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PROGRESS REPORT FOR AINGRA07126P

PROJECT TITLE	Hydrogen content determination of RF-plasma modified carbon surfaces for nanotechnological sensors	
INVESTIGATOR(S)		**Institution and Department**
Chief Investigator	**Dr Jamie Quinton**	Chemistry, Physics and Earth Sciences, Flinders University
Other Investigators	Dr. Mihail Ionsecu	
Students	Alec Deslandes Anders Barlow	
ANSTO Investigators	Mihail Ionescu	
Specialist Committee	M	

SCIENTIFIC OBJECTIVES

This project will provide crucial information to aid the development of hydrogen-terminated carbon surfaces modified via plasma treatments for new electrochemical sensors technologies. In particular, hydrogen content measurements made via elastic recoil detection analysis (ERDA) at ANSTO will complement surface characterisation studies undertaken in South Australia, such as STM and ToFSIMS, and electrochemistry studies made at UNSW, which will enable optimisation of the surface preparation and treatment procedures.
This AINSE project is part of a larger collaboration between Dr. Jamie Quinton's (Flinders) and Prof. Bryn Hibbert's (UNSW) research groups, which is supported by ARC Discovery Grant DP0559327.

PROGRESS REPORT, DATA and RESEARCH OUTCOMES

Our first visit to ANSTO to attempt ERDA on our surfaces was highly beneficial. We have established that not only is the technique suitable for determining the information we seek from our samples, but also that our protocols for preparing and analyzing the samples are acceptable.

Specifically, we have made crucial measurements of the hydrogen content of plasma-modified carbon surfaces. Substrates investigated included highly ordered pyrolytic graphite (HOPG) and pyrolyzed photoresist films (PPF). These were modified with hydrogen and methane plasma treatments to produce hydrogen-terminated surfaces (which is then used for further modification towards the development of electrochemical sensors by our collaborators).

The two pristine substrates used in these investigations were compared, with results shown in Figure 1. HOPG was found to have a very low surface hydrogen content (<1%). The PPF was also found to have a minimal hydrogen content of ~6-10% (depending on batch/preparation conditions). PPF was found to be too insensitive (too little variation in H-content using the plasma treatments employed) for meaningful data to be obtained.

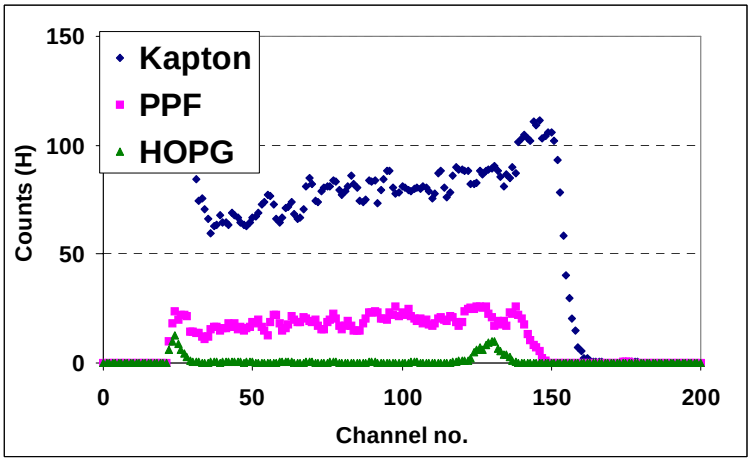


Figure 1. Comparison of substrates used in studies.

