PLASMA PROCESSING STUDIES WITH APPLICATION TO CARBON NANOTUBE FLUORINATION

A dissertation submitted by

Anders Barlow

for the degree of

Doctor of Philosophy

School of Chemical and Physical Sciences
Flinders University

OCTOBER 2011

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.

Anders Jack Barlow

October 2011

SUMMARY

The fluorination and growth of carbon nanotubes using plasma is a possible means towards controlling their properties. To develop a deeper understanding of these processes, a series of fundamental experiments were performed that studied sulphur hexafluoride (SF_6) plasma, its exposure to carbon nanotubes and finally the growth of nanotubes within a plasma environment. Plasma was characterised using a single cylindrical Langmuir probe, while carbon nanotube modification and growth treatments were studied using X-ray photoelectron spectroscopy, Raman spectroscopy and electron microscopy. Methods that allowed the fluorination and growth of nanotubes with desired properties are discussed.

Using an established Langmuir probe apparatus, plasma ignited within sulphur hexafluoride was characterised. Initially, a curious instability was observed within the main plasma density that oscillated with a frequency of ten's of Hertz. This instability was characterised with respect to experimental parameters such as applied power, gas pressure and probe position within the plasma chamber. From this research the instability is hypothesised to manifest as a wave that moves radially throughout the chamber from the plasma source with a speed of ~16 ms^{-1}. The instability interfered with Langmuir probe experiments by inducing fluctuations in the measured probe currents. The experiment was refined to account for this interference and allow the characterisation of the plasma with respect to experimental parameters.

The electron density within SF_6 plasma was observed to increase with absorbed rf power. Only marginal variations were observed with gas pressure. Typical densities were found to be ~10^8 cm^{-3}. Ion densities display a stronger dependence on the gas pressure in comparison with rf power and overall were significantly greater than that of the electron density, ~10^9 cm^{-3}, despite the assumption that plasma maintains quasineutrality. This is attributed to the strong electronegativity of the SF_6 molecule. The space potential of SF_6 plasma remained largely constant irrespective of applied rf power and gas pressure, while the floating potential is found to decrease with increasing power and pressure. For most SF_6 plasma the electron temperature is found to remain constant across the powers studied, although for high pressures the presence of a second population of high temperature electrons is observed.

Single-walled carbon nanotubes were exposed to sulphur hexafluoride plasma resulting in the attachment of fluorine moieties to the structures. Initial analysis found that smaller diameter nanotubes result in greater levels of functionality. Nanotubes with metallic band structure are also observed to show a greater susceptibility to the plasma fluorination mechanism. By varying the absorbed rf power the extent of these functionalities could be tuned, with a general increase in fluorination as power was increased. The oxygen content on the nanotube surfaces acted to interfere with the fluorination mechanism whereby increased oxygen content at the surfaces prior to a treatment resulted in a greater amount of fluorine attachment after exposure. This observation was then used to develop another level of control over the fluorination mechanism. Sulphur hexafluoride plasma containing low amounts of either oxygen or water vapour produce much greater levels of functionality. The cause of this was elucidated as an enhanced breakdown of the parent sulphur hexafluoride molecule resulting in a greater concentration of reactive fluorine ions in the plasma and thus greater reactivity overall.

Pure sulphur hexafluoride plasma resulted in carbon-fluorine bonding at the nanotube surface that was a mixture of covalent and semi-ionic types, thereby decreasing the overall quality of the functionalised sites. Through the addition of oxygen, either into the plasma or at the nanotube surface via pretreatments, the relative amounts of covalent and semi-ionic bonding could be tuned. Pretreatments using oxygen plasma result in almost purely covalent carbon-fluorine bonds.

The plasma chamber was modified to enable the growth of carbon nanotubes from mixed methane/argon plasma. The resultant nanotube growth displayed predominantly single-walled nature with very high homogeneity. The yield was very low however, with the nanotubes hypothesised to be very short in length. The variation of experimental parameters, such as time and temperature, afforded the growth of nanotubes with tailored diameters. Through Raman spectroscopy a transition from single- to multi-walled growth was observed to occur with increasing growth time and decreasing growth temperature. For temperature this is explained through a decrease in the energy of growth species at the catalytic sites and thus insufficient energy for the formation of single-walled nanotubes. The transition observed for growth time is explained through the enhanced etching of the smaller diameter nanotubes by plasma species, an effect that the larger multi-walled nanotubes could withstand for longer periods of time.

CONTENTS

ACKNOWLEDGEMENTS

I endured the highs and lows of PhD candidature alongside many of my peers. As I was writing this dissertation it was interesting to note the many different interpretations of what made a PhD thesis. Naturally everyone had different ideas about the body of the dissertation; from reference styles to page layouts, but it was *this* section that seemed to draw the greatest contrast in opinion. Personally, I felt it to be an opportunity to give thanks, not just to those who offered scientific input throughout my research, but also to those who have supported me through motivation, inspiration and compassion.

Before all else, I must thank my supervisor, Jamie Quinton. From the outset you guided me into an ideal project that was both engaging and novel. Although we never anticipated the troubles we faced during my candidature, and I know that you would never wish such problems upon any student, I am fairly certain that without those hard times I would not have the confidence that I now carry. You instilled upon me knowledge, experience, and patience. But most of all you taught me to be a careful scientist, to think before I act, and to make sure I consider all possibilities before arriving at a conclusion. Although my candidature was not as fruitful as it could have been with a working instrument, there is no doubt in my mind that my training was anything less than the most worthwhile experience of my life to date. I must also thank you for supporting me financially during the final stages of my candidature. Without that support I honestly do not know if I would have been successful.

