Three-dimensional hybrid silicon nanostructures for surface enhanced Raman spectroscopy based molecular detection


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Three-dimensional silver nanoparticles decorated vertically aligned Si nanowires (Si NWs) are effective surface-enhanced Raman spectroscopy (SERS) substrates for molecular detection at low concentration levels. The length of Si NWs prepared by silver assisted electroless etching is increased with an increase in etching time, which resulted in the reduced optical reflection in the visible region. These substrates were tested and optimized by measuring the Raman spectrum of standard dye Rhodamine 6G (R6G) of 10 nM concentration. Further, effective SERS enhancements of ~10^5 and ~10^4 were observed for the cytosine protein (concentration of 50 μM) and ammonium perchlorate (oxidizer used in explosives composition with a concentration of 10 μM), respectively. It is established that these three-dimensional SERS substrates yielded considerably higher enhancement factors for the detection of R6G when compared to previous reports. The sensitivity can further be increased and optimized since the Raman enhancement was found to increase with an increase in the density of silver nanoparticles decorated on the walls of Si NWs. Published by AIP Publishing. https://doi.org/10.1063/1.5000994

I. INTRODUCTION

In the quest for understanding and applying nanoscale processes, molecular detection has attained great interest due to its effectiveness in medicine, biology, and pharmacology. Raman spectroscopy is one of the most reliable techniques for the identification and characterization of molecules. However, in the case of a diluted solution, the Raman signal is very weak, which results in the limited identification of molecules as compared to fluorescent materials. Surface-enhanced Raman spectroscopy (SERS) is a powerful vibrational spectroscopy technique and is well established as a reliable technique for investigating the complexity of analyte molecules in diverse fields such as chemistry and medical sciences. Moreover, in a special configuration, SERS can detect molecules at single molecular level concentrations. The SERS phenomenon predominantly deals with the electromagnetic field enhancement due to localized surface plasmon resonance, which is directly associated with the morphology of nanometallic surfaces. The composed nanostructures (NSs) such as silver and gold have higher significance in SERS studies due to their favorable dielectric and plasmonic responses. However, application of colloidal metal nanostructures or metallic rough nanostructures based SERS for molecular detection still remains a great challenge due to their poor stability, reproducibility, and low responsiveness.

In the latest technology, low-dimensional semiconductor nanostructures are promising materials for exploring physics in reduced dimensions and in complex geometries. Nanowires (NWs) are capable of confining the electrons, photons, and phonons within their complex geometry. These structures have diverse applications involving the fabrication of devices in optoelectronics, energy storage, solar cells, and chemical sensing. The silicon nanowires (Si NWs), in particular, have attracted increasing interest in scientific and technical fields owing to their nontoxicity, biocompatibility, high surface to volume ratio, and matured manufacturing technologies. Various approaches are reported in the literature for the fabrication of Si NWs by utilizing the commonly used expensive techniques, with complicated operations such as vapor-liquid-solid, solution-liquid-solid, and laser ablation methods. Among all the conventional techniques, the silver-assisted electroless (SAE) etching is an easy and inexpensive wet chemical process adopted to synthesize Si NWs in a wide scale range. Specifically, in current research, metal nanoparticles (NPs) decorated three-dimensional (3D) semiconductor nanostructures (NSs) have been recognized as the promising SERS substrates for molecular detection. The superior performance of 3D SERS substrates is basically attributed to their large surface to volume ratio, which is beneficial for the formation of hotspots, and the capture of target analytes at lower concentration levels. In this communication, we present results from our recent work wherein we focused our efforts on preparing Si NWs decorated with silver nanoparticles (AgNPs) and achieving an ordered arrangement of high density hotspots along the third direction which were...
later used as SERS substrates for effective molecular detection. The high surface roughness is another critically important property of these substrates, which helps to hold the molecules on the substrates for superior SERS enhancements in the low concentration level. These substrates were tested and optimized by measuring the Raman spectrum of standard dye Rhodamine 6G (R6G). In addition, for the first time, we have achieved effective SERS enhancement for cytosine and explosive molecules at lower concentration levels.

