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Surface plasmon enhanced broadband spectrophotometry on black silver substrates

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We demonstrate surface plasmon-induced enhancements in optical imaging and spectroscopy on silver coated silicon nanocones which we call black silver. The black silver with dense and homogeneous nanocone forest structure is fabricated with a mass-producible nanomanufacturing method. It can efficiently trap and convert incident photons into localized plasmons in broad wavelength range, permitting the enhancement in optical absorption from ultraviolet to near infrared range by 12 times, the visible fluorescence enhancement of ~30 times and the Raman scattering enhancement factor up to $\sim 10^8$. We show the potential of the black silver in high sensitivity and broadband optical sensing of molecules. © *2011 American Institute of Physics*.
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Black silver refers to silver-coated black silicon. Black silicon is the silicon surface modified to have extremely low optical reflectivity from visible to infrared range and thus has black appearance.[1] Recently its applications including highly sensitive photodiode, superhydrophobicity, and biomedical sensing starts to be realized and produced intentionally.[2–4] Black silicon can be made by reactive ion etching or femtosecond laser machining.[5] On the other hand, the plasmonic enhancements on roughed coinage metals surface (silver, gold) are known as surface enhanced fluorescence and surface enhanced Raman scattering (SERS).[6–8] The enhancement is related with surface plasmon resonance (SPR) determined by the optical constant, size and geometry of the metal surface, and surrounding media.[9] Coinage metals have appropriate optical constants for SPR in visible or near infrared (NIR) range.[9] The nanostructures boost the optical enhancement with sharp tips by "lightning-rod" effect and plasmon coupling between adjacent particles.[9]

With a reactive ion plasma etching method,[7] we produce nanocone structured black silicon with wafer scale uniformity at room temperature in a short time and in no need of photomask. The black silver is completed by depositing a layer of silver on the black silicon. We call it black silver because it looks much darker than smooth silver. The enhanced broadband optical absorbance and photon trapping are demonstrated by comparing the reflectance spectra in the wavelength range from 200 to 800 nm on smooth silver and black silver. The fluorescence enhancement is characterized by comparing the fluorescence spectra of Rhodamine 6G (R6g) molecules adsorbed on black silver and smooth silver. Furthermore, SERS detection of R6G and oligopeptides is demonstrated, exhibiting the enhancement factor up to $\sim 10^8$ and the potential in high sensitive label-free sensing.

The nanocone forest structure on the black silicon is produced by reactive oxygen and bromine ion mixture plasma etching, in which bromine ion plays the role of etching while oxygen ion plays the role of oxidized passivation. In this process, the aspect ratio and the etching rate of the silicon nanocones can be controlled by oxygen passivation time, flux rate, and bromine etching time.[4] With this etching-passivation process, we can produce the dense and uniform nanocones all over the single crystalline silicon wafer (⟨100⟩ n-type), which makes the whole wafer "black" [Fig. 1(a)] or lithographically patterned areas black [Fig. 1(b)]. Reflection measurement indicates >99% optical absorption of black silicon in visible wavelengths. The nanocone structure is the key to black silicon as it provides a graded optical reflective index layer on surface to attenuate the reflection with match of dielectric constants at the interface.

To make the black silver substrate, we deposit 5 nm thick titanium and 80 nm thick silver onto the black silicon. Figure 1(c) shows the scanning electron microscope (SEM) image of the cross section of the black silver. The silicon

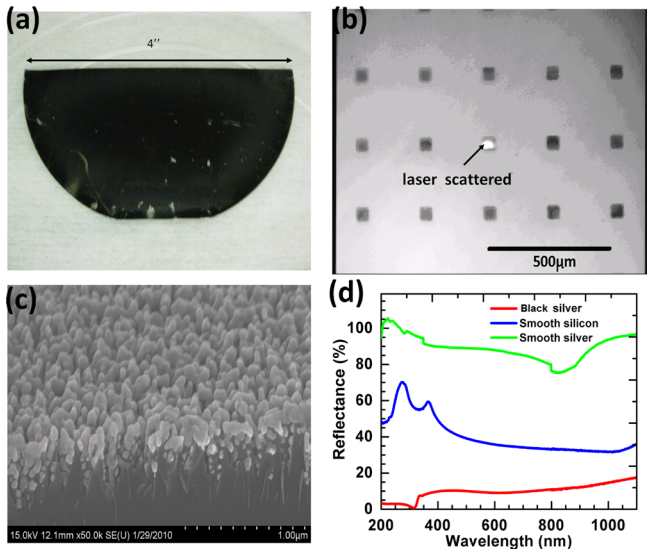

FIG. 1. (Color online) (a) Photograph of 4″ black silicon wafer. (b) Photograph of square array patterned black silver. The shining spot is induced by laser. (c) Cross section SEM image of black silver substrate. (d) Reflectance spectra of black silver, smooth silver, and smooth silicon.

