Fabrication and Application of Carbon Nanotube/Silicon Nanostructures

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The best things in life are beyond money, their price is agony and sweat and devotion...

- Robert A. Heinlein in *Starship Troopers*

The Scientific man does not aim at an immediate result. He does not expect that his advanced ideas will be readily taken up. His work is like that of the planter – for the future. His duty is to lay the foundation for those who are to come, and point the way. He lives and labours and hopes.

- Nikola Tesla

Any sufficiently advanced technology is indistinguishable from magic.

- Arthur C. Clarke

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Summary

The amazing electrical and mechanical properties of carbon nanotubes (CNTs) make them ideal for use in a variety of applications, many of which require the CNTs to be surface bound. Here the applicability of nanostructures based upon CNTs chemically attached to silicon to the fields of water filtration, field emission and as biomaterial interfaces is investigated.

Initial experiments studied the chemical attachment and alignment of different CNT types to silicon. Single-walled carbon nanotubes (SWCNTs) were found to form vertically aligned arrays on both flat silicon and porous silicon (pSi). Double-walled carbon nanotubes (DWCNTs) were found to exhibit both vertical and random alignment while multi-walled carbon nanotubes (MWCNTs) exhibited an exclusive horizontal orientation. The variation in alignment is attributed to the level of crystallinity and functionalisation of each CNT type as determined by Raman spectroscopy.

The control of the placement of SWCNTs on silicon was further investigated by fabricating both surface coverage gradients and patterns of SWCNTs. Gradients were fabricated following two protocols, both of which produced surfaces which consist of all possible SWCNT coverage's. SWCNT patterns were produced by forming an initial chemical pattern on the silicon surface for subsequent selective SWCNT chemical attachment.

CNT membranes for water filtration were fabricated by chemically attaching SWCNTs to permeable pSi membranes. Gaps between the SWCNTs were filled by spin coating polystyrene onto the surface. The SWCNT tips were revealed by etching the polystyrene matrix via water plasma treatment. The fabricated membranes were found to have a water permeability of 0.022 $mm^3\ cm^{-2}\ s^{-1}\ atm^{-1}$. Comparisons to commercial nanofiltration membranes and other published CNT membranes are made and improvements to membrane fabrication are discussed.

Field emission experiments were completed for all CNT types chemically attached to silicon. All samples exhibited field emission of electrons with characteristics varying with CNT diameter and vertical alignment. The emission

stability of each CNT type was investigated with the SWCNTs exhibiting the most stable emission. Comparison of emission characteristics and stability to other CNT field emission substrates are made.

The behaviour of a mammalian neuronal cell line on SWCNTs chemically attached to porous silicon was investigated. Fluorescence microscopy revealed that the cells had a strong affinity for the SWCNT substrate and that the SWCNTs may compromise the cell membrane allowing small fluorescent molecules to enter the nuclear envelope. Experiments to determine if plasmid DNA could be inserted into the cell via the SWCNTs was completed with results indicating the SWCNTs did not promote DNA transfection for the neuronal cell line.

Declaration

I certify that this Thesis does not incorporate without acknowledgment any material previously submitted for a degree or diploma in any university; and that to the best of my knowledge and belief it does not contain any material previously published or written by another person except where due reference is made in the text.

Cameron J. Shearer

Acknowledgements

This Thesis would not have been possible without the assistance of many people who I should acknowledge. Chapter 1 contains parts of a review article published in *Advanced Materials*; this work was co-authored with Kristina Constantopoulos, Amanda Ellis, Nico Voelcker and Joe Shapter. The pattern work presented in Chapter 4 was inspired by an original idea of Ben Flavel, Martin Sweetman then came up with a protocol to form silane patterns which I then used for nanotube attachment. The porous silicon membrane dye transport in Chapter 5 was completed by Leonora Velleman, she also analysed and interpreted the data. The pressure driven water transport, also in Chapter 5, was completed at the University of Bath in the laboratory of Davide Mattia with the help of Fernando Acosta. An ARNAM student travel grant assisted in the travel and accommodation costs for that trip. The field emission experiments shown in Chapter 6 were all completed at the University of Newcastle. I would like to thank Paul Dastoor for allowing me to visit on three occasions. The field emission experiments were assisted originally by Kane O'Donnell and Lars Thomsen, and by Adam Fahy and Matthew Barr on the final visit. The field emission work would never have been completed without the influence of Jamie Quinton, and I thank him for making the most enjoyable and successful aspect of my PhD possible. Fran Harding completed most of the cell culture, cell staining and fluorescence microscopy in Chapter 7, the remainder was completed by Qi Peng. The data presented in Chapter 7 was largely championed by Nico Voelcker who urged collaboration between Fran and myself which became a nice side-project to focus upon when other experiments weren't going as hoped.

I have had the privilege to work in the Smart Surface Structures group at Flinders. Despite only having a single fumehood and rarely containing a post-doc we seem to meet or beat the output of any other group. I think this is largely in part to the hard working culture imparted by Matt Nussio and Ben Flavel. Mark, Lachlan, Chris, Kate, Sam, Anders, Adam, Dan, Ash and others I have forgotten have all been fun to work with. I also spent some time in the Voelcker lab, particularly early in my PhD, where I was helped immensely by the pilots in the cockpit: Steve, Martin and Andy J.

Final professional thank you goes to my supervisors. Amanda and Nico were always willing to chat with me about my research and give advice when requested. Joe has been the perfect supervisor for me; his adaptability has suited my varying style perfectly. When I wanted meetings, Joe would make himself available. When I didn’t want meetings, Joe was content to have five minute chats. Thanks for making the entire PhD as stress free and enjoyable as possible.