II. EXPERIMENTAL DETAILS

A. Preparation of vertically aligned Si nanowires

After appropriate cleaning using the procedures reported elsewhere,44 single-crystalline p-type Si wafers \([1 \times 10 \Omega \text{ cm, orientation: (1 0 0)}\)] with \(1 \times 1 \text{cm}^2\) area were utilized for preparing Si NWs by a silver-assisted electroless etching method. Subsequently, these Si samples were cleaned with diluted HF to remove the native oxide layer. After proper cleaning the Si samples, the SAE procedure\(^{29–38}\) has been implemented at room temperature (RT) to prepare vertically aligned Si NWs with high aspect ratio and surface roughness. The SAE etching process involves Ag deposition and subsequent etching. As-cleaned Si samples were dipped in the aqueous solution containing AgNO\(_3\):HF::0.02 M:4.6 M for 2 min for Ag deposition (I). Next, Ag deposited Si is immersed in H\(_2\)O\(_2\):HF::1.9 M:15 M for 15 min, 1, 2, 5, and 7 h etching time to grow vertically aligned Si NWs (II). Immediately after completing the etching process, the Si NWs were rinsed in the cleaning solution containing NH\(_4\)OH and H\(_2\)O\(_2\) in the volumetric proportion of 3:1 for 5 min to remove unwanted Ag dendrites. Finally, the etched samples were rinsed in de-ionized water and left for N\(_2\) gas drying. Silicon nanowires prepared at 15 min etching time have been utilized for further Ag NPs deposition.

B. Preparation of Ag NPs decorated Si nanowires

An innovative two-step electroless deposition process was employed for the preparation of Ag NPs. This process has been used to improve the uniformity of Ag NPs decorated on Si nanowires. In the first-step, the successfully etched Si NWs were placed in 0.005 M AgNO\(_3\) at RT for 30, 60, 90 min, 8, 20, and 24 h for varying the density of Ag NPs. Thus, Ag ions can be physically adsorbed on the entire surfaces of Si NWs due to their high roughness sidewalls. The Si NWs incorporated with Ag\(^{+}\) ions were gently removed from AgNO\(_3\) contained solution and subsequently dipped in 4.6 M HF solution for 15 s to grow spherical NPs. The formation of Ag NPs is no longer limited to top surfaces and solely each Ag\(^{+}\)/Si interface can initiate the galvanic deposition of Ag. As a result, the uniformly decorated Ag NPs on Si nanowires are achieved. Finally, the Ag NPs decorated Si NWs were cleaned in double deionized (DDI) water and subsequently dried in an N\(_2\) gas blower. The schematic representation of fabrication of Ag NPs decorated vertically aligned Si NWs is presented in Fig. 1.

The morphology and thickness of successfully prepared Ag NPs decorated Si NWs have been studied by the field emission scanning electron microscope (FESEM: Carl ZEISS, Ultra 55–5 keV energy of electron used for the study) used to estimate the size distribution of Ag NPs decorated on the walls of Si NWs. The energy dispersive X-ray spectroscopy (EDS) with 20 keV energy was used to quantify the chemical contaminations present in the nanowires. The size distribution of Ag NPs on the walls of Si NWs is extracted from the transmission electron microscopy (TEM-Technai, equipped with a thermo-ionic electron gun working at 200 keV) measurements. The selected area electron diffraction (SAED) and dark field image confirm the presence of silver nanoparticles, authentically. The TEM samples were prepared by scratching the AgSiNW surface.

The confocal micro-Raman spectroscopy (HR 800 Horiba Jobin Yvon, He-Ne laser) with 632 nm excitation wavelength with 100X magnification has been utilized to study the enhancement in the Raman spectrum of standard dye like Rhodamine 6G (R6G) of \(10^{-8}\) M (10 nM) concentration. In the present experiment, R6G has been dissolved in ethanol solution. Further, this investigation has been

![FIG. 1. Schematic representation of Ag NPs decorated vertically aligned Si NWs that are loaded with analyte molecules.](image-url)
extended to study SERS on cytosine of 5 × 10^{-5} M (50 μM) and ammonium perchlorate (AP) with 10 μM concentration.

