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► **To cite this version:**

M Amraoui, M Fombonne, Marie Adier, A-M Jurdyc, F. Bessueille, et al.. Enhanced Raman Scattering of amorphous matrices for Fiber Optics Sensor. 3rd International Workshop on Metallic Nano-Objects (MNO 2016), Nov 2016, Lyon, France. . hal-02332400

HAL Id: hal-02332400

<https://hal.science/hal-02332400>

Submitted on 24 Oct 2019

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Enhanced Raman Scattering of amorphous matrices for Fiber Optics Sensor

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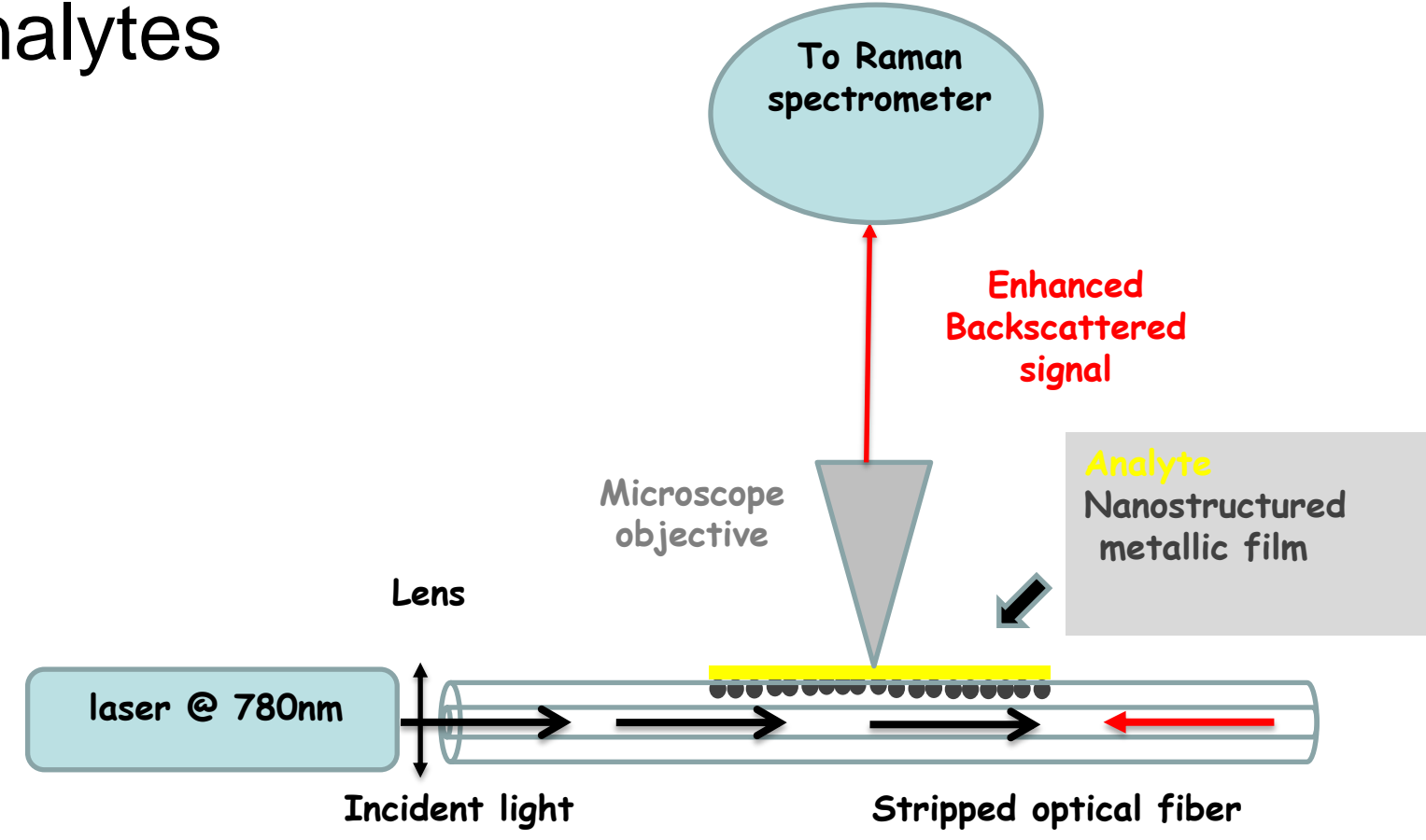
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Introduction and objectives

