SILICON NANO-STRUCTURE FABRICATION
AND APPLICATION FOR SURFACE-ENHANCED RAMAN SPECTROSCOPY

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ABSTRACT

We demonstrated fabrication of black silicon with slanted nano-pillar array on both planar and 3D micro- and mesoscale structures produced by a high-throughput lithography-free oblique-angle plasma etching process. Nano-pillars with gradual change in height were created on the same piece of silicon. The relation between the slant angle of nano-pillars and incident angle of directional plasma is experimentally investigated. In order to demonstrate the monolithic integration of nano-structures on micro- and mesoscale nonplanar surfaces, a nano-pillar forest is fabricated on nonplanar silicon surfaces in various morphologies such as silicon atomic force microscopy (AFM) tips and pyramidal pits. By integrating nano-pillars on inverse silicon micro-pyramid array devices, we further improved the surface-enhanced Raman scattering (SERS) enhancement property of this optimized commercial SERS substrate by severalfold even when using 66% less noble metal coating. We investigated the length gradient dependence and asymmetric properties of SERS effects for slanted nano-pillar with polarized excitation. This versatile and angle-controllable nano-pillar fabrication and monolithic 3D nano–micro–meso integration method provides new dimensions for production and optimization of SERS and other nano-photonic sensors.
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CHAPTER 1

INTRODUCTION

1.1 Black silicon

Black silicon is a semiconductor material whose surface is modified with micro- or nano-structures to become highly absorptive and thus appears black. It was discovered in the 1980s as an unwanted side effect of reactive ion etching (RIE) in the semiconductor industry [1]. It can be formed by laser treatment [2], electrochemical etching, metal-assisted chemical etching, stain etching and other processes [3].

Over the years, black silicon has been applied to improve the sensitivity of image sensors and the efficiency of photodetector and solar cells [4], to serve as an antibacterial surface [5], high sensitive photodetector, super-hydrophobic material, and biomedical sensor [6],[7]. Researchers are looking for methods to produce black silicon on purpose, especially at low cost and high repeatability. Besides RIE, other methods to produce black silicon include chemical wet etching [8],[9], laser pulse irradiation [2],[10], and nanoparticle-catalyzed etch [11]. Among these techniques, RIE has the advantages of high throughput and low cost, so it is still the most widely used method.

In order to produce sophisticated nanostructures such as 3D photonic crystal, angle-controllable engineering in micro- and nano-scale fabrication is pursued with
different methods. Oblique directional RIE with Faraday cage was developed in the 1980s and has been used for producing photonic crystal [12],[13]. Angle-controlled ion sputtering and focused ion-beam erosion are also used for creating nano-patterns [14]–[16]. The most prevalent method of producing slanted nano-structure is oblique angle deposition or glancing angle deposition (GLAD) [17],[18]. A self-organized nano-rod array can be produced with oblique angle deposition and has been used as humidity sensor [19], surface-enhanced Raman spectroscopy (SERS) substrate [20],[21], optical fiber sensor [22], plasmonic oligomer sensor [23], 2D–3D photonic crystal [24], and micro-battery [25]. Similar to GLAD, the slanted nano-cone black silicon (SNBS) fabrication process is a mask-free and self-organized process. GLAD is a growth process while SNBS is an etching process, which offers better cost-effectiveness and is more suitable for monolithic integration. In addition, as the silicon nano-cones are a part of the bulk silicon substrate, the interfacial material incompatibility issues are avoided.

1.2 Metal coated black silicon

On the homogeneous and dense conic forest structure coated by silver, we got an absorptive and diffusive metal surface which can be used to achieve surface-enhanced Raman scattering (SERS) and surface-enhanced fluorescence. The plasmonic enhancements on roughed noble metal surfaces (silver, gold) can be explained by surface plasmon resonance (SPR) and provide high sensitivity for cancer diagnosis and toxin detection.
1.3 Raman spectroscopy and surface-enhanced Raman scattering

Raman spectroscopy is a spectroscopic technique to observe rotational, vibrational, and other low-frequency modes in a system [26]. It is commonly used in chemistry to provide a fingerprint of molecules to be identified. It relies on inelastic scattering of monochromatic light from a laser. The light interacts with phonons (molecular vibrations) resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the vibrational modes in the system. Usually, a laser beam illuminates a sample. Electromagnetic radiation from the illuminated spot is collected with a lens and sent to an optical system. The light with wavelength equal to that of the incident wave (Rayleigh scattering) is filtered out and the rest is projected onto a detector with a grating and a CCD detector.

However, spontaneous Raman scattering is a weak phenomenon and the resulting spectrum is blended with intense Rayleigh scattered laser light. Mostly, researchers can get weak Raman signals even when large quantities of samples, high power of incident laser beam, and long exposure time are applied.

