

Silver-based SERS substrate fabrication using nanolithography and site selective electroless deposition

Maria Laura Coluccio^{a,b}, Gobind Das^{a,b}, Federico Mearini^{a,b}, Francesco Gentile^{a,b}, Luisa Bava^a, Rossana Talerico^a, Patrizio Candeloro^a, Carlo Liberale^{a,b},
Francesco De Angelis^{a,b} and Enzo Di Fabrizio^{a,b}

^a*BIONEM (Bio and NanoEngineering for Medicine), Università “Magna Graecia” di Catanzaro, Viale Europa, loc. Germaneto, 88100, Catanzaro, ITALY.*

^b*CalMED s.r.l., c/o Catanzaro C.da Mula Loc. Germaneto, c/o Campus Universitario Edificio Area Medicina, 88100, Catanzaro, ITALY*

In recent years, Surface-enhanced Raman scattering (SERS) has been widely studied as a method that can be used for the detection of molecules adsorbed on noble metal substrates (Cu, Ag, Au, etc) at sub-micro-molar concentrations. SERS signal arises from a huge enhancement of the local electromagnetic field close to metallic surfaces, due to the excitation of localized surface plasmons (LSP).¹ The enhancement in intensity of SERS substrate depends on the size, shape, and dielectric constant of the material so it is essential to choose these factors carefully. There are many techniques to fabricate SERS device, exhibiting the enhancement of signal to detect the molecules with concentration down to attomole, among them: electrochemically modified electrodes, colloids, island films, and regular particle arrays. The use of well-defined nanolithographic structures allows a better operation of SERS substrate, giving the possibility to fabricate the controllable and reproducible device. In this paper, we report the two-fold steps to fabricating an active SERS substrate; a) electron beam lithography to make the nano-pattern in order to control and restrict the diffusion of metallic nanoparticles on Si surface, b) Ag-based electroless deposition to have plasmonic enhancement due to metal nano-sphere. This approach is based on the assembling of silver nanoparticles on nano-patterned Si substrate with different shape and size, using an electroless method. The patterned Si wafer was dipped in a 0.15 M HF (hydrofluoric acid) solution containing 1 mM silver nitrate at 50°C for different times (10-60 sec),^{2,3} obtaining the Ag-based plasmonic SERS devices, shown in Figure 1(a,b). Rhodamine 6G (R6G) was used as probe molecules for SERS experiments, at known concentration ranging (10^{-4} M - 10^{-20} M). Raman spectra of R6G are shown in Figure 2. This SERS device, enabling to detect R6G with concentration down to 10^{-20} M, shows the great potential for chemical and biological sensors. The novelty of this work is that by combining these two techniques, e-beam lithography and electroless deposition, the device enhances the signal in such a way that we are able to detect the molecule of very low concentration.

1 R.K. Chang, T.E. Furtak (Eds.), Surface-enhanced Raman-Scattering, Plenum Press, New York, 1982; M. Moskovits, Rev. Mod. Phys. 57 (1985) 783; R. Aroca, Surface Enhanced Vibrational Spectroscopy, Wiley, Chichester, 2006.

2 Weichun Ye, Chengmin Shen, Jifa Tian, Chunming Wang, Lihong Bao, Hongjun Gao, Electrochemistry Communications 10 (2008) 625–629.

3 Shinji Yae, Noriaki Nasu, Kohei Matsumoto, Taizo Hagihara, Naoki Fukumuro, Hitoshi Matsuda, Electrochimica Acta 53 Issue 1 (2007) 35-41.

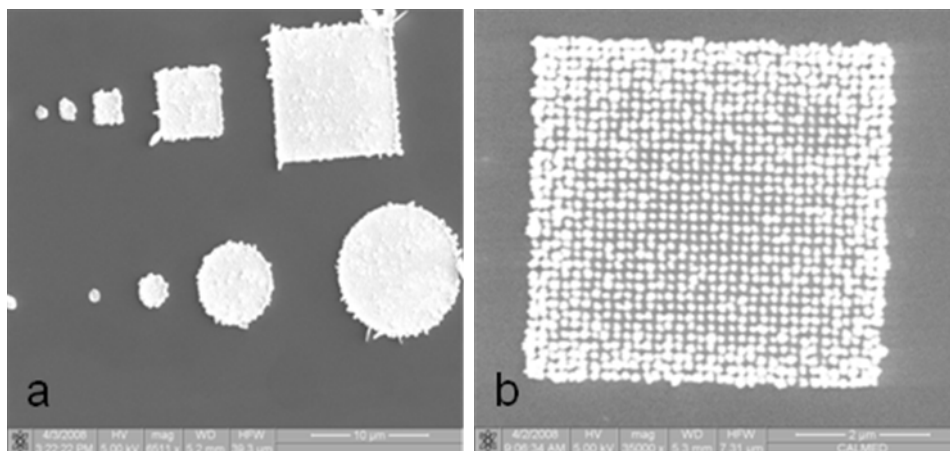


Fig 1.(a,b): SEM micrographs: Ag nanoparticles deposition on a patterned Si wafer after treatment in the HF-AgNO₃ solution.

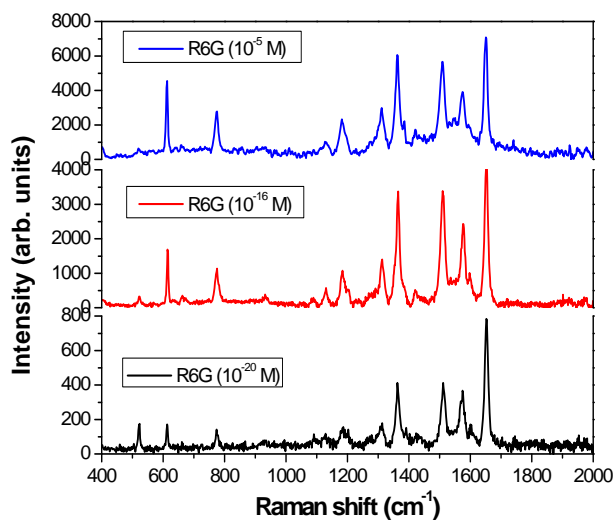


Fig 2: SERS spectra acquired from 10⁻⁵, 10⁻¹⁶ and 10⁻²⁰ M R6G, absorbed on the silver structures.