High aspect ratio SiNW arrays with Ag nanoparticles decoration for strong SERS detection

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Abstract
Well-ordered silicon nanowires (SiNWs) are applied as surface-enhanced Raman scattering (SERS) substrates. Laser interference lithography is used to fabricate large-area periodic nanostructures. By controlling the reaction time of metal assisted chemical etching, various aspect ratios of SiNWs are generated. Ag nanoparticles are decorated on the substrates via redox reaction to allow a good coverage of Ag over the SiNWs. As the height of the SiNWs increases, the light scattering inside the structures is enhanced. The number of the probing molecules within the detection volume is increased as well. These factors contribute to stronger light–matter interaction and thus lead to higher SERS signal intensity. However, the light trapping effect is more significant for higher SiNWs, which prevents the detection of the SERS signals. An optimized aspect ratio ~5:1 (1 μm height and 200 nm width) for the SiNW array is found. The well-ordered SiNWs demonstrate better SERS signal intensity and uniformity than the randomly arranged SiNWs.

Keywords: surface enhanced Raman scattering, nanowires, surface plasmons

1. Introduction
The plasmon resonance of surface metallic nanostructures can exhibit significant local field enhancement [1], leading to a dramatic increase in the intrinsically weak Raman scattering signals [2]. Meanwhile, charge transfer among metal surface and target molecules can also help enhance the Raman scattering [3]. Via these electromagnetic and charge transfer mechanisms, metallic nanostructures have been widely applied in surface enhanced Raman scattering (SERS) for applications such as fingerprinting bio-sensing and imaging. Recent developments in the fabrication and optical characterization of nanostructures boost the studies of SERS substrates with improved sensitivity and reproducibility. Various SERS substrates, such as Ag film on nanospheres and nanoprisms, have been studied [4–7]. The geometries were well designed to create hotspots at the resonance to improve the SERS performance. In recent years, three dimensional (3D) SERS substrates have been introduced to show...
impressive sensitivities [8–10]. Michael et al have demonstrated SERS substrates based on Au deposited Si nanowires (SiNWs) [11]. The leaning effect was studied to considerably enhance the SERS signals. Nevertheless, in this work, only the top area of the SiNWs contributed to the SERS detection. Glass nanowire arrays with nanogap-rich silver nanoislands for SERS detection were also demonstrated by Oh et al. Nanoislands were located on both top and sidewalls of the nanowires (NWs) to generate high-density hotspots [12]. However, the glass NWs used in this paper were limited in height. The advantages of the vertical dimension were not fully developed. Black Si surfaces fabricated by reactive ion etching were investigated by Gervinskas et al for SERS sensing [13, 14]. They discussed the influences on SERS signals at different thicknesses of the metal film coating and different solid angles (numerical aperture of excitation/collection optics) on the detection signals.

The higher aspect ratio (height/width) of SiNWs creates more surface area available for the formation of hotspots. It also improves the adsorption of probing molecules within the detection volume. Meanwhile, the SiNWs can increase light scattering within the structures, leading to intense light–metal and light–molecule interactions. These factors contribute to intense SERS signal enhancement. However, the light trapping effect is enhanced in higher SiNWs, which prevents the collection of the SERS signals [15]. Therefore, an optimization is needed to balance these effects.

In this paper, we report the 3D SERS substrates based on well-ordered SiNWs with Ag nanoparticle (NP) decoration. By combining laser interference lithography (LIL) and metal assisted chemical etching, we fabricate the 3D SERS substrates over a large area (cm²). By changing the reaction time, various aspect ratios of NWs are obtained. The SERS spectra of 4-methylbenzenethiol on the substrates are analyzed to optimize the aspect ratio. The optical reflection of these substrates is studied to evaluate the SERS performance. We also investigate the different SERS performance of well-ordered SiNWs and randomly arranged SiNWs. The well-ordered SiNWs exhibit better SERS signal intensity and uniformity due to the optimized height and the periodic configuration.

2. Methodology

The fabrication process is illustrated in scheme 1. A positive photoresist S1805 was firstly spin coated on 725 μm thick p-Si (100) substrates. The doping concentration of the Si substrates is around 5 × 10¹⁶ cm⁻³. The samples were baked at 90 ºC for 15 min. The photoresist was exposed using LIL with 325 nm light by two perpendicular exposures. The typical resolution of LIL using 325 nm light is around 200 nm. In the present work, the period of the nanowire array is set as 600 nm. The density of the NWs per unit area is around 2.78 × 10⁶ NWs mm⁻². After photoresist developing, a layer of Au (approximately 15 nm thick) was deposited by an e-beam evaporator (EB03 BOC Edwards). Then the samples were chemical etched in a solution of H₂O₂, HF and H₂O. The concentrations of HF and H₂O₂ were 4.6 and 0.44 M. The etching time varied from 30 s to 10 min to achieve SiNWs with different heights. The Au was then removed using gold etchant. To decorate Ag NPs on the SiNWs, the substrates
were dipped into an aqueous deposition solution of 5 M HF and 10 mM AgNO₃ for 1 min in the dark. After being washed with deionized water and ethanol, the Ag NPs were deposited over the nanostructures. The morphology of our 3D SERS substrates was characterized by a JEOL JSM-5600 field emission scanning electron microscope.