Because surface-enhanced Raman spectroscopy (SERS) gives a much stronger Raman scattering, it is my focus of research. Normally SERS is done in a gold or silver colloid or substrate containing gold or silver. Because Raman intensities are proportional to the electrical field, there is a significant increase in the measured signal.
As mentioned, metal coated black silicon has SPR. Here we need to introduce SPR briefly. A plasmon is the collective excitation of the electron gas of a conductor. A surface plasmon occurs if the excitation is confined near the surface. It can either be propagating or localized. Under conditions of surface plasmon excitation, the electromagnetic field of the light at the surface can be substantially enhanced. Both the incident laser field and the scattered Raman field under this condition constitute the SERS mechanism. Take, for example, a metal sphere in an external electric field; if the radius is much smaller than the wavelength of light, the electric field can be approximated by the Rayleigh scattering model. The field induced at the surface is related to the field of the laser for eqn. (1), where \( \varepsilon_1(\omega) \) is the frequency-dependent, complex dielectric function of the metal and \( \varepsilon_2 \) is the relative permittivity of the ambient phase. Resonance occurs at the frequency when \( \text{Re}(\varepsilon_1) = -2\varepsilon_2 \). Excitation of the surface plasmon greatly increases the local field experienced by a molecule absorbed on the surface of the particle. As the particle not only enhances the field of the incident laser but also the Raman scattered field, a small increase in the local field produces a large enhancement in the Raman scattering. Overall enhancement scales roughly as the fourth order of electrical field [27].

\[
E_{\text{induced}} = \left( \varepsilon_1(\omega) - \varepsilon_2 / \varepsilon_1(\omega) + 2\varepsilon_2 \right) E_{\text{laser}}
\]  

(1)

With the contribution of SPR, SERS provides substantially stronger signal than normal Raman scattering does. As Figure 1 shows, normal Raman signal of 0.1 M
rhodamine 6G (R6G) is only 1/10 the intensity of SERS signal of $10^6$ M R6G [28]. Thus, SERS in this work amplified the signal intensity by about $10^6$ so that targets with very low concentration can be identified.

Figure 1 Comparison between Raman and SERS under excitation laser of 633nm wavelength. Red: Raman intensity with 0.1M R6G. Blue: Intensity of SERS with $10^4$M R6G. [28]

In the following text, we will demonstrate our ability to integrate black silicon features which are random nano-pillar structures to assorted micro-structured silicon devices. Then we will investigate the abilities of SERS with these structures coated with silver [29].
CHAPTER 2

MANIFOLD SILICON NANO-PILLAR FABRICATION

2.1 Overview

This chapter describes the fabrication of black silicon with slanted nano-pillar array, on both planar and 3D micro- and mesoscale structures, produced by a high-throughput lithography-free plasma etching process.

On the same piece of silicon, we fabricated nano-pillars with gradual change in angle. We investigated the relationship between the slant angle of nano-pillars and incident angle of directional plasma. A nano-pillar forest was fabricated on nonplanar silicon surfaces in various morphologies such as silicon pyramidal pits and atomic force microscopy (AFM) tips, demonstrating the monolithic integration of nano-structures on micro- and mesoscale nonplanar surfaces.

2.2 Fabrication process of silicon nano-pillar

Our improved RIE process, a three-step O₂–CHF₃–Cl₂ process at room temperature which takes less than 20 min in total, was used to fabricate the black silicon. We have verified that this is a reliable and controllable three-step process. Figure 2a is the cross-sectional schematic of the three-step fabrication set-up for producing nano-pillar black silicon. First, a thin film of oxide is formed on silicon surface by oxygen plasma (Figure 2b), which takes 5 min. Second, CHF₃ is flowed in for 2 min after O₂ is shut
down (Figure 2c). This short period of CHF$_3$ plasma is for removing the thin oxide layer to form dispersed islands rather than for completely etching away the oxide.

Third, CHF$_3$ is shut down and the mixture of Cl$_2$ and Ar at the ratio of 10 to 1 is flowed in. This step is to etch the silicon to create the nano-pillars with the nano-mask of the oxide islands formed in step 2, as Figure 2d shows. Cl$_2$ is the etching gas while Ar is added to increase the etching rate by physical bombardment of the silicon surface. Without Ar, the etched rate was rather slow and the silicon did not turn black.

Step 3 is highly controllable because the etching rate is determined by the radio-frequency (RF) power. Under a certain etching rate, the etching depth is controlled by the etching time. In this article, we stick to the recipe with the etching rate of about 30 nm/min and 10 min-etching to get nano-pillars with about 300 nm-length. The result of the whole process is shown in Figure 2e as a scanning electron microscope (SEM) image. After dipping the silicon into BOE for 5 seconds, the top silicon oxide is removed and the result is shown in Figure 2f.

Even though it is a three-step process, all the three steps were carried out sequentially at room temperature and in the same reaction chamber. Therefore, it is still a one-step process in terms of maneuverability. Even though this three-step O$_2$–CHF$_3$–Ar + Cl$_2$ process is a bit more complex and time-consuming than previous one-step HBr–O$_2$ process from our group [4], it is more controllable. In the one-step HBr–O$_2$ process, HBr and O$_2$ are mixed; thus, the oxide mask formation and the etching of nano-pillars are simultaneous. Thereby different processes are entangled; it is rather difficult to
quantitatively control each individual process. In this three-step O₂–CHF₃–Ar + Cl₂ process, the first two steps are formation of oxide nano-mask and the third step is for etching; each step is separate thus can be precisely and tuned individually.

