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Solution chemistry approach to fabricate vertically aligned carbon nanotubes on gold wires: towards vertically integrated electronics

Benjamin S Flavel, Jingxian Yu, Amanda V Ellis, Jamie S Quinton and Joseph G Shapter

School of Chemistry, Physics and Earth Sciences, Flinders University, Sturt Road, Bedford Park, Adelaide, SA 5001, Australia
E-mail: joe.shapter@flinders.edu.au

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Abstract
A monolayer of hexadecyltrichlorosilane, 3-aminopropyltriethoxysilane or 3-mercaptopropyltrimethoxysilane was self-assembled onto a p-type silicon (100) substrate to provide a resist for electrochemical anodization with an atomic force microscope cantilever. Silane treatment of the oxide nanostructures created by anodization lithography allowed for the creation of a chemically heterogeneous surface, containing regions of $-\text{NH}_2$ or $-\text{SH}$ surrounded by $-\text{CH}_3$ functionality. These patterned regions of $-\text{NH}_2$ or $-\text{SH}$ provided the point of attachment for citrate-stabilized gold colloid nanoparticles, which act as ‘seed’ particles for the electro-less deposition of gold. This has allowed the creation of gold wires on a silicon surface. Carbon nanotubes, with high carboxylic acid functionality, were vertically immobilized on the patterned gold wires with the use of a cysteamine monolayer and a condensation reaction. Such a material may prove useful in the creation of future vertically integrated electronic devices where it is desirable for electron transport to be in three dimensions and this electron transport is demonstrated with cyclic voltammetry.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Current device and process scaling in the semiconductor industry has led to a continuous demand for increased density of silicon-based electronics and a decrease in the cost of manufacture. However, scaling techniques currently employed will soon reach physical and technical limitations and alternative methods are now being investigated [1, 2]. As a result many research efforts in the field of nanotechnology have been directed towards the development of new methods to create addressable, surface-immobilized metallic architectures [3, 4], which may form the components of future electronics, sensors and fuel cells [5]. One approach, which is proving to be particularly promising, is the controlled assembly of metal nanoparticles on solid surfaces [6, 7]. Due to their quantum scale dimensions, metallic nanoparticles are vastly different from bulk materials, exhibiting many interesting electronic, optical and catalytic properties, which could be advantageously exploited for future device design [8, 9]. The most commonly used metallic nanoparticle is colloidal gold due to its ability to simply and inexpensively, using wet chemical methods, create solutions of nanoparticles with average diameters from 3 to 150 nm [10]. Gold nanoparticles also have sufficient surface reactivity to facilitate adhesion to a variety of chemically functionalized surfaces [10], either through electrostatic attractions to a positively charged interface, such as a protonated amine [4, 6, 7, 11], or by covalent bonding to a thiol [9, 12]. In this manner it has been possible to use a variety of different techniques to create a patterned surface...
Au3

to perform using solution chemistry [11]. In this method on catalytic surfaces [4], which is simple and inexpensive deposition is an autocatalytic redox process, occurring only known as electro-less deposition [4, 11, 13, 14]. Electro-less particle size can have on surface coverage. Low nanoparticle colloidal gold particles, which demonstrates the dramatic effect have reported a surface coverage as low as 13% for 20 nm with vertical interconnects are especially promising for future integration, where multiple layers of active devices are stacked in series of metal interconnects [1]. However, three-dimensional a two-dimensional layer of silicon-based transistors with a investigated [1, 2, 15]. Current microprocessors consist of several micrometres in diameter. Anodization lithography with oxide nanostructures fabricated with anodization lithography was used to create regions of silicon oxide in an insulating self-assembled monolayer of –CH3, –NH2- or –SH-terminated using hexadecyl-trichlorosilane (HTS), 3-aminopropyltriethoxysilane (APS) or 3-mercaptopropyltrimethoxysilane (MPS), respectively, on silicon substrates. Further silane modification of the oxide nanostructures fabricated with anodization lithography resulted in a chemically patterned silicon surface consisting of –CH3 and –NH2 or –SH regions. As has been shown in the literature [4, 6, 7, 9, 11, 12] these –NH2 and –SH regions provide the point of attachment for citrate-stabilized gold nanoparticles, which facilitate the initiation of electro-less deposition, creating horizontal gold wires. Previously [3, 4], surface templates for electro-less deposition have been created by micro-contact printing of –NH2-terminated regions alone and the resultant gold wire was several micrometres in diameter. Anodization lithography used in our work allows wires on the nanoscale to be created. A monolayer of –NH2-terminated cysteamine is