III. RESULTS AND DISCUSSION

Vertically aligned silicon NWs were prepared by a silver-assisted electroless etching method. In this method, we have used HF, AgNO₃, and H₂O₂ as the main constituents for NW formation. The FESEM image shown in Fig. 2 confirms the formation of vertically aligned Si NWs. Silver dendrites are segregated on top of the NWs after completing the SAE etching process, which is clearly visible in the inset of Fig. 2. The silver dendrites were removed by rinsing the Si NWs in NH₄OH:H₂O₂::3:1 solution for 5 min. After this dissolution process, impurity-free vertically aligned Si NWs have been accomplished for further investigation. The size of Si NWs has been estimated by considering the planar and cross-sectional FESEM measurements. Figures 3(a)–3(e) illustrate the cross-sectional FESEM images of Si nanowires prepared at different etching times. The inset of Fig. 3 shows the plain (or planar) view of grown Si NWs. For clear discussion, these samples are labeled as SiNW1, SiNW2, SiNW3, SiNW4, and SiNW5 corresponding to 15 min, 1, 2, 5, and 7 h of etching times respectively. From the images presented in Fig. 3, it is evident that the Si NWs are vertically grown on the Si substrate with high aspect ratios. The average length of nanowires as a function of etching time is shown in Fig. 4. It is found that the length of NWs increases monotonically with an increase in the etching time.

The optical reflectance of Si NWs is found to be decreased with an increase in etching time as seen in Fig. 5. The minimum reflectance value achieved is ~1% for Si NWs of the length of ~35 μm in the wavelength range of 400–800 nm. The random multiple internal scattering events inside the NWs forest might be responsible for enhanced light absorption, which results in the consequent drastic reduction in the reflectivity at the frequencies absorbed by
the NWs. The quantitative estimation of the refractive index of the Si NWs prepared at different etching times is shown in Fig. 6. It is found that the refractive index of Si NWs decreases as a function of the length of NWs. It is in good agreement with the observed reflection properties.

Figures 7(a)–7(f) illustrate the cross-sectional FESEM images of Si NWs incorporated with Ag NPs at various deposition times (60 min, 90 min, 8, 20, and 24 h). For the convenience of discussion, the samples are labeled as AgSiNW1, AgSiNW2, AgSiNW3, AgSiNW4, and AgSiNW5, which correspond to 60 min, 90 min, 8, 20, and 24 h Ag NP deposition times, respectively. From the images of Figs. 7(a) and 7(b), it is clearly observed that the tips of Si NWs are highly decorated with Ag NPs. This is due to the agglomeration of primarily formed Ag NPs, intended to form nanoclusters near nanowire tips. The observed features lead us to infer that the NW tips could be the most energy favorable regions for employing the Ag ion reduction through the two-step electroless deposition process. At higher Ag deposition time, the Ag NPs were distributed...
throughout the nanowire surface, which is clearly observed in the insets of Figs. 7(c)–7(e). Figure 8 shows the TEM image, which illustrates the distribution of Ag NPs on the walls of Si NWs (AgSiNW). The inset shows the corresponding SAED and dark field image which confirms the presence of silver nanoparticles, authentically. The histogram shown in Fig. 9(a) presents the average distribution of silver nanoparticles decorated on the walls of Si NWs. The inter-particle distance of Ag NPs on Si NWs can affect the strength of hotspots, which can result in rapid changes in the resultant SERS enhancement factor (EF). In the present experiment, the estimated average inter-particle distance of Ag NPs is \( \sim 10 \text{ nm} \). The high-resolution TEM and Inverse Fast Fourier Transform (IFFT) image of Ag NPs decorated Si NW are shown in Fig. 9(b). The IFFT image has been extracted from the region of interest indicated. From the IFFT image, the d-spacing (0.23 nm) is matching with the Ag (111) d-spacing (0.23 nm) from JCPDS card No. 04-0783. Energy-dispersive X-ray spectroscopy measurements have been performed to identify the elemental compositions that are present in the samples. These results are presented in Fig. 9(c). This clearly demonstrates that the strong Si peak is related to Si NWs and weak Ag peak due to the presence of Ag NPs that are decorated on the walls of NWs. There are no detectable impurities other than a small concentration of oxygen present in the sample.

