Black-Si as a Platform for Sensing


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ABSTRACT

The nano-textured surface of black silicon can be used as a surface-enhanced Raman scattering (SERS) substrate. Sputtered gold films showed increasing SERS sensitivity for thicknesses from 10 up to 300 nm, with sensitivity growing nonlinearly from around 50 nm until saturation at 500 nm. At 50 nm, a cross over from a discontinuous to a fully percolated film occurs as revealed by morphological and electrical measurements. The roughness of the Au coating increases due to formation of nanocrystallites of gold. Structural characterization of the black-Si needles and their surfaces revealed presence of silicon oxide and fluoride. The sharpest nano-needles had a tip curvature radius of \( \sim 10 \) nm. SERS recognition of analyte using molecular imprinted gels with tetracycline molecules of two different kinds is demonstrated.

Keywords: black-silicon, SERS, tetracycline, food safety, water safety

1. INTRODUCTION

Surface area of surface-enhanced Raman scattering (SERS) sensor is one of contributing factors to an overall detection sensitivity but usually it is not measured. Determination of the actual surface area by an electrochemical cyclic voltammetry has been demonstrated using catodic peak of Au passivation. It was shown that surface area of Au sputtered over laser ablated SERS sensor on sapphire is up to 10 times larger as compared with surface area of Au on glass. Surface nano-roughening is contributing to the light scattering and, hence, to SERS. However, extremely rough surfaces produced by electrochemical, plasma, or laser assisted plasma etching such as black Si (b-Si) have surface areas even larger. They appear black due to low \( \sim 1\% \) reflectivity at visible spectral range. As SERS substrates, such surfaces are very sensitive to the numerical aperture of the focusing lens used to collect Raman signal. At the optimized focusing (numerical aperture 0.7-0.9) for a fixed aspect ratio (< 5) black-Si, efficient SERS substrates can be prepared using Au sputtering. A natural question arises what is the optimum reflectivity of the black-Si of a high surface area for a good overall sensitivity of analyte detection by SERS? Better understanding of b-Si surface properties, curvature and structure (amorphous vs crystalline) of the needles is required. Sputtering or evaporation of metal (Au, Ag) cause formation of none uniform layer, e.g., evaporation with a more directional metal flux tend to form a layer over top of the needles while sputtering causes more even and conformal deposition.

Black-Si can be used as a sensing platform with combination with Au-colloidal nanoparticles prepared by laser ablation in water without surfactant; in water ablated Au colloids are promising for more flexible chemical functionalization since surface has now residual surfactant contamination. Bactericidal properties of black-Si due to mechanical puncture of the bacteria/cell membrane is promising for SERS of the interior of the cells, e.g., malaria parasites in red blood cells. SERS combination with molecular imprint technology is another very...
promising technology for sensing. Very strong discrimination between two most common tetracycline molecules using imprinted gels has been recently demonstrated using surface plasmon resonance (SPR) in optical fibers.\(^7\) Where a wavelength shift up to 30 nm was observed at \(\sim 0.1\ \mu\text{M}\) concentration of the matching analyte.\(^7\) Since SPR via wavelength discrimination in fiber for white-light illumination has very broad spectral features there is a limitation on sensitivity which can be further improved using SERS with molecular imprint investigated in this study.

Here, we report on a structural characterization of a low-aspect-ratio b-Si which has the needle height comparable with the axial extent. SERS was carried out at typical focusing with a numerical aperture of \(N.A = 0.8 \pm 0.1\) which correspond to the conditions when axial length of the focus is comparable with the b-Si needle height. We show for the first time that molecular imprint is compatible with SERS on black-Si using the most simple drop cast preparation of sensors for the two varieties of tetracycline used in the tests. High rejection rate of non-matching analyze molecules is promising for food safety applications.

## 2. EXPERIMENTAL: SAMPLES AND PROCEDURES

The final goal of this study was creation of SERS substrates on b-Si for sensing with the molecular imprint. This is promising due to a very time efficient substrate preparation which requires minutes of dry etching and Au sputtering. The gel preparation by drop-casting and baking is a fast process. The final samples are shown in Fig. 1. Below, the used procedures of sample preparation, characterization and SERS measurements are described in more details.

### 2.1 Fabrication of black-Si

Plasma dry etching procedures are described for nano-texturing the Si surface via a controlled flow of SF\(_6\):O\(_2\) mixture, with voltages of the bias and inductively-coupled plasma that influence the anisotropy of surface etching together with a chamber pressure. The formation of nano-pillars of aspect ratio \(2.2 \pm 0.3\) takes 10 - 15 min of plasma etching, with full area coverage of 3- and 4-inch wafers.
Black-Si was fabricated from a single side polished p-type (100) orientation silicon wafer. Fabrication was performed using dry reactive ion etching (DRIE) method. A RIE-101iPH (SAMCO Inc.) tool capable of performing reactive ion etching (RIE) and inductively coupled plasma (ICP) assisted RIE was used in experiments: 150 W ICP and 15 W (for the RIE) bias powers were typically used, flows were set 35 sccm for SF$_6$ and 45 sccm for O$_2$, chamber pressure was 1 Pa and etching time was 15 min. Typical sample is shown in Fig. 2 (height vs preparation conditions summary is shown in Fig. 3). Magnetron sputter AXXIS (Kurt J. Lesker Ltd) then was used for gold deposition with well controlled thickness (Fig. 4).