Figure 1. Idealized representation of carbon nanotube vias on gold for future electronic devices.
then self-assembled onto the gold wires allowing the vertical attachment of −COOH functionalized carbon nanotubes via a condensation reaction. Previously [19–21], carbon nanotubes have been immobilized on flat gold substrates using cysteamine. However, to our knowledge this is the first example utilizing a nanoscale wire created by electro-less deposition. Finally, to demonstrate electron transport along a carbon nanotube and into the underlying gold, a further condensation reaction was performed on the free end of the carbon nanotube to immobilize the redox active molecule ferrocenemethanol for cyclic voltammetry.

2. Materials and methods

2.1. Atomic force microscopy (AFM)

Atomic force microscope images were taken in air with a multi-mode head and Nanoscope IV controller, Digital Instruments, Veeco, Santa Barbara, operating in tapping mode. Commercially available silicon cantilevers (FESP-ESP series, Veeco probes, Santa Barbara) with fundamental resonance frequency between 70–85 kHz were used. Topographic (height) images were obtained at a scan rate of 1 Hz with the parameters set point, amplitude, scan size and feedback control optimized for each sample. The method of anodization lithography has been outlined in detail previously [22, 23]. In brief, lithography was conducted in tapping mode with platinum/iridium-coated silicon cantilevers (SCM-PIT series, Veeco probes, Santa Barbara) with fundamental resonance frequency between 60 and 75 kHz and an applied cantilever voltage of −11 V with a tip velocity of 1 μm s⁻¹. Prior to patternning, the amplitude set point was reduced to 70% of its imaging value to reduce the tip–substrate distance. All images presented represent background subtracted data (using the flatten feature in the Digital Instruments or WS × M [24] software).

2.2. Synthesis of gold colloid nanoparticles

Prior to use all glassware was thoroughly cleaned with a 3:1 v/v solution of 36% hydrochloric acid (Univar) and 70% nitric acid (Univar). Colloidal gold nanoparticles were prepared using the method outlined by Chen et al [4] and Dong et al [11]. Firstly, 1 ml of a 1% aqueous solution of 99.9% gold (III) chloride (Sigma-Aldrich) was added to 100 ml of HPLC grade water produced by a MilliQ Plus (Millipore), hereafter referred to as MilliQ water, under vigorous stirring for 1 min. 1 ml of a 1% aqueous solution of 99% sodium citrate (Sigma-Aldrich) was then added and further stirred for 1 min. Finally 1 ml of a 0.075% solution of 99% sodium borohydride (Sigma-Aldrich) in 1% aqueous sodium citrate was added and the solution stirred for 5 min. An intense burgundy solution, which is characteristic of gold nanoparticles [10], was then obtained and stored at 4 °C until required.

2.3. Particle size analysis

Particle size analysis by dynamic light scattering was performed with a Malvern Instruments Ltd, Malvern, UK, High Performance Particle Sizer (HPPS—HPP5001) utilizing an enhanced quality set. Immediately after synthesis the gold nanoparticle solution was analysed at a temperature of 20 °C with a dispersant refractive index and viscosity set to 1.3320 and 0.890 cP, respectively.

2.4. UV–visible spectroscopy

A UV–vis spectrum of the colloidal gold nanoparticle solution was obtained from a Varian Cary 50 Scan UV–visible spectrophotometer with an incorporated xenon flashlamp. Dual beam mode was utilized with a scan rate of 60 nm min⁻¹ and resolution of 4 nm at a temperature of 20 °C.

2.5. Preparation of carbon nanotubes

The preparation of carboxylated single-walled carbon nanotubes (SWCNTs) has been described in detail previously [22]. In brief, single-walled carbon nanotubes (SWCNTs) from Carbon Solutions Inc., California, USA, RFP-SWNT, were refluxed in 3 M nitric acid for 24 h. The dilute nitric acid solution was then decanted off and the nanotubes were placed into a more aggressive oxidizer, namely a 3:1 v/v solution of concentrated sulfuric acid (98%) and concentrated nitric acid (70%) and ultrasonicated for 8 h at 0 °C [19, 20]. The shortened nanotubes were then diluted in 500 ml of MilliQ water and filtered through a 0.45 μm polytetrafluoroethylene (PTFE) membrane. The nanotubes were further washed with MilliQ water to bring the pH to 5–7 and dried under vacuum [20].

