Silicon Nanowire – Gold Nanoparticle Heterostructures for Surface-enhanced Raman Spectroscopy

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Abstract

In this paper, we report a facile approach for the fabrication of silicon (Si) nanowire-gold (Au) nanoparticle heterostructures and their application in molecular sensing using Surface-enhanced Raman Spectroscopy (SERS). Si nanowires were grown *via* an atmospheric pressure chemical vapor deposition (APCVD) method. The growth conditions such as silicon source feed rate, growth duration, temperature, and catalyst amount were studied to control the morphology and structure evolution of Si nanowires. Further surface decoration of Si nanowires with Au nanoparticles was achieved using a galvanic deposition approach combined with a subsequent annealing process. This process enabled the formation of uniformly- and tightly-packed Au nanoparticles on Si nanowires with controlled size and inter-particle spacing. Such novel Si nanowire-Au nanoparticle heterostructures were subjected to SERS-based chemical detection of water-containing organic dyes. The results indicate that these heterostructured substrates have significantly improved Raman sensitivity and uniformity, and will be potential for future SERS-based bio/chemical sensors.

Keywords

Silicon nanowires; Gold nanoparticles; Heterostructures; APCVD; SERS

1. Introduction

Coinage metals such as gold, silver, and copper have been widely used as favorable substrates for Surface-enhanced Raman Spectroscopy (SERS) [1-4]. The significant enhancement for normally-weak Raman signals up to several orders is believed to originate from the Localized Surface Plasmon Resonance (LSPR) of above metallic substrates, which generates a constant electromagnetic field on the surface of plasmonic nanostructures (called near-field) [5]. LSPR can be simply modulated by controlling the size, shape, and distribution of these nanostructures [6,7], or decorating them on special supporting materials [8]. For instance, direct dispersion of gold and silver nanostructures on flat substrates such as silicon wafer has been initially studied [9,10]. However, such substrate geometries were limited due to the uncontrollable spatial density, inevitable aggregation, and nonuniform distribution of the decorating nanostructures [11]. With this regard, heterostructures by combining these Raman-sensitive plasmonic nanomaterials with low-dimensional nanomaterials (e.g., Si nanowires) have been recently developed in great demand [12-14].

Si nanowires have been studied for several decades due to their unique electronic property, convenient surface tailorability and excellent industrial compatibility [15,16]. It was recently found that the utilization of Si nanowires in chemical sensors is of particular interest due to their good biocompatibility, vast surface-to-bulk ratio, fast response, and their oxide-coated or H-terminated surface [17-19]. However, the as-produced pristine Si nanowires only exhibit moderate sensitivity in SERS due to the lack of plasmonic properties. Towards this end, the subsequent surface modification or decoration of Si nanowires with plasmonic nanostructures can provide an efficient route to develop novel one-dimensional heterostructured substrate. Previously, combination of Si nanowires with foreign nanostructures such as platinum nanoparticles [20], boron and magnesium

[21], alkyl and nanotrees [22], diamond-like carbon (DLC) [23] and polymers [24,25] has been reported for electronic and photovoltaic applications. With respect to SERS sensors, Ag nanoparticle-decorated Si nanowires were also demonstrated for the detection of R6G [26], CV [27], DNA [28], and amoxicillin [29]. The significant Raman signal enhancement observed on these nanowire heterostructures was attributed to (1) the enlargement of specific surface area, which can absorb more target molecules per unit area, and (2) the closely-packed nanoparticles on the nanowires, which generate abundant “hot-spots” for SERS sensing [30].

Compared with these Ag-based heterostructures, Au nanoparticle-decorated Si nanowires are more potential for electronic sensors and optical devices due to their chemical stability, low-temperature processibility (low melting point), and excellent bio-compatibility [31-33]. The concept of combining Au nanoparticles with Si nanowires has been previously proposed in the studies of Tip-enhanced Raman Spectroscopy (TERS) [34-36]. Afterwards, the decoration of Si nanowires with extraneous Au nanoparticles were further explored to develop novel efficient SERS substrate. For instance, Sun et al. studied the charge-selective ability of Au nanoparticles decorated Si-C core-shell nanowires for the detection of Rhodamine 6G (R6G), acridine orange, fluorescein, and methyl orange in aqueous solutions [37]. Chen et al. demonstrated SERS sensing based on the tailorable optical properties of Au nanoparticle-decorated Si nanowires and further tested their photodetection ability [38]. Recently Peng et al. reported the direct decoration of Au nanoparticles on wet-etched Si nanowires as highly sensitive SERS substrate [39]. However, further progress and large scale application of such Au-Si nanowire heterostructures are still a big challenge due to (1) the high production cost, poor structural uniformity, and heavy crystal defects of Si nanowires [16], and (2) lack of methodologies for the effective combination of Si nanowire and Au nanoparticle with controlled particle size and distribution [40].

