

# Characterisation of Methane Plasma Treated Carbon Surfaces

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**Abstract**—Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) was used to investigate the chemical nature of methane plasma treated graphite surfaces. Principle Component Analysis (PCA) was applied to the SIMS data, revealing chemical changes to the surfaces, in particular the extent of hydrogenation. The hydrogen content of the HOPG surface is observed to increase with systematic increases in power of the plasma treatment. These results are supported by Elastic Recoil Detection Analysis (ERDA) measurements that show a similar increase in hydrogen content. Scanning Tunneling Microscopy (STM) measurements provide insight into the morphological changes to the surface caused by the treatment, via investigating plasma-created features that are observed to increase in coverage with the increases in plasma power.

**Keywords**—methane plasma; secondary-ion mass spectrometry; principle component analysis; elastic recoil detection analysis

## I. INTRODUCTION

Carbon surfaces have a range of properties, including a wide potential range and chemical stability, which make them the substrate of choice in numerous electrochemical applications [1]. The electrochemical performance of glassy carbon electrodes is improved on exposure to hydrogen or methane plasma as evidenced by enhanced signal-to-noise ratios [2]. Carbon films with controllable material properties are also regularly deposited using methane or methane-containing plasmas (e.g. commonly mixed with hydrogen or argon) [3-5]. It is our intention to produce a hydrogen-rich surface via plasma treatments, upon which electrochemical or biosensing chemical architectures can be developed through further chemical attachment.

In our investigations, highly ordered pyrolytic graphite (HOPG) was used as a model substrate to study the influence of various plasma treatments on carbon surfaces, particularly sp<sup>2</sup> bonded (or containing a significant amount thereof) or graphite-like surfaces. Exposure to methane plasma changes the chemical and structural characteristics of the carbon surface [6]. Due to its extreme surface sensitivity (ppm) and structural specificity, combined with its ability to detect all elements

(particularly hydrogen), ToF-SIMS is an ideal technique for probing the hydrogen content of carbon surfaces. To efficiently exploit the spectral data, principal component analysis PCA [7] was employed.

## II. EXPERIMENTAL

HOPG was cleaved and then placed inside a stainless steel plasma chamber, which was then pumped down to  $1 \times 10^{-6}$  Torr. Treatment pressure (methane) was 30 mTorr and exposure time was one minute. The applied plasma power ranged from 0 to 100 Watts. Power was provided by an RF signal generator operating at 13.56 MHz and was inductively-coupled to the plasma by a single loop internal stainless steel antenna.

The ToF-SIMS analyses were performed with a PHI TRIFT II (model 2100) spectrometer (PHI Electronics Ltd, USA) equipped with <sup>69</sup>Ga liquid metal ion gun (LMIG). A 15 keV pulsed primary ion beam was used to desorb and ionise species from a sample surface. Each spectrum was acquired from an area of 100  $\mu\text{m} \times 100 \mu\text{m}$  for 60 seconds. The total primary ion fluence per spectrum was less than  $6 \times 10^{11}$  ions  $\text{cm}^{-2}$  ensuring experiments are carried out in the static conditions regime. The peaks were normalized to the sum of the intensities of the selected prominent peaks before PCA. PCA was achieved using PLS Toolbox version 3.0 (Eigenvector Research, Inc., Manson, WA) along with MATLAB software v. 6.5 (MathWorks Inc., Natick, MA).

ERDA measurements were conducted using the STAR accelerator at ANSTO. The primary 1.8 MeV He<sup>+</sup> ion beam was incident on the sample surface at an angle of 70° relative to the sample normal. Collection time was typically 6 minutes per spectrum.

STM measurements were obtained with a Digital Instruments STM, using an A-scanner and Nanoscope IV controller. Tungsten wire (1.5 mm) tips were electrochemically etched in NaOH solution. Bias voltage was 20 mV, and tunneling current was constant at 2 nA.