2.6. Preparation of patterned gold colloid templates for electro-less deposition

The process to create patterned silicon surfaces of different chemical functionality, utilizing silane chemistry and anodization lithography, is shown schematically in the first six steps in figure 2. This has been described in detail elsewhere [22, 23]. In brief, highly boron-doped p-type silicon (100) (Virginia Semiconductor Inc., USA) was cut into 1 cm × 1 cm sized wafers and cleaned with a 1:3 (v/v) mixture of 30% hydrogen peroxide (Chem-Supply, South Australia) and 98% sulfuric acid (Labscan Asia Co. Ltd, Thailand) at 80 °C for 15 min to yield a hydroxylated silicon surface. After cleaning, the silicon wafers were rinsed with MilliQ water. Before self-assembled monolayer formation, the silicon substrate was blown dry under a stream of ultrapure nitrogen. The hydroxyl-terminated silicon wafers were then immersed into a 0.5% solution of 90% hexadecyltrichlorosilane (HTS) (Fluka Production GmbH) in 99% hexadecane (Sigma-Aldrich) for 40 min. After removal from solution the silicon wafers were rinsed in chloroform (Ajax-Finechem) and allowed to dry. Atomic force anodization lithography was then used to selectively remove the hexadecyltrichlorosilane layer, creating regions of silicon oxide on the surface. The now patterned silicon substrate was then placed into a 1:3 (v/v) mixture of 30% hydrogen peroxide and 98% sulfuric acid for 3 min at 80 °C to produce silanol groups on the oxide and then washed with MilliQ water and dried with nitrogen. The substrate was then placed into a 0.5%
solution of either 99% 3-aminopropyltriethoxysilane (APS) (Sigma-Aldrich) or 99% 3-mercaptopropyltrimethoxysilane (MPS) (Fluka Production GmbH) in 99% hexadecane (Sigma-Aldrich) for 40 min. The substrate was then removed from solution, washed in chloroform and allowed to dry. This allowed a silicon surface of predominantly $-\text{CH}_3$ functionality with regions of either $-\text{NH}_2$ or $-\text{SH}$ to be created.
2.7. Electro-less plating of gold

Prior to use the patterned silicon/nanoparticle surfaces were ultrasonicated for 2 min, thoroughly rinsed with water and then blown dry under a stream of ultrapure nitrogen. This was to ensure that only the nanoparticles which were either electrostatically or chemically attached to the surface remained when placed into the gold plating solution. Figure 2, step 8, shows the site-selective gold nanoparticles act as ‘seed’ particles to initiate the electro-less deposition of gold. The substrate was then placed into a solution of aqueous 0.4 mM 99% hydroxylamine hydrochloride (Sigma-Aldrich) and 0.1% gold chloride trihydrate for a period of up to 1 min before being thoroughly washed with water. This resulted in the creation of patterned gold nanostructures on silicon.

2.8. Attachment of carbon nanotubes to patterned gold nanostructures

Figure 2, steps 9 and 10, show the approach used to immobilize carbon nanotubes onto the electro-less plated gold nanostructures using a cysteamine monolayer as a molecular anchor. The patterned gold nanostructured substrate was immersed into a 1 mM 95% cysteamine (Sigma-Aldrich) ethanol solution for a period of 40 min. The substrate was then removed, thoroughly washed with ethanol and dried under a stream of ultrapure nitrogen. The patterned gold nanostructure was placed into a 5 ml 99.9% N,N-dimethyl formamide (DMF) (Southern Cross Scientific Pty. Ltd.) solution containing both 2.5 mg of 99.0% N,N’-dicyclohexylcarbodiimide (DCC) (Fluka Production GmbH) and 1 mg of carboxyl functionalized carbon nanotubes. Prior to introducing the gold nanostructure, the carbon nanotube/DCC/DMF solution was ultrasonicated for 5 h to evenly disperse the carbon nanotubes. Finally the silicon wafer containing the gold nanostructure with immobilized carbon nanotubes was rinsed in acetone and allowed to dry.

