
TABLE OF CONTENTS

Table of contents						
Dec	laratio	n		v		
Ack	Acknowledgements					
Summary						
Publications during the course of this work						
Nota	ation		-	х		
1	Dron	ortios o	f Carbon Nanotubos	1		
1 1	The	tructuro	and properties of the earbon penetube	1		
1.1		e structure and properties of the carbon nanotube				
1.2	Applications of carbon nanotubes					
1.3	Elect	ron emi	ssion applications	4		
	1.3.1	Motiva	ation for carbon nanotube emitters	6		
	1.3.2	Carbor	n nanotube field emission applications	9		
		1.3.2.1	Field emission displays	10		
		1.3.2.2	Carbon nanotubes applied to gated cathodes for parallel electron beam	11		
		1222	lithography	12		
		1.3.2.3	Other field emission applications	12		
14	Elect	ron giin	sources	13		
1.1	1 / 1	1.4.1 Current microscory electron source technology				
	1.4.1	1 / 1 1	L anthanum heyaboride emitters	15		
		1412	The tungsten thermionic emitter	15		
		1.4.1.3	The Schottky emitter	13		
		1.4.1.4	Cold field emitters	19		
	1.4.2	Tip cha	aracterisation	20		
	1.4.3	Tip ali	gnment	21		
	1.4.4	Alignn	nent in the column	21		
1.5	Field emission properties of carbon nanotubes					
	1.5.1	1.5.1 Fowler-Nordheim theory				
	1.5.2	1.5.2 Measurement of the energy spectrum				
	1.5.3	5.3 Emission stability				
	1.5.4	5.4 The vacuum level				
	1.5.5	5.5 Source brightness				
	1.5.6	1.5.6 Source lifetime and failure mechanisms		31		

		Table of contents	ii	
1.6	Sumn	nary	32	
1.7	Refer	ences	33	
2	Engiı	neering the synthesis of carbon nanotubes	38	
2.1	Carbon Nanotubes synthesis methods			
	2.1.1 Synthesis of CNTs by arc discharge			
	2.1.2	Synthesis of CNTs by laser ablation	40	
	2.1.3	Synthesis of CNTs by ball milling	41	
	2.1.4	Synthesis of CNTs by chemical vapour deposition	41	
		2.1.4.1 Formation of the catalyst for chemical vapour deposition	42	
		2.1.4.2 Growth by CVD and PECVD	43	
2.2	Grow	th of CNTs on three-dimensional surfaces	46	
2.3	Positi	oning a single CNT in the centre of a silicon chip	50	
2.4	Direc	t growth of carbon nanotubes onto three-dimensional surfaces.	55	
2.5	Sumn	nary	59	
2.6	Refer	ences	59	
3	The p	production of carbon nanotube electron sources	62	
3.1	Desig	n of a chamber to vertically aligned CNTs	63	
3.2	The effect of catalyst on dimension and orientation		66	
3.3	Grow	ing single CNTs on tungsten tips	68	
	3.3.1	Electron beam lithography	69	
	3.3.2	Focused ion beam lithography	69	
	3.3.3	Electron beam deposition	71	
	3.3.4	Electron beam emission	71	
	3.3.5	Geometrical manipulation	71	
3.4	Electi	costatic field simulations for multi-CNT tips	72	
3.5	Repro	oducibility of tungsten wire etching	76	
3.6	Optimizing catalyst deposition			
	3.6.1	Catalyst deposition by evaporation	77	
	3.6.2	Catalyst deposition by sputter coating	79	
3.7	Statistical analysis of CNTs grown on sharp tungsten tips			
	3.7.1 Yield of single CNT tips produced			
	3.7.2	Distribution of CNT radii	82	
	3.7.3	Variation in CNT length	83	

