Scientific Report on the Short-Visit Grant

Influence of the surface roughness of single particles on the SERS enhancement factor: reproducibility

(Ref. No. 4871)

Purpose of visit

The purpose of this visit was to carry out surface enhanced Raman scattering (SERS) measurements on electron-beam lithographically (EBL) fabricated gold nano-particles. A systematic variation of the particle plasmon resonance was intended to allow for a distinction of on and off-resonant SERS enhancement mechanisms. Particular emphasis was put to evaluate the reproducibility of the annealing effects on the SERS signal observed in previous experiments. During the visit in Paris, we planned to concentrate on the single particle SERS characterization of samples fabricated in Graz.

Description of work carried out during visit

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

1. Characterization of the SERS enhancement of EBL fabricated gold nano-particles: The nano-particles which are arranged in regular arrays of ~100x100 μm² on an ITO covered glass substrate, were first covered by probe molecules (usually methylene blue or rhodamine 6G) and subsequently a SERS spectrum was recorded in a Raman microscope (Horiba LabRam HR). The analysis of the SERS spectra allows the comparison of the SERS intensities between different particles and / or arrays.
2. Scientific discussions on the interpretation of past and present results and planning of future directions.

Description of the main results obtained

One of the major problems with SERS substrates fabricated by EBL is the undefined shape of the metal structures on a nanometer level. This uncertainty is caused by the poly-crystalline structure and the related inevitable surface roughness in the range of 1-1.5 nm RMS, as well as fabrication (liftoff~) defects[1,2]. This influences the optical near field enhancement and thus the SERS efficiency of such substrates, and is not discernibly by e.g. optical far-field spectroscopy. To asses the near field contribution of such features, we developed an approach based on a thermal treatment. By annealing a sample of gold nano-particles at 200°C for 10-30min, the surface roughness gets slightly reduced and the liftoff defects (larger protrusions on the edges of the particles) largely disappear by a healing process (Fig.1).

For dense arrays of such nano-rods (array period 300nm), optical extinction spectra and SERS spectra could be recorded and confirmed the previously[1] observed trend (Fig.2): After annelaing, the reduced roughness and the healing of the liftoff defects leads to an overall reduction of the observed specific (i.e. background subtracted) SERS intensities in the range of 10-50% for excitation at 633nm.

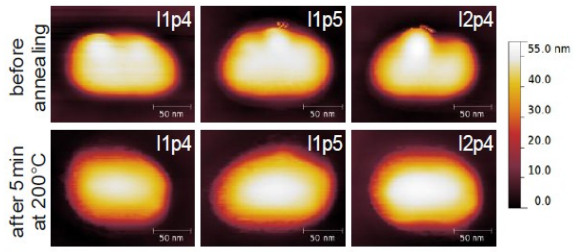

Fig.1: Atomic force micrographs of three individual gold nano-rods, as deposited (top row) and annealed (bottom row). The somewhat broader appearance of the annealed rods is attributed to a tip-artifact.

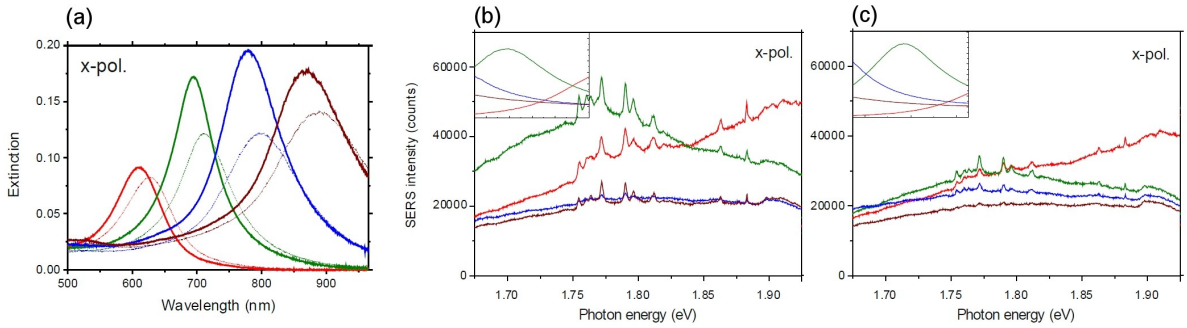

Fig. 2: Exitnction spectra (a) of gold nano-rod arrays, and corresponding SERS-spectra before (b) and after (c) annealing with rhodamine 6G.

To get a better comparability to simulations and to avoid the array-averaging in the measurement process, one attempt was to measure SERS on single gold nano-rods. Therefore arrays with large particle spacings of 3µm were fabricated and the particles characterized by AFM before deposition of the molecular Raman probe (Methylen Blue for its large resonant Raman cross-section if excited at 633nm)†. Unfotunately after several attempts it turned out, that although single-particle SERS spectra can be recorded on such samples, the signal to noise ratio of the intensity of single SERS peaks is in the range of 50% and thus does not allow to draw conclusions on the annealing effect on a single particle level.

Nontheless, we found that if the nano-rod arrays are excited not at 633 but at 785nm, the changes to SERS intensity induced by annealing are actually reversed, i.e., SERS intensity is larger after annealing than before. After several discussions we concluded, that this is not an artefact, but related to the annealing induced changes to the dielectric function of gold,[2] i.e. a reduction of its real and imaginary part which causes a spectral blue shift and narrowing of the particle plasmon resonance. This blue-shift moves the resonance position closer to the damping d-band absorption of gold. When the resonance is close to 633nm, the blue shift of the resonance position upon annealing brings it closer to the spectral region of the d-band absorption. In this case, the effect of the reduced imaginary part of the gold dielectric function is largely compensated and the improvement of the LSP resonance quality not very pronounced. In contrast, at 785nm, distant from the d-band absorption, the improvement of LSP-quality is more pronounced and lead to a stronger resonance enhancement overcompensating the reduced roughness induced near field enhancement. This is also visible

† Sample preparation and characterization was supported by J.-C. Tinguely in the context of his PhD thesis at the Institute of Physics, Karl-Franzens University Graz, Austria.

in the extinction spectra by the much larger and narrower curves at larger resonance wavelength after annealing (Fig. 2(a)).

Future collaborations with host institution

We currently plan further experiments to obtain single-particle SERS characterization and to overcome the experimental deficiencies. A common publication of the hitherto achieved results will be prepared in the comming months.

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] C. Leiner, Diploma-Thesis, Institute of Physics, Karl-Franzens-University Graz, Austria (2010).