The 3D SERS substrates were functionalized with a self-assembled monolayer of 4-methylbenzenethiol. The substrates were submerged inside a 10 mM 4-methylbenzenethiol solution made with ethanol for 8 h and then gently rinsed in an ethanol solution for 30 s, followed by drying of nitrogen. A laser Raman microscope system (Nanophoton RAMAN-touch) with non-polarized 532 nm laser excitation was used to characterize the SERS properties of the substrates. Signals were obtained through a 100× microscope objective lens and projected onto a thermoelectrically cooled CCD array with a 600 g mm⁻¹ diffraction grating. To characterize the fabricated samples, a UV–visible–NIR micro-spectrophotometer (CRAIC QDI 2010 based on a Leica DMR microscope) was used. A non-polarized normal incident light was applied to excite the nanostructures.

3. Results and discussion

Figure 1(a) shows the SEM images of the well-ordered SiNWs at different heights. The periodic surface structures were made by LIL. The metal assisted chemical etching process configured the SiNWs from 600 nm to 10 μm for different etching time. The etching relies on an electrochemical reaction between the Si surface and the solution of HF and H₂O₂ catalyzed by the Au layer. It only takes place at the Si–Au interface. The vertical SiNWs can be etched in an anisotropic way by using the patterned Au nanostructures as catalyst layer [15–17]. During the etching process, the cylindrical shapes of the structures are greatly influenced by the contact of the metal film and Si surface especially at the boundaries of the nanostructures. Despite the variance on the shape of the structures, the height and periodicity can be well controlled by the etching time and LIL. These factors are more significant for the application. The period of the NWs is controlled at around 600 nm and the diameter of the SiNWs is around 200 nm. The aspect ratio of the SiNWs varies from 3:1 to 50:1. The SiNWs can maintain very well defined periodicity at heights less than 5 μm. When further increasing the SiNW height, the mechanical strength of the nanostructure fails to support the NWs. Several adjacent SiNWs lean together to form clusters and the SiNW arrays lose the periodicity.

Figure 1(b) shows the SEM images of the SiNWs decorated with Ag NPs. To apply the SiNW arrays for SERS detection, the Ag NPs were deposited on the substrates via the electroless redox reaction between the oxidation of Si and the reduction of Ag+. The size of Ag NPs is approximately in the range from 50 to 200 nm. The Ag NPs have a good coverage on the top, sidewall and bottom surfaces of the SiNWs. Therefore, the large surface area of the SiNWs can be fully used for the molecules’ adsorption and light–matter interaction to enhance SERS signals. It should be noted that the size and density of Ag NPs can be tuned by changing the concentration of the AgNO₃ and HF in the water solution. The amount of time for which the samples are submerged into the solution also influences the size and density of Ag NPs [18].

Figure 2(a) shows the SERS spectra of monolayer 4-methylbenzenethiol molecules adsorbed on the Ag decorated SiNW arrays at different heights. The change of average SERS intensity at the 1083 cm⁻¹ Raman band is shown in figure 2(b). The SERS signal intensity of the 600 nm high SiNW array is approximately 230 counts at 1083 cm⁻¹ Raman band. At 600 nm height and 200 nm width (aspect ratio
around 3:1), the surface area of the SiNWs substrate is 2.05 times of a 2D planar surface. By gradually increasing the height of SiNWs, the aspect ratio is increased and the better SERS performance is observed. When the height of SiNWs reaches 1 μm (aspect ratio around 5:1), the surface area of the substrate is 2.74 times of a 2D planar surface. The SERS signal is maximized (approximately 580 counts). The better SERS performance can be attributed to the larger surface area of the higher SiNWs, which allows the decoration of more Ag NPs on the sidewalls and thus leads to a higher density of hotspots over the substrate. Meanwhile, there are more probing molecules allocated within the detection volume inside the SiNWs. The increase in both the hotspots density and the number of molecules results in higher SERS signal intensity. We assume that the measured SERS signal consists of three contributions from the top, bottom and sidewall areas of the SiNW arrays. Thus the SERS signal intensity can be described as 

\[ I_{\text{SERS}} \propto N_{\text{top}} M_{\text{top}} + N_{\text{sidewall}} M_{\text{sidewall}} + N_{\text{bottom}} M_{\text{bottom}}, \]