Thus, in this paper we report a fundamental study on the cost-effective and large-scale production of Si nanowires and their further surface decoration with Au nanoparticles. The form was conducted *via* a modified atmosphere pressure chemical vapor deposition (APCVD) method while the later was achieved using a unique galvanic deposition – annealing approach. The influence of growth parameters such as SiH₄ flow rate, duration, temperature and catalyst amount on the morphology and structure of Si nanowires were studied in detail. Si nanowires with different structure were further selected and subjected to a galvanic deposition process for the deposition of surface Au nanostructures (shell or flakes), of which the morphology and dispersion were optimized in a subsequent high-temperature annealing process. The obtained final products, Si nanowire-Au nanoparticle heterostructures, as well as various pristine Si nanowires were used as the SERS substrates for the chemical sensing of R6G in aqueous solution. Their Raman sensitivity (detection limit) and uniformity were evaluated and compared in detail.

2. Experimental details

2.1. Materials and Methods

(100), n-type silicon wafer was purchased from IWS (Colfax, CA). Gold (III) chloride trihydrate (HAuCl₄·3H₂O, 99.9%) was purchased from Sigma-Aldrich (St. Louis, MO). Sodium borohydride (NaBH₄, 98%) was purchased from Acros Organics (New Jersey, NJ). DI water (18.1 MΩ-cm) was obtained using a Barnstead International DI water system (E-pure D4641). All chemicals were used without further purification. Gold sputtering was carried out in a Bio-Rad gold sputtering and coating system, (Agawan, MN). Growth and annealing of the Si nanowires were conducted in a GSL-1100X Tube Furnace (MTI Corporation).

2.2. Growth of Si nanowires

An atmosphere-pressure chemical vapor deposition (APCVD) method was used for the growth of Si nanowires. Briefly, the Si substrate was treated in piranha solution for 30 min at 100 °C. This was followed by sputtering of gold film with required thickness. The substrate was then placed in the center of the quartz tube for the growth of Si nanowire according to the vapor-liquid-solid (VLS) mechanism. Various growth parameters were used to optimize the CVD process and further control the morphology and structure of Si nanowires (see Table S1 in supplementary information for detailed experimental parameters the sample labeling). 10% H₂/Ar with a feeding rate of 100 sccm (standard cubic centimeters) was constantly used as the carrier gas. When the growth was completed, the furnace was cooled down to room temperature with protection of Ar.

2.3. Fabrication of Si nanowire-Au nanoparticle heterostructures

The as-produced Si nanowires were treated with BOE solution for 5 s and then placed in a galvanic deposition solution (1 mM KAuCl₄ + 1% HF) for gold deposition [41,42]. The samples were then washed with DI-water and immediately dried in N₂. This was further followed by a high-temperature annealing process (10 min) at various temperatures. Such treatment leads to the fabrication of final product, Si nanowire-Au nanoparticle heterostructures, an efficient SERS substrate for detection of trace-amount organic dye molecules.

2.4. Detection of water-containing R6G

Both the as-produced Si nanowires and the Si nanowire-Au nanoparticle heterostructures were used for the detection of R6G *via* SERS. The nanostructures were first treated in BOE solution for 10 s to create surface Si-H bonds, which can effectively anchor R6G molecules onto the substrates. The samples were then washed with DI-water, dried in N₂ and immediately incubated in the R6G-

containing solution for 10 h under slight stirring. The dye-attached samples were washed with DI-water and dried in N₂ for Raman test.

2.5. Characterizations

Morphological and structural analysis of the Si nanowires and the Si nanowire-Au nanoparticle heterostructures were conducted using JEOL-7000 FE-SEM and Tecnai F-20 TEM. The average nanoparticle size and inter-particle spacing was estimated according to ~200 nanoparticles or nanowires counted from SEM and TEM images. Raman test on R6G-attached substrates were carried out on the Bruker Senterra Raman System (Bruker Optics Inc. Woodlands, TX), where a neon laser source with wavelength of 785 nm was used. The applied laser power was 1 mW and the integration time was 10 s. The average intensity of Raman peak for R6G were estimated from ~15 spectra obtained at various regions on the substrate.

