Regularity 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 electroleos 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<sub>dep</sub>) and Ag salt concentration (C<sub>AgNO3</sub>).

Uniform PS layers were formed by anodization of n-type (100) Si wafers in the 1:3:1 mixture of HF, H<sub>2</sub>O and C<sub>2</sub>H<sub>5</sub>OH at the 100 mA/cm<sup>2</sup> current density for 85 s. The Ag deposition was carried out by immersion of PS in water-ethanol solutions of AgNO<sub>3</sub> for different times. Samples for SERS measurements were prepared by incubation of Ag/PS substrates in the cationic Cu(II)-tetraakis(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 AgNO<sub>3</sub> solution.

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 caused by the peculiarities of the Ag growth, we assumed it 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<sub>dep</sub> 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 analyze’s molecules should drastically increase.

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 open 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<sub>dep</sub> by C<sub>AgNO3</sub>. 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.

This work has been supported by the Belarusian Foundation for Fundamental Research (Grant T13M-161).