### 2.2 Structural and surface characterization

X-ray photoelectron spectroscopy (XPS) using a Thermo Scientific K-alpha XPS system equipped was Al K$_\alpha$ source (1487.6 eV). Spectra were collected with the flood gun active to alleviate sample charging.

### 2.3 SERS measurements and preparation of molecular imprints

Fabricated b-Si was used as a substrate for SERS. The surface was coated by 200 nm Au layer to form plasmonic hot-spots for electric field enhancement. Coated b-Si wafer was diced into 0.5 × 0.5 cm$^2$ chips which were prepared for SERS by molecular imprint procedures described below.
Selective layer was formed on top of the coated black silicon. Two selective layers for different molecules were made by imprinting target molecules in acrylamide/N,N-methylolenediacrylamide (AM/BIS) matrix. In our case the target molecules were widely used antibiotics: tetracycline hydrochloride (TC) and oxytetracycline hydrochloride (OTC). Phosphate buffer of 0.1 M and pH 7 was prepared using (Na$_2$HPO$_4$)$_2$H$_2$O and (NaH$_2$PO$_4$)$_2$H$_2$O in Millipore water. The master solution was prepared by mixing AM/BIS (4 g AM + 0.2 g BIS) and 0.8 g TC (0.8 g OTC for OTC molecular imprints) molecules in Millipore water and stirring for 10 min in nitrogen atmosphere. Polymerization medium was made by adding 2.5 ml master solution, 4.5 ml buffer, 30 wt % Acrylic acid (AA), 7.5 mg ammonium persulfate (APS) and 20 µl of N-tetramethylethylenediamine (TEMED) in 10 ml Millipore water. The diced black silicon chips then was drop coated by the prepared solution and kept in oven at 50°C for 3 hours for polymerization. After polymerization has completed the substrates were taken out and dipped in aqueous solution of 10 wt% sodium lauryl sulphate (SDS) and 1 ml acetic acid for 2 hours at room temperature for the removal of the target molecules (TC or OTC). It was then washed with de-ionized water. For SERS detection 10 mM TC and OTC aqueous solutions were prepared separately. The SERS substrates designed for TC or OTC molecules were immersed in both solutions for 1 hour at room temperature for target molecules to inter inside imprint layer and reach the surface of coated gold. Then samples were rinsed with de-ionized water and dried. Fig. 1 shows images of the tested samples.

Raman microscope (Renishaw) was used for sample characterization. Microscope objective with 0.75 NA and 50 times magnification was used to deliver 785 nm laser light to the substrate.

3. RESULTS

Samples of b-Si were characterized by SEM and XPS for their morphology and surface properties. Then, SERS measurements were carried out using molecular imprints.

3.1 Morphology of b-Si

The morphology of b-Si surface greatly depends on all the conditions used in fabrication. An increase in SF$_6$ gas flow from 30 to 50 sccm creates a larger separation between the formed pillars. When ICP and RIE powers are varied, the etching time and/or a process pressure is changed, surface morphologies vary even more greatly: forming pyramids, pillars or tube-like structures on the sample surface. It is noteworthy that an increase of the RIE voltage cause a more anisotropic etching while a large bias voltage of ICP cause favors isotropic etching. Usually there is a limitation for application of simultaneous high RIE and ICP voltages.

3.2 Surface characterization

Figure 5 shows an XPS survey spectrum of the black Si surface. The adventitious surface carbon peak is centered at 285.3 eV indicating that minimal sample charging occurred. Several surface contaminations are present from the black Si fabrication process, in addition to a native surface oxide. The presence of strong oxygen and fluorine peaks is due to residual contaminates from the dry etching process, in addition surface oxide will continue to form once the sample is exposed to atmosphere. Sulphur (S) from the dry etching process is also present, however the relatively low intensity of this peak indicates that S as most likely not formed a surface compound like fluorine and oxygen. The Al seen likely originates from the Al$_2$O$_3$ sample holder, during the dry etching process some Al is removed and will redeposit on the sample surface. The doublet in the Si 2p peak indicates the formation of a second Si species, this second peak can be attributed to SiO$_2$ but likely has a component that can be attributed to SiF$_x$.

Table 1 shows the composition of the black Si surface as determined from the XPS survey spectrum. The presence of a significant amount of F further reinforces that the fluorine present has formed SiF$_x$. Other authors have attributed the fluorine peak to a combination of SiF$_x$ and Si-O-F bonds.

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Figure 5. XPS survey scan of black silicon created with 15 min etch time. Photoelectron peaks have been labeled.