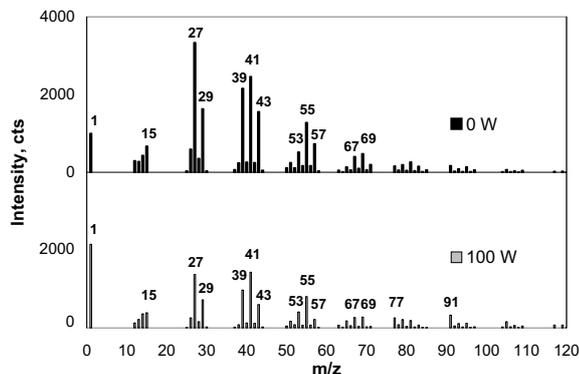


Figure 1. Positive static SIMS spectra of clean graphite (0 W), and methane plasma-treated graphite (100 W).

### III. SURFACE CHARACTERISATION: CHEMICAL MODIFICATION

ToF-SIMS spectra of clean graphite and methane plasma-treated graphite show a number of characteristic hydrocarbon moieties with varying intensities as shown in Fig. 1. The spectra shown were obtained from a fresh HOPG (0 W) and methane plasma treated (100 W) sample. The amu of prominent peaks in each spectrum have been labeled to aid identification of the secondary ions produced.

The relative intensities of specific peaks are observed to change with the plasma treatment, i.e. the 100 W spectrum is observed to have a much larger hydrogen-ion signal than the 0 W spectrum. Indeed, when all the measurements of this study are taken into consideration (data not shown here), it appears some peak height changes appear to be systematic with changes in the plasma power. However, the large number of fragment ion peaks makes the analysis of these changes difficult, and the relevance (i.e. weight) of these changes is hard to judge.

Thus PCA is used to determine the peaks that contribute the greatest variance between spectra. PCA produces scores for spectra on new principle component (PC) axes, where a score is a linear variable dependent on the intensities of peaks and the loading given to each individual peak. Analysis of the loadings allows us to characterize differences between samples.

Fig. 2(a) shows the scores plot for spectra obtained from samples treated at different methane plasma powers. The grouping of the spectra according to plasma power shows that different plasma powers produce surfaces that are chemically different. Higher plasma powers yield surfaces with more positive values PC1 values indicating a systematic change.

As seen in Fig. 2(b), the positive contributions to the scores on PC1 are dominated by a large positive loading of the  $H^+$  fragment. Negative contributions to the PC1 scores are dominated by the loadings of  $C_2H_3^+$  and  $C_3H_3^+$  (relatively hydrogen-poor fragments). Thus, increasingly positive scores on PC1 indicate increasing hydrogen termination of the surface. This is confirmed by observing the trend in the mean normalized yields for these fragments, as observed in Fig. 2(c): the hydrogen ion yield is observed to increase with increasing plasma power, while the  $C_2H_3^+$  and  $C_3H_3^+$  yields are observed to decrease.