SERS measurements were carried out for R6G with a concentration of \( 10^{-8} \text{ M} \) (10 nM) in the spectral range of 550–1800 cm\(^{-1}\). Typically, 20 \( \mu \text{l} \) of an R6G solution of 10 nM is drop-casted on AgSiNW based SERS substrates and then dried in the ambient environment. Figure 10 shows the Raman spectra of R6G molecules on Si NW substrates with Ag NP deposition of 30 min, 60 min, 90 min, 8, 20, and 24 h at fixed concentration of 10 nM. It is evident from the data presented in Fig. 10 that the intensity of Raman peaks corresponding to R6G increased with the increase in the density of Ag NPs present on the walls of Si NWs.

To extend the potential of these SERS targets explored by probing bio-organic molecules, we have also investigated the SERS spectrum of a nucleobase such as a cytosine.\(^{45,46}\) To characterize the nucleobase, different density of Ag NPs decorated vertically aligned Si NWs have been utilized. Figure 11 presents the Raman spectra of cytosine with a...
concentration of $5 \times 10^{-5}$ M $(50 \mu$M) in the spectral range of $550–1800 \text{ cm}^{-1}$. For the Raman measurements, $20 \mu l$ of cytosine solution of $50 \mu$M was drop casted on AgSiNW based SERS substrates with various distributions of Ag NPs and then dried in the ambient environment. Enhancement in the Raman signal of cytosine has been observed as a function of Ag NP distribution on the walls of Si NWs. Further, these studies have been extended to demonstrate the utility of these substrates for the detection of the explosive molecules. Ammonium perchlorate (AP) has found technological applications in explosives, pyrotechnics, and propellants. \cite{47} Figure 12 presents the Raman scattering data of AP explosives with $10 \mu$M concentration. We have observed the strong intense peak at around $\sim 760 \text{ cm}^{-1}$ in addition to other peaks, which clearly signifies the effective detection of explosives. We have also observed another interesting feature that the intensity of $\sim 760 \text{ cm}^{-1}$ Raman signal enhances as a function of Ag NP density.

The relation between intensity of Raman peaks and the density of Ag NPs has been quantified by considering a single peak, which is presented in Fig. 13. The peaks at $\sim 610 \text{ cm}^{-1}$, $\sim 792 \text{ cm}^{-1}$, and $\sim 760 \text{ cm}^{-1}$ were considered in R6G, cytosine, and AP molecules, respectively. The area under the peak was determined from the SERS spectra recorded at various Ag deposition times. The Lorentzian peak fitting has been used to estimate the area under the peak. Figure 13 shows the intensity dependence of Raman peaks of $\sim 610 \text{ cm}^{-1}$, $\sim 792 \text{ cm}^{-1}$, and $\sim 760 \text{ cm}^{-1}$ for R6G, cytosine, and AP molecules, respectively, as a function of various Ag NP deposition times. It is clearly observed that the intensity of SERS signal increases with an increase in the density of Ag NPs decorated on Si NWs. From these observations, we conclude that the density of plasmonic nanoparticles is the most favorable factor in SERS studies of molecular detection with micromolar concentrations. Hence, the capability of these substrates could be enhanced by simply employing alloy nanoparticle decoration instead of silver nanoparticle decoration. \cite{50}

The Raman enhancement factor (EF) is important for demonstrating the effectiveness of SERS substrates for measuring Raman spectra, \cite{48,49} which is given by the following equation:

$$\text{EF} = \frac{I_{\text{SERS}}}{{N_{\text{RS}}} \cdot I_{\text{Raman}}}$$
where $I_{SERS}$ and $I_R$ are the Raman intensity of molecules adsorbed on the AgSiNW and non-SERS substrate, respectively. $N_{SERS}$ is the number of molecules on the AgSiNW substrate and $N_{RS}$ is the number of molecules on the non-SERS substrate. In this calculation, as-prepared SiNW has been considered as a non-SERS substrate.