- Most of Surface Enhanced Raman Scattering Sensors (SERS) is applied to detection of molecules in solution
- Development of a Fiber Optic Sensor (FOS) allowing the detection of liquid and solid analytes



- Application to sol gel amorphous matrices (TiO₂, SiO₂) covering a nanostructured gold layer deposited on glass substrate and pieces of stripped optical fibers (model samples)

Surface-Enhanced Raman Scattering (SERS)

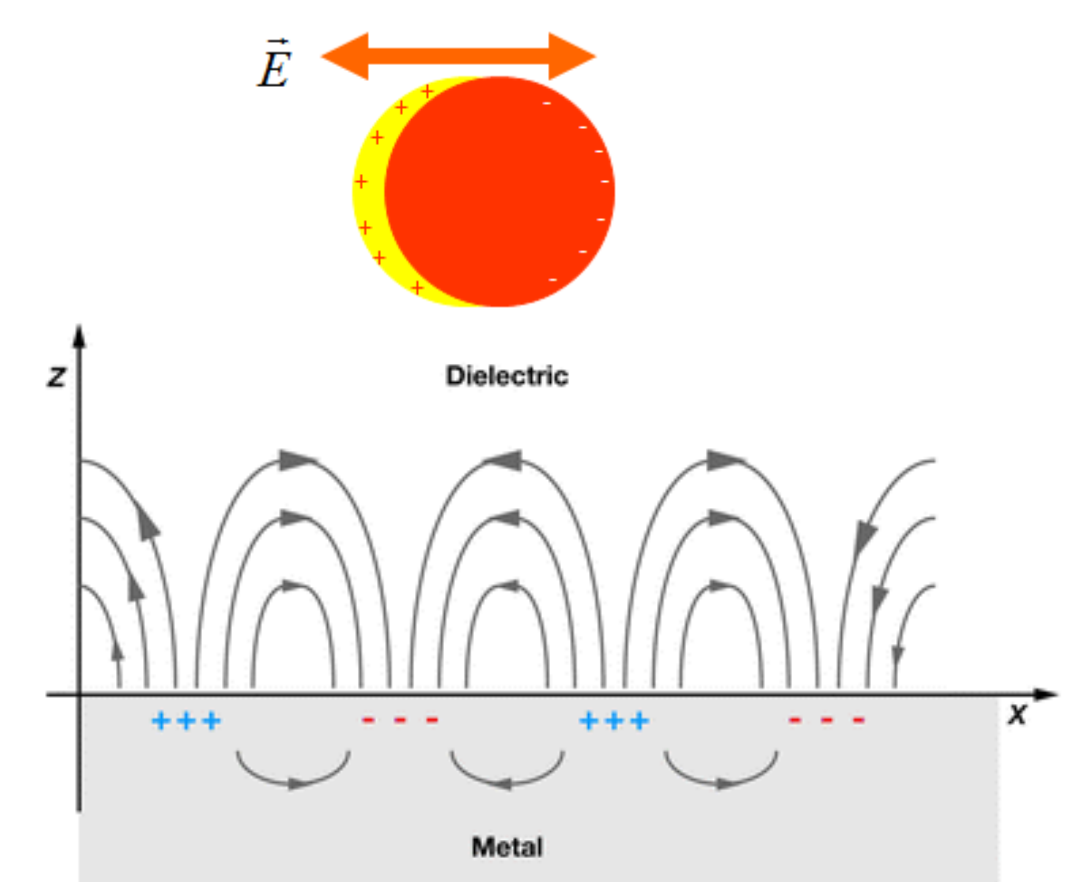
- SERS at the interface between Raman probed materials and a noble metal with a negative real part dielectric constant $\epsilon(\omega) < 0$ (Au, Ag...)
- Two mechanisms are responsible for SERS