2.9. Electrochemistry

Electrochemical measurements were performed with a BAS100B Electrochemical Analyser (Bioanalytical Systems Inc., USA), operating in cyclic voltammetry mode using a specially designed electrochemical cell [25]. All data was collected using the BAS100W (Bioanalytical Systems Inc., USA) software v2.3 with data presented representing a Fourier transform of the raw signal. The background capacitive current was subtracted using the UTLIS, Utilities for Data Analysis, software (Dirk Heering). Due to the inherent difficulty in electrically connecting a gold nanostructure for electrochemical analysis, electro-less deposition was used to create a complete gold layer on a silicon wafer, which due to the increased surface area could easily be connected. The chemical approach used remained exactly the same and is therefore believed to be comparable to the nanostructure systems [26]. As shown in figure 3,
a monolayer of either 3-aminopropyltriethoxysilane or 3-mercaptopropyltrimethoxysilane was assembled onto a silicon wafer, followed by the attachment of gold nanoparticles and the subsequent electro-less deposition of gold to fabricate a gold-coated silicon surface. The same method used for patterned gold nanostructures was then used to immobilize carbon nanotubes onto the gold surface using cysteamine. However, the nanotubes still have carboxylic acid functionality available after attachment which can then be used to further modify the nanotubes. In this case, the redox active molecule, ferrocenemethanol, was attached to the carboxylic acid end groups of the carbon nanotube using a condensation reaction [23, 26, 27]. The attached carbon nanotube substrate was immersed into 3 ml of 99.9% dimethyl sulfoxide (Sigma-Aldrich) containing 0.3 mg of 99.0% N,N′-dicyclohexylcarbodiimide and 1.5 mg of 97% ferrocenemethanol (Sigma-Aldrich) for 48 h at 25 °C. The substrate was then rinsed in acetone and dried with nitrogen. An electrolyte solution containing 1 mmol l−1 of 98% tetrabutylammonium perchlorate (Fluka) in acetonitrile (Scharlau Chemie) was used. The potential was swept initially in the anodic direction from 100 to 1200 mV at a scan rate of 100 mV s−1, with the working electrode connected directly to the gold surface.

3. Results and discussion

3.1. Gold nanoparticles

Immediately after preparation, UV–visible spectroscopy and particle sizing by dynamic light scattering was performed on the colloidal gold nanoparticles and is shown in figures 4(a) and (b), respectively. In the UV–visible spectra the maxima of the surface plasmon peak, λmax, was located at 528 nm and particle size analysis gave a size of 7 nm. This is the expected average particle size for gold nanoparticles prepared using the method of Chen et al [4] and Dong et al [11]. However, the width of the peak from particle size analysis indicates a nanoparticle size distribution of 4–15 nm. This, combined with the broad surface plasmon peak, which provides information about the polydispersity, indicates the presence of a large distribution in particle size. Furthermore, the observed redshift of the surface plasmon peak from the typical 518–520 nm [8, 10] to 528 nm suggests the formation of larger gold nanoparticles or possible aggregation [10]. Gold nanoparticles prepared with the method described should be negatively charged due to the presence of a citrate (−COO−) capping layer and hence ideally repel each other to remain evenly dispersed in solution [4, 11]. The observed aggregation of gold nanoparticles in our work may be due to inhomogeneous nanoparticle structure or the presence of electrolytes, such as sodium chloride, in the water used for dispersion. Despite the broad distribution in size and possible nanoparticle aggregation the prepared colloid could still be used effectively to attach −NH2- and −SH-terminated regions to ‘seed’ electro-less deposition. In the case of the −NH2-terminated regions, gold colloid assembly was driven by the electrostatic attraction between the negative, citrate-capped, gold nanoparticles and the partially protonated amine layer (pKa 7.5) [5, 6, 8, 28]. In the case of the −SH-terminated regions, well-known gold–thiol chemistry [9, 12, 13] was used to chemically attach the gold nanoparticles.

