Interfaces, **T**raitements, **O**rganisation et **DY**namique des **S**ystèmes

Final report *(Ref. No. 5033)*

Influence of the surface roughness on the SERS of lithographically fabricated gold nanoparticles: complementary experiments and publication

1 Purpose of the visit

Surface enhanced Raman scattering (SERS) is a very sensitive spectroscopic technique allowing the detection of molecules at very low concentration. In specific conditions, it is possible to detect the Raman signature of a single molecule. In order to describe the SERS effect, one important aspect is the control of the shape and the size of the plasmonic structures, which strongly determine the SERS efficiency. Among numerous SERS substrates, electron –beam lithographic structures are very good candidates since they allow reproducible Raman enhancement factors (REF) of adsorbed molecules. However, if many aspects of the SERS mechanisms have been resolved, there are still some open questions regarding the role of the nanoscale surface roughness (NSR) and the cristallinity of the particles on the magnitude of the REF. In the frame of the collaboration with the group of Graz, we focused our attention on the influence of the NSR of the lithographic structures on their optical properties and their SERS efficiency.

In the previous short-visit grants (Ref. No. 4577 and 4871)**,** we investigated the SERS enhancement on electron-beam lithographically fabricated gold arrays made of circular gold dots, where parameters as the particle roughness, shape of lift-off defects and the metal dielectric function were modified by thermal annealing. By comparing the SERS signals from differently modified samples, we could identify the contribution of these parameters [1, 2].

The purpose of this visit (Ref. No. 5033) was *(i)* to plan a final discussion of the results obtained on the different samples, in order to prepare two different publications, *(ii)* to make additional experiments on single particles (fabrication, optical properties and SERS experiments).

References

[1] J.-C. Tinguely, I. Sow, C. Leiner, J. Grand, A. Hohenau, N. Felidj, J. Aubard, J.R. Krenn, *Gold nanoparticles for plasmonic biosensing: The role of metal crystallinity and nanoscale roughness*, BioNanoScience, 1, 128 (2011).

[2] A. Trügler, J.-C. Tinguely, J.R. Krenn, A. Hohenau, U. Hohenester, *Influence of surface roughness on the optical properties of plasmonic nanoparticles*, Phys. Rev. B **83**, 081412(R) (2011)

<u>2 Description of the work carried out during the visit</u>

The work carried out by the applicant during the visit focused on two main tasks:

1- New measurements have been investigated and discussed on lithographic gold nanowires. We completed the experiments with optical extinction, SERS and AFM topographic images. A set of several wires were previously fabricated (100 mm length, 40 nm height, and width in the range of 50-200 nm). By changing the size of the nanowires, we expect to match the localized surface Plasmon (LSP) wavelength with the two laser lines 633 and 785 nm used for the Raman experiments. We expect strong differences in the Raman enhancement factors between annealed and non-annealed samples, at both excitation wavelengths. In order to confirm the experimental results, we plan to make calculations using the dipole discrete approximation (DDA) method.

2- Attempts towards a comparative study of SERS of single particles failed in a first attempt due to too low SERS signals, which did not allow to draw unambiguous conclusions. New experiments towards single particle SERS characterization are considered now. Therefore, the single particle SERS signal has to be improved over the samples investigated up to now. We thus plan to fabricate large gold nano-rods (~1µm length, 40nm height, width in the range of 100-200nm) with their in-plane longiudinal LSP resonances between 600-800nm. The large surface area and the large dipole strength of the LSP in combination hopefully improve the SERS signal sufficiently, whereas the particles are still small enough to warrant complete and individual characterization by high resolution atomic force and electron microscopy. The results would be important for a better comparison to simulations taking into account the realistic shapes in as much detail as possible.