3.7.3 Variation in CNT length

	3.7.4	Alignment of CNTs grown on tungsten tips	85		
	3.7.5	Discussion of possible fluctuation causes	86		
3.8	Grov	wth of CNTs on single crystal tungsten tips	87		
3.9	Crys	Crystallinity of CNTs			
3.10	Mod	ifying the production process	90		
	3.10.1	Growth on specially designed mounts	91		
	3.10.2	Growth on whole electron sources	93		
3.11	Hand	lling of tips	98		
3.12	Lifet	ime and robustness	100		
3.13	Summary				
3.14	Refe	rences	101		
4	Field	l emission from manufactured carbon nanotube electron sources	103		
4.1	Mou	nting of CNTs for data collection	104		
	4.1.1	Electron sources grown on single tungsten wire pieces	104		
	4.1.2	Mounting of electron sources with a Philips heating filament	105		
	4.1.3	Electron sources mounted in electron guns	106		
	4.1.4	Field emission configuration summary	107		
4.2	Field	l emission data	108		
	4.2.1	Completing the cap structure	108		
	4.2.2	The first few hours of emission from CNTs	111		
4.3	Stab	ility	114		
	4.3.1	Determination of drift and instability	116		
	4.3.2	Variation of instability with time	120		
4.4	CNT	tip lifetime	125		
4.5	Vari	ation of instability with pressure	127		
4.6	Wor	kfunction of CNT electron sources	129		
4.7	Ener	gy spread measurements	129		
4.8	Brig	Brightness determination			
4.9	Sum	nmary			
4.10	Refe	References			
5	Carl	oon nanotube electron sources: in the microscope	137		
5.1	The	The field emission vacuum system			
5.2	Imag	Imaging with a CNT electron sources			

Imaging with a CNT electron sources 5.2

	Table of contents	iv
	5.2.1 Schottky field emitter (SFE)	142
	5.2.2 Carbon nanotube emitter	143
5.3	Summary	146
5.4	References	146
6	Discussion, conclusions and proposed future work	147
6.1	Silicon-based CNT sources	147
6.2	Tungsten-based CNT sources	148
6.3	Electron-optical properties of CNTs	150
6.4	Microscope operation	152
6.5	Future work	152
6.6	Summary	152
6.7	References	153
7	Appendix	154

DECLARATION

This dissertation contains the results of research performed by the author between October 2004 and February 2008 in the Department of Engineering, University of Cambridge. This dissertation is the result of my own work and includes nothing which is the outcome of work done in collaboration except where specifically indicated in the text.

This work has not been submitted in whole or in part for any other University degree or diploma except where specifically indicated in the text.

Permission is granted to consult or copy the information and results contained within this dissertation for the purpose of private study only, and not for publication.

In compliance with regulations, this dissertation contains 39,638 words and 116 figures.

Mark Mann Cambridge

ACKNOWLEDGEMENTS

I would first like to thank my supervisor, Prof. Bill Milne, for his encouragement, guidance and support throughout my time at the Engineering Department. I would also like to thank Dr. Ken Teo for his help with my experimental work, guidance and by using his contacts throughout the field to help me finish (almost) on time. I would also like to thank many friends and colleagues in the Electrical Engineering Division for their friendship and assistance, in particular Sharvari Dalal, Martin Bell, Yan Zhang and Shupei Oei.

I would like to thank FEI for funding my studies at Cambridge, for funding many trips to America to work on their electron beam testing equipment, and for guidance from some of the leading experts in the field. Thanks go especially to Dr Ted Tessner, Dr Greg Schwind and Mike Lysaght. I would also like to thank the now extinct electron beam lab in Eindhoven, the Netherlands and all the people that assisted me there. In particular, Niels de Jonge and subsequently Mikhail Ovsyanko provided great help with field emission testing. At York University, Prof Mohamed El Gomati has given great support to me and I would like to thank Torquil Wells for his assistance and input.

In studying for this degree, I have had the best time in my life and I would like to thank the people who got me there. In particular I am grateful to Prof Mike Payne for introducing me to this field in 2002 and to Prof Bill Allison who encouraged me in my first research project.

I wouldn't be here without the support of my family. I will always be grateful to my Mum and Dad for helping me through school and university and to my brother David for being there. Finally, I would like to thank my fiancée Karen for proof-reading the first draft of my dissertation (which I hope she enjoyed), but more importantly for providing so much love and support during the course of my work.

CARBON NANOTUBES AS ELECTRON GUN SOURCES

Mark Mann

This dissertation presents the development of a manufacturable carbon nanotube (CNT) electron source for specific application to high-quality electron beam equipment. It first details the advantages CNTs have over other electron sources and then describes the various methods used to fabricate carbon nanotubes.

For an effective electron source, it is important that the electrons come from one CNT, because if there are two, they will interfere with each other. After controlling the geometry of the tungsten wire during etching so that the apex diameter is less than 100 nm, a new process was developed to grow one multi-walled carbon nanotube typically 50 nm in diameter and a few hundred nm in length at the apex by plasma-enhanced chemical vapour deposition (PECVD). This process resulted in a 49% yield of single CNT tips aligned with the optical axis; a significant improvement on methods mentioned elsewhere [1]. The process was then modified so that CNTs could be grown on etched wires mounted on hairpins and by putting an entire electron source module into the reaction chamber. These modified processes gave similar yields.

