

Patterned Attachment of Carbon Nanotubes to Silicon

Benjamin S. Flavel, Jingxian Yu, Daniel Tune, Joseph G. Shapter*, Jamie S. Quinton

School of Chemistry, Physics & Earth Sciences
Flinders University, Sturt Road, Bedford Park, Adelaide SA 5001

*Email: joe.shapter@flinders.edu.au

Telephone: (08) 8201200

Abstract - A variety of carbon nanotube based surface architectures are fabricated on silicon, which are ideal for use in future electronic devices

I. INTRODUCTION

Current device and process scaling in the semiconductor industry has led to a continuous demand for the increased density of silicon-based electronics and a decrease in the cost per bit. However, scaling techniques currently employed will soon reach physical and technical limitations [1] and alternative methods are now being investigated. One such method is molecular electronics which has been proposed to circumvent the limitations associated with current semiconductor devices allowing for scaling down to the molecular level [2] whilst dramatically decreasing the associated cost [1]. A promising approach within the field of molecular electronics is the use of single-walled carbon nanotubes as electronic interconnects [3, 4]. Conducting polymer composites have also received a great deal of attention [5-8], in particular with carbon nanotubes, as a result of nanotubes exceptional electronic and mechanical properties [4, 9]. Fabrication of hybrid materials in this way provides a possible avenue to enhance the characteristics of materials as the composite material often exhibits characteristics different to the individual components [5]. In the case of carbon nanotube/polymer composites it is expected that the electrical and mechanical properties may be able to be significantly improved compared to pure polymer films [6, 8, 10]. An order of magnitude increase in electrical conductivity using the conductive polymer polyaniline in a composite with carbon nanotubes compared to pure polyaniline has already been demonstrated by Maser et al. [7]. Furthermore, a suggested mechanical improvement of carbon nanotube/polymer composites is that nanotubes in the polymer could act as a nanometric heat sink, preventing device break down [6, 8]. However, for any molecular electronic approach to be successfully integrated into existing technologies the ability to precisely control the orientation and position of molecular interconnects and storage media is of crucial importance [11].

This work presents approaches to fabricate a variety of site selective carbon nanotube based surface architectures, which are ideal for use in electronic devices. Each of the approaches for producing these architectures utilise low energy solution chemistry and a scanning probe method called atomic force

anodisation lithography. Anodisation lithography is one of the many different forms of scanning probe lithography and it is proving to be particularly promising for nano-scale patterning, as it can be readily used to produce features with sizes below 100 nm [12]. Moreover, it offers a versatility in the material used and high patterning speeds (up to $1000 \mu\text{m s}^{-1}$) [13]. The technique relies upon the use of a self-assembled monolayer (in this case hexadecyltrichlorosilane on silicon), a conductive atomic force microscope cantilever and the ability to selectively oxidize and remove molecules on the surface. Patterning is made possible as the probe tip can be placed at a specific set of co-ordinates and then moved in a controlled fashion to 'write' oxidized features onto the surface [14]. Electrochemical oxidation occurs in a small electrochemical cell formed due to capillary forces between the conductive cantilever tip and the humidity-adsorbed sample surface as a result of the presence of atmospheric water [14]

A monolayer of methyl terminated hexadecyltrichlorosilane is self assembled onto a p-type silicon (100) substrate to provide a resist for electrochemical oxidation with an atomic force microscope cantilever. Through precise control of the cantilever's position on the surface and the voltage applied, a variety of different patterns have been etched into the substrate. These etched regions provide a site for a variety of further functionalization. For example, to these etched regions amine terminated 3-aminopropyltrimethoxysilane can be self assembled, which provides a point of attachment for condensation reactions. Carbon nanotubes, with high carboxylic acid functionality, can then be attached to these etched regions, forming an amide linkage between the silicon surface and the carbon nanotube. Once the SWCNT are immobilized the conductive polymer, polyaniline, can be selectively attached to the carbon nanotubes to create a patterned carbon nanotube/polyaniline composite material. Finally citrate stabilized colloidal gold nanoparticles can be self assembled onto the patterned amine terminated regions by electrostatic forces and provide an initiation point for the electroless deposition of gold, allowing the creation of high resolution gold nano-wires. To these gold nano-wires the alkanethiol, cysteamine can be self assembled, which provides a further reaction point for a carbon nanotube. By combining these gold wires with vertically aligned carbon nanotubes a possible route towards 3-dimensional electronics is demonstrated.