$$I_{Raman} \propto \alpha^2 E_{loc}^2$$

1. Electromagnetic effect :

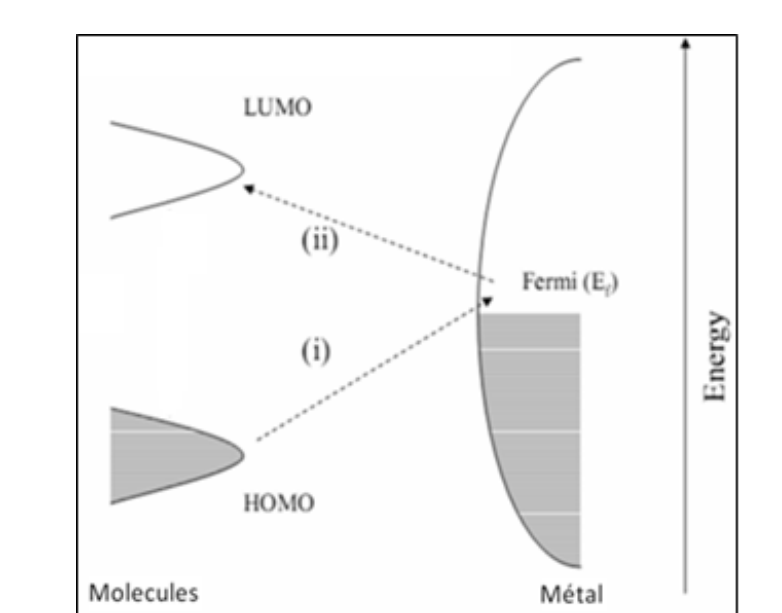
Surface plasmon resonance increases local electric field E_{loc} intensity experienced by Raman probed materials:

- Localized surface plasmon resonance (LSPR)
- Propagative surface plasmon (SPP)



2. Chemical effect :

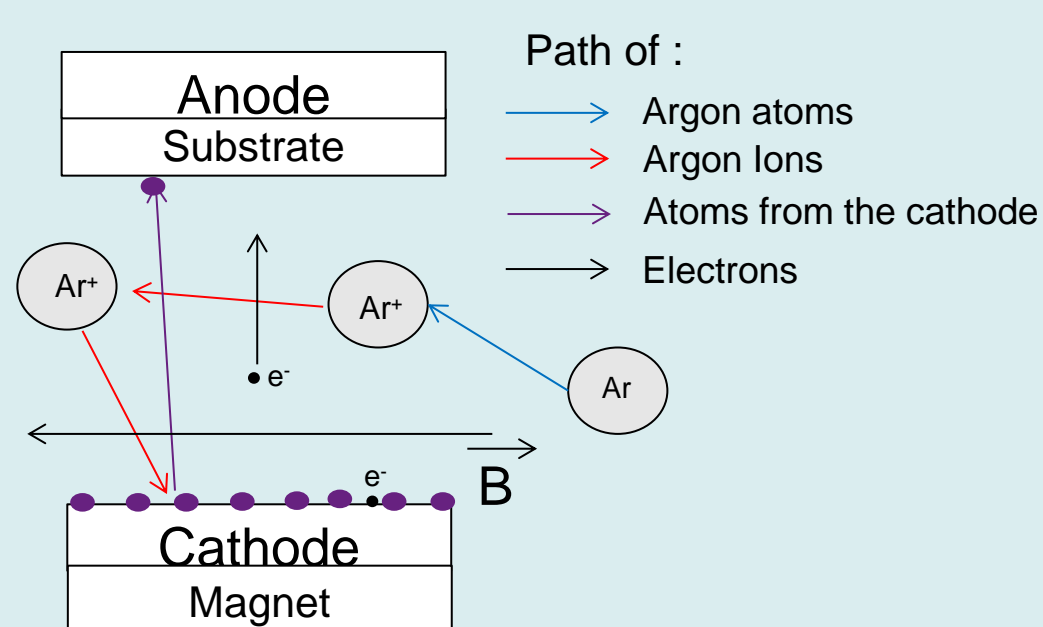
Charge transfer between metal and adsorbed molecules inducing an increase of dielectric polarizability α .



