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# Description of a technique based on the indirect nanoplasmonic sensing to probe the adsorption/reactivity of gas with nanoparticles.

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## SCIENTIFIC BACKGROUND

The large field of nanotechnology allows the interaction between different scientific disciplines especially in the development of chemical [1-3] and biological nanosensors [4-6] based on the extraordinary optical properties of noble metal nanoparticles. As based on the surface plasmon resonance (SPR) sensors, nanosensors based on the localized surface plasmon resonance (LSPR) are sensitive to small local changes in refractive index at the surface of metal nanoparticles during the adsorption/desorption of molecules. These changes induce a shift in the wavelength of the LSPR signal [3,7]. Variations of the reflectivity as a function of the angle of incidence for the SPR and the LSPR peak extinction are linked to the same physical phenomena: the collective oscillation of electrons in the metal. The minimum of reflection corresponds to a maximum of absorption.

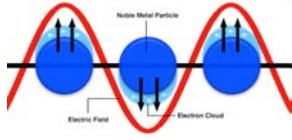
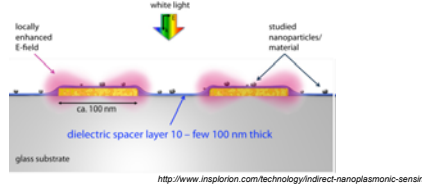


Figure: <http://simslab.uwaterloo.ca/research/biomems-sensors.php>

## THE INDIRECT NANOPLASMONIC SENSING (INPS)

In this work we propose to study the adsorption/reactivity of gas with nanoparticles absorbed on gold nanodisks acting individually as nanodetectors. To study the system gas/nanoparticles/Au nanodisks it is necessary to deposit an insulating layer (SiO<sub>2</sub>) on gold nanodisks. The work of Larsson [8] has shown indeed that this layer protects and makes more stable the detection nanostructure (gold nanodisks) at high temperature and it eliminates the interaction (mainly electronic interactions) between the nanoparticles and the gold nanodisks. Nanoparticles can react with gas molecules, they change the dielectric properties at the surface of the nanoparticle and generate a displacement of the LSPR wavelength of the underlying gold nanodetector. This is called an indirect LSPR phenomenon (or indirect nanoplasmonic sensing: INPS)



<http://www.inspiration.com/technology/indirect-nanoplasmonic-sensing>

## GOLD NANODISKS FABRICATION: A LIFT OFF PROCESS

Sample holder = borosilicate glass window, e = 1 mm, Ø = 25,4 mm  
Cleaning: acetone + US, then isopropanol + US, EDI rinsing, oxygen plasma oven at 150°C (300 W during 10 min)

PMMA spin-coating (resin 950 K at 4 %, speed : 4000 rpm, e = 270 nm annealing 10 min at 170°C)

Gold layer deposition (5 nm) to remove the charges (Edwards 306)

The gold film is irradiated with an electron beam (Raith PIONNEER)  
Areas of 90 x 90 µm<sup>2</sup> repeated 8 times in each direction (X, Y) a total area of 720 x 720 µm<sup>2</sup> (misfit < 50 microns)

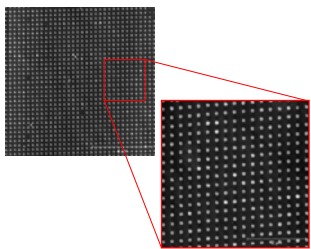
Revelation in acetone (or is removed) then with MIBK/IPA 1 : 3 during 45 s  
Then with IPA during 45 s (→ holes in the resin)

Cr and Au evaporation within the PMMA resin (Edwards 306)

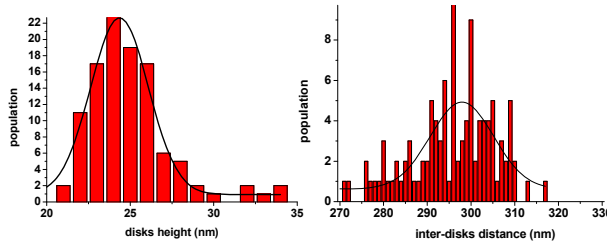
e<sub>Cr</sub> = 2 nm, e<sub>Au</sub> = 20 nm  
Lift-off of the resin (acetone + US)



## GOLD NANODISKS CHARACTERISTICS



Tapping mode topographical AFM images of gold nanodisks on borosilicate window (images obtained with a PSIA apparatus XE-100)



the average height is  $\langle h \rangle = 24.4 \pm 0.1 \text{ nm}$

center-to-center distance  $\langle d \rangle = 297.9 \pm 1.2 \text{ nm}$

## LSPR MEASUREMENTS: EXPERIMENTAL SET-UP



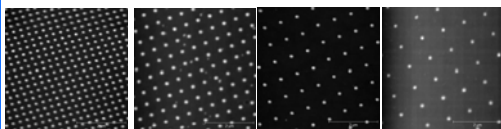
The sample holder (glass window) fits into an UHV reactor :

-UHV cube (CF DN 40) + 2 glass windows.