![Diagram of setup to produce black silicon with RIE. The gray parts are the top and bottom electrodes to create electric fields. The orange part is the plasma formed in the chamber. The pink part is the alumina carrier wafer. The blue part is the silicon piece to be etched.](image)

Three-step O₂–CHF₃–Ar + Cl₂ fabrication process. (b–d) A thin oxide layer (orange) formed on silicon surface (blue) by oxygen plasma. (c) Dispersed oxide nano-mask formed by etching thin oxide layer with CHF₃ plasma, the inset is the SEM picture of the nano-mask. Scale bar=300nm. (d) Nano-pillars etched by mixture plasma of Cl₂ and Ar (10:1). (e) SEM image of etched nano-pillar with SiO₂ nano-mask. (f) SEM image of nano-pillar after SiO₂ removal. [29]

2.3 Fabrication process of slanted silicon nano-pillar

In order to fabricate slanted nano-pillar black silicon (SNBS), we used some glass stacks to hold the sample so that there is an angle α between the carrier wafer and the silicon sample as Figure 3a shows. Angle α is determined by the height of the stack of glass at the right-hand side, H, and the space between the two glass stacks L. Thus, tangent α equals the quotient of H divided by L.
Figure 3 (a) Diagram of setup to produce slanted black silicon with RIE. One side (right side in this diagram) of the piece of silicon is blocked by a stack of glass slides, and the other side (left side in this diagram) is blocked with one glass slide. The thickness of the silicon piece is exaggerated for illustration. The titled angle $\alpha$ is determined by the height of the stack of glass slide $H$ and the distance between the two glass stacks $L$. $\tan(\alpha) = H/L$. (b–d) Three-step $O_2$–CHF$_3$–Ar + Cl$_2$ process for SNBS fabrication. The arrows of the radicals are the incident direction of the plasma relative to the sample. [29]

The following steps are quite similar as etching straight nano-pillars described in previous section, as Figure 3b–d shows. The differences are, first, that the energized radicals are projected slantedly onto the surface of silicon substrate, but there is no difference in terms of silicon oxide formation and selective etching compared with previous case; and second, that at the etching step (Figure 3d), the nano-pillars were formed at an angle between the normal angle of the silicon plane and the incident angle of the plasma radicals, which we will discuss specifically later.

2.4 Dependence of nano-pillar angle on etching tilted angle

Figures 4a–i are cross-sectional SEM images of SNBS after RIE treatment under
different etching angles. We can see that these nano-pillars are about 300–400 nm long. Some granular substances seen in Figure 4d came from the sputtered gold to avoid charging during SEM imaging. The pillar slant angle $\beta$ is defined as the angle between the normal of the silicon plane and the pillar. Figure 4a shows the SNBS after vertical etching without tilting ($0^\circ$ vertical etching means that the incident plasma flow is vertical to silicon). This is the common vertical nanocone black silicon demonstrated in our previous work [4].

Figure 4 Dependence of nanocone slant angle on etching tilted angle. Cross-section SEM of slanted nanocone black silicon when etching tilted angle of (a) 0°, (b) 8°, (c) 15°, (d) 20°, (e) 30°, (f) 40°, (g) 50°, (h) 60°, and (i) 70° (scale bar = 300 nm). (j) Plot of the angle dependence. [29]

The etching angles in Figures 4a–i are 0°, 8°, 15°, 20°, 30°, 40°, 50°, 60°, and 70°,
respectively. As the etching angle $\alpha$ increases, the pillar slant angle $\beta$ will also increase. But $\beta$ is always smaller than $\alpha$. When the etching angle $\alpha$ goes above 80°, the nano-pillars will not form and thus the silicon substrate surface will not turn black. For every SEM image in Figure 4, we measured and marked the complementary angle of cone slant angle $\beta$. The plot in Figure 4j shows the more explicit relationship between the etching angle $\alpha$ and cone slant angle $\beta$.

2.5 Gradual length of nano-pillars on SNBS

We already demonstrated that the nano-pillar slant angle is dependent on the etching angle. A photograph of two pieces of SNBS is shown in Figure 5a. Each piece of SNBS is not uniformly black. The piece shown on the left side of Figure 5a is the same one shown in Figure 4g with the etching angle $\alpha = 50^\circ$ while the piece shown on the right side of Figure 5a is the same one shown in Figure 4e, with the etching angle $\alpha = 30^\circ$. We can see that each piece is lighter on the upper side and darker on the lower side with gradual color change. The lighter side on the silicon piece in Figure 5a corresponds to the higher side shown in Figure 3a. All the SEM images in Figure 4 were taken on the black end of the silicon pieces.
Figure 5 (a) Gradient of darkness on two pieces of slanted nanocone black silicon with etching angle of 50° (piece on the left) and 30° (place on right). The lower side is lighter while the upper side is darker (scale bar = 1 cm). (b–g) Cross-sectional SEM images taken on the SNBS on the right (α = 30°) in (a) to show the gradient of cone lengths from light end to dark end of SNBS. The following percentages stand for the location where the SEM is taken in the path from the light end to the dark end. L is the measured length of one cone. (b) 0%, no cone, $L = 0$ nm; (c) 20%, $L = 166$ nm; (d) 40%, $L = 204$ nm; (e) 60%, 232 nm; (f) 80%, 301 nm; (g) 100%, 386 nm (scale bar = 300 nm). [29]