Field emission experimentation was carried out on the CNT tips. CNTs need to undergo a rapid thermal anneal to remove adsorbed gaseous species and to complete the cap structure at the top. Stability, poorly defined elsewhere, has been replaced by *drift* and *instability* to describe peak to peak and standard deviation fluctuations in emission currents respectively. Instability was found to be less than 1% after three weeks of emission, comparable to that measured by De Jonge [1], but was found to increase if not annealed rapidly frequently. It was also found that the CNTs should not be operated at pressures of 10⁻⁸ mbar and above because instability was found to be too high. Kinetic energy spread was found to be as little as 0.28 eV at 20 nA total current. The CNT could be as much as three times as bright as current commercially available Schottky emitters.

On placing the CNT source in an electron microscope, micrographs were taken to compare it with a typical Schottky source. With the same system geometry, the resolution of the CNT was found to be twice that of the Schottky indicating a smaller virtual source size.

This work shows that CNTs are a viable electron source and in performance are at least equal and in some cases better than state-of-the-art electron sources currently available.

 N. de Jonge, M. Allioux, M. Doytcheva, M. Kaiser, K.B.K. Teo, R.G. Lacerda and W.I. Milne. "Characterization of the field emission properties of individual thin carbon nanotubes", Applied Physics Letters 85, (2004).

PUBLICATIONS

- "Helium detection via field ionisation from carbon Nanotubes," D.J. Riley, M. Mann, D.A. MacLaren, P.C. Dastoor, W. Allison, K.B.K. Teo, G.A.J. Amaratunga and W.I. Milne, Nanoletters 3, 1455 (2003).
- "Statistical Mechanics and Reversible States In Quasi-Static Powders." A. Chakravarty, S. F. Edwards, D. V. Grinev, M. Mann, T. Phillipson, A. J. Walton. Quasi-static Deformations of Particulate Materials, Ed. K. Bagi, 123-135, Budapest University of Technology and Economics Publishing Company, Budapest (2003)
- "Direct growth of multi-walled carbon nanotubes on sharp tips for electron microscopy", M. Mann, K.B.K. Teo, W.I. Milne, and T. Tessner. NANO: Brief Reports and Reviews 1, 35 (2006).
- 4. "Carbon nanotubes as electron sources" M. Mann, K.B.K. Teo, W.I. Milne.
 Carbon Based Nanomaterials by Trans Tech Publishers, Switzerland. 2007*
- W. I. Milne, K. B. K. Teo, M. Mann, I. Y. Y. Bu, G. A. J. Amaratunga, N. De Jonge, M. Allioux, J. T. Oostveen, P. Legagneux, E. Minoux, L. Gangloff, L. Hudanski, J.-P. Schnell, L. D. Dieumegard, F. Peauger, T. Wells, and M. El-Gomati. Carbon nanotubes as electron sources, Phys. Stat. Sol. (a) 203, No. 6, 1058–1063 (2006).
- 6. "Fabrication of Carbon Nanotube-based Nanodevices using a Combination Technique of Focused Ion Beam and Plasma Enhanced Chemical Vapour Deposition, "J. Wu, M. Eastman, T. Gutu, M. Wyse and J. Jiao, S.-M. Kim, M. Mann, Y. Zhang and K.B.K. Teo, Applied Physics Letters 91, 173122 (2007).
- "Low temperature electron spin resonance investigation on SWNTs after hydrogen treatment." S. Musso, S. Porro, M. Rovere, A. Tagliaferro, E. Laurenti, M. Mann, K.B.K. Teo, W.I. Milne. Diamond & Related Materials 15 (2006) 1085 – 1089.

 "Apparatus and methods for growing nanofibres and nanotips." M. Mann, K.B.K.Teo, W.I. Milne. (Patent no. GB 0503139.8, filed 16-Feb-2005)

NOTATION

Units

As a general rule, S. I. units are used throughout this dissertation. The only exceptions to this rule are where accepted practice dictates otherwise. The two exceptions are gas flow rate, which is measured in standard cubic centimetres per minute (sccm), and gas pressure, which is measured in millibar (mbar). 1 sccm = $1.6667 \times 10^{-8} \text{ m}^3 \text{sec}^{-1}$, and 1 mbar = 100 Pa.

References

References to published literature are given in the text in the form [Authorⁿ], where Author is the surname of the first-named author, and n is a reference number which refers to the list of references to be found at the end of each chapter.

Abbreviations

All abbreviations are written in full at their first occurrence in the text, with the abbreviation given next to it in brackets, for example Plasma Enhanced Chemical Vapour Deposition ("PECVD").

Keywords

Carbon Nanotube Field Emission Plasma Enhanced Chemical Vapour Deposition Electron microscopy