

Surface-enhanced Raman characteristics of Ag cap aggregates on silicon nanowire arrays

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Abstract

A convenient nanotechnique is used to place analyte molecules between closely spaced silver-capped Si nanowires for investigating surface-enhanced Raman scattering (SERS). It is revealed that the SERS intensity (or sensitivity) is closely related to the etching time used to prepare the Si nanowires from wafer. As the etching leaves the nominal spacing between the nanowires unaffected, the observed effect can be explained based on different gaps between the Ag particles due to the different lengths of the Si nanowires. Large SERS intensity for short etching times can be elucidated in terms of the rigidity of the nanowires and the smaller SERS intensities for longer etching times can be explained by considering the bending of nanowires and the agglomeration of the Ag caps due to gravity and van der Waals forces.

1. Introduction

Since the demonstration of optical detection and spectroscopy of single molecules at room temperature by means of surface-enhanced Raman scattering (SERS) [1, 2], reproducible fabrication of metallic nanostructures with 'hot geometries' in which the molecules can be manipulated to produce reliable, stable, and uniform SERS signals with a wide dynamic range is of importance [3–6]. Two types of such hot geometries can be SERS active and have applications in molecular sensing. They are small nanoparticle aggregates with gaps of less than 2 nm and large fractal aggregates [6]. The evolution of the large fractal network tends to be random and it is thus difficult to control the morphology. Periodic sub-10 nm 2D nanostructures with controlled junctions have attracted much attention due to interparticle-coupling-induced Raman enhancement [3, 5, 7]. However, precise control of the gaps with dimensions less than 2 nm (necessary for intense

SERS enhancement) is still extremely difficult using existing nanofabrication methods [5, 6].

Lee and co-workers have proposed a simple method to obtain sub-10 nm hot geometries of the 'metal/molecule/metal' arrangement. In this technique, analyte molecules spontaneously occupy the space between adjacent tips of the Ag nanowires that are produced in porous aluminium oxide by controlled dissolution of the alumina matrix [6]. Although the protocol is quite innovative from the perspective of fabrication of hot geometries, the tips of the nanowires can bend towards each other and there is room for optimization. Moreover, the only hot geometries that have been produced have the 'tip/analyte/tip' arrangement with the rest of the Ag nanowires used to stabilize the system. It is thus of practical importance to be able to use other materials to substitute for the stabilizing bars. In this work, we utilize a promising technique to assemble visible light-emitting nanomaterials on the tips of Si nanowires [8–10]. By extending the technique, SERS-active silver-capped Si nanowires with hot geometries were produced.

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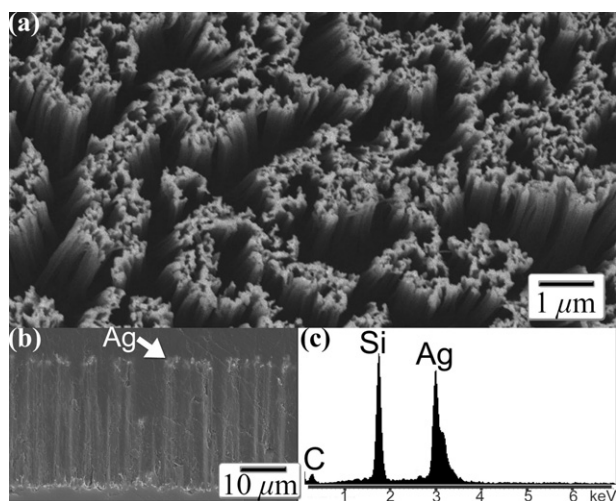


Figure 1. (a) SEM image of the Ag caps on the silicon nanowire arrays. (b) Cross-sectional SEM image of the silver-capped silicon nanowire arrays. (c) EDS spectrum of the as-grown silver-capped silicon nanowire arrays.

The SERS sensitivity depends on the lengths of the Ag-capped silicon nanowires that can be controlled by the etching time.

2. Experimental details

Silver-capped Si nanowires were fabricated using an electrodeless metal deposition method based on the self-assembled localized microscopic electrochemical cell model [8]. B-doped silicon (100) (1–5 Ω cm) wafers were first cleaned by acetone to degrease the Si surface; this was followed by etching in diluted aqueous HF (~10 wt%) for 10 min. The silicon wafers were then etched in a 5.0 mol l⁻¹ HF solution containing 0.02 mol l⁻¹ of silver nitrate at 50 °C for different periods of time. The container was a conventional Teflon-coated stainless steel vessel. After etching, the silicon wafers were rinsed with de-ionized water and air dried. The thick silver dendrites covering the silicon wafer were detached before microstructural investigation. The morphology and chemical composition of the samples were determined using an FEG JSM 6335 field-emission scanning electron microscope (SEM) and an EDAX PV7715/89 ME energy dispersive x-ray (EDS) detector.

