08

Surface-Enhanced Raman Spectroscopy on „Black Silicon“ Substrates

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In this work, an array of „black silicon“silicon nanofibers was formed on a silicon substrate by cryogenic reactive ion etching and studied as a substrate for surface-enhanced Raman spectroscopy. According to scanning electron microscopy, silver particles deposited by thermal sputtering uniformly coated the black silicon nanofibers, which leads to plasmon resonance and enhancement of signal intensity. The Raman spectra of the reference samples showed no responses, while the sample coated with silver particles showed a main peak at $1436\,\mathrm{cm}^{-1}$ corresponding to the $C_\alpha = C_\beta$ bond of the PEDOT:PSS polymer, which was deposited on the substrate at a low molar concentration of $7 \cdot 10^{-4}$ mol/L.

Keywords: black silicon, plasma-chemical etching, scanning electron microscopy, Raman spectroscopy.

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Raman scattering spectroscopy (RS) has proven itself to be a good method making it possible to accurately identify a wide row of chemical substances. This method is based on inelastic collisions of particles upon interaction of laser radiation with the studied molecules, changes in the photon energy may provide information on interaction of molecules [1]. However, when this method is used, a problem of defining the composition of low-concentration aqueous solutions arises, since the intensity of Raman scattering response in this case is very weak. To solve this problem, an improved method of surface-enhanced Raman scattering spectroscopy (SERS) is proposed.

This method makes it possible to study the interaction of molecules in real time mode using surface-enhanced Raman scattering using special substrates, presenting nanostructures from noble metals (Au, Ag, Cu) [2]. Therefore, photos interact with free metal electrons, causing plasmon resonance, which makes it possible to enhance the signal up to 6 times. Usually such arrays are created with the help of applying nano- and microstructures of metal on a glass substrate. However, such structures have considerable disadvantages, such as: low heterogeneity of the surface and low sensitivity [3].

This paper proposes to create a periodical array of plasmon nanoparticles, by sputtering a thin layer of silver on the surface of the nanostructured black silicon. Black silicon is an array of microcones, which effectively reduces the reflection from the surface, enhancing light scattering and absorption at the same time. The surface of the black silicon coated with nanometer layer of metal is an attractive candidate for use in the surface-enhanced Raman scattering spectroscopy.

The black silicon substrate was created using dry plasma-enhanced chemical etching in the mixture of gases SF_6/O_2 at cryogenic temperature without using the mask with additive of Ar [4]. Application of the thin silver layer was carried out using the method of resistive vacuum sputtering from the tantalum tray.

A test solution was the high-conducting polymer poly(3,4-ethylene dioxite-iofen)-polystyrene sulfonate (PEDOT:PSS) of Orgacon grade in concentration of 1%wt (approximately $7 \cdot 10^{-2}$ mol/l). The test solution was applied on the substrate of the source black silicon and substrate with the applied thin layer of silver, with subsequent washing in deionized water. Therefore, a very small quantity of substance remains on the substrate, which is hard to detect for the Raman scattering method.

Using scanning electron microscopy (SEM) in Zeiss Supra 25 unit, the structural properties and surface morphology of black silicon formed on the silicon substrate, and the structure with silver sputtered on it were studied. SEM-image of the source specimen (Figure 1, *a*) showed that the height of the black silicon fiber is approximately 5.4 mkm, and width — below 1 mkm, fibers are smooth and are cone-shaped. In Figure 1, *b* one can see that silver coats nanofibers evenly and is deposited in the form of nanoparticles, which cause plasmon resonance and enhance the Raman scattering signal from the specimen [5].