where the \( N_{\text{top}}, N_{\text{sidewall}} \) and \( N_{\text{bottom}} \) are the numbers of adsorbed molecules at the top, sidewall and bottom surfaces of the Ag decorated SiNWs, respectively, and \( M_{\text{top}}, M_{\text{sidewall}} \) and \( M_{\text{bottom}} \) are the corresponding SERS enhancement factors. We assume that \( M_{\text{top}}, M_{\text{sidewall}} \) and \( M_{\text{bottom}} \) are constants in these substrates, considering the same Ag NP decoration process and the same diameter of the SiNWs. The higher SiNW increases \( N_{\text{sidewall}} \) and thus enhances the contribution from the sidewall area of the SiNWs for the overall SERS signals. Meanwhile, the high aspect ratio of the SiNWs also promotes the light–matter interaction. The large surface area creates more opportunities for the interaction among the incident light, probing molecules and the Ag NPs, which leads to higher SERS signal intensity. However, the SERS performance becomes worse when the height of SiNWs is further increased. When the height of SiNWs is larger than 1 μm, the SERS signal intensity decreases and saturates at around 400 counts. The suppression of the SERS signals can be mainly attributed to the light trapping effect of the SiNWs with high aspect ratios. The SERS signals at the deep part of the SiNWs cannot escape and be detected.

Figure 2. (a) SERS spectra (50 × 50 μm²) of 4-methylbenzenethiol molecules adsorbed on SiNWs at different heights and (b) average SERS signal intensity at the 1083 cm⁻¹ Raman band of these substrates.

![Figure 2](image)

Figure 3. (a) Wavelength range of the Raman measurement (Raman shift from 0 to 2000 cm⁻¹) in the visible spectrum and (b) the average reflection of Ag decorated SiNWs at different heights in the wavelength range from 532 to 600 nm.

![Figure 3](image)
SERS signal consists of three contributions from the top, bottom and sidewall areas of the SiNW arrays. The expression for the SERS signal intensity from the SiNWs can be modified as

$$I_{\text{SERS}} \propto C_{\text{top}} I_{\text{CNMSERS\ top\ top\ top}} + C_{\text{sidewall}} I_{\text{CNMSERS\ sidewall\ sidewall\ sidewall}} + C_{\text{bottom}} I_{\text{CNMSERS\ bottom\ bottom\ bottom}}$$

where the $C_{\text{top}}$, $C_{\text{sidewall}}$ and $C_{\text{bottom}}$ are the collection efficiencies of the signals from the top, sidewall and bottom surfaces of the Ag decorated SiNWs, respectively. The strong light trapping effect greatly influences the signal collection by largely reducing $C_{\text{sidewall}}$ and $C_{\text{bottom}}$. Consequently, the average SERS signal intensity is suppressed by the SiNWs higher than 1 $\mu$m.

When further increasing the height of the SiNWs to around 10 $\mu$m by longer metal assisted chemical etching time, the SiNWs randomly lean together to form SiNW clusters. The period (600 nm) and density of NWs in a unit area ($2.78 \times 10^6 \text{ NWs mm}^{-2}$) are the same for these two substrates. Figure 4(a) shows the reflectance spectra of SiNWs at 1 and 10 $\mu$m in the visible spectrum. Compared to the 1 $\mu$m SiNWs, the 10 $\mu$m SiNWs exhibit much lower reflectivity (below 8%) in the visible spectrum range due to the enhanced light trapping of higher SiNWs. Figure 4(b) shows the SERS spectra of the monolayer 4-methylbenzenethiol molecules adsorbed on the well-ordered and randomly arranged SiNWs while figure 4(c) illustrates the corresponding Raman map images at the 1083 cm$^{-1}$ Raman band of these two substrates.

In the previous research on SiNW-based SERS substrates, the large surface area of the SiNWs is featured for enhancing SERS signals [9, 10, 12–14]. On the other hand, high aspect ratio SiNWs are also applied as black Si surfaces to exhibit an anti-reflection property. Experimentally, we demonstrated that the SERS signal intensity can be enhanced by increasing the aspect ratio of the SiNWs when their height is less than 1 $\mu$m. However, when further increasing the height of SiNWs, the light trapping effect of the SiNWs becomes dominant and weakens the SERS signal intensity. It should be noted here that the reflection and SERS detection are also determined by the diameter of the SiNWs, the size of Ag NPs and the solid angle during SERS detection. These factors also result in different optimal heights of the SiNWs.
4. Conclusions

In summary, 3D SERS substrates based on highly ordered SiNWs with Ag thin film deposition and Ag NPs decoration are designed and fabricated. By combining LIL and metal assisted chemical etching, we fabricated the well-ordered SiNWs over a large area (cm²). The redox reaction decorates assisted chemical etching, we fabricated the well-ordered are designed and fabricated. By combining LIL and metal assisted chemical etching, we fabricated the well-ordered SiNWs with Ag thin film deposition and Ag NPs decoration

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