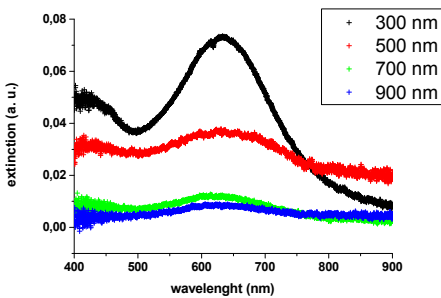
-The sample is illuminated by an optical fiber (Avantes, IR200-FC-2) connected to a tungsten halogen source (Avantes, AvaLight-HAL-S). The fiber is mounted on a collimating lens (Avantes, COL-UV/VIS) allowing the sample to have a coherent beam of parallel light.

-The signal transmitted by the sample is collected by a second fiber mounted on an other collimator lens (Avantes, COL-UV/VIS), it is collected and analyzed by a UV-VIS spectrometer (CCD detector, Avantes Avaspec-ULS3648 USB2) which is monitored by the Avantes "Avasoft-Full" software.

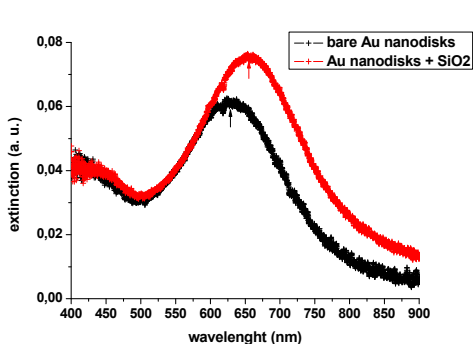
## EFFECT OF THE INTERDISTANCE d ON THE LSPR SIGNAL



From left to right : tapping mode topographical AFM images of gold nanodisks obtained with a PSIA apparatus (XE-100), respectively with d = 300 nm, d = 500 nm, d = 700 nm, d = 900. Below: LSPR signals corresponding to these different samples



## EFFECT OF THE SiO<sub>2</sub> LAYER ON THE LSPR SIGNAL



	Bare Gold Nanodisks	Gold Nanodisks + SiO <sub>2</sub>
Peak Area	6.34	6.72
LSPR peak position (nm)	625	654
FWHM (nm)	147.3	139.8

## WATER ADSORPTION/REACTIVITY ON SOOT PARTICLES

Soot particles can act in the atmosphere as ice nuclei and it is important to well characterize the water/soot interaction mechanism.

### Blank measurement

This shift is almost linear vs the relative humidity, at saturation (ie RH = 100%, P<sub>0</sub> = 18.7 Torr) we measure a shift  $\Delta\lambda_{\text{max}} = 2.42 \text{ nm}$ .

From equation (1) this shift corresponds to a thickness of the water layer of d = 0.37 nm (about 1 ML of water)

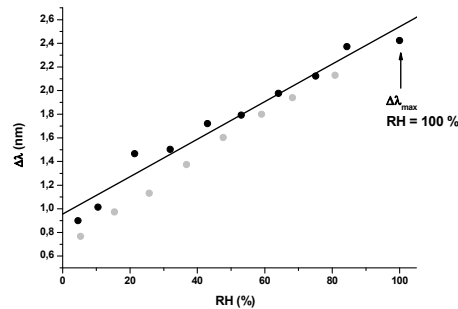


Figure : evolution of the shift  $\Delta\lambda$  of the LSPR signal vs the relative humidity of the reactor (room temperature) during the adsorption of water vapor on the bare gold nanodisks (+ SiO<sub>2</sub> layer). Black points are obtained during the adsorption, gray points are obtained during the desorption.

### Remarks:

- Hypothesis: m = 200 nm / RIU and l<sub>0</sub> = 20 nm
- n<sub>2</sub> - n<sub>1</sub> = n (H<sub>2</sub>O<sub>v</sub>) - n (vacuum) = 1.3330 - 1 = 0.3330.
- good reversibility of the adsorption and desorption curves
- mainly H<sub>2</sub>O physisorption and no chemisorption of water molecules on SiO<sub>2</sub>.

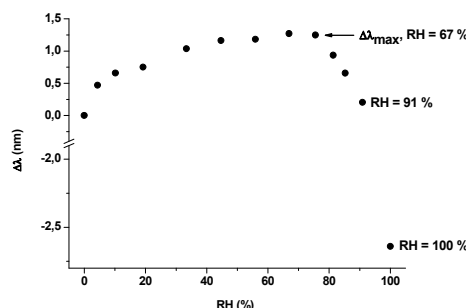


Figure: evolution of the shift  $\Delta\lambda$  of the LSPR signal vs the relative humidity of the reactor (room temperature) during the adsorption of water vapor on soot particles deposited on gold nanodisks (+ SiO<sub>2</sub> layer). Black points are obtained during the adsorption.

## RESPONSE OF THE LSPR NANOSENSORS

The response of LSPR nanosensors follows a simple model described by the group of Campbell [9]:

$$\Delta\lambda = m (n_2 - n_1) [1 - \exp(-2/l_0)] \quad (1)$$

$\Delta\lambda$ : wavelength shift

m: sensitivity of the refractive index (RI)

n<sub>2</sub> and n<sub>1</sub>: RIs of different surrounding media

d: effective thickness of the adsorbate layer

l<sub>0</sub>: characteristic decay length of the evanescent electromagnetic field.

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