Preparation and characterisation of vertically aligned single-walled carbon nanotube arrays on porous silicon

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ABSTRACT

Vertically aligning carbon nanotubes (VACNTs) onto 2D porous materials is advantageous for many conceivable electronic applications but also for investigating the unique water transport properties of CNTs and the molecular separation of molecules during fluid transport through their inner shell. Here we report a wet chemical technique to produce vertically-aligned single walled CNT arrays on porous silicon (pSi). The nanotubes were first acid treated to produce carboxylic acid functionalities on the single-walled CNT. The carboxy-functional nanotubes were then covalently immobilised on a pSi surface that had been either ozone treated or silanated with aminopropyl triethoxysilane (APTES). The VACNT surfaces were analysed with atomic force microscopy (AFM), confocal Raman spectral imaging and Fourier transform infrared (FTIR) spectroscopy. Dense arrays of VACNTs were observed with the obtained CNT orientation and surface coverage depending upon attachment method and attachment reaction time.

Keywords: Single-walled carbon nanotubes; porous silicon; vertically aligned carbon nanotubes; atomic force microscopy

1. INTRODUCTION

Since 1991, carbon nanotubes (CNTs) have attracted significant attention due to their unusual mechanical and electrical properties.1-7 Interest has recently been shifted toward investigating the flow of fluids through the inner shell of CNTs for purposes of investigating flux with various fluids or as size-based chemical or biological separation devices.8-10 CNTs are advantageous for these purposes over other carbon based nanopores such as chemical vapour deposition (CVD) grown nanotubules based on porous alumina templates11 because the smoothness of the inner walls of CNTs leads to an almost frictionless transport of some fluids.12, 13 At the same time, the size of CNTs is much smaller and more controllable leading to both a higher flux and selectivity.

However, experimentally producing CNT arrays suitable for the study of fluid transport has proven to be difficult. The generally adopted approach is to grow an aligned array of CNTs using CVD, fill in the gaps between the CNTs with polymer (or similar) and finally remove the substrate under the CNTs as well as the tops of the CNTs via an etching technique. This process has been used to create multi-wall carbon nanotube (MWCNT) and double wall carbon nanotube (DWCNT) arrays14, 15 to investigate flow of gases9, liquids8 and for ionic separation.10 The limitations of this process are the incomplete removal of catalyst particles which inhibits flow, the use of large radius MWCNT and DWCNTs limiting size-based separation, and the lack of support of the CNT membrane after removal of the substrate, which compromises the stability of the system.

A simple method to produce vertically aligned single-walled carbon nanotubes (VASWCNTs) has recently been developed where pristine SWCNTs are treated with concentrated acid to both shorten the nanotubes and produce carboxylic functionalities on the ends.16 The carboxylic acid groups are then reacted with either a hydroxylated surface or an aminopropyl triethoxysilane (APTES) layer to form VASWCNT arrays.17, 19 Arrays such as these could be advantageous over the CVD-grown CNT arrays in fluid transport/separation experiments since there is no blocking from unremoved catalyst because catalyst particles are removed during the acid treatment and because SWCNTs synthesised by arc-discharge have a smaller diameter than those produce by CVD. Such experiments will require the substrate (commonly silicon) to either be removed by etching14 or be porous.
Porous silicon (pSi) is produced through the chemical, photochemical or electrochemical etching of flat, crystalline silicon with fluoride solutions. The pores formed can be in a range of tuneable sizes from micropores (<5nm) to mesopores (5-50nm) to macropores (>50nm) with a depth depending on the etching time. After etching in hydrofluoric acid (HF) the pSi surface is left hydrogen terminated, which can be further reacted to perform a range of surface chemistries. Porous silicon membranes, open at both ends, can be generated by either extending the etching time until the whole thickness of the wafer is etched or by using the "lift off" technique which results in porous membrane detachment from the silicon substrate.

Here, SWCNTs will be chemically attached to pSi using various methods similar to techniques that have previously been used to successfully create VASWCNTs arrays on flat silicon. The suitability of each created SWCNT array as a potential substrate for investigation of fluid flow and molecular separation will be discussed based upon the orientation and density of chemically attached SWCNTs.

2. EXPERIMENTAL

2.1 pSi formation

Porous silicon substrates were prepared from p-type (boron doped) silicon wafers with (100) orientation and a resistivity of 3-6 Ω cm (Silicon Quest International). The silicon wafers were etched in a custom made Teflon cell with an etching area of 1.767 cm². Prior to etching, the wafer was washed with methanol, acetone and dichloromethane (DCM) and dried under a stream of nitrogen. Etching was carried out at a constant current of 66mA (supplied by a Keithley 2425 source meter) for 120 seconds in a solution of 1:1 (v/v) 48 % aqueous hydrofluoric acid (HF, Merck)/ethanol (100 %undenatured, Chem-Supply). The hydrogen terminated etched pSi substrate was then rinsed consecutively with methanol, acetone and DCM then dried under a stream of nitrogen.