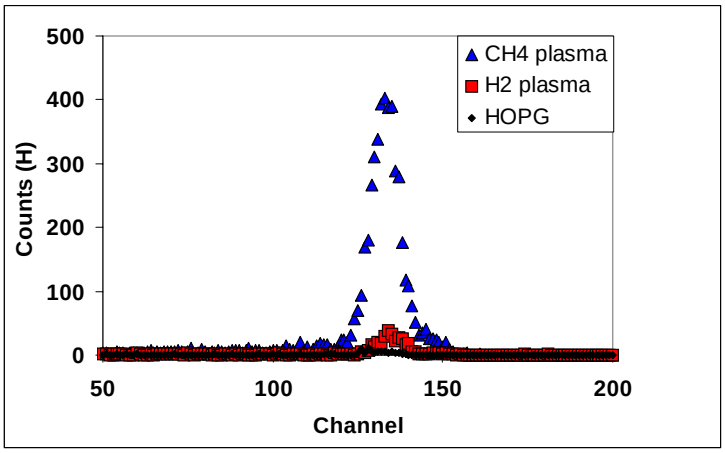


Figure 2. Methane and hydrogen plasma modification of HOPG.

HOPG was treated with methane plasma or hydrogen plasma and an increase in the hydrogen content of the surface region was observed (Figure 2). The methane plasma-treated surface was found to have a higher degree of hydrogen termination than the hydrogen plasma-treated surface.

For the PPF surface (Figure 3), the effects of the hydrogen plasma modification are indistinguishable above the native hydrogen content of the surface. As previously described, the HOPG results (Figure 2) were successful in comparing the modification to the hydrogen content brought about by the plasma treatments, and thus confirmed our previous SIMS-PCA (principle component analysis) conclusions. Thus, this ERDA data is used in our first paper on this topic which is about to be submitted to the journal 'Carbon'.

A key objective of our studies and the focus of the provisional grant that is to follow this one is to investigate the evolution and thus surface modification mechanisms of hydrogen as a function of various experimental parameters (time, plasma density, power). To establish whether this is achievable, a pilot ERDA study we conducted was performed on samples that had been treated with methane plasma under varying driving power conditions. The results for these samples are shown in Figure 4. Although the exposure time was only 1 minute for each sample, the advantage of using HOPG (with very low native hydrogen content) is highlighted. Despite low counts, the trend of increasing modification on exposure to higher power plasma is clearly observable. This result also helps to highlight the good resolution of our SIMS-PCA method, which showed an analogous trend. Through comparison with STM and SIMS results for this study, insights into the growth of carbon films via plasma are also possible (such as the relationship between the number/nature of STM observed features and the measured hydrogen content). These results are currently being used to prepare a second journal article.

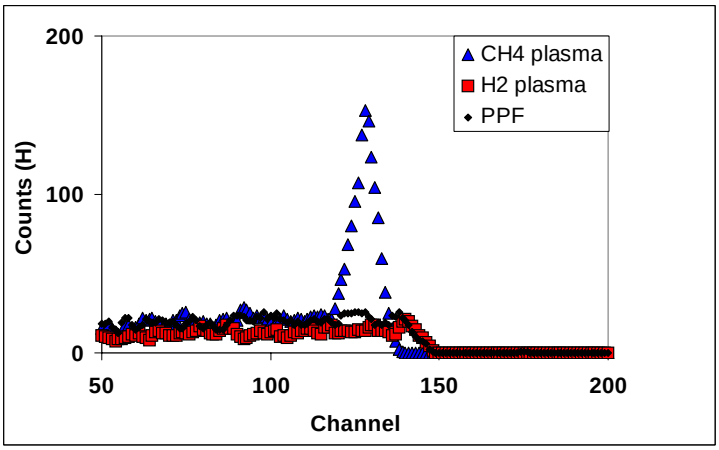


Figure 3. Methane and hydrogen plasma modification of PPF.