3.2. Electro-less deposition of gold

To investigate the effect exposure time in the electro-less plating solution had on the vertical and lateral dimensions of the resultant gold structure, a silicon substrate covered with a monolayer of hexadecyltrichlorosilane (CH3 terminus), with etched regions containing either 3-aminopropyltriethoxysilane...
(NH₂ terminus) or 3-mercaptopropyltrimethoxysilane (SH terminus), see figure 2, step 6, was immersed in the colloidal gold solution followed by the electro-less plating solution for periods of 0, 2.5, 5, 10, 15, 22.5, 30 and 60 s. Figure 5 shows the obtained vertical and lateral dimensions of gold structures with increased exposure time to the electro-less plating solution, where 0 s represents exposure to gold nanoparticles alone. Both the lateral and vertical growth reported represent an average of nine measurements taken with the section analysis feature in the Digital Instruments software using AFM data of a gold structure. Vertical growth was obtained by subtracting the initial height of the silicon oxide, created by anodization lithography, from the final height of the overall gold nanostructure. The measurement of lateral growth was slightly more complicated due to the potential for gold to deposit either side of the initial silicon oxide line. This is unlike vertical growth, where deposition is confined to one direction, out of the surface plane. To ensure that gold growth was comparable both vertically and laterally the initial width of the silicon oxide was subtracted from the final width of the gold nanostructure and then divided by two to obtain the width increase in one direction. To provide an example a cross-section analysis has been performed on a patterned silicon substrate both before and after 22.5 s electro-less deposition and is shown as an inset to figure 5. It can clearly be seen that the deposition rate of gold by the surface catalyzed reduction of Au³⁺ is a nonlinear process. For deposition times less than 20 s both the vertical and lateral dimensions increase rapidly to approximately 37 nm before reaching a plateau. Initially, this could be interpreted as a concentration effect caused by the plating solution. However, it is more accurately described by equation (1), the Gibbs–Thompson equation [11, 14], which relates the excess free energy ($\Delta E$) of a small metal particle to its dimensions ($\Gamma$):

$$\Delta E = \frac{2\sigma V_m}{\Gamma F}$$  \hspace{1cm} (1)

where $V_m$ is the molar volume of metal, $\sigma$ is the specific free surface energy of the interface with the electrolyte and $F$ is Faraday’s constant. From the Gibbs–Thompson equation it can be seen that, as the gold nanoparticle increases in size, the initial high surface free energy, which is required to catalyze electro-less deposition, decreases. The plateau in lateral and vertical deposition after 20 s suggests that, after this time, the gold nanoparticles have coalesced to form a complete layer, which is no longer capable of catalyzing electro-less deposition. In fact, for extended deposition times, up to 2 min, no increase in lateral or vertical gold deposition was found to occur on the patterned oxide. Instead small surface-absorbed gold particles from the plating solution were observed by AFM to grow in size, resulting in the eventual coverage of the entire silicon surface with a porous gold layer. Previously electro-less deposition times of 5 min to 24 h [3, 4, 11, 14] have been used. However, this was for a patterned surface of several micrometres in resolution. In this work due to the nanoscale dimensions of the patterned gold structure, deposition times of approximately 25 s were to create all gold nanostructures shown in this work.

Figure 6 shows an AFM image of a patterned silicon substrate from anodization lithography before (a) and after (b), (c) electro-less deposition of gold for 25 s. Prior to deposition a silicon oxide pattern, approximately 5 nm in height, can be seen and is independent of the silane monolayer used for patterning. To obtain the gold wire structure (b) a monolayer of hexadecyltrichlorosilane was patterned with anodization lithography followed by the attachment of 3-aminopropyltrimethoxysilane to the oxide line, creating a
chemically heterogeneous surface containing $-\text{CH}_3$ and $-\text{NH}_2$ functionality. The inverse of this gold structure, a gold channel (c), was obtained by initially patterning a silicon oxide line in a 3-mercaptopropyltrimethoxysilane ($-\text{SH}$ terminus) monolayer. The same resultant gold structure is obtained in (b) and (c) if the use of 3-aminopropyltriethoxysilane and 3-mercaptopropyltrimethoxysilane is interchanged as both provide sufficient attached gold nanoparticles for electro-less deposition. As expected after electro-less deposition it can be seen that gold selectively plates on regions containing the gold nanoparticles, which are attached to either a $-\text{NH}_2$- or $-\text{SH}$-terminated monolayer. It can be seen that electro-less deposition has resulted in the coalescence of gold nanoparticles into a complete layer. However, gold layers created by electro-less deposition are typically porous [11, 14, 29], which is not entirely obvious in the images presented due to convolution of the AFM cantilever. In both cases a patterned region 160 nm in width was created and is a significant resolution improvement over previous work [4]. Such gold structures may find application in future electronic [6, 7] or micro-fluidic devices [30].