Thank you to my co-supervisor, Joe Shapter. We didn’t spend a tremendous amount of one-on-one time during my PhD, but any contact we did have regarding my work was always productive. Even if you weren’t aware, you helped strengthen my scientific and critical thought process, and gave me the motivation to aim higher than I otherwise would.

The Smart Surface Structures Group at Flinders is an ensemble of fantastic scientific minds. Every time I would stand in front of the group to give a talk about my work I always came out inspired and motivated and often with new ideas to test. The group provided companionship and a great sense of camaraderie, especially when on conference trips where the downtime together was essential to surviving a PhD intact. To the entire group, including the many peers who have come and gone over the years, thank you.

There are some specific names from the group I must acknowledge. Cameron Shearer provided the oxidised and cut CNT samples that were part of the 2010 study at the Australian Synchrotron. While the PECVD research was in the back of my mind for a long time during my candidature, the research of Mark Bissett on carbon nanotube photovoltaics became the final push to attempt to grow CNTs and I am certainly glad we did. The 2008 synchrotron trip was exhausting as I was alone almost the entire time. In 2010 however, myself, Jamie, and two peers Adam Blanch and Ashley Slattery arrived at the synchrotron *en masse* to perform research into nanotube fluorination. To all of you, thank you for dedicating some of your precious time to my work, we couldn't have achieved what we did if we hadn't worked so well together as a team. Chris Gibson managed the Raman instrument used in this work and as such trained me and imparted as much of his knowledge as he could, so thank you Chris. Thank you also to Alec Deslandes. Not only did you show that it was in fact possible to complete a PhD, by doing so right in front of me, you have always provided a different level of insight into my research, especially with the Langmuir probe work. I am extremely grateful.

There is also a myriad of support staff I must acknowledge. Thank you to the Electronics and Mechanical Workshops in the School of Chemical and Physical Sciences. Specifically Bill Drury, Wayne Peacock, Mark Ellis, Mike Mellow, Bob Northeast and Chris Price. Throughout all the troubles we had with the XPS, each and every one of you were willing to drop things at a moment's notice to provide assistance. We would never have the LHS in such fine working order without your help. Thank you to Bruce Cowie, Lars Thomsen and Anton Tadich of the soft X-ray beamline at the Australian Synchrotron. Your assistance during our research was invaluable. On an official note I must also thank the Australian Synchrotron Research Program for funding assistance during each of our trips.

To all my friends and family, thank you. You have provided me with friendship and compassion for the duration of my candidature, even if I was somewhat of a hermit towards the end. I am eternally grateful. To my mum and grandmother, thank you for always being there for me and for pitching in whenever possible, I love you both.

And finally, to Kate, thank you for dealing with me through this the final stage in my education. Thank you for putting up with my rollercoaster emotions, and loving me regardless. I know that it has been equally hard on you as it has me, especially while I was writing this dissertation, but I could never have survived without you. I love you.

PUBLICATIONS

The following is a list of publications made during the author's candidature resulting from work either directly related to the research herein or performed as a result of the research.

Journal Articles

Barlow, A.J., Deslandes, A. and Quinton, J.S., Langmuir Probe Characterization of Low-Frequency Oscillations in Radio-Frequency SF_6 Plasma. *Plasma Sources Sci. Technol.,* **20**, 065011 (2011).

Bissett, M.A., **Barlow, A.J.**, Shearer, C., Quinton, J.S. and Shapter, J.G., Carbon Nanotube Modified Electrodes for Photovoltaic Devices. *Carbon*, doi:10.1016/j.carbon.2012.01.065 (2012).

Bissett, M.A., **Barlow, A.J.**, Shapter, J.G. and Quinton, J.S., Transition from single to multi-walled carbon nanotubes grown by inductively coupled plasma enhanced chemical vapor deposition. *J. Appl. Phys*, **110**, 034301 (2011).

Quinton, J.S., Deslandes, A., **Barlow, A.J.**, Shapter, J.G., Fairman, C., Gooding, J., & Hibbert, D.B., RF Plasma Functionalized Carbon Surfaces for Supporting Sensor Architectures. *Curr. Appl. Phys.*, **8**, 376-379 (2008).

Refereed Conference Proceedings

Bissett, M. A., **Barlow, A. J.**, Shapter, J. G., Quinton, J. S., Raman Characterisation of Carbon Nanotubes Grown by Plasma Enhanced Chemical Vapour Deposition. *Materials Science Forum*, **700**, 112-115 (2011).

Barlow, A.J. and Quinton, J.S., Radio Frequency SF_6 Plasma Modified Single-Walled Carbon Nanotubes: Synchrotron Spectroscopy and Plasma Characterisation Studies, *International Conference on Nanoscience and Nanotechnology, 22-26 February, Sydney Australia* (2010).

Barlow, A.J. and Quinton, J.S., Synchrotron Soft X-ray Studies of Single-Walled Carbon Nanotubes Functionalized by Radio-Frequency SF_6 Plasma. *AIP Conference Proceedings*, **1151**, 21-24 (2009).

Barlow, A.J., Shapter, J.G., & Quinton, J.S., Fluorinated carbon surfaces using radio frequency plasma modification. *Proceedings of the 18th Biennial Australian Institute of Physics Congress*, 85-88 (2008).