To see what induced this gradual change of appearance at nanoscale, we took cross-sectional SEM images at different locations on the silicon piece, as shown in Figures 5b–g. We let the percentages stand for the location where the SEM is taken in the path from the light end to the dark end. Figure 5b is taken at the light end. As we move from the light end to the dark end, the nano-pillars tend to be longer. Even though the nano-pillar length varies at different places, the slant angle stays almost the same, about 20° everywhere on this piece.
Figure 6 shows the top view images of the SNBS in Figure 5. The images convey similar information; i.e., pillars are shorter at the light end. We did not see the difference in the density of nano-pillars.

The reason for this gradual length phenomenon can be explained by the differences in ion speed at different heights. When the plasma is ignited, a plasma cloud occupies the chamber while leaving a space of several millimeters from the carrier wafer,
which is called sheath. Across this sheath, a strong electric field from the DC bias is applied [30]. For the part far from the carrier wafer, the field is much weaker and the ion speed is slower. Thus, when the step 2 of CHF$_3$ was in process, the silicon oxide did not get removed, which explains why the top part was smooth; and during step 3, the etch rate was much slower, which explains why the pillars get shorter with increasing distance from the carrier wafer.

2.6 Integration of nano-pillar on micro-structure

After investigation of etching nano-pillars on horizontal silicon and tilted silicon pieces, we demonstrate that it can also be applied to 3D nonplanar silicon surface, especially on existing micro-structures. We chose three kinds of silicon microstructures including positive pyramids, inverse pyramidal pits, and sharp AFM tip. SEM images of these micro-scale surfaces before (insets of Figures 7a,c,e) and after (Figures 7b,d,f) the monolithic integration of slanted silicon nano-pillars are shown in Figure 7.

The positive micro-scale pyramids are on the surface of commercial solar cells, produced by KOH anisotropic etching of silicon (Figures 7a,b). The inverse pyramidal pits are on the surface of Klarite SERS substrate (Renishaw), produced by photolithography and KOH anisotropic etching (Figures 7c,d).
Figure 7 (a) Scale bar = 5 μm and (b) scale bar = 2 μm. Nanocone forest made on silicon pyramids. (c) Scale bar = 2 μm and (d) scale bar = 1 μm. Nanocone forest made on inverted pyramids on silicon (black Klarite). (e) Scale bar = 10 μm and (f) scale bar = 1 μm. Nanocone forest made on silicon AFM tip. For each row, the SEM image in the right column is the magnified image of the region cropped by the white square in the SEM image in the left column. The insets in the bottom left corners of (a), (c), and (e) are SEM images of silicon pyramids, original Klarite after gold being removed, and silicon AFM tip before RIE treatment, respectively. The scale bars in the insets in (a), (c), and (e) are 2, 1, and 4 μm, respectively. The insets in the upper right corners of (b), (d), and (f) are photographs to compare the appearances of silicon pyramids (solar cell), silicon inverted pyramids (Klarite), and AFM tip chips with (black) and without (original) nanocone forest. The scale bars in the insets in (b), (d), and (f) are 8 cm, 1 cm, and 5 mm, respectively. [29]

Figure 7e,f shows nano-pillars formed on an AFM silicon cantilever tip. All these surfaces turn black after the nano-pillars are formed on the 3D micro-structures. The insets on the upper right corners of Figure 7b,d,f show the comparison of the appearances of these surfaces before and after being treated by our plasma etching
process. We give the inverse silicon pyramids with slanted silicon nano-pillars the name *black Klarite*. Both the positive pyramids and pyramidal pits are created by anisotropic chemical etching of the silicon (100) plane, so both have exposed (111) planes with the angle of 54.7° with respect to the horizontal plane [31]. In this case, the angle of the incident plasma with the normal of the wall of pyramids is also 54.7°. For the AFM silicon cantilever tip in Figures 7e,f, we notice that nano-pillars are formed on most surfaces except for those sidewalls which are too steep. In Figure 7e, the sidewalls of the long sharp spike are almost vertical, and they are smooth without any nano-pillars. But on the tip of the spike that is a bit flat, the nano-pillars are formed. This matches the phenomenon in section 2.4 that when SNBS is tilted more than a certain degree, no nano-pillars are formed.
CHAPTER 3

SURFACE-ENHANCED RAMAN SPECTROSCOPY ON NANO-STRUCTURE SILICON

3.1 SERS measurement on metal coated silicon nano-pillar and black Klarite

Surface-enhanced Raman spectroscopy (SERS) is a surface-sensitive technique that enhances Raman scattering by molecules adsorbed on rough metal surfaces. The enhancement factor can be as high as $10^{10}$ to enable single molecule detection [32]. The enhancement factor is strongly dependent on the material and morphology of the rough metal surface. Our group member have already demonstrated that straight cone black silicon deposited with 80 nm silver can enhance the Raman scattering of rhodamine 6G more than $10^7$ times and the fluorescence of rhodamine 6G by 30 times.