As previously mentioned gold particles from the plating solution can occasionally absorb on surrounding regions, especially for long exposure times. However, as these suspended particles have no affinity to the absorbed region an adhesive tape peel was used to remove them post-plating. The adhesive tape peel test is a qualitative test often performed to measure the adhesion of a thin film and its substrates, where the amount of material transferred to the tape is a measure of the adhesive strength [11]. This test has previously been used to examine the adhesion of electro-less deposits of gold on $-\text{NH}_2$ patterned substrates of several microns in dimension [4] or monolayer coverage [11, 14]. Poor adhesion of the gold film to the substrate was found with the removal of up to 50% of the gold film prepared on a $-\text{NH}_2$ monolayer and 100% in the case of a patterned gold substrate. In the work presented here no delamination of the gold film was observed for structures created on a $-\text{SH}$-terminated region and only very slight removal was observed for $-\text{NH}_2$-terminated regions. This dramatic increase in gold adhesion compared to previous patterned substrates [4] is obvious in the case where a chemical bond instead of electrostatic attraction is used to anchor the gold nanoparticles to the surface. A reduction in size to the nanoscale and a silane layer containing a higher density of vertically aligned functional groups may explain the increased adhesion for $-\text{NH}_2$-terminated regions observed in this work.
3.3. Attachment of carbon nanotubes to lateral gold wires

Typically a self-assembled monolayer of cysteamine (−NH₂-terminated) on flat gold substrates is created by exposure to a cysteamine solution for a period of 5–24 h ensuring a dense well-aligned layer [19, 20, 31, 32]. However, in this work due to the porous nature [11, 14, 29] of the gold nanostructures, extended exposure to the cysteamine ethanol solution was found to completely delaminate the gold. For extended exposure times it was believed that the cysteamine was able to penetrate under the gold nanostructure, displacing it from the surface. This is likely due to the high affinity of gold for sulfur-containing molecules [33, 34]. An exposure time of less than 1 h was therefore used and was found to leave the gold intact whilst also providing a sufficient coating.

Figures 7 and 8 show AFM images of a gold wire created by electro-less deposition with a cysteamine monolayer before and after attachment of carboxylic acid functionalized carbon nanotubes, respectively. Graphs 1–6 are a cross-section analysis of the patterned gold and gold/nanotube structures. Prior to the attachment of carbon nanotubes, small regions of increased height (defects) on the gold wire are present and have been highlighted, figure 7(II). Such defects in the prepared gold layer are often present and are attributed to nanoparticle aggregation or a localized increase in Au³⁺ reduction during deposition. This aggregation of the gold nanoparticles is in agreement with the UV–visible and particle size analysis previously discussed. Upon looking at the AFM image of the attached carbon nanotubes it is difficult, due to the image contrast, to easily identify each nanotube. To make it clearer each nanotube has been highlighted, figure 8(II). Furthermore, to ensure that a clear distinction between deposited carbon nanotubes and existing defect locations can be made, defects are shown in the same image. With careful examination of the cross sections of the gold wire before and after exposure to the nanotubes, it is possible to determine a nanotube coverage in the active area of about 5%. Immediately it can be seen that there is little or no adsorption of carbon nanotubes on the surrounding −CH₃-terminated silane layer. Long carbon nanotubes are also observed to align themselves with the gold nanostructure in preference to the surrounding layer. Despite the fact that the final goal of this work is to have only vertically aligned carbon nanotubes a significant number of nanotubes are found to ‘lie down’ along the gold wire. This is unlike our previous work [22, 23, 25, 27, 35, 36] attaching carbon nanotubes to silicon using condensation reactions, where predominantly vertical alignment is observed. It is believed that the increase in horizontal lying carbon nanotubes is a result of the reduced time for cysteamine assembly producing a poorly aligned monolayer for nanotube attachment coupled with the relatively rough gold surface. Furthermore, due to the poorly aligned cysteamine layer there is expected to be an increase in exposed hydrophobic hydrocarbon chains, which will promote attachment to the hydrophobic carbon nanotube sidewalls. However, some vertical alignment of carbon nanotubes was observed and a cross-section analysis has been performed on a variety of regions, as shown in figures 7 and 8, to demonstrate the height increase upon attachment. It can be seen that, prior to carbon nanotube deposition, figure 7, the prepared gold wire has a vertical height of between 31 and 40 nm. After attachment of carbon nanotubes, figure 8, the vertical height has increased by between 16 and 46 nm.
Figure 8. AFM images of a gold nanostructure after attachment of carbon nanotubes.