2.2 Hydroxylation of the pSi

The hydrogen-terminated freshly etched pSi substrate was hydroxylated using two different methods: ozone and wet chemical treatment. Ozone hydroxylation was carried out by exposing freshly etched pSi to ozone using a Fischer ozone generator with the current set at 1.2 A and an O₃ flow rate of 3.2 g hr⁻¹ for 10 to 60 min. Wet chemical hydroxylation was carried out by adding a freshly etched pSi wafer to piranha solution, 3:1 (v/v) H₂SO₄ (98 %, Labscan Asia Co. Ltd.):H₂O₂ (30 %, Chem-Supply), for 20 to 60 min at 80 °C. The pSi substrate was then washed with MilliQ water and dried under a stream of nitrogen or further reacted with a solution of 1:1:5 (v/v) NH₄OH (30 %, Sigma-Aldrich):H₂O₂:MilliQ water for 5 min at 80 °C then washed with MilliQ water and dried under a stream of nitrogen.

2.3 SWCNT cutting

P2-SWCNTs (Low Functionality; purified) were purchased from Carbon Solutions Inc., California, USA. The nanotubes are produced via electric arc discharge using Ni-Y catalysts and have a carbonaceous purity of 70-90 % with minimal functionality as determined by solution-phase near-IR spectroscopy. P2-SWCNTs (20mg) were shortened/cut by adding to 20 mL of 3:1 (v/v) solution of concentrated H₂SO₄ (98 %):HNO₃ (70 %) in an Elma S30 H ultrasonic bath kept at 0 °C for 8 h by periodically adding ice. The cutting was stopped after 8 h by adding a 50 fold excess of MilliQ water. The shortened SWCNTs were then filtered under vacuum through a 0.45 µm PTFE (polytetrafluoroethylene) filter (Adelab Scientific, Thebarton, South Australia). The filtered carboxylated SWCNTs were further washed with MilliQ water until a pH of between 5 and 7 was obtained then placed to dry in an oven at 80°C for 12 hours.

2.4 Direct ester attachment of SWCNTs to pSi

The dried carboxylated SWCNTs were suspended in 100 mL of dimethyl sulfoxide (DMSO, 99.9 %, ACS Spectrophotometric Grade, Sigma-Aldrich) along with 20 mg of the activating agent N,N'-dicyclohexylcarbodiimide (DCC, 99 %, Aldrich) creating a 0.2 mg mL⁻¹ SWCNT suspension and sonicated for 4 h prior to use. 2 mL of activated shortened SWCNT suspension (0.2 mg mL⁻¹) was then added to a round-bottomed flask containing a hydroxylated pSi substrate, inside a nitrogen filled glove box. The flasks were then stoppered and wrapped in parafilm and fibreglass tape to ensure a good seal before being taken out of the glove box and placed into an oven at 80 °C for varying amounts of time (2 to 24 h). The substrates were then rinsed thoroughly in acetone to remove any unbound reagents and dried under a stream of nitrogen.
2.5 **Phosphorus pentasulfide attachment of SWCNT to pSi**

A pSi substrate, hydroxylated by 10 min ozone treatment, was added to a pre-sonicated (5 min) solution of cut SWCNTs (1 mg), 1% (v/v) pyridine, and 1 mg of phosphorus pentasulfide in 10 mL of dried toluene. The substrate and solution were then sonicated for 20 mins at 50°C. The substrate was then removed, washed with dichloromethane (DCM) and acetone and dried under a stream of nitrogen.

2.6 **Aminopropyl triethoxysilane attachment of SWCNTs to pSi**

A pSi substrate, hydroxylated by 10 min ozone treatment, was placed into a 0.5% solution of 3-aminopropyl triethoxysilane (APTES, 99%, Sigma–Aldrich) in anhydrous toluene for 5 min. The substrate was then removed from solution, washed by rinsing sequentially in chloroform, acetone and water and dried under a stream of nitrogen. The substrate was then placed into approximately 3 mL of the 0.2 mg mL⁻¹ SWCNT, 0.2 mg mL⁻¹ DCC in DMSO solution that had been pre-sonicated for 4 h. The wafer was allowed to sit in the SWCNT solution for times varying from 5 min to 24 h until, then removed and washed thoroughly with acetone and dried under a stream of nitrogen.