II. MATERIALS & METHODS

A. Preparation of Carbon Nanotubes

The preparation of the single-walled carbon nanotubes (SWNTs) has been described in detail previously [15]. In brief, single-walled carbon nanotubes (SWNTs) from Carbon Solutions Inc, California, USA, RFP-SWNT, were refluxed in dilute nitric acid (HNO_3) for 24 hours. The dilute nitric acid solution was then removed and the nanotubes were placed into a more aggressive oxidiser, namely 3:1 v/v solution of concentrated sulphuric acid (98 %) and concentrated nitric acid (70 %) and ultrasonicated for 8 hours at 0 °C [16, 17]. The shortened nanotubes were then diluted in 500 mL of ultrapure water and then filtered through a 0.45 μm polytetrafluoroethylene (PTFE) filter membrane. The nanotubes were further washed with MilliQ water to bring the pH to 5-7 and dried under vacuum [16].

B. Atomic Force Microscopy

Atomic force microscope (AFM) images were taken in air using commercially available silicon cantilevers (FESP-ESP) with fundamental resonance frequency between 70-85 KHz. Anodisation lithography was conducted in tapping mode with platinum/iridium coated silicon cantilevers (SCM-PIT) with fundamental resonance frequency between 60-75 KHz. Precise movement of the cantilever was controlled using scripts written in house. All patterns were written with an applied cantilever voltage of -11 V, a tip velocity of 1 μms^{-1} and an atmospheric humidity level between 30-45 %. The tip-substrate distance was reduced prior to patterning by reducing the amplitude set point to $\sim 70\%$ of its original value. All images presented represent background subtracted data (using the flatten feature in the WSxM software) [18].

C. Self Assembly of Silanes on Silicon

Highly boron doped p-type silicon (100) with resistivity 0.001 Ωcm (Virginia Semiconductor, Inc. USA) was cut into 1 cm \times 1 cm sized wafers and ultrasonically cleaned in acetone for 30 seconds before being thoroughly rinsed with MilliQ water. The wafers were then cleaned with a 1:3 (v/v) mixture of 30 % H_2O_2 and 98 % H_2SO_4 , (Piranha solution) at 80 °C for 15 minutes followed by rinsing with MilliQ water. It has been shown that treatment of silicon with piranha solution affords a highly hydroxyl terminated silicon surface with a density of approximately 10^{15} $-\text{OH}$ groups cm^{-2} [19]. The hydroxyl terminated silicon wafers were then immersed in a 0.5 % solution of 90 % hexadecyltrichlorosilane in hexadecane for 40 minutes, then rinsed with chloroform and allowed to dry. Once anodisation lithography had been carried out the same procedure is used to assemble 3-aminopropyltrimethoxysilane onto the etched regions.

D. Attachment of Carbon Nanotubes

The substrate is 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'-di-cyclohexylcarbodiimide (DCC) (Fluka Production GmbH) and 1mg of functionalised carbon nanotubes. Prior to use the

carbon nanotube solution was ultra-sonicated for 5 hours to evenly disperse the carbon nanotubes within solution. Finally the silicon wafer was rinsed in acetone and allowed to dry, shown in Fig. 1 (Structure B). For the attachment of carbon nanotubes to gold wires the substrate was first placed into a 1 mM cysteamine in ethanol solution to create the monolayer of cysteamine, Fig 1. (Structure C).

