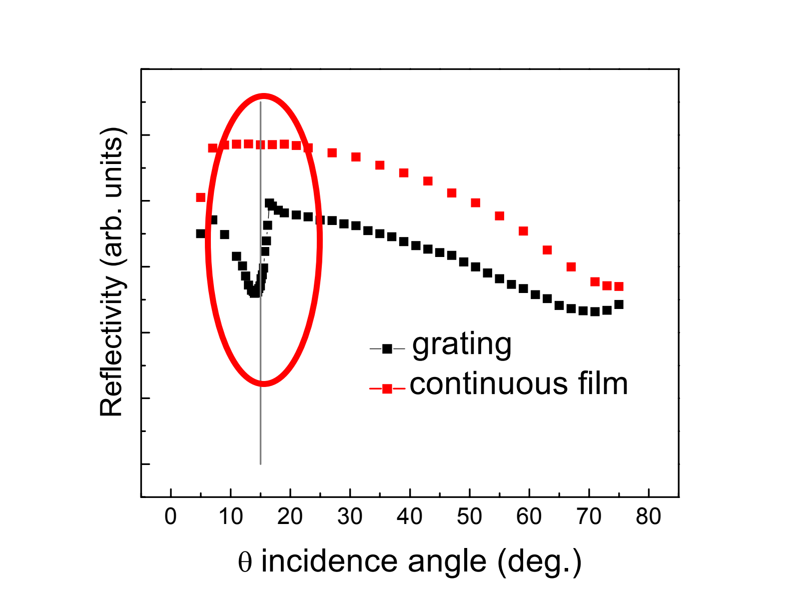
- We have explored e-beam lithography to nanopattern magneto-plasmonic materials with two goals in mind:
  - Use diffraction gratings for photons-plasmons coupling
  - Explore localized enhancement of the electromagnetic field to further enhance the magneto-optical activity