3. Results and discussion

3.1. Atmosphere-pressure chemical vapor deposition of Si nanowires

Scheme 1 illustrates the process for the fabrication of Si nanowire – Au nanoparticle heterostructures and their application as SERS substrate. As mentioned above, Si nanowires were grown *via* an atmospheric-pressure chemical vapor deposition (APCVD) process, of which the growth mechanism can be directed from the well-defined vapor-liquid-solid (VLS) principle [16]. As shown in Scheme 1, first sputtering of gold film was conducted on silicon substrate. This was followed by a high-temperature annealing process, which led to the dewetting of gold film to form island-like Au nanoparticles. These Au nanoparticles were further served as catalysts for the growth of Si nanowire. Silicon atoms decomposed from SiH₄ were diffused into liquid gold

droplets and alloyed due to the high solubility of silicon in gold. As the silicon content reached saturation in the alloy, solid silicon started to precipitate. This process is most favorable at the low-energy interface region of gold droplet and silicon substrate (due to the lattice mismatch). As a result, the gold droplet was lifted up and present as a typical tip on the Si nanowires [16]. It is worth mentioning that similar CVD process were normally conducted in a high vacuum system to prompt the decomposition and diffusion of SiH_4 and avoid possible oxidation of the Si nanowires. In this study, we develop an atmosphere pressure CVD process by involving a H_2 environment and further optimizing various growth conditions (see Table S1 in supplementary information), which leads to the large-scale production of Si nanowires with low cost.

Figure S1 (supplementary information) shows the SEM images of the silicon substrates decorated with as-sputtered gold film and the dewetted Au nano-islands after annealing. One can observed that the Au film is uniform all over the substrate and numerous cracks can be observed between crystalline grains. These self-separated crystalline grains have been found to take an important role in the following annealing/dewetting process and lead to the formation of Au nanoparticles or islands [43]. As shown in Figure S1B, the resulting Au nano-islands were uniformly dispersed on the substrate with inter-particle spacing of $\sim 92 \pm 31$ nm and average size of $\sim 113 \pm 21$ nm. These Au islands were used as catalysts in the subsequent Si nanowire growth process.

To improve the growth of Si nanowires, various parameters including SiH_4 flow rate, growth duration, temperature, and catalyst amount were evaluated (see Table S1, Figure S2-S5, supplementary information). The influence of SiH_4 flow rates (10 sccm, 20 sccm and 30 sccm) were first demonstrated. When the flow rate is small (10 sccm), the decomposed silicon atoms were not sufficient to saturate the gold-silicon droplets. As a result, no nanowire was formed, instead we only observed the enlarged Si-Au droplets ($\sim 230 \pm 50$ nm, see Figure 1A). The growth

of Si nanowires occurred when SiH_4 flow rate was 20 sccm (Figure 1B). Au nanoparticle tips with a slightly larger diameter than the diameter of Si nanowires was constantly observed according to the VLS mechanism [16]. SEM image for the cross-section of Si nanowires on the Si substrate indicates a “zig-zag” shape for the as-grown nanowires (Figure S2C, supplementary information). Approximately the average length of the Si nanowires is $\sim 1.6\text{-}2.4\ \mu\text{m}$, which suggests a nanowire growth speed of $\sim 27\text{-}40\ \text{nm/s}$. The nanowires obtained with a SiH_4 flow rate of 30 sccm show increased length due to the fastened silicon precipitate speed (Figure 1C). The morphology of the nanowires became relatively straight at this case while the “zig-zag” structure was still observed for some nanowires (Figure S2E, supplementary information).

In addition, it is worth mentioning that Si branches were constantly observed on the nanowires. The branches for the 20 sccm sample were crooked and with a high spatial density (Figure 1B). However, with increased flow rate (30 sccm), these branches became straight and less (Figure 1C). The formation of Si branches is due to the non-uniform diffusion of gold droplet during the growth [47]. The main gold tip was lifted up by the precipitation of Si nanowire however some small Au particles still remained on the nanowire surface. These small gold nanoparticles acted as the new catalyst center for the growth of nanowire branches.