The Raman peaks at $\sim 610$ cm$^{-1}$, $\sim 792$ cm$^{-1}$, and $\sim 760$ cm$^{-1}$ in R6G, cytosine, and AP molecules, respectively, have been considered as reference peaks to calculate the EFs. In the present study, the minimum detectable concentrations of R6G, cytosine, and AP are 10 nM, 50, and 10 $\mu$M, respectively. The corresponding enhancement factors are summarized in Table I. The observed enhancement factors for R6G are considerably higher than the reported values.31,51–53

The observed effective Raman enhancement factors can be attributed to the high density and uniform distribution of the Ag NPs on Si NWs. Hence, this technique can be used to push the detection limits of SERS to further lower concentrations. Our future endeavor will be to improve the enhancement factors of different analyte molecules to be used with these hybrid nanostructures. This can possibly be achieved by (a) tailoring the size and concentration of Ag nanoparticles on Si NWs, (b) changing the metal from Ag to Ag-Au (alloy) with superior plasmonic properties, and (c) increasing the sharpness of the Si NWs thereby achieving superior electric fields at the tips of the NWs. Furthermore, we also wish to demonstrate the versatility of these targets by recording the SERS spectra of other common molecules of interest and test the recyclable nature of these substrates. We expect, at least, nM to pM detection using our substrates with the above mentioned appropriate optimization procedures.

**IV. CONCLUSIONS**

Three-dimensional SERS substrates have been prepared by decorating the vertically aligned silicon nanowires with Ag nanoparticles. Significant enhancements in the Raman signals from diverse molecules at low concentration levels have been achieved. The length of Si nanowires monotonically increases with an increase in etching time. It was observed that the optical reflectance of Si NWs decreases with an increase in etching time. The minimum reflectance value achieved was $\sim 1\%$ for $35 \mu$m long Si NWs in the wavelength range of 400–800 nm due to multiple scattering. The SERS spectra of standard dyes such as R6G (as low concentration as 10 nM) were measured with an effective enhancement factor of $10^7$. Furthermore, Raman enhancements of $10^5$ and $10^4$ were observed for cytosine protein and ammonium perchlorate, respectively, for higher distribution of Ag NPs decorated on the walls of Si NWs. The Raman peak at $\sim 760$ cm$^{-1}$ clearly signifies the detection of ammonium perchlorate (AP) molecules. This study demonstrates the importance and versatility of these 3 D SERS substrates for molecular detection at low level concentrations.

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**TABLE I. Estimated enhancement factors as a function of Ag NP deposition time.**

<table>
<thead>
<tr>
<th>Molecules</th>
<th>AgSiNW1</th>
<th>AgSiNW2</th>
<th>AgSiNW3</th>
<th>AgSiNW4</th>
<th>AgSiNW5</th>
</tr>
</thead>
<tbody>
<tr>
<td>R6G</td>
<td>$3.4 \times 10^6$</td>
<td>$7.2 \times 10^6$</td>
<td>$7.4 \times 10^6$</td>
<td>$3.9 \times 10^7$</td>
<td>$4.8 \times 10^7$</td>
</tr>
<tr>
<td>Cytosine</td>
<td>$3.6 \times 10^4$</td>
<td>$5.1 \times 10^4$</td>
<td>$7.2 \times 10^4$</td>
<td>$1.0 \times 10^5$</td>
<td>$2.1 \times 10^5$</td>
</tr>
<tr>
<td>AP</td>
<td>$3.7 \times 10^3$</td>
<td>$4.5 \times 10^3$</td>
<td>$2.1 \times 10^4$</td>
<td>$2.8 \times 10^4$</td>
<td>$4.0 \times 10^4$</td>
</tr>
</tbody>
</table>