I am lucky to have two families that have helped me throughout these years of study. Both my parents and Lauren’s parents have been happy for me to be poor for another few years in the hope that I will eventually get a real job. I am extremely lucky to have Lauren in my life, she has been very supportive and happy to be the bread winner for the past few years. Hopefully I can repay your kindness in the future.

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Glossary of abbreviations

Abbreviation	Definition
AFM	atomic force microscopy
APTES	3-aminopropyl triexthoxysilane
b	electric field enhancement factor
CMRA	CellTracker orange cytoplasm stain
CNT	carbon nanotube
CTA	chain transfer agent
CVD	chemical vapour deposition
D-band	disorder Band
DCC	dicyclohexyl carbodiimide
DETA	Diethylenetriamine
$DIOC_{18}$ (3)	green fluorescent cell membrane stain
DMEM	Dulbecco's modified eagle medium
DMF	dimethyl formamide
DMSO	dimethyl Sulfoxide
DNA	deoxyribosenucleic acid
dPBS	Dulbecco's phosphate buffered saline
DWCNT	double-walled carbon nanotube
E_F	Fermi energy
E_{to}	turn-on voltage
FDA	fluoroscein diacetate
FE	field emission
FET	field effect transistor
F-N	Fowler-Nordheim
FTIR	fourier transform infrared
G-band	graphene band
GFP	green fluorescent protein
GO	graphene oxide
HEK	human embryonic kidney
HF	hydrofluoric acid
ITO	indium tin oxide
LCD	liquid crystal display
MD	molecular dynamics
MWCNT	multi-walled carbon nanotube
pAl	porous alumina
pDNA	plasmid DNA
PECVD	plasma-enhanced chemical vapour deposition

Abbreviation	Definition
PEGS	polyethylene glycol silane
PEI	poly(ethylimine)
PFDS	Fluorinated silane
PI	propidium iodide
PMMA	poly(methylmethacrylate)
PS	poly(styrene)
pSi	porous silicon
PTFE	poly(tetrafluoroethylene)
PTMS	propyl trimethoxysilane
RAFT	reverse addition fragmentation chain transfer
RB	rose bengal
RBM	radial creathing mode
RNA	ribosenucleic acid
RO	reverse Osmosis
Rubpy	ruthenium based dye
SA	self assembly
SAM	self assembled Monolayer
SEM	Scanning Electron Microscopy
Si	Silicon
SK-N-SH	mammalian neuroblastoma cell line
STM	scanning tunnelling microscope
SWCNT	single-walled carbon nanotube
TEM	transmission electron microscopy
VA	vertically aligned
WCA	water contact angle
XPS	X-ray photoelectron spectroscopy

List of publications

[1] C. J. Shearer, J. G. Shapter, J. S. Quinton, P. C. Dastoor*, et al.*, "Highly resilient field emission from aligned single walled carbon nanotube arrays chemically attached to n-type silicon", *Journal of Materials Chemistry*, **18**, 5753 - 60 **(2008)**.

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[3] C. J. Shearer, K. T. Constantopoulos, N. H. Voelcker, J. G. Shapter*, et al.*, in *SPIE Smart Materials, Nano+Micro-Smart Systems, Vol. 7267*, Melbourne, 72670I **(2008).**

[4] Z. Poh, B. S. Flavel, C. J. Shearer, J. G. Shapter*, et al.*, "Fabrication and electrochemical behavior of vertically-aligned carbon nanotube electrodes covalently attached to p-type silicon via a thioester linkage", *Materials Letters*, **63** *(9-10)*, 757-60 **(2009)**.

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[6] C. J. Shearer, A. V. Ellis, J. G. Shapter, and N. H. Voelcker, "Chemically Grafted Carbon Nanotube Surface Coverage Gradients", *Langmuir*, **26** *(23)*, 18468-75 **(2010)**.

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[12] K. E. Moore, B. S. Flavel, C. J. Shearer, A. V. Ellis, J. G. Shapter, "Electrochemistry of Polystyrene Intercalated Vertically Aligned Single- and Double-Walled Carbon Nanotubes on Gold Electrodes", *Electrochemistry Communications,* **13**, 1190 **(2011).**

[13] M. A. Bissett, A. Barlow, C. J. Shearer, J. S. Quinton, J. G. Shapter, "Carbon Nanotube Modified Electrodes for Photovoltaic Devices", *Carbon, accepted (25/8/11)* **(2011).**

[14] C. J. Shearer, F. Harding, M. J. Sweetman, J. G. Shapter*, et al.*, "Nanostructured biointerfaces based on carbon nanotube-decorated porous silicon films", *Soft Matter*, *(under review)* **(2011)**.

[15] C. J. Shearer, A. Fahy, M. Barr, K. E. Moore, *et. al.*, "Field emission from single- double- and multi-walled carbon nanotubes chemically attached to silicon", *Journal of Applied Physics, (under review)* **(2011)**.

Parts of the above publications have been reproduced in this Thesis as follows:

- Chapter 1 contains parts of [5]
- Chapter 3 contains parts of [2] and [3]
- Chapter 4 contains parts of [6] and [14]
- Chapter 5 contains parts of [8] and [9]
- Chapter 6 contains parts of [1] and [15]
- Chapter 7 contains parts of [14]

Science is made up of so many things that appear obvious after they are explained.

- Frank Herbert in *Dune*

We are at the very beginning of time for the human race. It is not unreasonable that we grapple with problems. But there are tens of thousands of years in the future. Our responsibility is to do what we can, learn what we can, improve the solutions, and pass them on.

- Richard P. Feynman

You want a reason? How's about "Because"?

- Joshua Homme in *Turnin' on the Screw*