Influence of growth duration on the structure and morphology of Si nanowires was demonstrated in Figure 1D-F. Branched and “zig-zag” nanowires were again observed when the growth was conducted for 2 min. However, as the growth continued for 5 min or 10 min, the nanowires become straight and branchless (see the insets in Figure 1E and F). The disappearance of the Si branches can be well-explained by the Ostwald’s ripening effect, which reveals that the branches can slowly fuse into the main nanowires at high temperature [44]. To further control the growth process, the influence of temperature was investigated (Figure 1G-I). The growth at relatively lower

temperature (675 °C, Figure 1G and S4B) led to similar “zig-zag” and branched nanowires. However, as the temperature increased, straight nanowires with relative straight branches were obtained (Figure 1H and I). The influence of temperature on the morphology of nanowires is mainly attributed to the varied diffusion rate of silicon atoms in gold droplets at different temperature. Higher temperature leads to increased growth speed, as a result, the Si nanowires becomes more straight and longer [45].

The growth of Si nanowires is based on the alloying and saturation of gold droplets [16]. Thus, the deposition and subsequent annealing of gold catalysts are of importance for the geometry evolution of Si nanowires. This was further demonstrated in Figure 1J-K. Sputtering for 15 s leads to less deposition of gold film on the substrate and results relatively small gold nanoparticle catalyst [46]. During the high-temperature growth, these small gold droplets presented high surface energy. Rather than keep a completed gold tip, they prefer to disperse as the defect sites on the nanowires [47], leading to the pronounced growth of side branches. As a result, no obvious large gold tips were observed on these nanowires (Figure 1J). This reasoning was further confirmed by the growth of Si nanowires with gold catalysts from long-time sputtering (30 s and 45 s). In these two cases, less branches were observed and the gold tips became large and round (Figure 1K and L).

Based on above observation, the influence of various growth conditions on the morphology and structure of Si nanowires was schematically summarized in Figure 2A-D. Correspondingly, the influence of these parameters on the average diameter of the main nanowires and the gold tips was further estimated (Figure 2E-H). In general, the average diameter of the gold tips is larger than that of main nanowires due to the low melting point of Au nanoparticles [16]. It is worth mentioning that the consistent diameter variation trend for gold tips and main nanowires was observed as a function of growth conditions, indicating the gold tips have significant directing effect on the

growth of Si nanowires. For instance, the diameter of gold tips and main nanowires decreases with the increase of SiH_4 flow rate, which is due to the faster growth rate of Si nanowires at higher feeding of Si source. At the same time, the diameter first decreases and then increases with the increase of growth time (Figure 2F), which is consistent with the appearance and disappearance of Si branches (Figure 1B, D-F).

The microstructure demonstration was conducted for two representative Si nanowires: (1) “zig-zag” – branched Si nanowires (Figure 1D) and long – straight Si nanowires (Figure 1F). Figure 3A-C show the TEM images of Si nanowires at various resolutions for the “zig-zag” – branched Si nanowires. Gold tips were constantly observed on the main nanowires and the branches, which further indicates the growth was determined by VLS mechanism. High resolution image in Figure 3C indicates that the main nanowire and the branches have the same crystal structure. A lattice spacing of ~ 0.3 nm corresponding to (111) plane of silicon was observed for both. This is further confirmed by the FFT image in Figure 3D. TEM images of the long – straight Si nanowires were shown in Figure 3E-H. The nanowires are uniform and branchless in Morphology, with a thin SiO_2 shell encapsulated on the surface of gold tips (Figure 3F) [16]. The lattice evaluation by the high resolution TEM (Figure 3G) and the corresponding FFT image (Figure 3H) reveals the gold (111) plane for the tips and the silicon (111) plane for the main nanowires.

3.2. Surface decoration of Si nanowires

The surface decoration of Si nanowires with Au nanoparticles was achieved *via* a galvanic deposition – annealing process as illustrated in Scheme 1. Three representative Si nanowire samples (#4A, #8A, and #11A, see Table S1 in supplementary information) were used. SEM

images of these samples after galvanic deposition were shown in Figure 4. The inset high resolution SEM images indicate that the deposited gold was in a form of shell or flakes. Fundamental mechanism for galvanic deposition of gold (shell) on Si nanowires was illustrated in Figure 4D. The deposition is based on electroless replacement reaction between Si and Au^{3+} in HF-containing solution [48,49]. The obtained Au-coated Si nanowire heterostructures were labelled as #4B, #8B, and #11B. Sample #11B was further subjected to a subsequent high temperature annealing process for the evolution of Au nanoparticles on nanowire surface. The authors observed that the annealing temperature and environment have a dominant influence on the size and distribution of Au nanoparticles. The samples annealed in Ar environment were labelled as #11a, #11b, and #11c according to the temperatures (700 °C, 625 °C, and 500 °C), and the sample annealed in air at 625 °C was labelled as #11d (see Table S1 in supplementary information).

