Diversiform Black Silicon Covered with Nanometer-Thick Gold Layer for Surface Enhanced Raman Scattering Spectroscopy

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Black silicon (bSi) is obtained from a flat silicon wafer through one of the etching methods (metal-assisted chemical etching, laser chemical etching, wet chemical etching, reactive ion etching (RIE), etc.). As a result, silicon surface acquires various nano- and microstructures of different shapes, regular or not, causing suppressed specular reflection and increased wide-range absorbance. These properties make bSi suitable for vis-NIR sensors, photodetectors, solar cells. Being covered with a layer of noble metals (gold, silver, copper, aluminum), it becomes beneficial for surface-enhanced Raman scattering spectroscopy (SERS). Raman signal enhancement occurs due to the phenomenon of surface plasmon resonance (SPR). However, in most attempts to apply bSi for SERS the resultant substrates are covered with a very thick noble metal layer (from 100 nm to 1000 nm) to obtain sufficient Raman signal enhancement. Moreover, the production of a stable, uniform, large-scale, low-cost, simple in fabrication and at the same time sensitive, efficient, reproducible, reliable substrate for SERS is still very challenging.

In the present research we addressed these challenging through the fabrication of bSi by RIE approach varying etching parameters, simplifying it by shifting to room temperature (RT) synthesis, and reducing the thickness of a gold (pseudo-)layer up to tens of nanometers, trying to preserve the sensitivity of the bSi-based SERS substrate and enhancement efficiency at the acceptable level. As a result, three types of bSi were produced and tested: (i) cone-like bSi fabricated by cryogenic ICP-RIE (500 nm height of Si structures) and sputtered with approx. 50 nm gold pseudo-layer, (ii) lace-like bSi fabricated by RT-ICP-RIE (1000 nm height of Si structures) and sputtered with a gold pseudo-layer forming Au hemispheres of sizes (diameters, average) 10.8 nm, 34.6 nm, and 109.7 nm on the Si surface, and (iii) pillar-like bSi fabricated by RT-ICP-RIE (600-2500 nm height of Si structures) and sputtered with a gold pseudo-layer forming Au 'island' on the Si structures. All types of bSi sputtered with gold were demonstrated to provide significant Raman signal enhancement, when excited with 785 nm irradiation, with experimentally estimated enhancement factor to be around 10^8 and 10^6 for cone-like and lace-like bSi, respectively, and determined using a standard chemical compound 4-mercaptobensoic acid (4-MBA). The substrates were uniform, with relative standard deviations of SERS intensity less than 13%, 9%, and 4%-6% for cone-like, lace-like and pillar-like bSi-based substrates, respectively. In contrast to lace-like and pillar-like bSi substrate, cone-like substrate was hydrophilic and biocompatible, suitable for the living cells growth (>98 % of cells were viable) and allowed determining SERS spectra from C6 rat glioma cells, making this version of bSi applicable for living cell analysis. Lace-like bSi-based SERS substrate was demonstrated to be re-usable for at least 10 cycles when treated with oxygen plasma, although the plasma cleaning was accompanied by efficiency loss. The performed numerical simulations of the interaction of plane wave with the fabricated structures allowed us to explain the Raman signal enhancement provided by the bSi-based substrates when excited with NIR irradiation. We revealed that for fabricated structures the SPR coincides with experimental 785 nm excitation, red-shifts for core-shell Si@Au particles with Au layer thinning and becomes more pronounce and red-shifts for overlapped Au nanoparticles with the interparticle distance increase.

Thus, in the present study we demonstrated that simplification of bSi fabrication, modification of its geometry and significant gold reduction allows production of large-scale, low-cost, reliable, efficient, reusable, and stable SERS substrate which can be beneficial in many areas of research.