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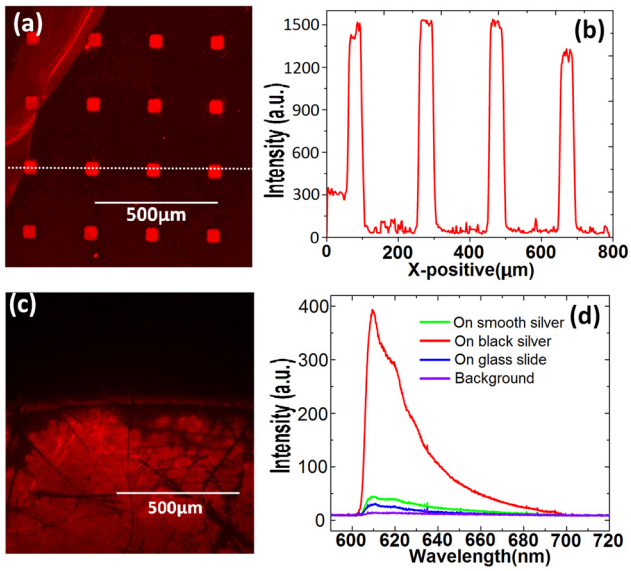

FIG. 2. (Color online) (a) Fluorescent image on square array patterned black silver. (b) Intensity profile across the white dashed line on (a). (c) Fluorescence image on the edge of a R6g on a uniform black silver substrate. (d) Fluorescence spectra of R6g on smooth silver, glass slide, and black silver.

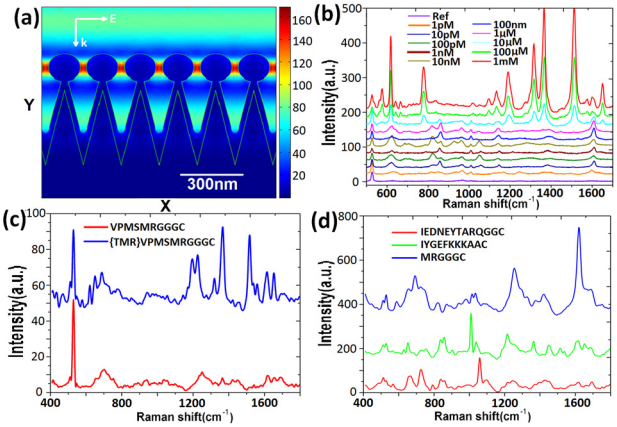

FIG. 3. (Color online) (a) 2D FEM simulation of electric field distribution on black silver. (b) SERS of R6g with different concentrations. (c) SERS of 100 nM peptides of the same sequence with and without TMR label. (d) SERS of 100 nM unlabeled peptides with three different sequences.

nanocone forest is covered by a layer of silver, especially on the tips of cones. The nanocones are around 500 nm tall, 180 nm wide at the base. The spacing between two adjacent silicon nanocones is about 100 nm that is reduced to sub-50 nm after silver coating. The smooth silver looks shining like mirror while the black silver looks much darker and more diffusive, shown in Fig. 1(b). To quantify the optical reflectance and absorbance of black silver, we measured the reflectance spectra [Fig. 1(d)] with all angle integration and in the wavelength range from 200 to 1100 nm by a integration sphere setup (Varian Gary 5G). The distinctions between reflectance on smooth silver, black silver, and smooth silicon wafer are significant. The reflectance of smooth silver is above 80% while that of black silver is below 20% in the entire wavelength range. The reflectance of smooth silicon resides in between the former two. The averaged reflectance over all wavelength range is 92.5% for smooth silver, 51.2% for smooth silicon, and 9.9% for black silver. With no transmission, the averaged absorbance of black silver is 90.1%, 12 times higher than the averaged absorbance of smooth silver (7.5%), which agrees with the reported calculation.[8] Since silver is known with low loss plasmon, we assume most of incident photons are trapped in the nanocone forest and converted to localized surface plasmons. The reflectance spectra of black silver is different from that of smooth silver, whose reflection is primarily specular and diffuse reflection. For black silver, a portion of reflection is the scattering photon emission from the resonating surface plasmons. This is confirmed by the absorption around 320 nm, where is the bulk silver plasmon resonance.