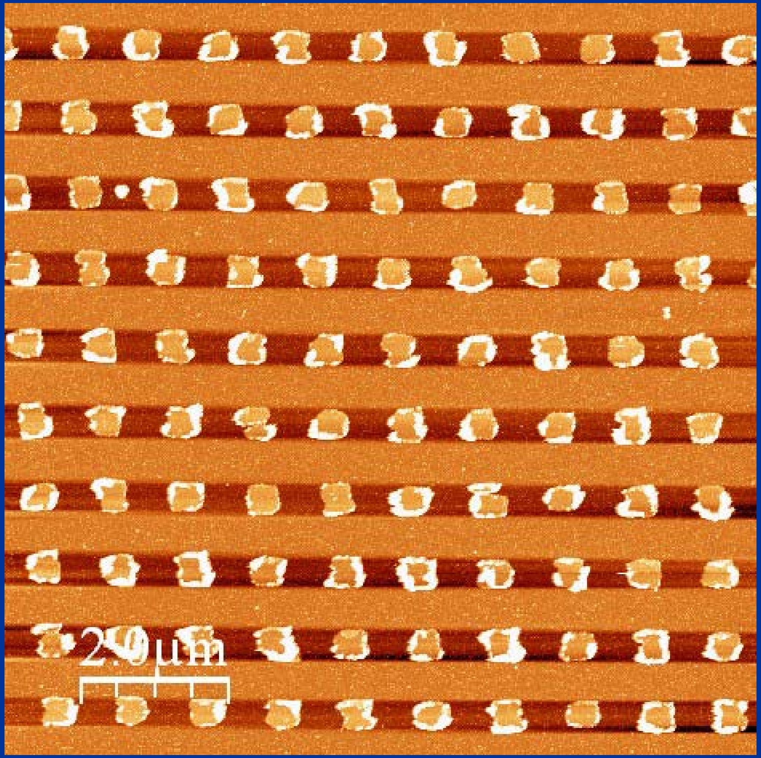
Au film with e-beam patterned grating

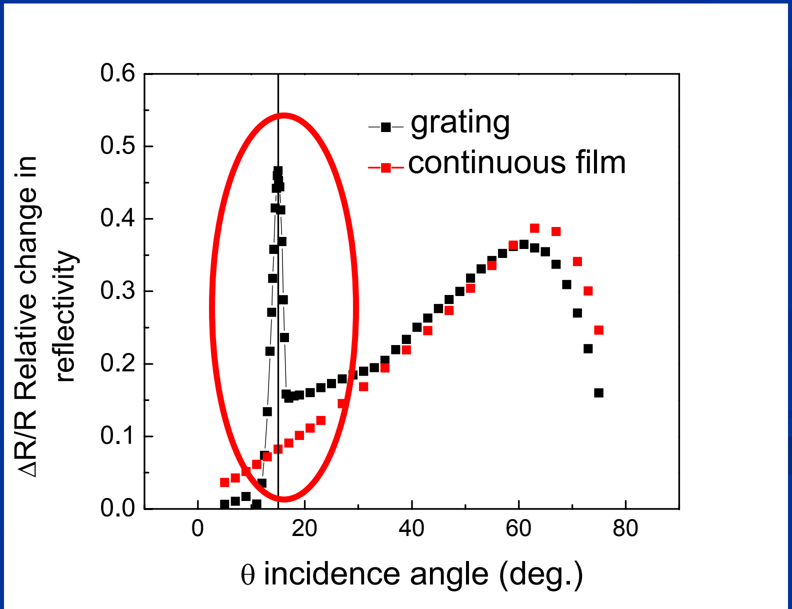




Au-Co-Au trilayer and Nano-patterned grating on top





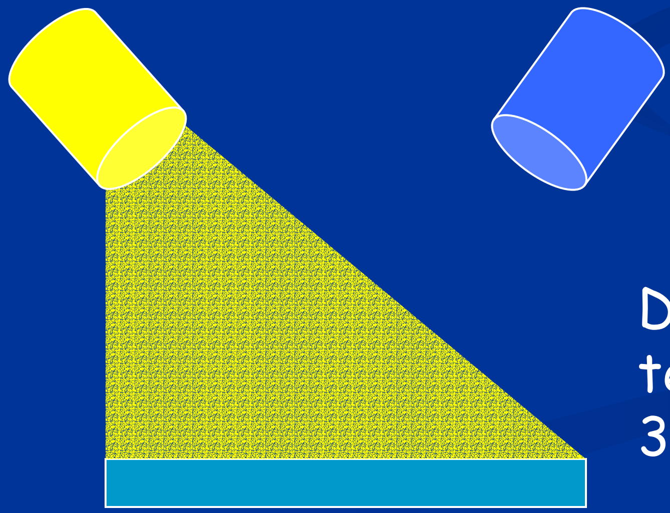


Au-Co nanocomposites

Sputtering codeposition of Au and Co

- Alternative solution for the adherence issue
- Decrease Co Absorption
- Easier to prepare