Figure 5 shows the SEM images of the Si nanowire-Au nanoparticle heterostructures annealed in above conditions. One can observe that all these annealing processes can lead to the formation of Au nanoparticles on the nanowires [50]. The heterostructures obtained in Ar environment constantly show a silicon shell on the surface of Au nanoparticles (Figure 5A-C) compared with that obtained in air environment (Figure 5D). This is probably because the diffusion and alloying of silicon atoms in Au nanoparticles are much faster in an inert environment [51]. During the subsequent cooling process, the oversaturated silicon precipitated, leading to the formation of the silicon shell. With respect to the annealing temperature, we observed that lower temperature resulted small Au nanoparticles with decreased inter-particle spacing (Figure 5E), which is probably due to the decreased migration rate of gold on Si nanowires [51]. Most importantly, it is worth noting that heterostructures annealed in air show increased Au nanoparticle size but smaller

inter-particle spacing (Figure 5D and E). This is probably because the surface oxidation of silicon and gold in air environment limited their diffusion and migration [52], and more gold shell dewetted to form single nanoparticle. The influence of Ar and air environment on the morphology of Si nanowire-Au nanoparticle heterostructures was illustrated in Figure 5F. The nanoparticle distribution geometry on the latter heterostructures is very important for SERS due to the increased possibilities of plasmonic coupling to form strong LSPR.

TEM images of the Si nanowire-Au nanoparticle heterostructures before (sample #11B) and after annealing in Ar (#11b) or air (#11d) environment were shown in Figure 6. One can observe that the as-coated gold presents a nano-film or flake structure and randomly disperses on the nanowires (Figure 6B). After the annealing process, effective dewetting was observed for these Au flakes or films, leading to the morphological evolution of Au nanoparticles (Figure 6C and E). The estimated nanoparticle size is 23 ± 13 nm for the Ar-annealed heterostructures and 26 ± 15 nm for the air-annealed heterostructures, which is consistent with above SEM results. Lattice evaluation (Figure 6B) indicates that the as-coated Au flakes present randomly distributed crystal structures. However, after the Ar-/air-annealing, standard low energy (111) plane for gold was constantly observed for the Au nanoparticles. In addition, no obvious lattice variation was observed for the Si nanowire before and after annealing, indicating the main nanowires are chemically and structurally stable to stand for such multi-step fabrication process.

3.3. Surface-enhanced Raman Spectroscopy

We evaluated the performance of pristine Si nanowires and the Si nanowire-Au nanoparticles heterostructures for the detection of trace-amount water-containing dyes using SERS. Rhodamine

6G (R6G) was used as a Raman probe. Si nanowires obtained at various growth conditions (sample #1A-#11A) as well as the Si nanowire-Au nanoparticle heterostructures before (sample #4B, #8B, and #11B) and after air-/Ar-annealing (sample #11a-#11d) was investigated (Note: sample labelling can be found in Table S1 in supplementary information). As contrast, the initial blank Si substrate, Si substrates coated with Au film or dewetted Au nanoparticles were also tested. The samples were first treated with BOE for 5 s and then immersed in 10^{-6} M R6G solution overnight to anchor the target molecules. The Raman signals of R6G were directly collected from these R6G-attached nanostructures. Schematic in Figure S6A (see supplementary information) shows the Raman test conducted on Au nanoparticles decorated Si substrate. The obtained Raman spectra were further shown in Figure S6B. No obvious signal was observed on blank Si substrate or Au film-coated substrate. However, the Au nanoparticle-coated substrate shows enhanced Raman signals due to the generation of LSPR [6,7].

