# Preparation of Carbon Surfaces for Sensing Applications via Plasma Hydrogenation

Alec Deslandes, Joseph G. Shapter, Emma L. Lawrance, Jamie S. Quinton*

Smart Surface Structures Group
School of Chemistry, Physics and Earth Sciences
Flinders University, GPO Box 2100 Adelaide 5001, Australia
*Corresponding Author, Email: jamie.quinton@flinders.edu.au

*Abstract*—**Graphite (HOPG) has been exposed to radio frequency (RF) plasmas of hydrogen and methane to produce hydrogen-terminated carbon surfaces, and hence model the use of plasma hydrogenated carbon as a substrate in sensing applications. Etching and/or growth and nucleation features are observed in scanning tunneling microscopy images. Surface coverage and size of features are found to depend upon the choice of source gas. Preliminary time of flight secondary ion mass spectrometry measurements suggest these features and the hydrogen content of the surfaces are related.**

*Keywords - graphite; plasma surface modification; STM; ToFSIMS; hydrogren termination*

## I. INTRODUCTION

Carbon surfaces are being investigated for use as substrates for developing chemically modified electrochemical sensors as they offer many advantages over traditional substrate systems. In particular, chemically modified glassy carbon structures are expected to have increased stability when compared to thiol-gold interfaces, which have been shown to be unstable under certain conditions [1]. The advantageous qualities of carbon have been shown to be further enhanced (with regard to stability) after exposure to hydrogen or methane plasmas [2]. Plasma hydrogenation of the carbon surface is being used as an initial step in sensor preparation. Hydrogen-termination will allow further functionalisation through attachment of short chain, carboxyl-terminated alkyl groups. Additional reaction will see attachment of peptides or enzymes to produce the electrochemical sensor. The ability to attach further molecules to the hydrogenated carbon surface is expected to be influenced by surface characteristics such as the distribution and coverage of hydrogen, as well as morphological properties such as roughness.

## II. EXPERIMENTAL

### A. Plasma Treatment of Graphite

In these initial investigations, highly ordered pyrolytic graphite (HOPG) was used as a model substrate to investigate the effects of the plasma treatment upon carbon surfaces. The $sp^2$-bonded basal plane of graphite offers good qualities for nanoscale imaging, while the $sp^3$ bonding exposed at defect sites provides useful information with respect to further investigations of the plasma's influence upon other carbon surfaces. In particular, HOPG is being used as a model surface for glassy carbon, which is known to contain a mixture of $sp^2$ and $sp^3$ regions.

The HOPG (ZYH grade) was cleaved using adhesive tape and then placed inside a plasma-processing vacuum chamber (stainless steel, cylindrical in shape with internal dimensions of 0.3 m high and 0.4 m in diameter), which was pumped down to a base pressure of $1 \times 10^{-5}$ Torr. High purity hydrogen (99.99%, obtained from CIG) and methane (99.95% from Linde) were used as source gases. Gas pressures adopted for each plasma ranged from $6.5 \times 10^{-3}$ to $3.0 \times 10^{-2}$ Torr, as desired. The applied plasma power was varied from 3-100 Watts, which was provided by an RF signal generator operating at 13.56 MHz and was inductively-coupled to the plasma by a single loop antenna. Exposure times were chosen between 1 minute and 60 minutes, as desired.

### B. Surface Characterisation

The chemical compositions of each surface was characterized using a Leybold LHS-11 X-ray photoelectron spectroscopy (XPS) analysis system, using Al $K_\alpha$ X-rays (1486.6 eV), at 14kV acceleration voltage and an emission current of 30 mA.

Features on the HOPG surface caused by the plasma treatments were imaged using a Digital Instruments scanning tunneling microscope (STM) and Nanoscope IV software, using a 5277A scanner for atomic scale images, or E scanner for larger scale images (i.e. 100 nm x 100 nm). Tips were prepared using 1.5mm Tungsten wire, which were mechanically cut with wire clippers and then electrochemically etched in 1M NaOH solution. When obtaining images, a bias voltage of 20 mV was applied between surface and tip, and for height-mode images the tunneling current was constant at 2 nA. Images were processed using the Nanoscope control and data analysis software. First the images were flattened using a second order polynomial to remove tilt and bow, and then processed using a low-pass filter.

Time of Flight Secondary Ion Mass Spectrometry (ToFSIMS) data was acquired using a Physical Electronics TRIFT II, which utilized a Gallium ion source operating at 15 keV. Static mode data was obtained for periods of 60 seconds, over areas of 100 x 100 microns. For each sample, ten positive ion spectra from were obtained from different areas. Impurity

peaks (such as Na) were removed, and the individual spectra were used to produce an average spectrum for that sample. The peaks within each average spectrum were normalized (as a fraction of the total counts of all peaks within that spectrum). Principle Component Analysis (PCA) was performed to enable further comparisons to be made between samples that had been exposed to different plasma treatments.

