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STRONGLY POLARIZED SCATTERING IN SURFACE ENHANCED RAMAN SPECTROSCOPY OF RANDOMLY DISTRIBUTED MOLECULES ON GOLD NANOWIRES

B. FAZIO,[a] P. G. GUCCIARDI,[a]* C. D'ANDREA,[a] A. IRRERA,[a] F. BONACCORSO,[a]
G. CALOGERO,[a] C. VASI,[a] M. ALLEGRINI,[b] A. TOMA,[c] D. CHIAPPE,[c]
C. MARTELLA,[c] AND F. BUATIER DE MONGEOT [c]

ABSTRACT. We study the polarized Surface Enhanced Raman Scattering from randomly oriented molecules adsorbed on near-field coupled gold nanowires. We show that the scattering is polarized always along the wire-to-wire nanocavities. We find the exact angular dependence for the polarized, unpolarized, parallel- and cross-polarized SERS intensity. Finally we develop a model that fits the experimental data and allows to measure the field enhancement and the re-radiation enhancement factors, independently, and retrieve the depolarization ratio of the probe molecules.

1. Introduction

The Surface Enhanced Raman Scattering (SERS) of molecules deposited on rough metallic substrates is generally unpolarized due to the random orientation of the molecular dipoles[1]. Nanostructured substrates, such as metallic dimers, nanoparticle aggregates and arrays of nanorods have highlighted a strict intensity dependence of the SERS emission intensity versus the polarization of the incident electric field, due to the anisotropic excitation of localized surface plasmons (LSP) responsible of the SERS enhancement[2, 3, 4, 5].

In this paper we show that the SERS from randomly oriented molecules, adsorbed on self-assembled gold nanowires arrays produced by controlled ion beam sputtering[6, 7] is strongly polarized along the wire-to-wire nanocavity axis no matter the excitation field polarization direction[8]. We measure the exact angular dependences of the polarized, unpolarized, parallel- and cross- polarized SERS intensity.

2. Results and Discussion

Measurements are carried out using the apparatus depicted in Figure 1(A). A polarization rotation up to 90deg is observed when the nanowires are turned under the excitation beam and the polarization degree is found to depend on the excitation angle q. We show

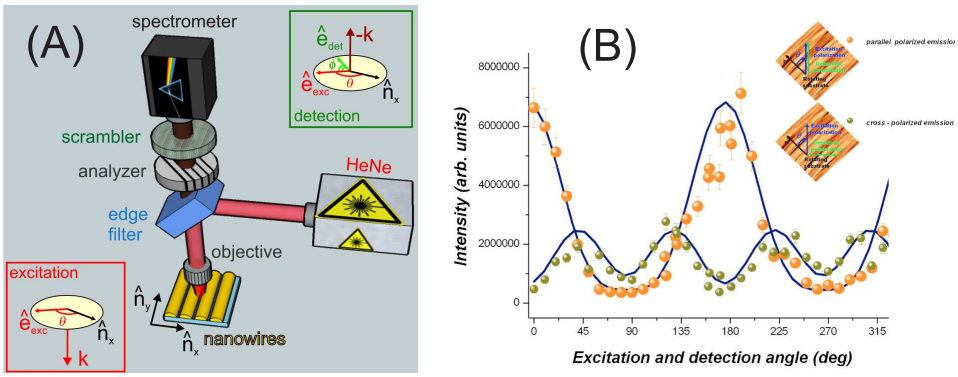

Figure 1. (A) Schematics of the experiment. Measurements are carried out in backscattering. The excitation polarization is varied by turning the sample underneath. The polarization analysis of the SERS radiation is carried out with a rotating Polaroid sheet. (B) Experimental behaviour of the parallel- (orange symbols) and of the cross-polarized (green symbols) components of the SERS emission. The blue lines are fits according to the theoretical model.

that the unpolarized SERS intensity is proportional to $\cos^2\theta$ and that only the SERS component polarized parallel to the excitation field displays the $\cos^4\theta$ behavior (Figure 1B, orange symbols). The cross-polarized component, as expected but never observed before, behaves like $\cos^2\theta \cdot \sin^2\theta$ (Figure 1B, green symbols). Our observations are explained in terms of the SERS electrostatic model and evidence the failure of the $|E|^4$model to provide a correct understanding of the polarization properties of SERS.