In order to evaluate the Raman-enhancing capability of the Ag cap aggregates, a 10⁻⁴ M aqueous rhodamine 6G (R6G) solution was prepared by magnetic stirring. The samples were submerged in the R6G solution for 30 min, taken out, and rinsed thoroughly. Raman measurements were performed at room temperature on a Jobin-Yvon T64000 triple Raman system with the 514.5 nm line of an argon laser. The probed area was ~10 μm in diameter with a 10× objective lens and the incident power was 5 mW. It should be noted that the accumulation times and the laser power are the same for all the Raman spectra; further, the enhancing power is uniformly consistent over the entire sample. All the measurements were performed at room temperature.

3. Results and discussion

The lengths of the Si nanowires have been shown to depend on the etching time [8, 9]. Figure 1(a) shows the top view

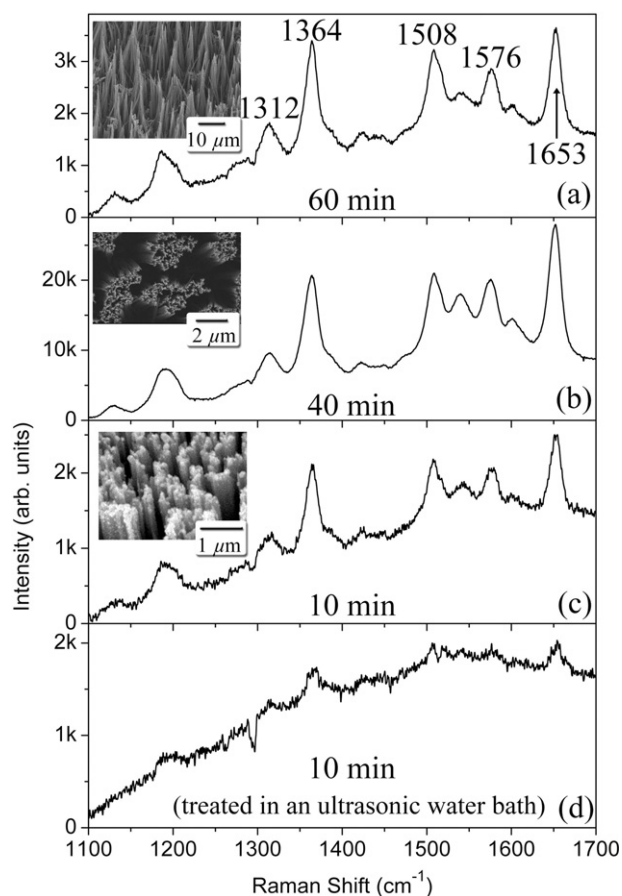


Figure 2. SERS spectra acquired from R6G adsorbed on the silver-capped silicon nanowire arrays etched for different times: (a) 60 min, (b) 40 min, and (c) 10 min. The insets show the corresponding morphologies of the samples, respectively. For comparison, the silver-capped silicon nanowire arrays shown in the inset of (c) were treated in an ultrasonic water bath for 10 s to remove the Ag caps and (d) shows the reduced Raman signals from this sample.

of the Si nanowire arrays with Ag caps on the tips that have been etched for 40 min. The nanowires can be observed to bend toward each other. The cross-sectional SEM image of the as-grown silver-capped Si nanowires is obtained by using a solidified agent to affix the sample and improve the contrast. The white spots on the tips of the Si nanowires in figure 1(b) are silver nanoclusters. The etched depth (i.e. the lengths of the Si nanowires) into the Si wafer is approximately 25 μm. Figure 1(c) shows the typical EDS spectrum taken from the top view of the sample; Ag and Si are the main constituents.

Figure 2 illustrates the variation in the SERS efficiency with different etching times. The R6G fluorescence and Raman spectra overlap in the range of 540–580 nm (Stokes shift, 920–2200 cm⁻¹) so that the Raman spectra have a fluorescence background [2]. The Si nanowires formed after etching for 10 min are primarily in the upright position. The inset in figure 2(c) is the SEM image of the as-grown vertical silver-capped Si nanowires. Due to random growth of the Si nanowires, some Ag caps are found in random locations and some tiny silver nanoclusters are also observed to attach on the walls of the Si nanowire tips. The SERS spectrum of the 10⁻⁴ M R6G molecules adsorbed on the Ag caps is shown

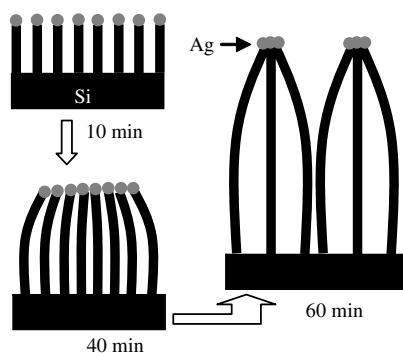


Figure 3. Schematic illustration of the rigidity of the Ag-capped silicon nanowires with different lengths as determined by the length of the etching time.

in figure 2(c). Pronounced peaks at 1312, 1364, 1508, 1576, and 1653 cm^{-1} can be readily identified above the fluorescence background and they can be assigned to the symmetric in-plane C–C stretching vibrations [11].