- In the case of solid analytes: surface (SERS) or volume (VERS*) effect?
* Volume Enhanced Raman Scattering?

Model samples elaboration

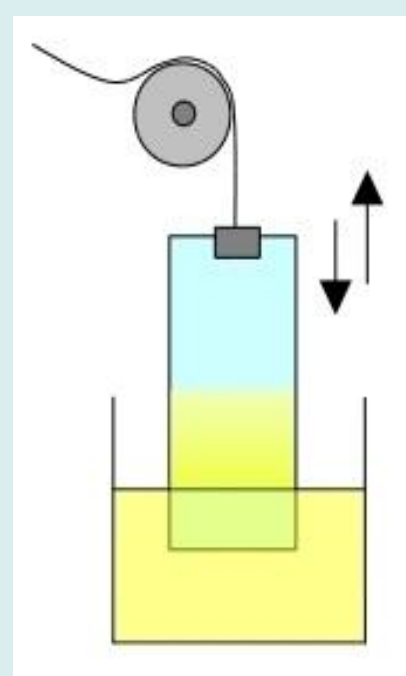
Step 1 : Gold sputtering



Step 2 : Sol elaboration

- SiO₂ precursors: TEOS + Ethanol + Chlorhydric acid
- TiO₂ precursors: Titanium isopropoxyde + Methanol + acetic acid

Step 3 : Dip-coating of amorphous gel layer



Step 4 : Annealing (solvent removing)