2.7 **Atomic force microscopy (AFM)**

AFM tapping mode images were taken in ambient conditions with a multimode head and a Nanoscope IV controller (Digital Instruments, Veeco, Santa Barbara). Silicon cantilevers (Mikromasch) with fundamental resonance frequency of between 200-400 kHz were used. Images were obtained using a scan rate of 1 Hz with the parameters of set point, amplitude and feedback control optimised manually for each sample. The images presented have been flattened using Nanoscope 6 software.

2.8 **Confocal Raman spectral imaging**

Confocal Raman spectra were recorded on a Witec alpha 300 Confocal Raman Spectrometer fitted with a 532nm laser (60 mW) using both a x100 (0.9 numerical aperture (NA), working distance (WD) 0.23 mm) and a x40 (0.6 NA WD 3.7 to 2.7 mm) objective. The presented spectra were taken as an average of 2 scans over a collection time of 50 sec. Confocal images were completed by taking 100 lines of 100 spectra with an average integration time of 0.1 sec. The Confocal Raman images represent the relative height of the G-band (1530-1630 cm⁻¹) for each individual spectrum. The experiments were carried out using Witec Control 1.42 software and the analysis was completed using Witec project 1.90 software.

2.9 **Fourier transform infrared spectroscopy**

FTIR spectra were recorded on a Nicolet Avater 370MCT spectrometer (Thermo Electron Corporation). The spectrometer was fitted with a transmission accessory, all spectra were recorded over a range of 650-4000 cm⁻¹ at a resolution of 2cm⁻¹ as an average of 64 scans and analysed using OMNIC version 7.3 software. All FTIR spectra were collected with a background of clean flat/non-functionilised silicon wafer of the same type as the samples.

### 3. RESULTS AND DISCUSSION

3.1 **Preparation and hydroxylation of pSi**

![AFM of freshly etched pSi](image_url)
The pSi substrates created were characterised by AFM. A freshly etched pSi substrate with pores ranging from 6.5 nm to 20 nm (11.6 nm average) is shown in Fig. 1. The thickness of the porous layer was calculated to be approximately 6 \( \mu \text{m} \) by scanning electron microscopy (not shown). The calculated pore size is in agreement with previous AFM studies of pSi substrates created under the same etching conditions. All SWCNT attachment methods described here require silanol (Si-OH) groups on the pSi surface. The most common method of producing these groups on freshly etched pSi is through ozonolysis, however all methods of attaching SWCNTs to flat silicon use wet chemical methods. Therefore the effectiveness of each method was investigated by FTIR. Freshly etched, hydrogen terminated, pSi (Fig. 2 (a)) is characterised by three different Si-H stretching vibrations (Si-H at 2091 cm\(^{-1}\), Si-H\(_2\) at 2120 cm\(^{-1}\), and Si-H\(_3\) at 2140 cm\(^{-1}\)) and a Si-H\(_2\) scissor vibration at 906 cm\(^{-1}\). The freshly etched pSi also shows a weak oxidation (Si-O) peak at 1070 cm\(^{-1}\) which occurs spontaneously when pSi is exposed to ambient conditions. Upon oxidation by both ozone (45 min, Fig. 2 (b)) and the wet chemical method (Fig. 2 (c)) the Si-H\(_x\) peaks disappear and are replaced by a strong broad peak at 1100 cm\(^{-1}\) attributed to Si-O valence vibrations, a small weak oxidation peak also appears at 1600 cm\(^{-1}\) attributed to Si-OH bending, as well as a broad –OH stretching band around 3400 cm\(^{-1}\) due to hydrogen bonded –OH groups and perhaps some chemisorbed H\(_2\)O. The small peak at 3715 cm\(^{-1}\) is attributed to isolated silanol stretches on the pSi surface. The presence of silanol peaks for both oxidation processes indicates that they are both suitable for SWCNT attachment.

FTIR was carried out for pSi substrates exposed to 10 to 60 mins of ozone showing a slight increase in the –OH and Si-OH peak intensities observed. Ozone is considered the better of the two oxidation methods since it does not damage the pSi substrate while the chemical oxidation changed the colour of the pSi film from brown/yellow to green which indicates a concurrent change in pore morphology.