The observed polarization of radiation emitted by molecules strongly coupled with optical nanoantennas will have a significant impact on the engineering of plasmonic devices such as molecular sensors[9, 10] or SPASERS[11].

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References

[1] E. C. Le Ru, M. Meyer, E. Blackie, and P. G. Etchegoin, "Advanced aspects of electromagnetic SERS enhancement factors at a hot-spot", *J. Raman Spectrosc.* **39**, 1127-1134, (2008).

[2] E. C. Le Ru, J. Grand, N. Flidj, J. Aubard, G. Lvi, A. Hohenau, J. R. Krenn, E. Blackie, P. G. Etchegoin, "Experimental Verification of the SERS Electromagnetic Model beyond the E4 Approximation: Polarization Effects", *J. Phys. Chem. C* **112**, 8117 (2008).

[3] J. Grand, M. Lamy de la Chapelle, J.-L. Bijeon, P.-M. Adam, A. Vial, and P. Royer, "Role of localized surface plasmons in surface-enhanced Raman scattering of shape-controlled metallic particles in regular arrays", *Phys. Rev. B* **72**, 033407 (2005).
[4] T. Shegai, Z. Li, T. Dadosh, Z. Zhang, H. Xu, and G. Haran, "Managing light polarization via plasmon-molecule interactions within an asymmetric metal nanoparticle trimer", *Proc. Natl. Acad. Sci. U.S.A.* **105**, 16448-16453 (2008).
[5] S. M. Nie, and S. R. Emory, "Probing Single Molecules and Single Nanoparticles by Surface-Enhanced Raman Scattering", *Science* **275**, 1102-1106 (1997).
[6] A. Toma, D. Chiappe, B. Setina Batic, M. Godec, M. Jenko, and F. Buatier de Mongeot, "Erosive versus shadowing instabilities in the self-organized ion patterning of polycrystalline metal films", *Phys. Rev. B* **78**, 153406 (2008).
[7] A. Toma, D. Chiappe, D. Massabo, C. Boragno, and F. Buatier de Mongeot, "Self-organized metal nanowire arrays with tunable optical anisotropy", *Appl. Phys. Lett.* **93**, 163104 (2008).
[8] B. Fazio, *et al.*,"Re-radiation Enhancement in Polarized Surface-Enhanced Resonant Raman Scattering of Randomly Oriented Molecules on Self-Organized Gold Nanowires" *ACS Nano*, accepted (2011).
[9] S. Shanmukh, L. Jones, J. Driskell, Y. Zhao, R. Dluhy, and R. A. Tripp, "Rapid and Sensitive Detection of Respiratory Virus Molecular Signatures Using a Silver Nanorod Array SERS Substrate", *Nano Letters* **6**, 2630 (2006).
[10] J. R. Anema, and A. G. Brolo, "The Use of Polarization-dependent SERS from Scratched Gold Films to Selectively Eliminate Solution-phase Interference", *Plasmonics* **2**, 157 (2007).
[11] M. A. Noginov, *et al.*, "Demonstration of a spaser-based nanolaser", *Nature* **460**, 1110 (2009).

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[a] CNR-IPCF, Istituto per i Processi Chimico-Fisici
Via F. Stagno D'Alcontres 37
I-98158 Messina, Italy

[b] Università di Pisa and INO-CNR Sezione di Pisa
Dipartimento di Fisica "Enrico Fermi"
Largo Bruno Pontecorvo 3
56126 Pisa, Italy

[c] Università di Genova and Consorzio Nazionale Interuniversitario per le Scienze Fisiche della Materia (CNISM)
Dipartimento di Fisica
Via Dodecaneso 33
I-16146 Genova, Italy

[*] To whom correspondence should be addressed | Email: gucciardi@me.cnr.it

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