and is attributed to the vertical alignment of carbon nanotube bundles on the gold. This is in agreement with our previous work where nanotubes 8–57 nm in length were shown to be vertically aligned on silicon [22, 23, 25, 27, 35, 36] and the work of Liu et al [19, 21], which has shown that the adsorption kinetics facilitates the assembly of shorter vertically aligned carbon nanotubes. To ensure that carbon nanotubes were indeed chemically attached, the control experiment of a gold nanostructure immersed in the carbon nanotube solution without exposure to cysteamine was carried out. It was found that no chemically attached carbon nanotubes were present. Furthermore, after attachment, the immobilized carbon nanotubes could not be removed with adhesive tape, indicating a high level of adhesion. Obviously if this is to become a commercial reality a method to create a greater density of significantly longer, addressable, vertically aligned carbon nanotubes will need to be devised.

3.4. Electrochemistry

It is believed that the vertically aligned carbon nanotubes presented in this work may offer a new approach to fabricate carbon nanotube vias on a lateral gold wire for future electronic applications. To demonstrate electron transport along an immobilized carbon nanotube and into a gold surface (as shown in figure 1), the redox active molecule ferrocenemethanol was attached to the free end of the carbon nanotube. Figure 9(a) shows the raw data obtained from cyclic voltammetry at a scan rate of 100 mV s\(^{-1}\) and (b) the background subtracted voltammogram for ferrocenemethanol-modified carbon nanotubes, where the working electrode was connected directly to the gold surface. Distinct redox waves can clearly be seen for ferrocenemethanol-modified carbon nanotubes. The anodic and cathodic peak positions were found from the background-subtracted data to be at 717 and 680 mV with peak currents of 66 and 65 nA, respectively. This represents a peak separation of 37 mV and is in agreement with previous work where a small separation between oxidation and reduction peaks is observed, which is attributed to the highly efficient electron transfer down the length of a carbon nanotube [23, 26]. To ensure that the observed redox waves were indeed from ferrocenemethanol-modified carbon nanotubes a variety of control experiments were performed and are shown in figure 9(a). Firstly a cysteamine monolayer was assembled on a gold layer created by electro-less deposition; secondly, carbon nanotubes were immobilized on the cysteamine and finally carbon nanotubes were immobilized on the gold and exposed to the ferrocenemethanol solution in the absence of N,N’-dicyclohexylcarbodiimide (DCC); hence no attachment of ferrocenemethanol is expected. As can be seen in figure 9(a) no ferrocenemethanol redox waves were observed in each of the control experiments. However, a small amount of oxidation can be seen at approximately 500 mV and is attributed to oxidative desorption of the underlying cysteamine monolayer [37–39] and is observed in each experiment. We have now begun work to perform a full electrochemical characterization of the ferrocenemethanol-modified carbon nanotubes on gold layers formed by electro-less deposition to determine the long term stability and viability for use in future electronic devices.
4. Conclusion

Anodization lithography has been used to pattern a monolayer of hexadecyltrichlorosilane, 3-aminopropyltrimethoxysilane or 3-mercaptopropyltrimethoxysilane to create a nanoscale chemically heterogeneous silicon surface containing regions of −CH₃, −NH₂ and −SH functionality. Colloidal gold nanoparticles were then assembled onto the regions containing −NH₂ or −SH functionality to catalyze the electro-less deposition of gold. Electro-less deposition of gold enabled the creation of nanostructures, which could be reproducibly created in a matter of seconds. These nanostructures also showed a dramatic increase in adhesion to the substrate, especially those created on a 3-mercaptopropyltrimethoxysilane layer. Carbon nanotubes were then assembled onto the gold nanostructures using a monolayer of cysteamine and a condensation reaction. A significant number of nanotubes were found to lie horizontally; however, vertical alignment was also observed. Such gold nanostructures may find application in future electronic or micro-fluidic devices. Furthermore, the attachment of vertically aligned carbon nanotubes to lateral gold wires may provide a new, low energy, solution chemistry approach to fabricate carbon nanotube vias.

References


Figure 9. (a) Cyclic voltammogram at 100 mV s⁻¹ of ferrocenemethanol-modified carbon nanotubes immobilized on gold and (b) background-subtracted data.