To demonstrate fluorescence enhancement on the black silver, we deposit R6g solution with the concentration of 10 μM on black silver, smooth silver, and glass slide, let dry and excite the fluorescence with green light (550 nm center wavelength). The image is taken with a microscope objective lens with 20× magnification and numerical aperture (NA) of 0.5. Figure 2(a) is the intensity image taken on the square array patterned black silver. Obviously, the intensity on the black silver square region is higher than the surrounding smooth silver region, which is also illustrated in Fig. 2(b), the intensity profile across the white dashed line in Fig. 2(a). Figure 2(c) is the fluorescence intensity image on the edge of a R6g drop stain on uniform nonpatterned black silver. The red region is covered by R6g and uniform molecule distribution ensures fair intensity comparison. In Fig. 2(d), the comparison of fluorescence emission spectra over the entire microscopic field of view (400 μm×400 μm) taken on uniform black silver, smooth silver, and regular glass slide, all captured with the integration time of 5 s, we see the intensity is much stronger on black silver than on smooth silver or glass slide. After subtracting the background, we divide the area under spectra curve from 600 to 700 nm of black silver by that of smooth silver and glass slide. The fluorescence enhancement of black silver is calculated as 15 times compared to smooth silver and nearly 30 times compared to glass slide. In most metal enhanced fluorescence like with gold particle, the emission photons are not likely to be trapped, therefore most emission photons are acquired by detector. However, with the photon trapping property, black silver may trap most emission photons within the nanocone forest from being detected. But in this case we still observed 30 times fluorescence enhancement. We propose an explanation for this: most fluorescence emission photons are converted into plasmons and later re-emitted through the plasmon scattering which account for the 10% "reflectance" measured from the black silver.

As a surface plasmon enhanced phenomena, SERS can be modeled with electromagnetic theory and the enhancement factor G can be estimated as the fourth power of the electrical field amplitude E.[10] With finite element method implemented by the software COMSOL, we simulate the two-dimensional (2D) electric field distribution around silver covered silicon nanocone structure, shown in Fig. 3(a). To approximate the structure shown in Fig. 1(c), we set an array of close-packed silicon nanocones with the height of 500 nm, width of 180 nm at the bottom, and the period spacing of 180 nm. Although the real nanostructures do not have the perfect periodicity as in the simulation, in principle the local electric field enhancement should be similar since simulated and actual nanostructures share the basic nanoscale profiles and material properties. The discrepancy between the simu-

lated and actual cases is the discrete resonance modes for the period photonic crystal structure in simulation which do not agree with the actual randomly distributed nanocone arrays. Evidenced by the SEM image in Fig. 1(c), most of the deposited silver is likely to reside on top of the nanocones and the deposition on the side wall is thinner. In the simulation model we set the side wall covered by only 15 nm thick silver and a silver bead with diameter of 80 nm on the tip of each nanocone. The optical constants of silver and silicon are polynomial fitting to the data in the handbook.[11] With the incident 785 nm transverse magnetic polarized plane wave propagating in Y direction,[9] the excited scattering electric field is calculated. The color bar on the right of Fig. 3(a) indicates the normalized amplitude of scattering electric field with respect to that of incident electric field. We can see the scattering electric field is largely enhanced in the regions between adjacent silver beads due to plasmon coupling. The maximum electric field enhancement in the proximity of the bead surface can reach 160 times. The electric field inside the cavity sandwiched by two adjacent nanocones is also amplified, especially near the valleys. Due to the unique "nanocavity" profiles of the nanocone arrays, multiple plasmon resonance modes in a very broad wavelength range exist and contribute to the high field enhancement.[12] To experimentally interrogate SERS of black silver, we measure the Raman spectra of R6g solutions with the concentrations from 1 mM to 1 pM diluted by ten times between each on black silver substrate [Fig. 3(b)]. The solution is deposited on the substrates and let dry. 10 mM R6g is measured on smooth silicon wafer for reference. By analyzing the intensity of the R6g characteristic peak at 1370 cm^{-1} in each case with a common calculation method,[7] the averaged enhancement factor on black silver is calculated as 6.38×10^{7}.

For black silver SERS, we also demonstrate its potential in labeled and nonlabeled biomolecule detection, e.g., peptide sensing. Figure 3(c) shows the SERS spectra of 100 nM tetramethylrhodamine (TMR) labeled and unlabeled peptide with the same amino acid sequence VPMSMRGGGC on a black silver. Figure 3(d) shows the SERS spectra of 100 nM unlabeled peptides with three different sequences, MRGGGC (blue curve), IEDNEYTARQGGC (red curve), and IYGEFKKKAAC (green curve) on black silver. Different characteristic peaks in Raman spectra for all three sequences allow them to be distinguished and identified without labeling.

All SERS measurements are carried on with the same setup and configuration. A laser with wavelength of 785 nm and power of 30 mW is used for Raman excitation. The scattered light is collected with an objective with 10× magnification and NA=0.28. We keep integration time of 5 s for capturing all the spectra. Prior to the analysis and plotting, the fluorescence background has been removed from all the spectra with an automated iterative polynomial fitting algorithm.[13] All peptides we use have cysteine (C) with a thiol group for bonding to silver.

In summary, we present a nanomaterial substrate, the black silver, produced by depositing silver on black silicon fabricated with plasma etching process and we demonstrate the broadband strong enhancement effects for multiple optical properties including absorption, fluorescence, and Raman scattering. The label-free peptide sensing with black silver SERS is demonstrated.

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