SERS sensing on the as-produced Si nanowire substrate was demonstrated in Figure 7. The signal enhancement is mainly attributed to Au nanoparticles on the tips of Si nanowires. Especially, when the tips of two or more Si nanowires get close to each other, significant Raman enhancement can be observed due to the coupling of LSPR [35]. This has been described as TERS (see schematic in Figure 7A) [36]. Figure 7B-E further show representative Raman spectra of R6G obtained on various as-produced Si nanowires (#1A-#11A). The alloyed Si-Au particles coated Si substrate (sample #1A) shows weak Raman signals, which is probably due to the large inter-particle spacing. However, the signals collected from the “zig-zag” nanowires were highly enhanced (sample #2A and #3A). The variation of Raman signals on Si nanowires obtained at different growth duration were shown in Figure 7C. The nanowires grown for 2 min (sample #4A) show the strongest signals due to the high spatial density of gold nanoparticle tips. In Figure 7D we observed that the Si

nanowires obtained at other temperatures has no further enhancement on Raman signals. Moreover, it is worth noting that variation of gold sputtering time has a significant influence on the morphology of Si nanowires (Figure 1J-L), leading to a dominant change of Raman enhancement. As shown in Figure 7E, Si nanowires with no tips (sample #9A) or small tips (sample #10A) show weak signals of R6G. The highest Raman enhancement was observed on sample #11A due to its high spatial density of Au tips.

Such TERS-based chemical sensing is interesting but still cannot provide desired Raman enhancement due to the limited amount of Au nanoparticles. Thus it is necessary to study the SERS sensing based on the Si nanowire-Au nanoparticle heterostructures. The schematic for corresponding Raman test was shown in Figure 8A. The closely-packed Au nanoparticles on Si nanowires are expected to exhibit strong plasmonic coupling and thus form a constant electromagnetic field on the heterostructures, which are able to give Raman enhancement up to several orders [7]. The Raman test was first conducted on the as-deposited Si-Au core-shell nanowires (Figure 8B). Depression of Raman signals were observed on these samples due to the random lattice structure and shell-like shape of the as-deposited gold. However, interestingly, significant Raman enhancement was observed on the heterostructures after annealing (Figure 8C). One can observe that the Raman intensity of R6G on these annealed samples are increased up to ~10 times as compared with the best pristine Si nanowire samples in Figure 7.

To further evaluate the uniformity and reproducibility of above TERS/SERS sensors, Raman mapping of R6G signals was conducted on selected nanostructure substrates (sample #11A and #11d). Figure 9A shows a representative optical images of the Si nanowire-Au nanoparticle heterostructured substrate marked with numbers of spots for conducting the Raman mapping. The mapping results were shown in Figure 9B and C. These two images were generated using the

indicative Raman signal of R6G at 1360 cm^{-1} . One can observe that the distribution of “hot-spots” on the Si nanowire-Au nanoparticle heterostructures are much more uniform and stronger as compared with that on the as-produced Si nanowires. Accordingly, the Raman sensitivity (detection limit) of these two samples were further evaluated using R6G solution with various concentrations (10^{-8} M , 10^{-10} M , and 10^{-12} M). The obtained Raman spectra were shown in Figure 9D and E. The variation of enhanced Raman intensity as a function of R6G concentration were also estimated accordingly (Figure 9F). One can observe that the detection limit of both the as-produced Si nanowire and the Si nanowire-Au nanoparticle heterostructures can reach 10^{-10} M . Meanwhile, the linear trend of Raman intensity vs. $-\log(C_{\text{R6G}})$ is also promising and critical for future development of practical SERS sensors.

4. Conclusions

In summary, we studied the growth of Si nanowires *via* an atmosphere-pressure chemical vapor deposition (APCVD) method. This was achieved by employing SiH_4/H_2 as the precursors and gold nano-islands dispersed on Si substrate as the catalysts. We found that the morphology and structure of Si nanowires can be controlled by varying the growth conditions. Accordingly Si nanowires with a “zig-zag” morphology or with a branched structure can be obtained. The subsequent surface decoration of selected Si nanowires was achieved *via* a unique galvanic deposition – annealing approach. This led to the fabrication of Si nanowire heterostructures with uniformly-dispersed and tightly-packed Au nanoparticles. The final Si nanowire-Au nanoparticle heterostructure products were used as substrates for SERS-based chemical sensing. We found that surface-decorated Au nanoparticles can introduce strong plasmonic coupling on the heterostructures and thus lead to

significantly enhanced Raman sensitivity. Raman signals on such heterostructured substrates are more uniform and can reach a detection limit of 10^{-10} M (for R6G). The studies in this paper filled the blank of research on cost-effective and large-scale production of Si nanowires as well as their further heterostructure evolution for SERS sensing.

