

Regularities of Electroless Deposition of Silver on Porous Silicon for Fabrication of SERS-Active Substrates

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Unique sensitivity of surface-enhanced Raman scattering (SERS) provides detailed information on the composition of analyzed materials at extremely low concentrations. Nanorough metallic films are usually used as SERS-active substrates. Recently, Ag electroless deposition on porous silicon (PS) has been found to yield SERS-active substrates of high sensitivity and storage stability [1, 2]. However, systematic study of dependence of SERS signal intensity on the regimes of Ag deposition has not been presented yet. In this paper we reported the intensity regularities of SERS signal from the analyte's molecules adsorbed on the Ag/PS substrates. It was shown that SERS-activity is directly related to the peculiarities of the structure of Ag deposit which can be managed by deposition time (t_{Ag}) and Ag salt concentration (C_{AgNO_3}).

Uniform PS layers were formed by anodization of n^+ type (100) Si wafers in the 1:3:1 mixture of HF, H₂O and C₃H₇OH at the 100 mA/cm² current density for 85 s. The Ag deposition was carried out by immersion of PS in water-ethanol solutions of AgNO₃ for different times. Samples for SERS measurements were prepared by incubation of Ag/PS substrates in the cationic Cu(II)-tetrakis(4-N-methylpyridyl) porphyrin (CuTMpyP4) aqueous solution for 2 h. SERS spectra were recorded by Solar TII DM160-MS3504I spectrometer with excitation at 441.6 nm by He-Cd laser (Liconix).

Figure 1 shows SEM images of top views of PS after Ag deposition from 1 mM AgNO₃ solution.

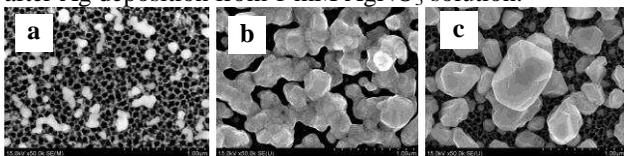


Figure 1. SEM images of top views of PS after deposition of Ag from 1 mM AgNO₃ solution for (a) 15, (b) 120 and (c) 180 min.

It demonstrates typical morphology changes of Ag deposit. At the initial stage the surface of PS was slightly covered with Ag NPs of diameter of a few to several tens nanometers (Fig. 1 a). The distance between Ag NPs varied from 150 to 500 nm. Further deposition led to the multiplication of the particles and their size increase resulted in formation of Ag agglomerates most of which are connected or extremely close to each other (Fig. 1 b). Than Ag agglomerates coalesced to the large particles of average diameter of 400-800 nm (Fig. 1 c). The disconnection of Ag agglomerates in some places at the coalescence process allowed reopening the PS surface for the new Ag NPs growth. Summarizing, the regularity of the Ag deposition consists in the alternation of the formation of the following deposits: the layer of the individual particles (Fig. 1 a, c) and quasi-continuous film (Fig. 1 b). The size and package density of Ag particles are the parameters which mostly characterize the structure of the deposit. The same behavior of the Ag deposit was observed for all applied C_{AgNO_3} . The duration of each stage of deposition decreased with the increase of C_{AgNO_3} . The comparison of Raman spectra of CuTMpyP4

adsorbed on the fresh PS and Ag/PS substrates revealed the SERS-activity of the silvered samples. The t_{Ag} alternation in the range of 15-200 min as well as C_{AgNO_3} from 1 to 10 mM resulted in the fabrication of the substrates provided 5 orders of magnitude enhancement of the Raman intensity in comparison with non-silvered PS. However, the spectra for the samples formed in 3 mM solutions are two times more intensive than those for 1 mM and 10 mM. The analysis of the SEM top views of Ag/PS samples showed that in case of 3 mM solution the content of Ag particles of 10-150 nm for all t_{Ag} was no less than 75-80%. Such sizes of particles are the best for the SERS effect promotion. Other C_{AgNO_3} resulted in the maximum 65% amount of the optimal particles during the whole deposition. In addition we found the SERS intensity oscillates depending on t_{Ag} . Figure 2 shows two-maximum dependence of the SERS intensity of the 1365 cm⁻¹ band on t_{Ag} ($C_{AgNO_3}=1$ mM). The similar character is typical for such dependencies respected to the samples fabricated in solutions 3 and 10 mM. Assuming it is caused by the peculiarities of the Ag growth, we compared the stages of Ag deposition and peaks of SERS intensity. At the beginning of deposition Ag NPs are separated to a considerable extent (Fig. 1 a). That resulted in a low level of Raman signal (Fig. 2 a). Further increase in the t_{Ag} led to the formation of the structure which is favorable to the maximum SERS enhancement, since closely package of Ag agglomerates promotes the abundance of vacancies for so-called "hot spots", i.e. the scattering cross section of the analyte's molecules should drastically increase.

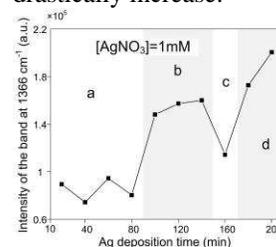


Figure 2. CuTMpyP4 1366 cm⁻¹ band intensity dependence on t_{Ag} .

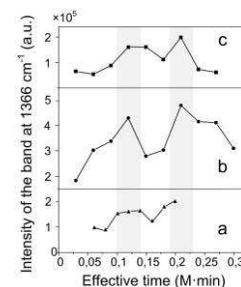


Figure 3. CuTMpyP4 1366 cm⁻¹ band intensity dependences on "effective time" of Ag deposition from (a) 1, (b) 3 and (c) 10 mM AgNO₃ solutions.

So, the first peak of SERS intensity appeared (Fig. 2 b). At the moment of large particles formation and their disconnection (Fig. 1 c) the fall-off of the SERS signal is observed (Fig. 2 c). Finally, we suggest that the second peak of the largest SERS enhancement is caused by the growth of new Ag NPs on the opened PS surface and their repacking. We proposed the universal parameter crucial for the optimal regimes of Ag/PS substrates formation – "effective time", which is calculated as multiplication of t_{Ag} by C_{AgNO_3} . The dependence the SERS signal intensity on the "effective time" is demonstrated in Figure 3. In fact, two distinct maxima (in grey) of SERS enhancement are observed for three types of Ag-PS substrates at the same "effective time" ranges. Applying the optimal "effective time" allows improving the sensitivity and is going to promote the technology optimization of Ag/PS SERS-active substrates.

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