3 Description of the main results obtained

1- We investigated the influence of the nanoscale surface roughness (NSR) of gold stripes by thermal annealing, and the changes induced to the SERS enhancement factor. In these experiments, we demonstrate that the NSR strongly determines the SERS intensity of molecular probes such as methylene blue or rodhamine 6G, by comparing structures with different roughness parameters. In particular, we show that SERS signal on realistic gold structures remains very efficient far from the LSP resonance, in agreement with numerical simulations based on the discrete dipole approximation (DDA).

The gold nanowires display LSP resonances when the incident polarization is set along the width of the structures (perpendicular polarization). No LSP excitation is expected along the length of the structures (parallel polarization). Thus, such structures are very well adapted for analyzing the SERS efficiency *on* and *off* LSP resonance by changing the polarization direction of the incident light.

SERS experiments were investigated on annealed (smooth surface) and non-annealed (rough surface) gold wires. For the non-annealed samples, it was possible to detect a strong SERS signal of adsorbed methylene blue (MB) for perpendicular (*on* LSP resonance) and parallel (*off* LSP resonance) polarizations (laser excitation at 633 nm). SERS experiments were also investigated on smooth nanowires (where the NSR is mostly reduced by the annealing process). When the polarization is parallel to the wires length, no more SERS signal is observed as expected (in this case, no LSP resonance takes place in such configuration). For a perpendicular excitation, the SERS signal of MB is observed, which was expected. All the set of experiments made on the nanowires are nicely confirmed by the DDA (discrete dipole approximation) calculations (figure 1). In particular, the DDA calculations show that the NSR at the wires surface gives rise to a strong local electric field leading to a SERS signal of MB, although the polarization is parallel to the wires length.

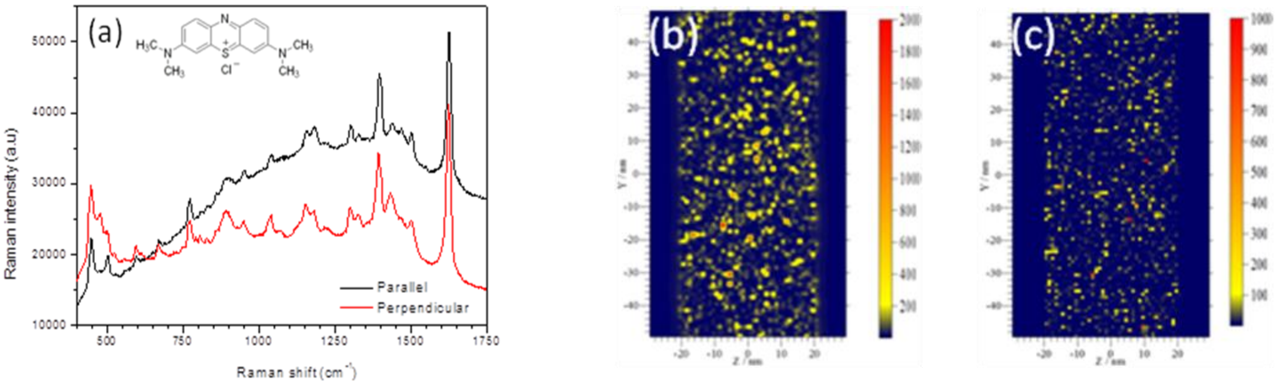

Figure 1: (a) SERS spectra of MB (parallel polarization, excitation at 633 nm); (b) DDA calculation of the local electric field from a stripe presenting NSR at the surface (polarization is perpendicular to the stripe); (c) DDA calculation of the local electric field from a stripe presenting NSR at the surface (polarization is parallel to the stripe).

At 785 nm, all the structures are *off* LSP resonance. However, it was still possible to detect a SERS signal of MB for the non-annealed samples. The DDA calculations confirm the SERS results and show that the NSR is even more efficient in the red part of the visible range (with stronger local electric field). At last, it was not possible to detect any SERS signal of MB for the smooth samples, also confirmed by the DDA calculations (figure 2).