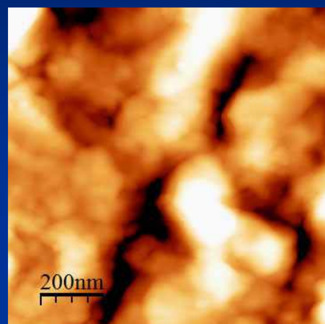
Au 95% - Co 5 % → Au 40% - Co 60 %



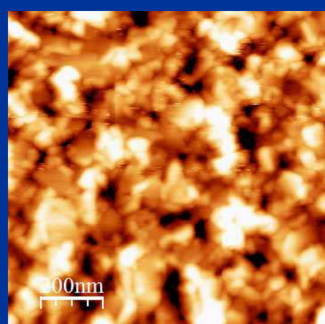
Deposition temperature RT, 300 C, 600 C

Au-Co nanocomposites: morphology

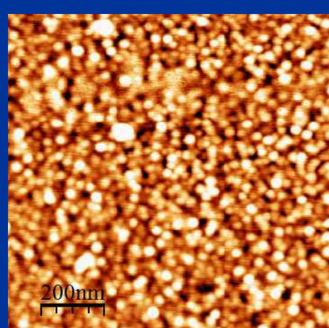
600 C



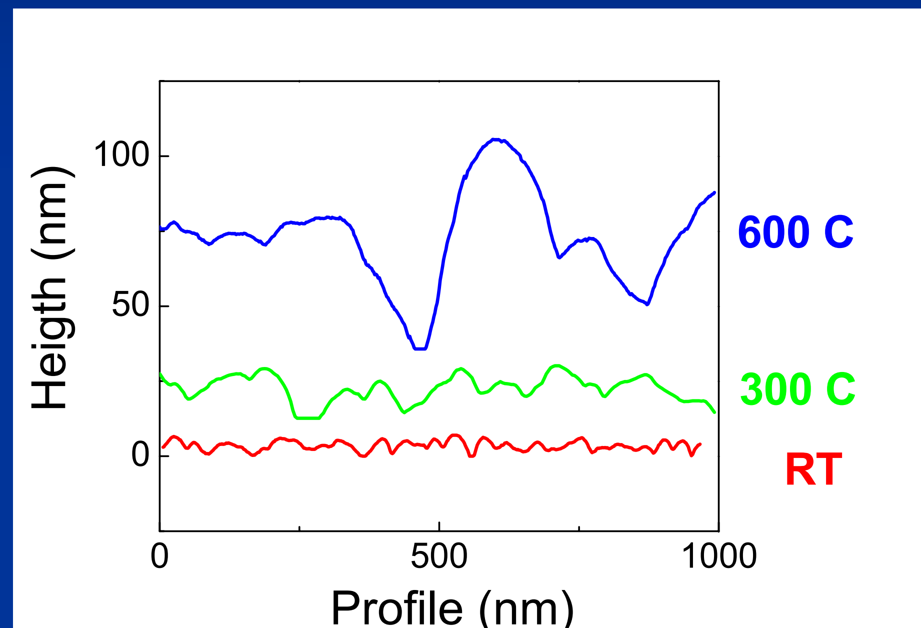
300 C



RT

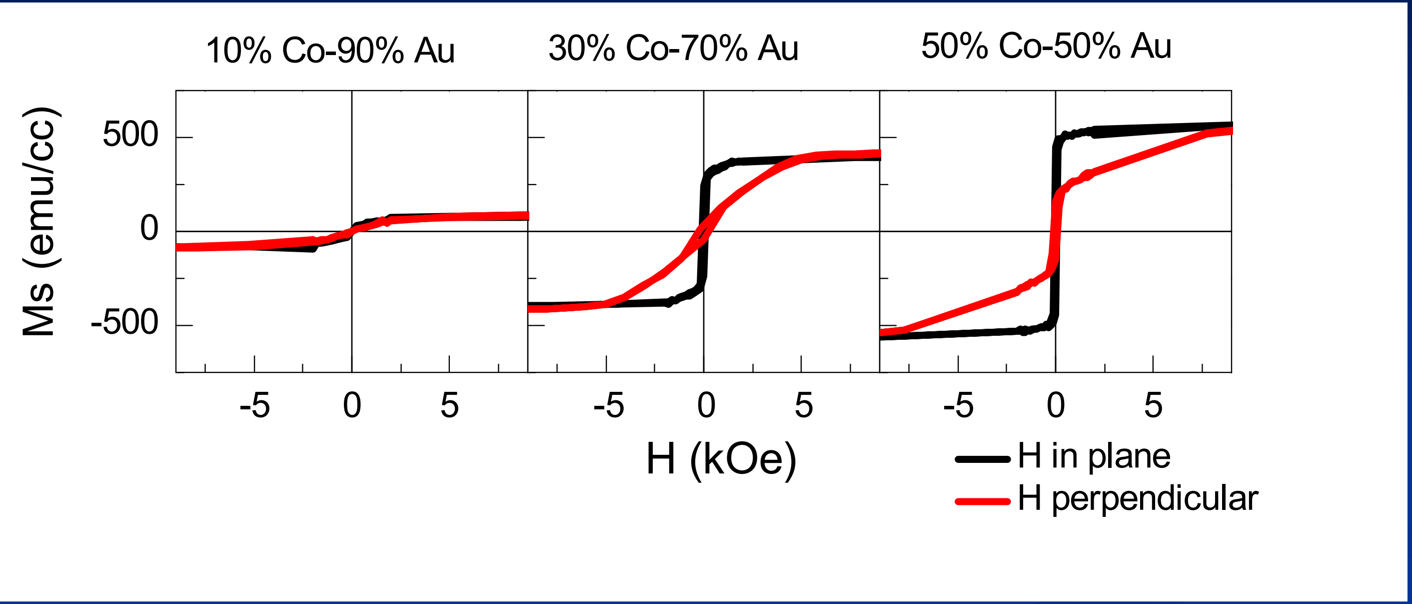


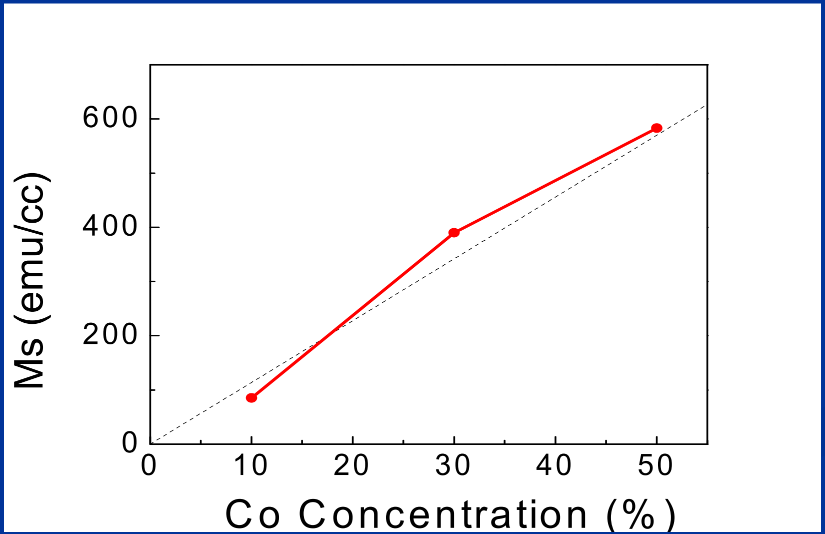
50 nm thick films



Good adhesion to glass.