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Appendix A: Supplementary Material

Detailed experimental parameters for Si nanowire growth; SEM images for Au catalyst and Si nanowires obtained at various conditions; SERS sensing test on blank/Au catalyst decorated Si substrate. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/>

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Figures

Scheme 1. Approaches for the growth of Si nanowires and further their surface decoration with Au nanoparticles for developing heterostructural SERS substrate.

Figure 1. SEM images of Si nanowires or arrays obtained at various SiH_4 flow rate (A- 10 sccm; B- 20 sccm; C- 30 sccm), various growth duration (D- 2 min; E- 5min; F- 10 min), various temperature (G- 675 °C; H, I-725 °C), and various gold film sputtering times (J- 15 s; K- 30 s; L- 45 s). Note: the inset SEM images show the morphology of representative Si nanowires (scale bar for all the insets: 100 nm).

Figure 2. Schematic illustrating the influence of (A) SiH_4 flow rate, (B) growth time, (C) temperature, (D) gold sputtering time on the morphology and structure of Si nanowires. (E-H) Influence of growth conditions on the diameter of Si nanowires: (E) flow rate set, (F) grow time set, (G) sputtering time set, (H) temperature set.

Figure 3. (A-C) TEM images of the branched Si nanowire (sample #4A). (D) FFT image corresponding to C. (E-F) TEM image of the straight Si nanowire (sample #6A). (H) FFT image corresponding to H.

Figure 4. Galvanic deposition of gold film on various Si nanowires: (A) sample #4A, (B) sample #8A, (C) sample #11A. The insets show corresponding individual Au-coated Si nanowire after galvanic deposition of Au film. *Note: scale bar for all the insets: 100 nm. The Si-Au nanowire heterostructures after galvanic deposition were labelled as #4B, #8B, and #11B, correspondingly (see Table S1, supplementary information).* (D) Schematic showing the galvanic deposition of gold shell on silicon nanowires.

Figure 5. Annealing of Au-coated Si nanowires (sample #11B) at different temperature and environment. (A) 700 °C in Ar, (B) 625 °C in Ar, (C) 500 °C in Ar, and (D) 625 °C in air. *Note: scale bar for all the insets: 100 nm.* (E) Variation of diameter and inter-particle spacing of the Au nanoparticles on Si nanowires as a function of the annealing conditions. (F) Schematic showing the influence of annealing temperature and environment on the morphology of obtained Si nanowire-Au nanoparticle heterostructures.

Figure 6. TEM images of (A, B) Au-coated Si nanowire after galvanic deposition (The inset shows morphology at the tip side), (C-F) Si nanowire-Au nanoparticle heterostructures annealed in Ar environment (C, D) and in air environment (E, F).

Figure 7. (A) Schematic illustrating TERS sensing on the as-produced Si nanowires. (B-E) Raman spectra of R6G obtained on various Si nanowires showing in Table S1: (B) SiH₄ flow rate set, (C) growth time set, (D) temperature set, and (E) gold sputtering time set. *Note: the sample labeling can be found in Table S1 (supplementary information).*

Figure 8. (A) Schematic illustrating SERS sensing on the Si nanowire-Au nanoparticle heterostructures. (B) Raman spectra of R6G obtained on the Au-coated Si nanowires corresponding to Figure 4. (C) Raman spectra of R6G obtained on various annealed Si nanowire-Au nanoparticle heterostructures corresponding to Figure 5. *Note: the sample labeling can be found in Table S1 (supplementary information).*

Figure 9. (A) Optical image of Si nanowire-Au nanoparticle heterostructured substrate for conducting Raman mapping. (B, C) Raman mapping obtained on (B) the as-produced Si nanowire substrate (sample #11A) and (C) the Si nanowire-Au nanoparticle heterostructured substrate (sample #11d). *Note: The Raman mapping was generated by analyzing intensity of Raman peak at 1360 cm^{-1} .* (D, E) Raman spectra obtained on (D) the as-produced Si nanowire substrate (sample #11A) and (E) the Si nanowire-Au nanoparticle heterostructured substrate (sample #11d) by detecting R6G solution with different concentration. (F) Calibration curve of Raman intensity as a function of R6G concentration for the as-produced Si nanowire substrate (sample #11A) and the Si nanowire-Au nanoparticle heterostructured substrate (sample #11d).