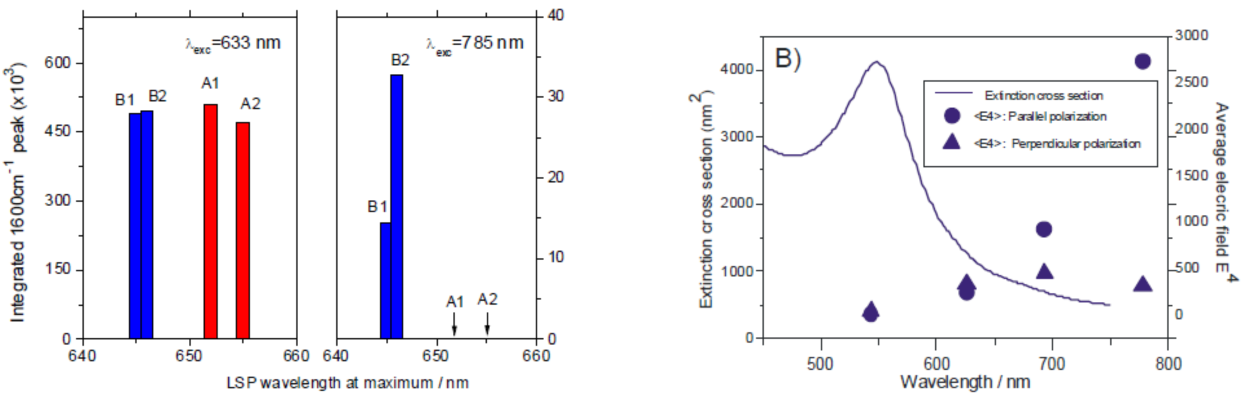

Figure 2: (left) Specific SERS intensity of EBL wire-like structures. The bar plots show the integrated area of the SERS peak at 1600cm^{-1} of MB on the non-annealed (blue) and the annealed sample (red), presenting a comparable tendency at resonant wavelength excitation (633nm, left) and considerable differences at a non-resonant wavelength (785nm, right).(Right): DDA calculations of a gold wire ca. 10µm long and 40nm high/wide. The spectra display calculated extinction vs. near-field intensity on a rough stripe.

- SERS experiments have been also investigated on single gold nanoparticles. For the first time, it was possible to detect the SERS signal of MB on non-annealed and annealed isolated structures with a laser excitation at 633 nm. We plan now to correlate the NSR of each single particle with the SERS efficiency. Depending of the position of the NSR on the particle surface, we expect important differences in the SERS enhancement factor.

4 Future collaboration with host institution

First, the collaboration between the host institution and our laboratory will continue through this project. We submitted in May 2012 an Egide (Amadee) application on a project dealing with the elaboration of hybrid plasmonic structures. We also plan to submit an application, ANR France-Austria in 2013. The project will be focused on SERS effect.

5 Projected publications / articles resulting or to result from the grant

Two papers are in progress:

1- J.-C. Tinguely, G. Charron, A. Hohenau, S. Lau, J. Grand, N. Felidj, J. Aubard, J. R. Krenn *Template assisted deposition of gold nanorods with nanoscale resolution*, in preparation.

This paper, written by J. C. Tinguely (Experimental Institute of Graz), deals with a novel approach for positioning gold colloidal nanorods. The substrate binding sites are genretaed through electron beam lithography, creating trenches with access to a surface functionalized with silane molecules.

2- I. Sow, J. C. Tinguely, A. Hohenau, J. Aubard, J. Grand, G. Lévi, J. Krenn, N. Félidj, *Revisiting surface enhanced Raman scattering on realistic gold lithographic structures*, in preparation.

This paper deals with the study of the influence of the surface roughness and cristallinity of lithographically designed gold nano-wires by thermal annealing. We show that the surface roughness contributes significantly to the SERS enhancement. We conclude that SERS effect is a multi-scale phenomenon, arising from both the particle LSP and the particle surface roughness.