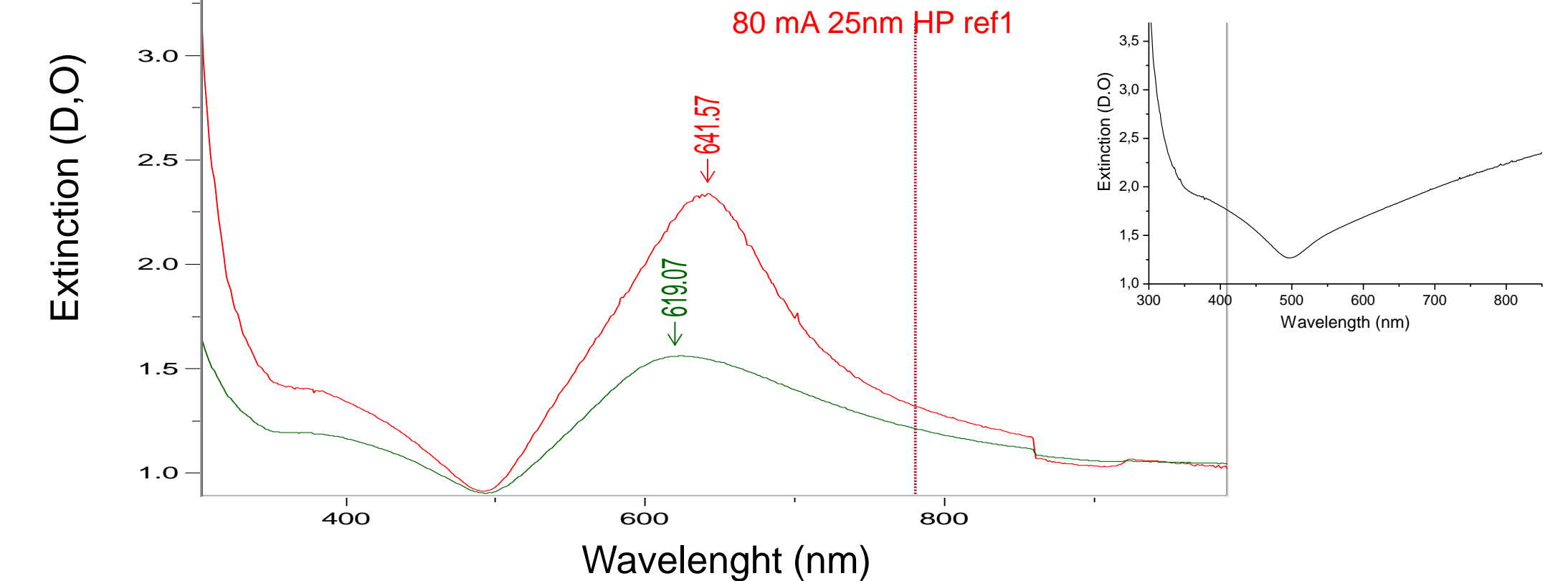


250° C
30 min

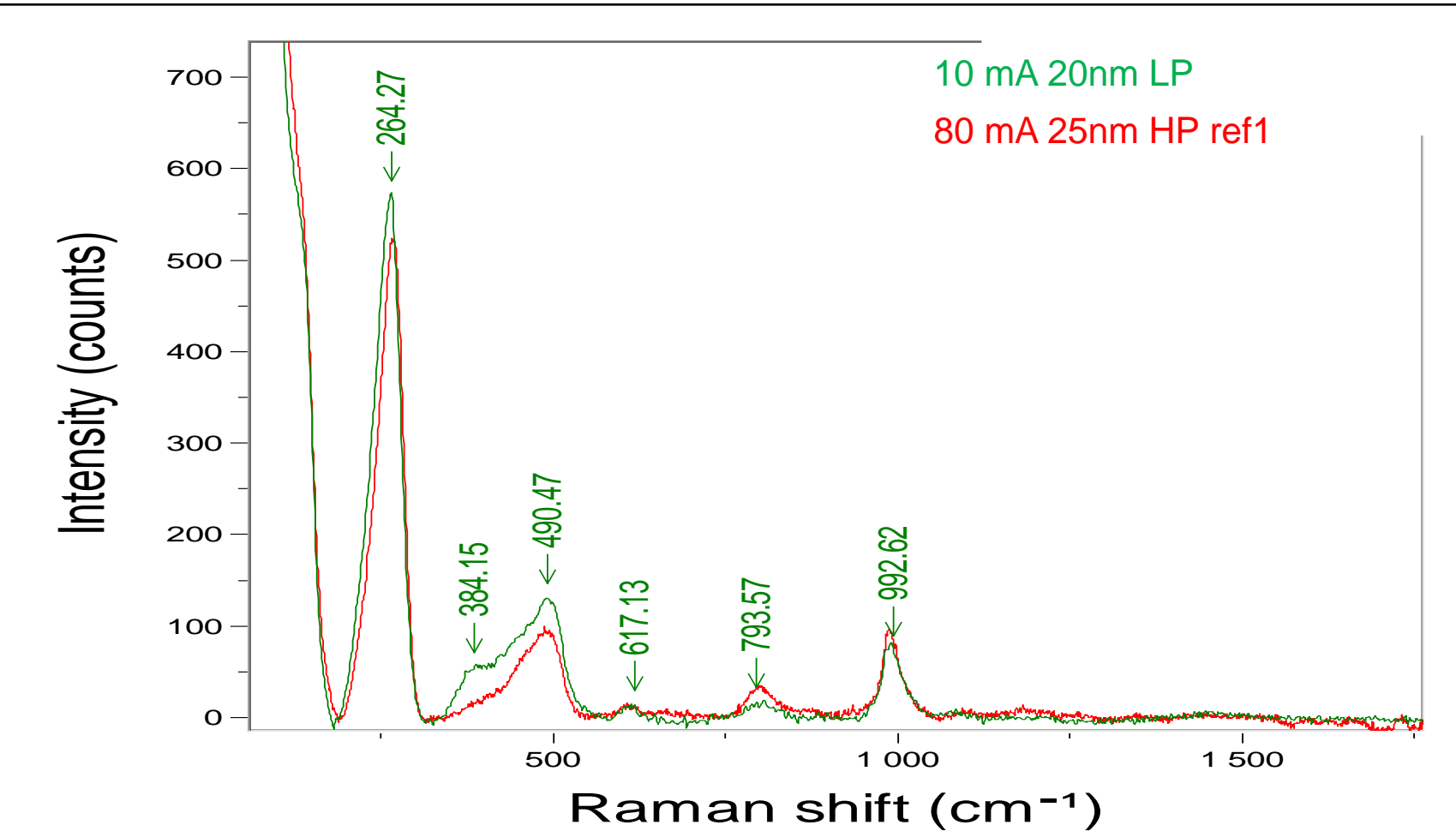
Experimental results

$\lambda_{exc} = 780 \text{ nm}$, $P_{inc} = 14 \text{ mW}$, $t_{integration} = 1 \text{ min}$, ObjX20 (NA=0,40)

