

## Fabrication of SERS-active Substrates by Electrochemical and Electroless Deposition of Metals in Macroporous Silicon

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Since its discovery surface enhanced Raman scattering (SERS) has been attracting a constantly increasing attention of the scientific community as this method demonstrates an extremely high sensitivity and allows detection of the lowest possible concentration of substances including biological specimens up to single molecule [1]. The enormous increase of the Raman signal is observed for the molecules adsorbed on the surfaces consisted of metallic nanoparticles (NPs), especially of the noble metals. The electromagnetic mechanism plays the most valuable role in such enhancement and is caused by plasmon resonance in the certain places on the metallic surfaces. Recently, use of ordered arrays of metallic nanovoids has been found to significantly improve reproducibility and enhancement of SERS signal due to specificity of the plasmon modes within metallic cavities which geometry is well controlled at the fabrication process [2, 3]. However, engineering of such arrays is often connected with an alternation of a number of liquid and dry operations which is desirable to avoid for technology simplification [4]. An urgent problem as well is still a development of the technology that provides an integration of SERS-active substrate with other elements on the single Si substrate. In the present work we propose fabrication of SERS-active metallic/macro porous silicon (PS) nanovoid arrays consisted of only electrochemical and electroless liquid steps.

As an initial template we used PS formed by anodizing of p-Si (100) wafer in solution of HF:DMSO=10:46 at 8 mA/cm<sup>2</sup> for 7 min. The depth and diameter of pores varied in the ranges 700-1200 nm and 500-1500 nm, respectively. It is in good agreement with the dimensions of nanovoids usually applied for SERS [2-4]. Two types of metallized nanovoids (single and hybrid) were fabricated by liquid deposition of Ag and Ni on PS. To form first type of substrate based on single metal (Ag), PS was immersed into the 3mM AgNO<sub>3</sub>+0.5M HF water solution for 40-200 min. As reaction of Ag reduction has positive standard potential, Ag ions attract electrons from Si atoms. In that way in water-based solutions Si is oxidized to SiO<sub>2</sub> while Ag is reduced. The addition of HF provides removing of SiO<sub>2</sub> for continuous supplying of Ag ions with electrons. To form hybrid metallization (Ag/Ni), Ni was electrochemically deposited on PS from the solution of 213 g/l NiSO<sub>4</sub>·7H<sub>2</sub>O+5 g/l NiCl<sub>2</sub>·6H<sub>2</sub>O+25 g/l H<sub>3</sub>BO<sub>3</sub>+3 g/l saccharin at 10 mA/cm<sup>2</sup> for 2.5 min. Such regime resulted in covering PS surface with continuous Ni film of 70 nm thickness. After that Ag was deposited by electroless method from the previously described solution for 5-30 min. The morphology and structure of the samples were studied with SEM Hitachi S-4800. SERS activity of substrates was tested using water-soluble CuTMpyP4 as an analyte compound. Raman spectra were registered with the spectrometer Solar TII DM160- MS3504I, equipped with CCD-detector. The source of continuous excitation was the He-Cd laser Liconix (λ=441.6 nm).

Figure 1 shows typical spectra of CuTMpyP4 on

the initial PS (a), Ag/PS (b) and Ag/Ni/PS (c). Both of metallized substrates demonstrated SERS-activity. However, hybrid metallization resulted in six orders of magnitude increase of the signal intensity in comparison to pure PS while Ag/PS provided enhancement of five orders of magnitude.

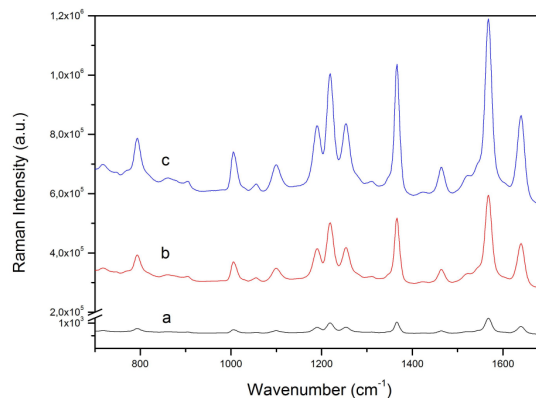


Figure 1. CuTMpyP4 (a) Raman spectrum on PS and (b, c) SERS spectra on Ag/PS, Ag/Ni/PS, respectively.

Figure 2 presents SEM of (a, c) top and (b, d) cross sectional views of PS after (a, b) 120 min of Ag deposition and (c, d) 5 min of Ag deposition followed by Ni electroplating. Ag covered PS and Ni/PS surface as a grainy quasi-continuous film. We revealed that duration of PS immersion in Ag solution does not significantly influence the sizes of silver NPs and coverage degree of pore walls but affects those on the external areas of PS surface. There was observed periodical coalescence of Ag NPs into the greater agglomerates simultaneously with decrease of coverage degree of the external PS surface which caused some lessening of the SERS signal intensity (no more than 20%).

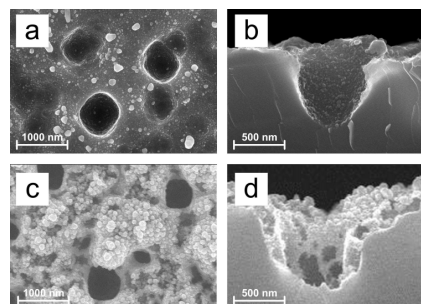


Figure 2. SEM top and cross sectional views of (a, b) Ag/PS and (c, d) Ag/Ni/PS.

Deposition of Ag NPs on Ni/PS led to partial dissolution of Ni film (Fig. 2 c, d). It was found that immersion of Ni/PS into Ag solution for more than 30 min caused complete removing of Ni film resulting in decrease of SERS signal intensity which did not exceed 20%.

Simple and effective technology of SERS-active substrates based on liquid electrochemical and electroless methods was proposed. MacroPS was demonstrated to be a template for metallized nanovoid arrays fabrication. Hybrid metallization of PS with Ag/Ni showed greater SERS effectiveness in contrast to Ag/PS substrates. SERS signal intensity was revealed to be slightly dependent on the time of metal deposition.

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