300 C samples



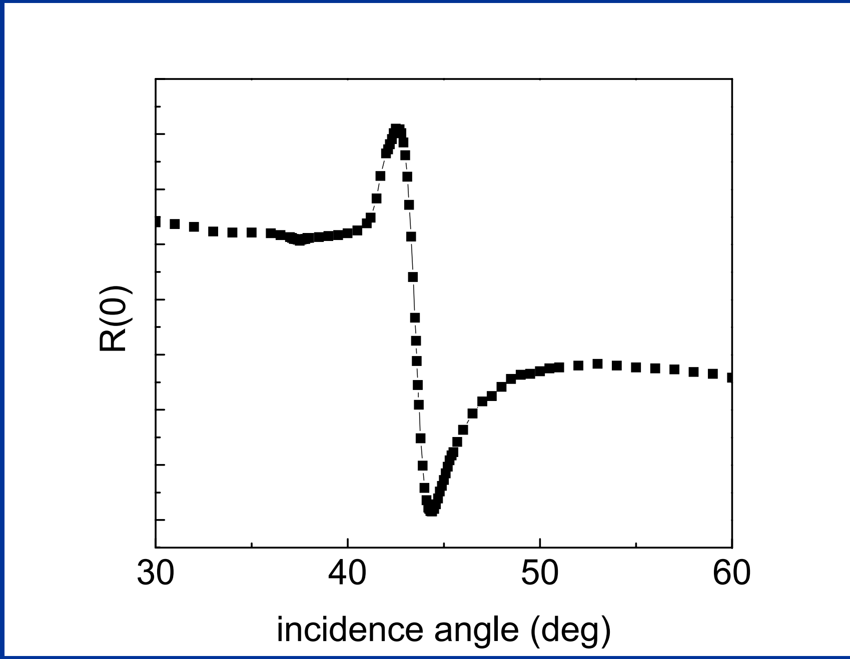


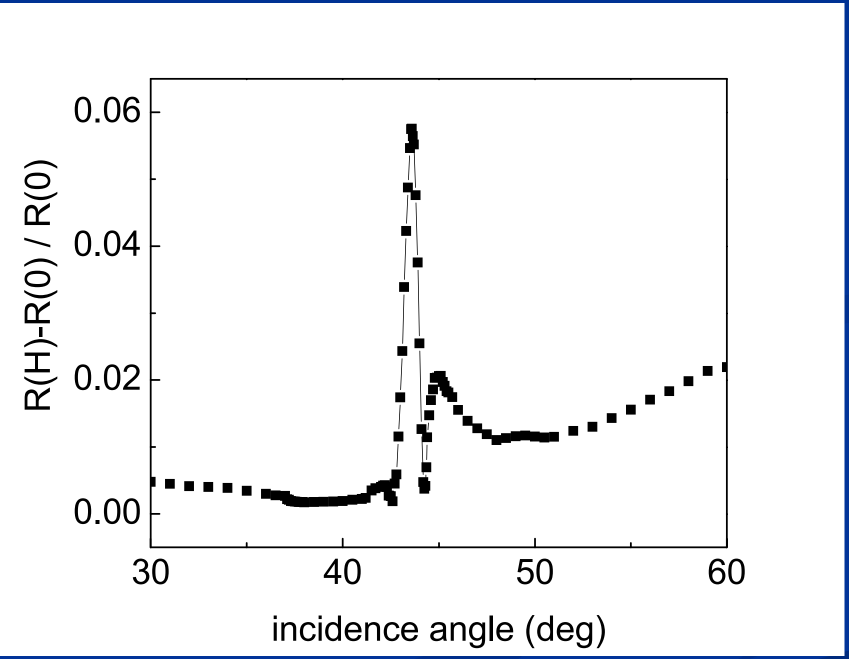
- In plane magnetic anisotropy
- Magnetic moment scales with Co concentration

Au-Co nanocomposites: MO-SPR

Measurements in air

Au 20%- Co 80 %   grown @ 300 C





The future

- Investigate the metal-insulator transition in VO_2 films grown on glass.
- The films will be excited with IR laser radiation following Cavalleri's work (PRL, 2001)
- We will then investigate the effect of this MI transition on plasmonic structures deposited/patterned on VO_2 films.