Extinction spectroscopy: LSPR and transmission window (absence of LSPR)

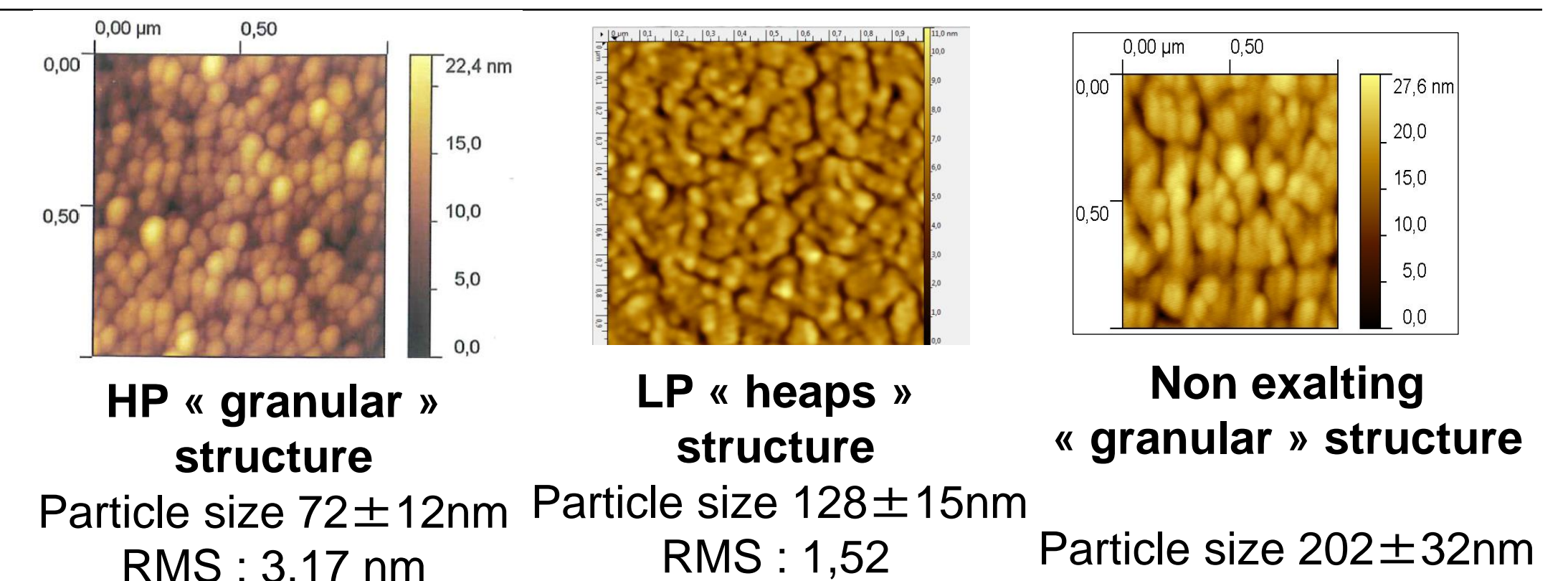


Enhanced Raman spectra of SiO₂ (200nm) with both gold structure (HP and LP) on glass slide (baseline removed)