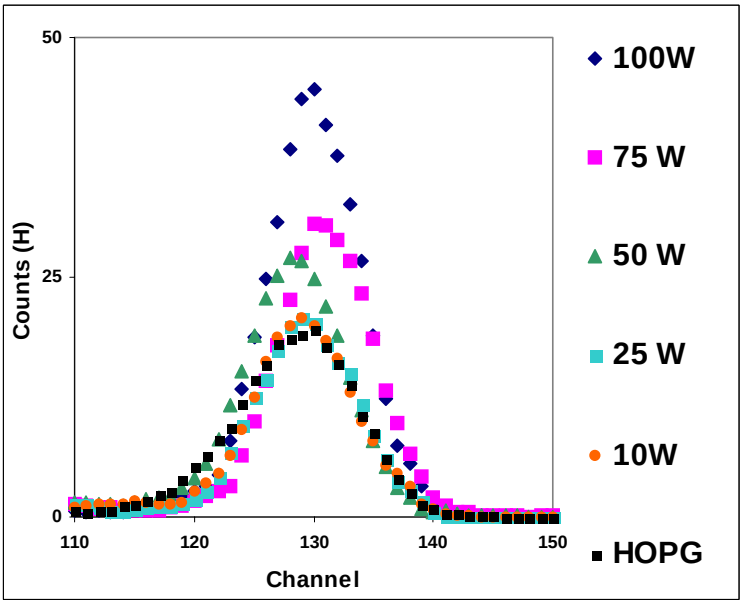
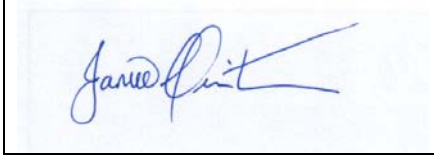


Figure 4. Effect of plasma power on the extent of modification (hydrogenation) by methane plasma.

Unfortunately a large number of investigations for this visit used PPF as a substrate and, combined with the nature of the plasma treatments used (in particular the plasma exposure times), there was little or no change observed via the ERDA results. Armed with a better understanding of the limitations of the ERDA measurements and a better understanding of the optimal ranges for the plasma treatment-variables (i.e. from the studies that did and did not produce serviceable results in this visit), we look forward to future visits being even more successful.

While this was a success, further work is needed to expand upon the studies currently underway (and support other SIMS and STM data already collected). The modifications to our plasma reactor that are currently underway will also permit investigation of the hydrogen content of boron-doped carbon films, as well as carbon films deposited using gas mixes. Hence, we would like the provisional award associated with this award to be activated in time for another visit in November 2007.

In summation, this visit was successful in showing that the conclusions drawn from principle component analysis (PCA) of ToFSIMS data were correct. This is a key result, as SIMS has not previously been used to investigate carbon films, or hydrogen/methane plasma modified carbon surfaces, in such a detailed manner. This is also the first time that such a relevant analysis of the hydrogen content of hydrogen/methane plasma modified carbon was conducted using SIMS and as such there were few methods or published work that could be used to confirm our analysis. Thus, results provided from this visit to ANSTO and utilization of ERDA (STAR) facilities were crucial to establishing these methods. We are most keen to further explore the application of the technique to our research.

Signature of Investigator preparing the report for **After signing this report please fax this page with your signature for our files**	**Proj: AINGRA07126P** **Date:**
	9 July 2007

PUBLICATIONS / REPORTS arising as a result of your work.

A. Deslandes
Methane plasma modified carbon surfaces characterized via ToF-SIMS and STM (contributed talk)
ARC Network for Advanced Materials (ARNAM) Workshop, 2007, 8-11 July 2007, ANU Kioloa Campus

Alec Deslandes, Marek Jasieniak, Mihail Ionescu, Joe G. Shapter, Callie Fairman, Justin J. Gooding, D. Brynn Hibbert, Jamie S. Quinton
Characterisation of Methane and Hydrogen Plasma Modified Graphite Surfaces
in preparation for submission to 'Carbon'

PhD STUDENTS For each student involved with the project, please indicate the date or anticipated date of conferment of a PhD or other award, and give the title of the thesis.

Alec Deslandes (Flinders) – *Plasma Modified Carbon Surfaces* - expected completion 10/2008

Callie Fairman (UNSW) – expected completion 10/2008