Doctoral Dissertation
Doctoral Program in Metrology (31st cycle)

Tailored fabrication of nanostructured substrates for surface-enhanced Raman spectroscopy applications

Eleonora Cara
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Supervisors
Dr. Luca Boarino, Istituto Nazionale di Ricerca Metrologica, Supervisor
Prof. Giuseppe Spoto, Università degli studi di Torino, Co-Supervisor

Politecnico di Torino
9th May 2019

Summary

Surface-enhanced Raman spectroscopy (SERS) is a vibrational spectroscopic technique providing selective information for sensing of chemical and biological species. It is based on the amplification of the Raman signals of molecules due to their interaction with the surface of plasmonic metals. Since SERS discovery, the morphology of the metallic substrate was recognised as a fundamental feature to provide a significant enhancement of the Raman signal. The modern advancement of the nanotechnologies has boosted the research activity on nanostructured substrates, pushing forward the hot spots engineering and the capabilities of SERS in ultrasensitive sensing and molecular identification. State-of-the-art 3D SERS substrates are commonly realised by means of conventional top-down nanolithography and etching techniques. These methods lead to adequate performances but are limited by time-consuming processes, high costs and low throughput.

In this dissertation, nanospheres lithography (NSL), a bottom-up technique, is exploited for the realisation of SERS substrates requiring regular plasmonic nanostructures produced over large area in a timewise manner and with affordable materials and methods. Particularly, NSL was employed in combination with a deep wet etching technique, metal-assisted chemical etching (MACE), for the realisation of gold-coated silicon nanowires (SiNWs) with hexagonally close-packed (HCP) symmetry. The high-aspect-ratio nanostructures exhibited high flexibility and the possibility to form bundles upon the evaporation of water. The location of the hot spots was found at the tip-to-tip sites of the leaning nanowires where probe molecules were adsorbed profiting from extremely high enhancement. Moreover, a quantitative analysis of the degree of order of HCP crystals of nanospheres in NSL was conducted in terms of the correlation length parameter ξ to optimise the distribution and density of the hot spots across the substrate.

The substrate with the highest long-range order (ξ larger than 1 µm), and correspondingly largest SERS enhancement, was found to display noteworthy homogeneity with inter-maps RSD of 8% evaluated over 600×600 µm^2. Moreover, the characterisation of SERS substrates relies on the evaluation of the enhancement factor (EF). However, its practical computation is often affected by a significant uncertainty in the determination of the number of molecules contributing to the SERS signal. Geometrical considerations are often used for such estimate, leading

to artificial variations of the EF of two orders of magnitude or more. A study of the EF was conducted to propose the use of synchrotron-based reference-free X-ray fluorescence for an accurate quantitative determination of the amount of analyte. The EF of the long-range ordered substrate was found equal to $(3.5 \pm 0.8) \cdot 10^4$. In addition, the gold-coated silicon nanowires SERS substrate showed promising results for its application to analytical chemistry. It was tested for the detection of melamine, a food contaminant, demonstrating high sensitivity with a limit of detection of 2.3×10^{-7} mg l^{-1} and limit of quantification of 1.3×10^{-5} mg l^{-1} in the picomolar range of analyte concentration.

Finally, in order to expand the fabrication protocol of SERS substrates based on NSL, a study on the directed self-assembly (DSA) of nanospheres was conducted. Employing topographical templates to confine the nanospheres allowed to overcome some intrinsic limitation of NSL, concerning the formation of domains with irregular shape, size and orientation. The correlated HCP domains of nanoparticles were extended to the area of tens of micrometres corresponding to the confining structures and distributed in patterns with regular shape and uniform orientation over square centimetres areas. This was especially observed in the linear templates with depth 0.6 times the spheres diameter, where 96.2 % of the domains were aligned to the template in the range $-10°$ - $10°$. The use of micrometre-sized templates exhibited remarkable results allowing to extend the use of NSL to a variety of advanced applications including biological, pharmaceutical and environmental analyses.

Part of the work reported in this dissertation has been previously published in references S. A. Kara, et al. *"Fabrication of Flexible Silicon Nanowires by Self-Assembled Metal-Assisted Chemical Etching for Surface-Enhanced Raman Spectroscopy"*; RSC Advances, 6, 96, 93649-93659 (2016) and E. Cara et al. *"Influence of the long-range ordering of gold-coated Si nanowires on SERS"*; Scientific Reports, 8, 1130 5 (2018).