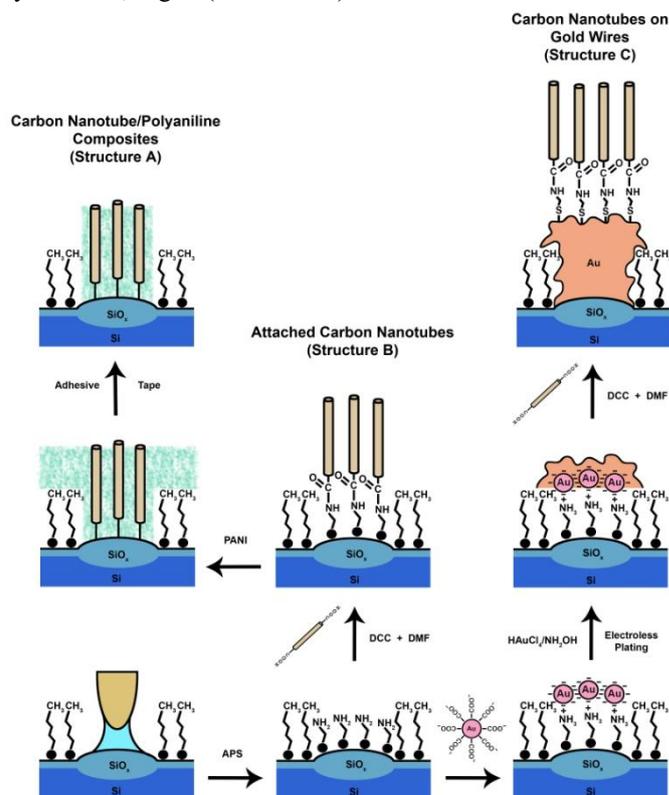


Figure 1. Mechanism for creation of carbon nanotube based structures

D. Fabrication of Carbon Nanotube/Polyaniline Composites

The patterned carbon nanotube substrates were then immersed in an aqueous solution containing 1 mL of purified aniline in 50 mL of 1M HCl (Ajax-Finechem). A second solution containing 0.575 g of 99 % ammonium persulphate (Analar) in 25 mL of 1M HCl was added to initiate polymerisation. The solutions were briefly stirred to ensure complete mixing and then allowed to rest and polymerisation took place at 18-25 °C. After 50 minutes the substrate was removed and placed into an aqueous solution containing 2mL of aniline in 1M HCl for 30 minutes to reduce the oxidation state of the deposited polyaniline from the pernigraniline to the emeraldine [20, 21]. Finally the substrate was placed into a 1M HCl solution for 5 minutes to ensure complete protonation of the polyaniline. After deposition of polyaniline a piece of adhesive tape (Highland Invisible Tape, 3M, U.S.A.) was firmly pressed to the silicon surface to ensure homogenous contact before being slowly peeled off, hence creating the patterned carbon nanotube/polyaniline composite upon removal of polyaniline from surrounding hydrophobic regions as shown in Fig. 1 (Structure A).

E. Gold Nanoparticles & Electroless Deposition

Colloidal gold nano-particles were prepared by the addition of 1 mL of 1 % aqueous $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ to 100 mL of water under vigorous stirring for 1 minute. 1 mL of 1 % aqueous sodium citrate is then added and further stirred for 1 minute. Finally 1 mL of 0.075 % NaBH_4 in 1 % sodium citrate is added and the solution stirred for 5 minutes, at which point the solution is observed to change colour from a pale yellow to a rich pink. Patterned silicon substrates containing a region of 3-aminopropyltrimethoxysilane were then immersed into the solution of nanoparticles for a period of 40 minutes, as shown in Fig. 1 (Structure C). These substrates, now having a patterned monolayer of colloidal gold nano-particles were then placed in a solution of aqueous 0.4 mM hydroxylamine hydrochloride and 0.1 % $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ for a period of 15 seconds before being washed thoroughly with water.

III. DISCUSSION

A. Attachment of Carbon Nanotubes

Fig. 2, structure B shows an AFM image of a patterned silicon substrate followed by the subsequent attachment of carbon nanotubes from an 8 hour exposure to a suspension of carbon tubes and coupling agent. Immediately it can be seen that the attached carbon nanotubes are vertically aligned forming a distribution of heights and that there is little or no adsorption of carbon nanotubes to the $-\text{CH}_3$ terminated silane monolayer. A distribution of nanotube heights is to be expected as it has been previously shown that introducing carboxyl functionality into carbon nanotubes through acid treatment leads to a log normal distribution of nanotube lengths [16, 22, 23]. For an 8 hour acid treatment carbon nanotubes are expected to have an average length of 380 nm and a maximum length of 850 nm [22, 23]. Upon looking at Fig. 2 however, it can be seen that the length of attached carbon nanotubes is significantly less with most having lengths between 8 – 20 nm with only a few nanotubes from 20nm to the maximum height of 57 nm. This dramatic decrease in the observed height has been observed previously [22] is attributed to the following. Firstly it has been shown in the literature by Liu et al. [17, 24] that adsorption kinetics facilitate the assembly of shorter carbon nanotubes over their slower moving longer counterparts. It is therefore possible that by the time a longer carbon nanotube reaches the surface most of the reactive sites are already obscured by smaller more mobile nanotubes. Secondly it is possible in that in using an AFM to image vertically aligned carbon nanotubes there is an interaction with the cantilever as it scans across the surface causing the nanotube to bend and sway, hence providing underestimates in the vertical height [22].

B. Carbon Nanotube/Polyaniline Composites

Fig 2, structure A, shows AFM images of each of the surface treatment steps involved in the fabrication of the patterned carbon nanotube/polyaniline composite material. When polyaniline is deposited onto this patterned array of carbon nanotubes it is found to cover the entire surface as aniline monomer can adhere to the hydrophobic carbon

nanotubes and hexadecyltrichlorosilane layer to facilitate polymerisation. Surprisingly upon removal of the polyaniline from the substrate, polyaniline was found to remain on the patterned region containing carbon nanotubes. This can be explained by consideration of the carbon nanotube structure. Due to the concentrated acid treatment, the end caps and sidewalls of the carbon nanotube are decorated with hydrophilic, oxygen containing functional groups such as carboxylic acids [15, 16, 22, 25]. It is the presence of hydrophilic regions in the form of both carboxylic acid groups on the carbon nanotube along with the underlying $-\text{NH}_2$ pattern to which the nanotubes are attached which facilitate adhesion. The adhesive tape can be used to remove selectively remove the polyaniline from the surrounding hexadecyltrichlorosilane layer as it is essentially a homogenous, hydrophobic $-\text{CH}_3$ terminated layer with no adhesion.