3.2 Direct ester attachment of SWCNTs to pSi

Direct ester attachment of SWCNTs has previously been carried out on flat silicon but not on pSi. Initial attempts involved ozone oxidation for 10 mins or piranha treatment for 20 mins. AFM imaging after SWCNT attachment (not shown here) showed little or no SWCNT attachment to pSi. Longer ozonolysis and piranha treatment times were attempted with little improvement. Gun'ko et al. chemically attached ferrocene to pSi using a 1 h of piranha treatment then 5 min in 1:1:5 (v/v) NH\(_4\)OH:H\(_2\)O\(_2\):MilliQ. This method was used to hydroxylate the pSi substrate followed by 4 h of SWCNT attachment. The SWCNT coverage after 4 h is shown in Fig. 3 where vertically-aligned bundles of SWCNTs are clearly observed with measured heights between 20 to 50 nm. Features like this have been seen before on flat silicon as well as on gold and silver. The bundling of the SWCNTs is expected and is due to tube-tube interactions brought about by van der Waals and hydrophobic interactions of the side wall. The vertical-alignment of the SWCNTs is due to two main effects; the hydrophilic hydroxyl groups on the hydroxylated pSi substrate repelling the hydrophobic walls of the SWCNTs thereby forcing the SWNTs away from the surface and van der Waals forces from the side-walls of adjacent SWCNTs supporting the vertical-alignment of other nanotubes. We assume that the shorter height of the attached SWCNT is due to the shorter nanotubes diffusing faster (longer mean free path) in solution and reaching the surface faster. The imaged SWCNTs may also be higher than they appear due to AFM tip convolution.
The calculated SWCNT coverage of SWCNT on pSi in Fig. 3 is 7% compared to 22% for the same attachment on flat Si. This reduction in coverage is thought to be due to the formation of geminal silyl esters on the pSi substrate. Silyl esters are susceptible to degradation because the bond can be cleaved by attack at either the carbonyl or the silicon atom. Degradation of silyl esters has been found to increase depending upon the environment of the silicon. Hydroxylated flat silicon (100) involves one silicon atom with one hydroxyl group. Porous silicon on the other hand can have 1, 2 or 3 hydrogens on the surface silicon atoms after etching which means it could have 1 to 3 hydroxyl groups on each surface silicon atom after hydroxylation. If a silicon atom forms an ester linkage with two or more SWCNTs (known as a geminal ester) the degradation is found to be much faster because of the loss of steric and electronic stability.

### 3.3 Phosphorous pentasulfide mediated attachment

The attachment of SWCNTs using the versatile catalyst phosphorous pentasulfide has recently been achieved on flat silicon to produce vertically aligned arrays. Fig. 4 shows the results of attaching nanotubes using phosphorous pentasulfide with hydroxylated pSi (10 min ozone). The 3D AFM image (Fig. 4 (a)) appears similar to Fig. 3 where there are VASWCNTs of 20 to 50 nm in height. However the top down view (Fig. 4 (b)) reveals that there is a large number of SWCNTs lying down. This orientation was consistently observed throughout a number of P$_{4}$S$_{10}$ mediated attachments but never observed with the direct ester attachment. We attribute this effect to the different mechanism of attachment involving the conversion of surface hydroxyl groups to thiols. On the pSi surface, the geminal hydroxyl groups are converted to geminal thiol groups (in the presence of P$_{4}$S$_{10}$) these newly formed thiols may oxidise to form a disulfide bond. These bonds render the surface more hydrophobic which might encourage adsorption of the SWCNTs sidewalls, resulting in side-on attachment.
3.4 Attachment of SWCNTs on APTES functionalised pSi

Fig. 5: AFM images of (a) pSi after 5 min of APTES treatment (0 % surface coverage, 1 x 1 µm², z scale 5 nm) and SWCNT attachment on APTES functionalised pSi (5 x 5 µm images, z scale 50 nm) for attachment times of (b) 5 min (18 % coverage), (c) 1 h (48 % coverage), (d) 24 h (52 % coverage) and (e) 3D image of (c) after 1 h attachment.
To further increase the coverage of SWCNTs on the pSi surface, the surface was silanated with APTES to produce an amine-terminated monolayer. After APTES functionalisation (5 min, Fig. 5(a)) the pSi surface looks identical to the freshly etched case (Fig. 1). This surface now is amine-terminated and when reacted with a carboxylic acid will form a more stable amide bond than the previously described ester bond. Fig. 5 (b-d) shows the AFM images of the SWCNT attachment to pSi via an amide linkage. All images show similar features to those observed in Fig. 3 but yielding higher coverages. The higher coverages are due to the favorable and stable amide linkage as well as the fact that the silane layer does not include any germinal groups, further increasing the stability of the attachment. Various SWCNT attachment times (the time that the hydroxylated pSi wafer was incubated in SWCNT solution) were completed and imaged by means of AFM with the lowest coverage observed after 5 mins (18 %, Fig. 5 (b)), the coverage increased rapidly up to 48 % after 1 h of nanotube suspension exposure (Fig. 5 (c)) then continues to rise to 52 % after 24 h of exposure (Fig. 5 (d)). This change in surface coverage with attachment time is shown graphically in Fig. 6. This trend has previously been observed for the direct ester attachment of SWCNTs on flat silicon and is caused by SWCNT attachment occurring in two phases. The first phase is when there are many available attachment sites and attachment continues rapidly. The second stage is where most sites are used up or sterically hindered and attachment continues at a very slow rate. In the flat silicon case the first stage continues for 24 h, which is much slower than the 1 h reported here. Previous work on SWCNT attachment to APTES functionalised flat Si has shown that the amide linkage is much more favorable and that the maximum SWCNT coverage occurs after 4 h of attachment. However, that work involved attaching SWCNTs to lithographically defined areas, which would slow the reaction. The 3D image (Fig. 5 (e)) clearly demonstrates the vertical alignment of CNTs on these surfaces.