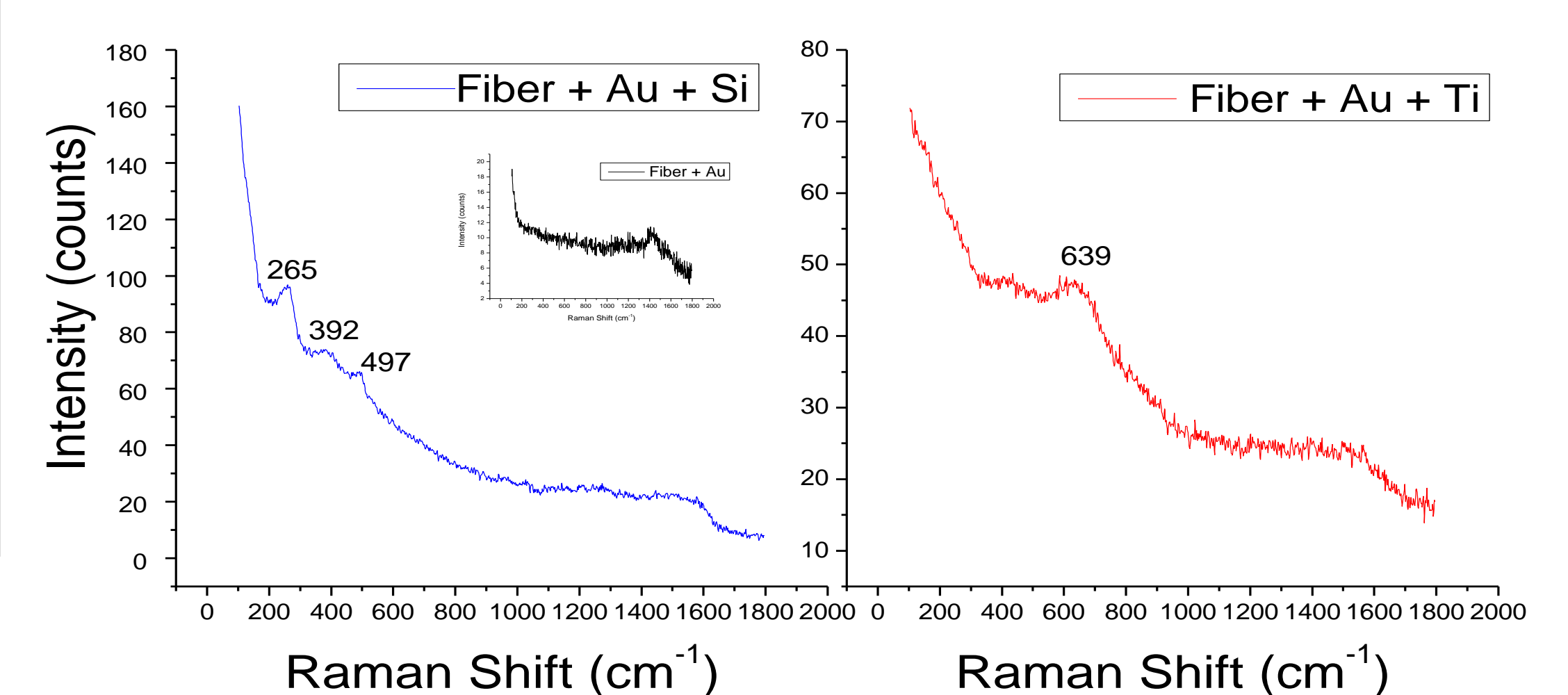


- Similar Raman exaltation with 2 different nanostructured gold layer HP, LP (nanostructures size and roughness)

AFM images (after removing the sol gel layer of SiO₂)



Application to a silica fiber (25nm Au (HP) + 200nm sol gel)