C. Gold with Vertically Aligned Carbon Nanotubes

Fig. 2, structure C, shows an AFM image of the steps involved to assemble carbon nanotubes onto an electrolessly plated gold wire. It can initially be seen that with an electroless plating time of 15 seconds produces a gold wire of thickness 25 nm. Whilst plating is most noticeable in the vertical direction, due to the height increase, it should be noted that gold plating is not uni-directional and also occurs laterally. This has the effect of slightly increasing the line width of the surface structure compared to the original patterned oxide. By increasing the amount of time that the patterned substrate is immersed in the plating solution, thicker gold wires can be produced, however, site selectivity begins to diminish with small islands of gold beginning to form on the surrounding hexadecyltrichlorosilane layer with increasing time. Upon comparing the cross section of a plated gold wire with that of a gold wire which has been exposed to carbon nanotubes, small bundles of nanotubes can be seen attached to the gold. As with the carbon nanotubes assembled onto the patterned oxide with 3-aminopropyltrimethoxysilane these nanotubes are found to be around 10 nm in height. If more control could be gained over the location of the attached bundles it may be possible to have an electron travel vertically down a carbon nanotube, laterally along the gold wire and then once again vertically out of another nanotube, hence making such three dimensional structures of significant importance to future electronics.

IV. CONCLUSION

A monolayer of $-\text{CH}_3$ terminated hexadecyltrichlorosilane was self-assembled onto a silicon substrate and used as a resist for AFM anodisation lithography. Chemical modification to form $-\text{NH}_2$ groups on the silicon oxide was then performed allowing carbon nanotubes to be attached through an amine bond. In both cases, no carbon nanotubes were observed on the $-\text{CH}_3$ functionalised silane regions due to a lack of reaction with the surface. Due to the hydrophobic side walls and high carboxylic acid functionality, polyaniline was able to polymerise around the carbon nanotube forming a composite

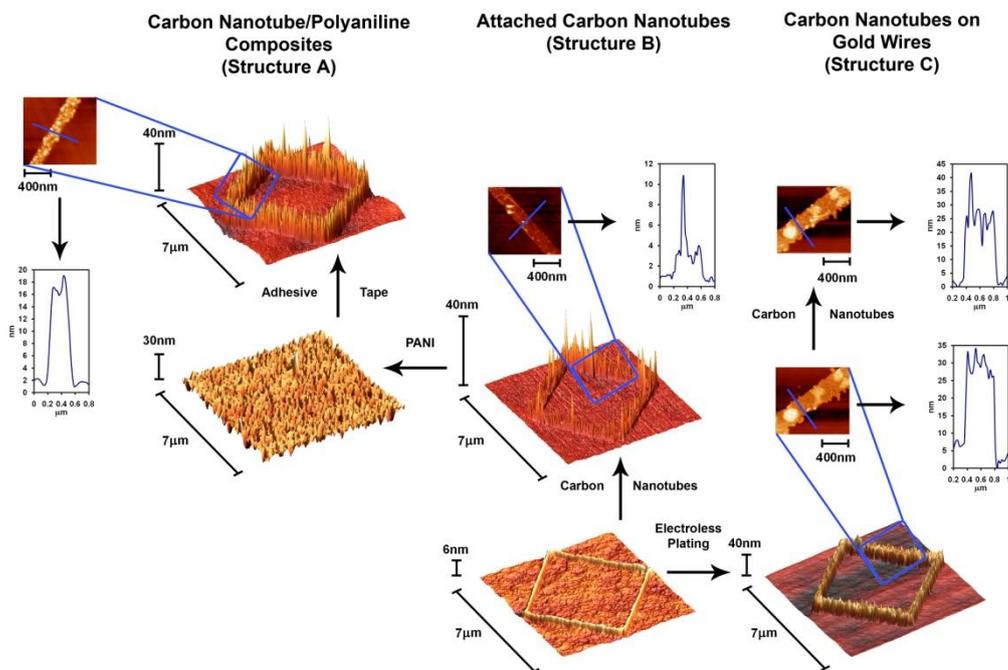


Figure 2. AFM of carbon nanotube based structures on silicon

material. Finally gold was electrolessly plated onto a silicon wafer to form lateral wires of gold to which carbon nanotubes were attached. Such a structure may prove to be particularly useful in the electronics industry as it may facilitate the conduction of electrons both horizontally and vertically on a surface, leading to true 3 dimensional electronic circuits.

V. REFERENCES

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