In this article, our major purpose is to use SERS as a tool to characterize the various surface morphologies of the SNBS. We will find the relationship between the SERS enhancement and surface morphology as well as other fabrication conditions. This will contribute to the design and optimization of SERS substrates.

First, we compare the SERS enhancement on the sub-micrometer pyramids structure with and without nano-pillars. Since we can make nano-pillars on the inverse pyramids array structure (Figures 7c,d), which is the Klarite SERS substrate after gold being removed, we compare this structure with original Klarite SERS substrate for SERS. We call it black Klarite here, a photograph of which is shown in inset of Figure
7d. We also take the planar silicon with nano-pillar (planar black silicon) for SERS comparison. For the black Klarite and planar black silicon with the nano-pillars with height of 300 nm, we deposited 80 nm of gold by electron beam (e-beam) evaporation. Before the deposition of gold, 5 nm of titanium was deposited as an adhesion layer between gold and silicon. The original Klarite SERS substrate has a 300 nm thick gold layer on the surface [31]. In the visible and near-infrared range, the SERS enhancement of silver is usually higher than that of gold by 2 orders under the same nano-structure [33], but silver will eventually get oxidized and lose enhancement. The reason we use gold instead of silver here is for fair comparison with original Klarite. Simple dropping and physical adsorption of analyte on the surface will form nonuniform coverage called the coffee stain effect. To get a uniform and quantitative characterization, a monolayer of the target molecule benzenethiol was formed on the gold surface by thiol–gold conjugation chemistry. The benzenethiol monolayer is formed by immersing the substrate in the solution of benzenethiol in ethanol with the concentration of 4 mM for 1 h [34]. Then we acquire the Raman spectra of benzenethiol by a Renishaw Raman system with the 785 nm laser with power of 1 mW and exposure time of 10 s.

Figure 8a shows the SERS spectra of benzenethiol on smooth gold surface (black curve), original Klarite SERS substrate (green curve), planar black silicon (red curve), and black Klarite (blue curve). The characteristic Raman peaks of benzenethiol are marked out at the wavenumber of 695 cm\(^{-1}\) (\(\beta_{\text{CCC}} + \nu_{\text{CS}}\)), 1073 cm\(^{-1}\) (\(\beta_{\text{CH}}\)), and
1575 cm\(^{-1}\) (\(\nu_{CC}\)); \(\beta\) and \(\nu\) indicate the in-plane bending and the stretching modes, respectively [35]. In Figure 8a, the smooth gold surface hardly shows any Raman peaks while black Klarite and planar black silicon show higher peaks than original Klarite.

![Graph](image)

Figure 8 (a) Raman spectra of benzenethiol monolayer on different substrates including smooth gold surface (black), original Klarite SERS substrate (green), planar black silicon coated with 80 nm gold (red), and black Klarite substrate coated with 80 nm gold (blue). The exciting laser is with the wavelength of 785 nm, power of 1 mW, and exposure time of 10 s (a.u. stands for arbitrary units). (b) Reflection spectra of different substrates including original Klarite SERS substrate (green), planar black silicon coated with 80 nm of gold (red), and black Klarite substrate coated with 80 nm of gold (blue). The smooth gold surface is regarded as 100% reflection mirror for reference. [29]

For a quantitative analysis of SERS enhancement, we calculated the enhancement factors of each substrate based on the peak intensity at 1073 cm\(^{-1}\) since all the Raman peaks are proportional in intensity on each substrate. As original Klarite substrate is proved to have enhancement factor of \(\sim 10^6\) [31], we use it as a reference to compute the enhancement factors for other substrates. The enhancement factor (EF) is calculated using the formula

\[
EF = 10^6 \times \frac{I_{\text{specimen}}}{I_{\text{Klarite}}} \tag{2}
\]
in which $10^6$ is the enhancement factor of original Klarite and $I_{\text{specimen}}$ and $I_{\text{Klarite}}$ are the Raman peak intensity at 1073 cm$^{-1}$ of the substrate of interest and original Klarite, respectively. The calculated enhancement factors (EF) of different substrates are listed in Table 1.