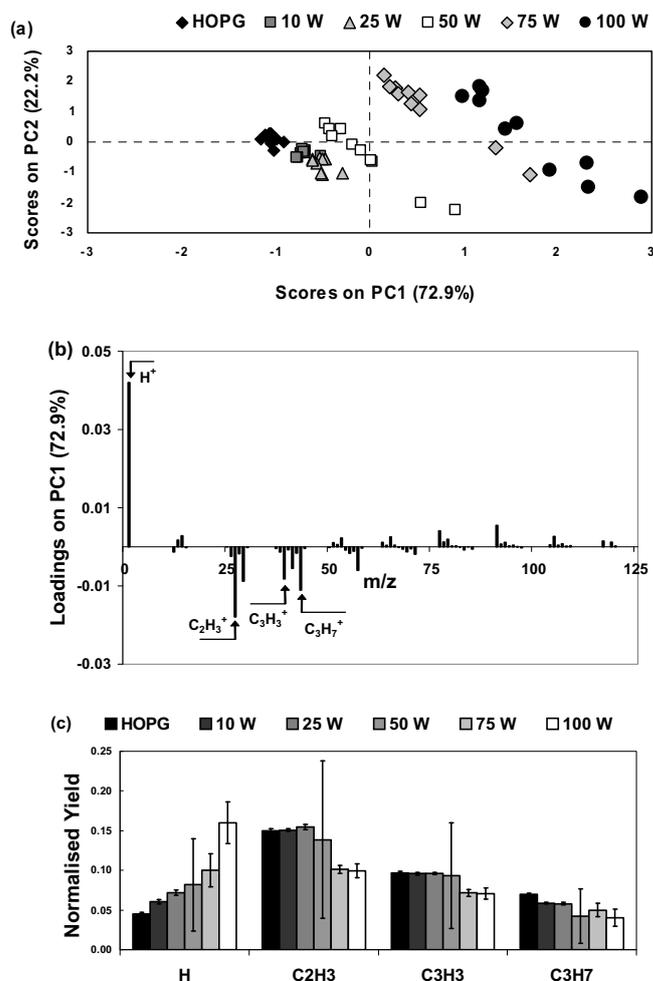


Figure 2. (a) Scores plot on PC1 and PC2, (b) loadings on PC1 for SIMS spectra (c) mean normalized yields for peaks highlighted by PCA analysis, from HOPG samples exposed to different power plasmas.

It is also noted that the  $C_3H_7^+$  fragment has a fairly large negative loading on PC1. It is thought that this fragment is related to the aliphatic nature of the graphite surfaces [6], rather than hydrogen termination. The negative loading for this fragment implies that the spectra that score more negative on PC1, i.e. the clean HOPG and low-power plasma treated HOPG, have relatively larger  $C_3H_7^+$  ion yields and thus a greater aliphatic nature. This result is unexpected, as the less-damaged HOPG surfaces (clean HOPG and low power treatments) would be expected to retain the aromatic nature of HOPG, while the more damaged or modified surfaces may have more aliphatic nature (due to possible growth of polymer-like material). The mean normalized ion yields for the  $C_3H_7^+$  ion are observed in Fig. 2(c). When the confidence intervals for the  $C_3H_7^+$  fragment are observed, it is questionable whether these ion yields follow the trend suggested by the loadings on PC1.

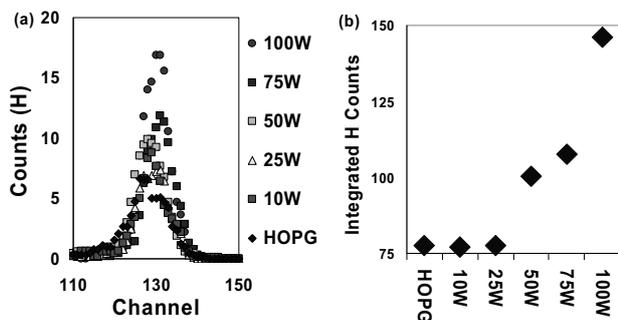


Figure 3. (a) Surface H counts, and (b) integrated H counts from ERDA measurements conducted on methane plasma-treated HOPG.

The close grouping of spectra scores observed in Fig. 2(a) for each of the HOPG, 10 W and 25 W sample groups indicate each these surfaces are fairly homogeneous. As the plasma power increases, the scores for spectra from the 50 W, 75 W and 100 W samples are observed to be more variable suggesting each of these surfaces are less homogeneous. This is also reflected in the confidence intervals for mean peaks from the sample spectra, as observed in Fig. 2(c). The large confidence interval and score spread of spectra for the 50 W (as well as 75 W and 100 W) spectra may be due to instabilities in the plasma, related to a possible transition from capacitive- to inductive-coupling of the plasma in the region near 50 W.

The results from ERDA measurements of samples exposed to methane plasmas with different plasma powers are shown in Fig. 3. In Fig. 3(a), the channel number is an indication of the energy of the detected hydrogen (4.67 keV/channel). At low channel numbers the amount of detected hydrogen is negligible, indicating that bulk HOPG has a very low hydrogen content. The lack of a broad peak (i.e. stretching to lower channels) indicates the modification is limited to near-surface layers of the HOPG. The hydrogen content of the surface is observed to increase with increasing plasma power, as shown in the integrated H counts plot in Fig. 3(b).