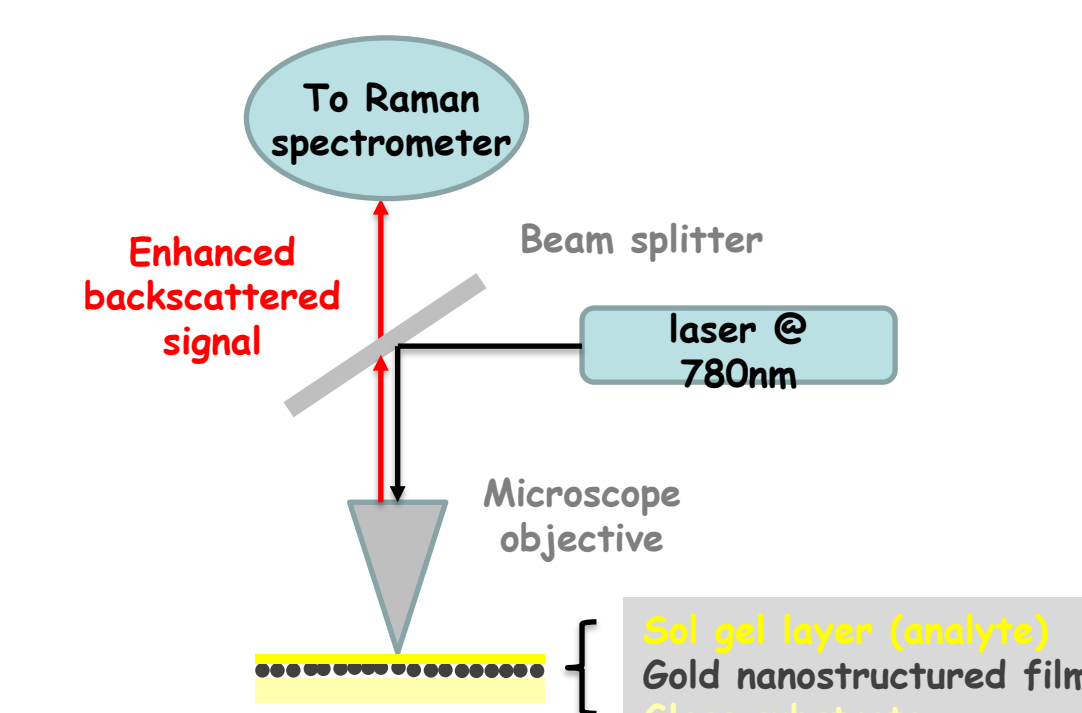
- Raman signal exaltation of amorphous matrices (TiO₂ and SiO₂) obtained after metallization of the stripped fiber pieces

Tested samples

Sol gel layer (200nm)
Gold nanostructured film (25nm)
Glass slide / Optical fiber substrate

Sputtering Intensity (mA)	Sputtering pressure (mbar)	Gold structure
80	0,1	HP
10	0,05	LP

Raman experimental setup



Discussion and conclusion

Raman bands exaltation of amorphous matrices (TiO₂ and SiO₂) obtained after metallization (nanostructured gold layer) of model samples (glass slide and pieces of stripped optical fibers). No Raman signal is obtained without this underlying gold layer.

Amorphous SiO₂ identified Raman bands :

- D₀ band at 490 cm⁻¹ => O₃Si-OH symmetric stretch
- D₂ band at 617 cm⁻¹ => ring breathing of three-membered siloxane
- Band at 793 cm⁻¹ => bond-bending vibration of Si-O-Si
- Band at 992 cm⁻¹ => symmetric stretch vibrations of silan ≡Si-OH
- Strong band at 264 cm⁻¹ => unidentified, might be due to phase transformations.

Amorphous TiO₂ identified Raman bands :

- Band at 639 cm⁻¹ => Ti-O stretching vibration
- Lowering the pressure during the sputtering allow to get two different nanostructures (gold nanostructures size and roughness) but both Enhanced Raman spectra are almost identical: the number of interstices between gold grains, where hot spots take place, and where sol can penetrate during the dip coating process, could be an important factor for this enhancement effect.
- The next step will be to test Raman Enhancement by guided optics allowing a coupling between the optical mode of the fiber and the gold plasmon wave.