Table 1. Calculated Enhancement Factors of Original Klarite SERS Substrates, Planar Black Silicon, and Black Klarite

<table>
<thead>
<tr>
<th>substrate</th>
<th>original Klarite</th>
<th>Planar black Si</th>
<th>black Klarite</th>
</tr>
</thead>
<tbody>
<tr>
<td>EF</td>
<td>$1\times10^6$</td>
<td>$3.5\times10^6$</td>
<td>$3.9\times10^6$</td>
</tr>
</tbody>
</table>

From Figure 8a and Table 1, we can see that planar black silicon and black Klarite have larger SERS enhancement than original Klarite. The original Klarite is made with inverse pyramidal pits for plasmon resonance at 785 nm to optimize SERS excited by this wavelength [31]. The enhancement factor (EF) of black Klarite and planar black silicon are $3.9 \times 10^6$ and $3.5 \times 10^6$, respectively, larger than the EF of original Klarite. Previously, we got the enhancement factor of the order of $10^7$ by depositing 80 nm of silver on planar black silicon [36]. It is reasonable for gold to have lower enhancement factor than silver with the same nanostructure by 2 orders in visible and near-IR range. The result that black Klarite and planar black silicon have similar EF indicates that the micro-size inverse pyramid structure does not remarkably help the SERS of nano-pillar black silicon.
Our explanation is that even though the nano-pillar forest creates more SERS hotspots for scattering light, at the same time it makes the reflection more diffusive and thus destructs the plasmon resonance mode at 785 nm of the smooth inversed pyramid array. This explanation is simply verified by the appearance of the substrates. The black Klarite does not show the iridescence seen on original Klarite, shown in the inset of Figure 7d. The reason why the EF of black Klarite is slighter higher than that of planar black silicon is probably only that inverted pyramids have more surface area than the planar surface. In the photograph in inset of Figure 7d, we can see the region of black inverse pyramids is darker than the surrounding regions of planar black silicon but with no iridescence.

The comparison of reflection spectra of black Klarite and original Klarite in the wavelength range from 650 to 850 nm in Figure 8b gives a more quantitative and convincing proof of our explanation. In Figure 8b, we can see that the original Klarite shows a dip around 760 nm (close to 785 nm) while the planar black silicon and black Klarite do not show a dip there. But the reflection of black Klarite is lower than that of planar black silicon, which confirms our observation on the inset of Figure 7d; that is, black Klarite is darker than planar black silicon. We improved the EF of Klarite SERS substrate by almost 4 times by making nano-pillars on the inverse silicon pyramid array. Even if the improvement is within 1 order of magnitude, we only need to deposit 80 nm of gold, less than one third of the 300 nm of gold on the original Klarite.
3.2 SERS measurement on metal coated slanted silicon nano-pillar with different angles

Since SERS is strongly dependent on the size, structure, and material of metal surfaces, we also use SERS to characterize the surface of the SNBS. There are multiple factors that may affect SERS, including the type and thickness of metal being deposited, length, density, and slant angle of nano-pillars. For the purpose of SERS optimization, it is of great interest to investigate how the SERS enhancement factor depends on these factors. The first factor we want to investigate is the effect of the slant angle of nano-pillars.

To characterize the slant angle dependence, we deposited 80 nm of gold on to SNBS with different slant angles, including the normal black silicon with straight up cones (zero slant angle). A monolayer of benzenethiol was formed on the surface as the analyte for SERS. Then Raman spectra were taken at the dark end of SNBS because, according to the results in Figure 5, the nano-pillar in this region has length, 300 nm, comparable to that of the straight up nano-pillar on vertical back silicon. Concerning the asymmetry of the slanted nano-pillar, we need to consider polarization. Figures 9a,b are the schematics to show how the propagation and polarization directions of laser excitation are related to the slant direction of the nano-pillar and the normal of the substrate. Figure 9a shows the polarization parallel to the slant direction while Figure 9b shows the polarization perpendicular to the slant direction. We did not use polarizer for the collection of scattered light. Figure 9c shows the relation of Raman
intensity at the 1073 cm\(^{-1}\) peak along with its corresponding enhancement factor with different slant angles, for both polarization directions. However, we did not see a clear monotonic trend of the Raman intensity with the slant angle. But the polarization does matter for slanted nano-pillars.

![Diagram showing laser excitation and polarization](image)

Figure 9 (a) and (b) are schematics showing the propagation direction and polarization of laser excitation relative to the slanted nanocones and the normal of substrate. (a) Polarization is parallel to the slant direction. (b) Polarization is perpendicular to the slant direction. S is Poynting vector or the propagation direction. E is direction of electric field or polarization. (c) Peak intensities at 1073 cm\(^{-1}\) measured at the dark end of SNBS after 80 nm gold deposition with different slant angle. The right vertical axis shows the enhancement factors calculated based on the peak intensities at 1073 cm\(^{-1}\). The letter M stands for million or \(\times 10^6\). [29]

For normal black silicon with slant angle of zero, the polarization direction makes no difference. For other slant angles, the Raman intensity is always higher when the polarization is perpendicular to the slant direction than when it is parallel. And this difference becomes more prominent with increased slant angle.
3.3 SERS measurement on metal coated slanted silicon nano-pillar with different length and metal thickness