FTIR analysis of the APTES functionalised pSi (Fig. 7 (a)) shows that while the silanol and –OH stretches have disappeared in the region of 3300-3700 cm⁻¹, two small primary amine peaks at 3361 cm⁻¹ and 3295 cm⁻¹ appear, as well as two broad peaks at 1640 cm⁻¹ and 1560 cm⁻¹ attributed to N-H scissoring and N-H bending. The peaks at around 2900 cm⁻¹ are attributed to C-H stretching (2932 cm⁻¹, 2877 cm⁻¹) and a C-H-NH₂ stretch at 2972 cm⁻¹. The Si-O stretch at 1100 cm⁻¹ is still present from Si-O bonds in the backbone structure of the pSi. Upon SWCNT attachment (Fig. 7 (b)) the primary amine peaks disappear, the C-H stretching peaks remain and two new peaks appear at 1638 cm⁻¹ and 1528 cm⁻¹ which are attributed to the N-H bending and C-N stretching of secondary amides. The FTIR spectra support the formation of an amine-terminated monolayer and the creation of an amide linkage between the APTES and functionalised SWCNTs.
Fig. 7: Transmission FTIR spectra of hydroxylated pSi substrates (ozone; 10 min) followed by (a) APTES functionalisation and (b) SWCNT attachment to APTES monolayer (24 h attachment). Inset shows zoom of amine peak area (3500cm⁻¹ to 3100cm⁻¹) for the APTES functionalised pSi substrate. Spectra offset for clarity.

Raman spectroscopy was performed to ensure that the tall features in the AFM images indeed corresponded to SWCNTs. Fig. 8 (a) shows a spectrum taken of SWCNTs attached to APTES monolayer on pSi (24 h attachment). The peaks observed in the spectrum are attributed to the radial breathing mode (RBM, 166 cm⁻¹), the disorder-induced mode (D-band, 1337 cm⁻¹), the graphitic (E₂g) mode (G-band) which is split into the G-band (1570 cm⁻¹) and the G’-band (1586 cm⁻¹), the M-band (1725 cm⁻¹) and the G’'-band (2664 cm⁻¹). The Raman data confirms the presence of SWCNTs on the surface showing the RBM band which is only present in SWCNTs. The position of the RBM (\(\omega_{\text{RBM}}\)) gives information on the diameter of the SWCNTs using the expression:

\[
\omega_{\text{RBM}} = 223.5/d_t + 25.5
\]

where \(d_t\) is the radius of the SWCNT investigated. The radius of the SWCNTs on the pSi surfaces was calculated to be 1.5 nm; which is in good agreement with the diameter quoted by the supplier. The confocal Raman spectral image (Fig. 8 (b)) shows change in relative peak counts for the G-band region. The variation in brightness indicates a variation in SWCNT density across the surface, indicating that the surface is covered by SWCNTs, in consistence with our AFM results.

Fig. 8: (a) Raman spectrum of SWCNTs chemically attached to pSi via the APTES attachment method and (b) confocal Raman spectral image from the relative peak height of the G-band region at each point (1500cm⁻¹ to 1630cm⁻¹).
4. CONCLUSIONS
Vertically-aligned SWCNTs (VACNTs) have successfully been covalently attached to pSi via three different attachment protocols. Namely, direct ester attachment, phosphorus pentasulfide mediated (thioester attachment), and to an APTES monolayer (amide attachment). Direct ester attachment produces well oriented VACNTs but with low density, $P_{10}$ mediated produces a higher density but loss of vertical-alignment. The attachment to the APTES monolayer on pSi produces high density and well orientated VACNTs. These attachment protocols could potentially be used in the formation of VACNT membranes for the study of fluid transport or molecular separations.

REFERENCES


