Revisiting Surface-Enhanced Raman Scattering on Realistic Lithographic Gold Nano-stripes

I. Sow, J. Grand, G. Lévi, J. Aubard, and N. Félidj*

Interfaces, Traitements, Organisation et Dynamique des Systèmes, Université Paris Diderot, Sorbonne Paris Cité, CNRS UMR 7086, 15 rue Jean de Baïf, 75205 Paris Cedex 13, France

J.-C. Tinguely

University of Tromsø, Department of Physics and Technology, Tromsø, N-9037, Norway

A. Hohenau and J. R. Krenn Karl-Franzens University and Erwin Schrödinger Institute for Nanoscale Research, A-8010 Graz, Austria (Dated: November 4, 2013)

 $^{^{\}ast}$ corresponding author: nordin.felidj@univ-paris-diderot.fr

Figures



Figure 1: (a): AFM image of a non-annealed gold stripes array (gold was deposited by thermal vacuum deposition onto an ITO substrate). (b) Lateral section of a single stripe. A grain size estimation led to grain sizes of ca. 10-30 nm.(c): AFM image of annealed gold stripes, with a grain size estimation in the range of 50-100 nm, as shown in the lateral profile with a reduced surface roughness (d).



Figure 2: (a) and (b): AFM images of a non annealed (a) and an annealed (b) gold film. The profiles show smaller grains (of ca. 30 nm) in the case of the non-annealed film, and large domains on the annealed one (ca. 100 nm). The RMS has been estimated by AFM: ca. 2.4 non annealed film), and ca. 1.6 nm (annealed film). (c): polar graph of the SERS intensity of MB molecules on samples A and B. In both cases, no dependence with the incident angle is observed. However, as in the case of the gold stripes, the SERS intensity is systematically lower in the case of the annealed gold film, whatever the incident angle.



Figure 3: Extinction spectra of the non-annealed gold stripes recorded in air (perpendicular polarization). The width of the stripes is varying from 126 nm to 238 nm. A significant red-shift of the LSP resonance ($\Delta \lambda_{LSP} = 53$ nm) is observed from sample B1 ($\lambda_{LSP} = 646$ nm) to sample B6 ($\lambda_{LSP} = 699$ nm).



Figure 4: SERS spectra of methylene blue (MB) molecules $(10^{-5}M)$ recorded at 633 nm (acquisition time:2×5*s*., laser power 1mW) on arrays A (a) and B (b) (the stripes features are described on table I). Note that the SERS spectra are vertically shifted for more clarity. The arrays display a SERS intensity of MB systematically lower on the annealed samples (b) compared to the non annealed ones (a). It is noteworthy that the intensity of the SERS spectra of MB is decreasing for wider stripes (for both annealed and non-annealed ones). Experiments show that increasing the stripe width shifts the LSP resonance further from the laser line and thus counterbalances the greater number of roughness features.



Figure 5: (a): Polar graph of the extinction spectra for samples A1 (black squares) and B1 (red squares), displaying the dipolar character of the LSP resonance of the gold stripes; (b): polar graph of the extinction cross section of a smooth target.



Figure 6: SERS intensity of the 1620 cm^{-1} peak of MB molecules, versus the LSP wavelength at maximum, for samples A and B. The excitation takes place at 785 nm. For the annealed samples (red bars), no SERS signal of MB is observed when the LSP wavelength is far from the 785 nm laser line (samples A1 and A2). However, a residual signal is obtained for arrays A3, A4, and A5, located closer to the 785 nm line. For the non annealed samples, a SERS signal is observed for all the arrays, whatever the LPS wavelength at maximum.



Figure 7: DDA calculation of the optical near-field enhancement for a roughened target (incident wavelength: 785 nm); mapping of the NF enhancement in transverse polarization (a), in longitudinal polarization (c); lateral cross section profile together with the 3d-dimensional mapping of the NF enhancement in transverse polarization (b), in longitudinal polarization (d).

Tables

Table I: Characteristics of the arrays used in this article

N#	Stripe Width (nm)		$\lambda_{\rm LSP}({ m max}) \ ({ m nm})$		Absorbance A.U.	
_	Non annealed (B)	Annealed (A)	Non annealed	Annealed	Non annealed	Annealed
1	126	149	646	652	0.83	0.83
2	131	152	645	655	0.90	0.88
3	178	204	687	684	0.90	0.79
4	187	210	690	688	0.87	0.77
5	233	266	697	690	0.73	0.67
6	238	284	699	688	0.72	0.66