In order to identify the origin of the SERS enhancement, the silver-capped silicon nanowire arrays etched for 10 min were treated ultrasonically for 10 s to remove most of the Ag caps (inset in figure 2(c)) and SERS measurements were carried out again after the sample was submerged in the R6G solution for 30 min, taken out, and rinsed thoroughly. Figure 2(d) displays the corresponding Raman spectrum. This sample yields very weak R6G Raman signals over the fluorescence band, and there is evidence that the R6G Raman signals are enhanced due to the Ag cap aggregates.

The longer Si nanowires produced by etching for a longer time such as 40 or 60 min are not as rigid as those produced by etching for 10 min. Bending of the nanowires leads to large Ag caps that can sometimes be bundled together, as observed in figure 1(a) and the inset in figure 2(b). This phenomenon can be explained by the irregularity of the individual nanowires [12] as well as van der Waals attraction between them [6]. This phenomenon is schematically illustrated in figure 3. According to the typical formation mechanism of Si nanowires reported in [12], if the shape of nanowires is irregular, the centre of gravity of each individual nanowire is not aligned with those of other nanowires. The longer nanowires which are off axis to gravitation will bend more, and eventually the torque leads to bending and agglomeration of the nanowires. The van der Waals attraction among the atoms may also play a part in this effect [6]. Our results illustrate that the spacing between the Si nanowires can be adjusted and controlled by using different etching times.

Figure 2(b) shows the SERS spectrum acquired from 10^{-4} M R6G molecules adsorbed on the Ag caps that have been etched for 40 min. Compared to the sample etched for 10 min (figure 2(c)), the SERS intensity shows a ten-fold increase. The SERS intensity is proportional to the Ag aggregate amounts, and the intense SERS spectrum observed from the silver-capped Si nanowires etched for 40 min can be attributed to the hot electromagnetic geometries composed of small nanoparticle aggregates with interstitial junctions. Our results are consistent with the

intense electromagnetic field enhancement expected of the cap/analyte/cap arrangement [6, 13–15].

García-Vidal and Pendry have proposed a model to quantitatively measure the electromagnetic interaction between adjacent metallic objects [13]. In their model, the complex particles are close enough on the surface to interact strongly. The incident radiation excites a plasmon trapped between the neighbouring metallic objects, creating a huge local electric field. The plasmon obviously has a strong dipole component. Their results suggest that SERS is a local phenomenon occurring in crevices or pores on a rough surface. It should be noted the distance between the centres of two adjacent particles (d) and the particle diameter ($2R$) are important parameters. Their calculation shows that the average enhancement increases from 10^3 for ‘isolated’ particles to a maximum of 10^6 for the case $d = 2R$ where the particles are in direct contact. They have also analysed the quantitative dependence of this localized plasmon mode on the surface roughness (different values of the ratio $d/2R$ with $d \leq 2R$) and observed that the enhancement effect diminishes with decreasing roughness. Our experimental data thus match very nicely the theoretical prediction [5] that large SERS enhancement can be achieved on a substrate with particle gaps in the sub-10 nm regime.

As the etching time increases to 60 min, the nanowire bundles become smaller, and consequently the SERS intensity decreases, as shown in figure 2(a) and the inset. This decrease in the SERS intensity is believed to stem from the reduced stability of the long Si nanowires and smaller number of Ag caps that are SERS active. In other words, only a fraction of the adsorbed molecules can occupy the sites between the very close Ag caps (figure 3).

4. Conclusion

We report a simple technique to place analyte molecules between adjacent Ag caps on silicon nanowires to investigate the SERS. The gaps between individual the Ag caps are altered by the length of the silicon nanowires and can be controlled by the etching time. The shorter silicon nanowires are more rigid and exhibit enhanced SERS sensitivity. On the other hand, the longer silicon nanowires (longer etching time) are less rigid, and gravity as well as van der Waals attraction cause bending and agglomeration of the Ag caps subsequently reducing the SERS intensity. Our technique has potential applications in SERS-based biosensors.

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