Thus, these ERDA results support the conclusions from the PCA applied to the ToF-SIMS measurements. That is, an increase in hydrogen content is observed on the treated HOPG surface when the applied power of the methane plasma is increased.

#### IV. SURFACE CHARACTERISATION: MORPHOLOGICAL MODIFICATION

Scanning tunneling microscope (STM) images show features developing on the graphite surface that are caused by methane plasma treatment, as observed in the 100 nm x 100 nm micrographs shown in Fig. 4 (a) and (b). In height mode (constant current) these features are observed as an increase in tunneling current, thus suggesting an increase in height or growth of material upon the surface.

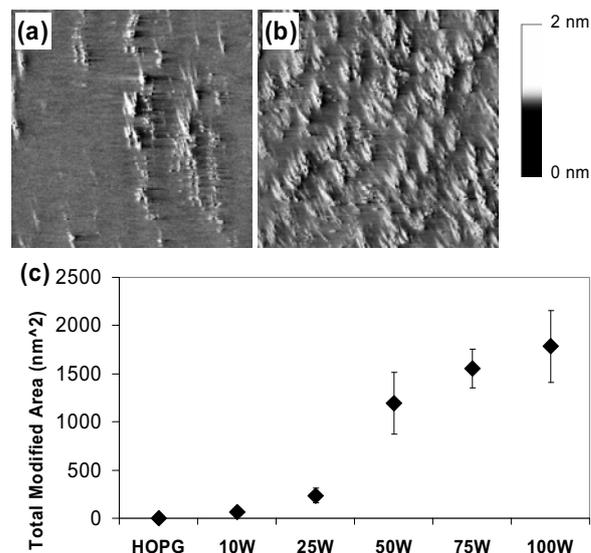


Figure 4. STM measurements of graphite treated with different power methane plasmas. 100 nm x 100 nm images of 25 W (a) and 75 W (b) plasma treated surface, and (c) area of plasma-created features.

The Nanoscope software was used to measure the average size and number of features on each image, and from this the area of features was calculated. The area of these features increases with increasing plasma power, as observed in Fig. 4(c). This trend has similarities to the increase in hydrogen content observed in Fig. 2(c) and Fig. 3(b). This suggests these growth features are likely to be sites with increased hydrogen content. Given the composition of the features is likely to be the same or very similar to the surrounding substrate, the observed features which appear as an increase in height are very likely due to topographical bumps on the surface. This indicates deposition of material on the surface. This is likely to be carbon from the carbon and hydrocarbon species present in the plasma. Thus, we are observing the initial growth stages of a hydrogenated carbon film on the HOPG surface.

#### V. FURTHER ATTACHMENT

Hydrogenation of carbon surfaces by plasma treatment has been shown to enable attachment of further molecules via photochemical functionalisation [8,9], which may be further modified to develop chemical sensing architectures. The methane plasma treatment in this study has been observed to modify the carbon surface by creating local sites (imaged by STM), which are likely to be sites of increased hydrogen content. Thus, further chemical addition may favour these sites yielding inhomogeneous coverages. If complete coverage, i.e. near-monolayer coverage, of subsequent attached species is desired, then larger areas of plasma-modified sites may be required. Using the methane plasma treatment used in these experiments, this could likely be achieved through further increasing plasma power. Longer exposure times may also be used, however this could lead to deposition of further carbon material (i.e. vertical growth, not just lateral modification) thus producing a new hydrogenated-carbon coating of some thickness atop the substrate. This could have detrimental

repercussions for the electrochemical performance of the surface particularly if this coating has low conductivity. Experiments investigating the hydrogenation of carbon surfaces via methane and hydrogen plasmas and further modifications and characterization of the surfaces are continuing in our laboratories.

#### ACKNOWLEDGMENT

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