Table 1. The composition of black Si surface as determined by XPS measurements.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic %</th>
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<tbody>
<tr>
<td>Si</td>
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<tr>
<td>O</td>
<td>35</td>
</tr>
<tr>
<td>F</td>
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</tr>
<tr>
<td>S</td>
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<tr>
<td>C</td>
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<tr>
<td>Al</td>
<td>10.7</td>
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<tr>
<td>N</td>
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3.3 SERS substrate preparation

Black-Si samples coated with Au showed a change from a non-continuous metal island film to distinct nano-gaps formation at the thicknesses of Au from 10 to 200 nm. At thicker coatings of ∼400 nm Au (Fig. 4) a continuous layer of Au with apparent grains was formed. For the best SERS performance we used 200-nm-thick coating when nano-gaps are present. For the higher aspect ratio b-Si, we have observed formation of conformal coating of Au sputtered at similar conditions.

To test the dependance of a formed pillar height on b-Si surface versus gas flow rates used in fabrication, the flow of SF$_6$ and O$_2$ was varied from 30 to 50 sccm in 5 sccm increments. Figure 3 demonstrates a schematic representation of the obtained results; the flow of 50 sccm of O$_2$ and 30 sccm of SF$_6$ produced the highest pillars of ∼1300 nm. Interplay of ICP and RIE voltages are the main control knobs to change the balance between more anisotropic (by RIE) vs isotropic (by ICP) etching. Usually, it is not possible to set both bias voltages high due to hardware and electronic constraints.

3.4 SERS sensing

Molecular imprinted gels for tetracycline recognition on Au-coated b-Si were tested as SERS platforms. Raman response spectra from 200 cm$^{-1}$ to 2000 cm$^{-1}$ were measured. Figure 6(a) shows spectra from TC imprint itself and TC imprint after immersion into a TC solution. The molecules and imprint match each other and this allows TC molecules enter into the imprint polymer and reach proximity of the Au nano-rough regions with hot spots. The measured TC imprint spectra was subtracted from TC imprint with TC molecules data to improve a TC peak recognition. The subtracted spectrum is plotted in Fig. 6(b). Reference spectra of TC powder was also measured and compared with the SERS data. Distinct TC peaks between 1200 cm$^{-1}$ and 1400 cm$^{-1}$
Figure 6. SERS spectra of TC imprint with matching and mismatching molecules: (a)&(b) TC molecules in TC imprint, (c)&(d) OTC molecules in TC imprint.

clearly indicates recognition of the matching molecules. A crosscheck of the substrate was done by immersing TC imprint in the OTC solution. In this case OTC molecules should not be detected as they can not enter into the polymer and reach vicinity of gold layer. Figure 6(c,d) shows recorded and subtracted spectra, respectively. The spectrum does not show well expressed peaks of the OTC molecules due to mismatch between imprint and molecules as one would expect.

The same procedure was repeated with OTC imprint ant results were similar: OTC molecules were detected with the OTC imprint and very low signal from TC molecules were obtained on the OTC imprint.

4. DISCUSSION

The concentration of the solution for molecular recognition was considerably high 10 mM and this allowed shortened time for permeation of the gel of the imprint. Typical thickness of the drop-casted gel used in the imprint was varied from 20 to 60 µm, obtained by mixing gel components in different ratios. In all cases SERS measurements were successful demonstrating a good permeability of the gel matrix.

In future work spin coating of gel will be made over larger areas of b-Si and this should improve performance of SERS recognition due to thinner gel film. By intentionally shifting the focal spot from the Au surface into gel by ~ 2 µm caused almost total loss of a SERS signal (doubled Rayleigh length of the beam was ~ 1.6 µm). Hence, only the pre-surface regions are active for SERS. This favors b-Si with needle height of 1.5 µm as a good match for SERS measurements with \( NA = 0.8 \sim 0.9 \) objective lenses.

Black-Si is a promising SERS sensing platform\(^2\) and can find applications along SERS sensors made by surface nano-texturing by ablation.\(^12\sim14\) Laser fabrication with ultra-short pulses has unique capability to create...
textures from tens-of-nanometers to wavelength scale, however, b-Si has also potential for tuning surface morphologies via processing parameters and is a faster parallel method as compared with laser direct write. Future work is required to investigate potential of b-Si as a metal island SERS substrate at thinner Au coatings when additional light enhancement effects can be created due to Fresnel enhancement effect. The proposed sensor can be integrated into micro-fluidic sensing platforms and be used with laser/plasmonic tweezers and to explore gel phase transitions for concentration of analyte.

5. CONCLUSIONS

Black-Si of the aspect ratio $\sim 2.2 \pm 0.2$ closely matching the axial extent of the light beam with $NA = 0.8 \pm 0.1$ objective lens widely implemented for SERS measurements was fabricated and characterized. Au coating of $\sim 200$ nm was chosen for SERS measurements using tetracycline molecular imprints in gel.

Recognition of tetracyclines by molecular gel imprints is a promising result of this work. It is noteworthy, that gel imprints were prepared and SERS measurements were carried out in collaborating labs in Delhi and Melbourne. We used the same chemicals ordered from different suppliers. Considering courier shipping conditions and approximately an one week duration from gel preparation to the actual measurements, the demonstrated SERS recognition using molecular imprints on b-Si has a promising future for real life applications. Moreover, gels of different thicknesses of tens of micrometers performed well in SERS measurements demonstrating good permeability.

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REFERENCES