To investigate the effect of pillar length and metal thickness on SERS, we deposited gold with thickness of 30 and 80 nm onto a 30° SNBS for SERS. We have shown in Figure 5 that there is a gradient in darkness, which is essentially a gradient in the height of the nano-pillar on the piece. Figure 10(a)-(d) show the SERS measurement of benzenethiol on SNBS coated with (a),(b) 30 nm and (c),(d) 80 nm of gold with the excitation of polarization (a),(c) perpendicular and (b),(d) parallel to the slant direction of the slanted nano-pillar. The percentage stands for the location where the spectrum is taken from the light end to dark end of the silicon piece (Figure 5a). For instance, 50% means the spectrum is taken when the laser spot is located halfway between the light and dark ends, and 0% means at the edge of the light end. From the spectra we can see the SERS signal intensity increases from the light to the dark end. SERS enhancement factor calculated based on the Raman peak at 1073 cm\(^{-1}\) with eqn. (2) is indicated on the right vertical axis. Figure 10e shows that the SERS enhancement factor increases from the light to the dark end in an almost linear relationship for both polarizations. It also indicates there is no significant difference in SERS intensity at the same location for the two polarizations. However, the enhancement factor in this case is only around the order of 10\(^4\)–10\(^5\), much weaker compared than that of 10\(^6\)–10\(^7\) on black silicon deposited with 80 nm of gold. Figure 10f shows enhancement factor from light to the dark end of a 30° SNBS with 80 nm gold for perpendicular and parallel polarizations. With 80 nm gold deposited, the...
intensity–location relation is not monotonic like 30 nm gold sample in Figure 10e. The enhancement factors for both polarizations are of the order of $10^6$–$10^7$ with the maximum enhancement factor around $7 \times 10^6$ except at the light end, where it is of the order of $10^5$. That means most places except the light end of SNBS with 80 nm of gold have comparable SERS enhancement with vertical nano-pillar planar black silicon with 80 nm of gold. Similar to the result shown in Figure 9, the enhancement factor for perpendicular polarization for SNBS with 80 nm of gold is always higher than that for parallel polarization at the same location.

To see what caused the difference in SERS results when SNBS is deposited with 30 and 80 nm of gold, we took top-view and cross-sectional SEM images of SNBS with 30 and 80 nm of gold, shown in Figure 11. Figures 11a,e are top-view SEM images of SNBS with 30 nm gold and 80 nm gold, respectively, where the arrow indicates the slant direction of the nano-pillar. After the gold being deposited on the nano-pillar, it forms a particlelike structure on the pillar. By comparing Figures 11a and 11e, we can see the feature size of 80 nm gold deposition is bigger than that of 30 nm gold deposition; thus, the spacing between adjacent particles is smaller. Closer spacing between particles creates stronger local electric field for stronger SERS enhancement as long as the particles are not touching, which is proven in the literature [37].
Figure 10 SERS spectra of benzenethiol on slanted nano-pillar black silicon coated with (a)-(b) 30 nm and (c)-(d) 80 nm of gold with the excitation of polarization (a)&(c) perpendicular and (b)&(d) parallel on the slant direction of the slanted nano-pillars. The percentage labeled for each curve stands for how far away the data is captured from the light to the dark end on the silicon piece in Figure 5a. (e)-(f) Enhancement factor calculated from the peak intensity at 1073 cm$^{-1}$ from the light to the dark end of SNBS with etching angle = 30° for 30 nm (e) and 80 nm (f) gold deposition. The letter k stands for thousand or $\times 10^3$, and M stands for million or $\times 10^6$. [29]

Another explanation for stronger SERS on 80 nm gold samples is that the red-shift in the plasmonic band aligns more closely with the excitation wavelength (785 nm), providing higher enhancement than for smaller particles which do not show such a
Figure 11 SEM images of 30° slanted nano-pillar black silicon deposited with gold of thickness of (a–d) 30 nm and (e–h) 80 nm. The top view SEM images of slanted nano-pillar black silicon deposited with (a) 30 nm of gold and (b) 80 nm of gold; the arrow indicates the slanted direction of nano-pillar. Cross-sectional SEM images of light end of the piece deposit with (b) 30 nm of gold and (f) 80 nm of gold, middle of the piece deposited with (c) 30 nm of gold and (g) 80 nm of gold, and the dark end of the piece with (d) 30 nm of gold and (h) 80 nm of gold (scale bar = 300 nm). [29]

great red-shift.
Figures 11b–d are cross-sectional SEM images of SNBS deposited with 30 nm gold at the light end, halfway, and dark end, respectively. Figures 11f–h are cross-sectional SEM images for 80 nm gold deposition.

3.4 Discussion

We have demonstrated slanted nano-pillars produced on planar and micro-structured silicon and investigated their SERS properties. Several questions need be answered.