RS spectra of four specimens were studied: 1) source black silicon substrate; 2) black silicon substrate with applied PEDOT polymer:PSS; 3) black silicon substrate with applied thin layer of silver and PEDOT polymer:PSS. RS spectra measurements were carried out using ENSPECTR R532 with 532 nm laser source, with an

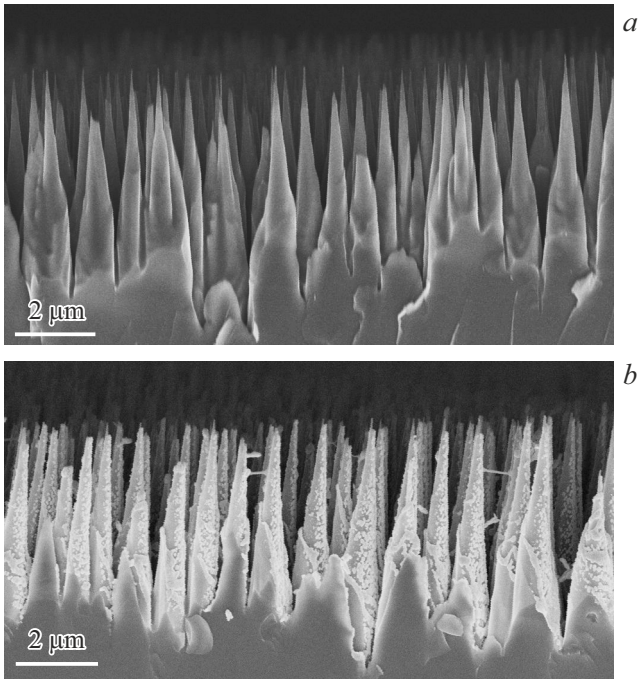

Figure 1. Images of scanning electron microscopy of black silicon substrate before (*a*) and after (*b*) silver sputtering.

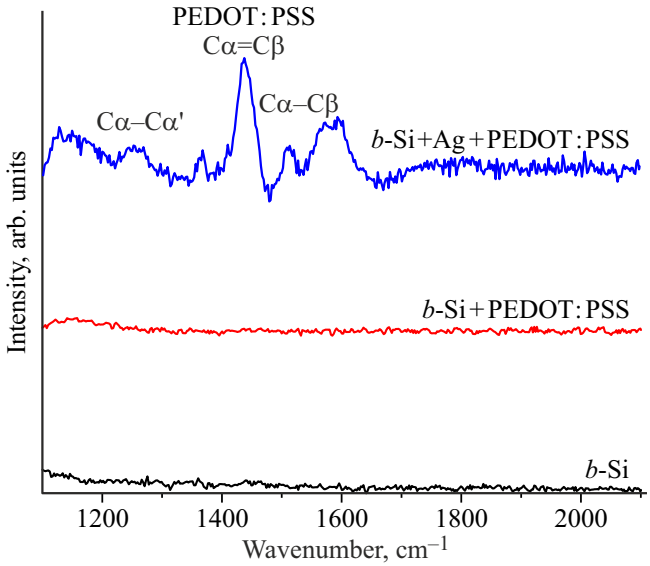

Figure 2. RS spectra of black silicon substrates: *1* — source black silicon substrate; *2* — black silicon substrate with applied PEDOT polymer:PSS; *3* — black silicon substrate with applied thin layer of silver and PEDOT polymer:PSS.

optimal integration time of 500 ms and with averaging by 200 times.

Figure 2 presents RS spectra of black silicon substrates. The spectra of the source substrate and substrate with the applied polymer show no response. The final test specimen with the thin silver layer and small quantity of PEDOT:PSS polymer applied on the surface demonstrates the main peak corresponding to shift 1436 cm^{-1}, which is a strong bond of symmetric $C_\alpha = C_\beta$ valent vibrations in PEDOT:PSS, and also a row of additional PEDOT:PSS peaks[6].

Therefore, it was shown that the black silicon substrates formed by method of plasma-chemical deposition with the applied thin layer of silver may be used for detection of extremely small quantity of the substance using surface-enhanced Raman scattering spectroscopy.

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Conflict of interest

The authors declare that they have no conflict of interest.

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