What caused the difference in SERS results shown in Figure 10 when SNBS is deposited with 30 and 80 nm of gold? In the experimental results part, we already explained that 80 nm gold SNBS has stronger SERS because of stronger coupling and red-shift of plasmonic band aligned closely with laser excitation. Why does SERS intensity increase monotonically as the cone length increases on the 30 nm gold sample but not on the 80 nm gold sample? Figures 11b–d show that as 30 nm gold deposition is so thin, there are lots of nanoparticles deposited on the slanted silicon nano-pillars. There is mostly particle plasmon, but little surface plasmon along the slanted nano-pillars or the whole substrate surface. In this case the SERS intensity should be proportional to the number of nano-particles, which increases with the height of the nano-pillars. Figures 11f–h show that for the 80 nm gold sample we start to have a continuous film covering the nano-pillar surface. In this case, the pillar-pillar plasmon coupling is the key to SERS. Previous results on polarized SERS
on slanted silver nanorod array also demonstrated that perpendicular polarization gives stronger SERS due to stronger rod–rod coupling [38]. However, this is not exactly pillar-pillar coupling. Figures 8e–h show that after 80 nm gold deposition the cone is not fully covered by a uniform gold film. Actually, most of gold stays on top of the cone like a bead. The local field enhancement for SERS mainly comes from the coupling between those gold beads or particles on top of the nano-cones. So for the 80 nm gold SNBS, the enhancement is determined by the formation of those gold nanoparticles rather than by the silicon nano-pillars. That explains why the SERS intensity in 80 nm gold sample does not increase monotonically as in case of the 30 nm thick gold sample. The SERS intensity on the 80 nm gold SNBS is relatively uniform except at the light end, where the nano-pillars are too short for gold nano-particles to form the particle-like shape as in the region with longer cones. Figure 9c shows that SERS intensity does not have a clear trend with slant angle, which can also be explained with the formation of gold nanoparticles as described below. The enhancements on SNBS with different slant angles for the same polarization are of the same order even though they are not identical. In Figures 9 and 10, at the same spot on an 80 nm gold SNBS, SERS is always stronger for perpendicular polarization compared to parallel polarization (with reference to slant direction). In Figure 11e, we can see that in the slant direction the adjacent gold nano-particles are farther apart than those in the perpendicular direction. With larger spacing between gold particles in the slant direction, the coupling is weaker and plasmonic band is less aligned with laser excitation (785 nm). Therefore, SERS is
weaker. With larger slant angle, the spacing between particles in the slant direction is even larger. But the spacing between particles in the direction perpendicular to the slant angle does not change. That explains why the difference in SERS between two polarizations becomes more prominent with increased slant angle.

A more general question is: What is the additional contribution of the black silicon, over the normal silicon nanostructure, to the SERS enhancement factor? The major advantage of black silicon on SERS is its broadband and omnidirectional enhancement due to its irregular corrugated surface structure. For silicon with periodic nano-structure, the coupling is highly wavelength and angle selective. Thus, it is usually iridescent. But black silicon looks black from all directions. That means black silicon can efficiently absorb light in very broad bandwidth from wide angles. Even with metal deposited (which is supposed to give rise to a mirror surface), it still couples light from broad bandwidth and wide angles [4]. The absorption or coupling can be attributed to two factors. One is the gradient effective refractive index of the sharp nano-pillar layer. The other is diffraction of the irregular subwavelength nano-pillar array. In addition, after metal deposition, the sharpness of the nano-pillar helps create hot spots for SERS, known as the “lightning rod” effect. Because of randomness in the structure, there is the possibility of overwhelming interference (constructive) of surface plasma at some location, which will give rise to very high electromagnetic field (“hot spot”). The irregular corrugated nano-structure also provides an additional surface plasmon coupled scattering path for the photons. All
these factors contribute more to SERS than periodic silicon nano-structure.
CHAPTER 4

CONCLUSION

We demonstrated that the nano-pillar forest can be formed on a variety of silicon surfaces with 3D microstructures, including AFM cantilever tips, inverse pyramid array on commercial SERS substrate, and positive pyramids on solar cell, with a three-step self-masked reactive ion etching process. All these silicon surfaces become black after the treatment. SERS enhancement factor of $3.9 \times 10^6$ was achieved after depositing 80 nm of gold onto Klarite SERS substrate we made black, which is better than the EF of $10^6$ for the original Klarite SERS substrate coated with 300 nm of gold. SNBS was produced with a tilted etching process. SNBS deposited with 30 and 80 nm of gold shows the enhancement factor on the order of $10^4$–$10^5$ and $10^6$–$10^7$, respectively. The SERS intensity on SNBS with 30 nm of gold shows an almost linear dependence on the darkness or nano-pillar length, but no dependence on the polarization of excitation light, while the SERS intensity on SNBS with 80 nm of gold shows no dependence on the darkness or nano-pillar length, but shows dependence on the polarization of excitation light. The SERS intensity is stronger when the polarization is perpendicular to the slant direction. We explain the SERS results with the formation of gold nanoparticles on the slanted silicon nano-pillars. The slanted nano-pillar black silicon integrated on 3D microstructures provides new dimensions for fabrication and optimization of SERS sensors as well as other nano-photonic sensors.
REFERENCES