## III. RESULTS

### A. XPS

In Fig. 1, XPS spectra of a clean HOPG surface (top), a hydrogen plasma treated surface (middle) and methane plasma treated surface (bottom) are shown. The strong carbon core photoelectron (C 1s) peak is observed at a binding energy of 285 eV. The presence of oxides on the surfaces is indicated by the O 1s peak at 534 eV. The peak observed at 842 eV at first glance may appear to be a F 1s photo peak (and thus contaminant), but is in fact a 'copper ghost' C 1s peak (due to a 557 eV shift of the Al $K_\alpha$ line), from wear of the anode in the X-ray source.
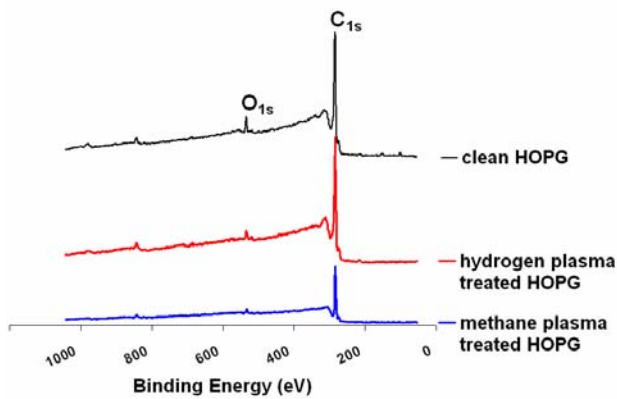


Figure 1. XPS spectra of (top) an untreated HOPG surface, (middle) a hydrogen plasma treated HOPG sample, and (bottom) a methane plasma treated HOPG sample.

The presence of oxygen is due to exposure to air after the HOPG was cleaved. The XPS spectra indicate that the cleaved and treated surfaces are free of other impurities. In particular, it suggests the hydrogen and methane plasma treatments used are free of impurities (such as from the chamber walls), and furthermore, that features imaged using STM (shown later in section III. B.) must be caused by the interaction between hydrogen and hydrogen-containing carbon groups, and the surface.

### B. STM

Features on the plasma treated HOPG surface were observed as atomic and nanometer-scale protrusions in STM measurements. Fig. 2 shows STM images of various plasma-treated samples. Each scan is 100 nm by 100 nm.
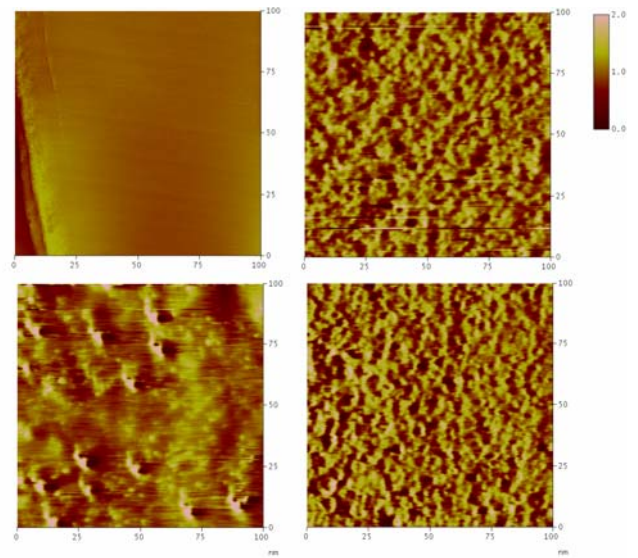


Figure 2. STM images of HOPG samples. Top left: clean HOPG, bottom left: HOPG exposed to CH4 plasma for 60 minutes, top right and bottom right: HOPG exposed to H2 plasma for 1 and 60 minutes, respectively.

In Fig. 2 the top left image shows a flat, clean HOPG surface. In the bottom left of this same image, a scratch-like defect caused during the cleaving process can be seen. The bottom left image in Fig. 2 shows a surface that has been exposed to a methane plasma for 1 hour. A number of protrusion-like defects are observable on this surface, which (determined over the fifteen most prominent features) are an average 1.5 nm high and 6 nm wide. The top right and bottom right images of Fig. 2 show hydrogen plasma treated surfaces. Both surfaces have a mottled appearance, with a high coverage of features whose heights are approximately 1 nm (with few features above this height).

Features are distributed randomly due to the homogeneity of the interaction between the plasma and the surface. However, the extent of plasma-induced features appears to be much greater for samples treated with hydrogen plasmas, while methane plasma treated surfaces have more sparsely distributed features.

The features induced by the methane plasma treatment are shown in more detail in Fig. 3. This image is a 20 nm x 20 nm atomic resolution image of a HOPG sample exposed to a methane plasma. Some regions of the periodic lattice structure (as observed for a pristine HOPG surface) are observable, which suggests these areas are unaffected by the plasma.

In Fig. 3, features induced by the methane plasma treatment can be observed to disrupt the periodic lattice structure of the HOPG surface, spanning tens of nanometers. The increase in tunneling current of the features indicates an increase in height, which suggests the plasma produces some deposition or growth upon the surface, likely sourced from the carbon contained in the plasma precursor gas. This is expected, as plasmas using hydrocarbon source gases have previously been used for the deposition of carbon films [3].
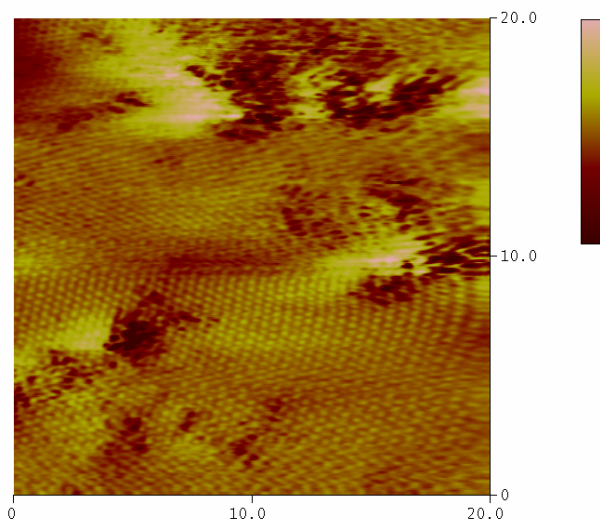
Figure 3. STM current-mode 20 nm x 20 nm image of a HOPG surface treated with a methane plasma.
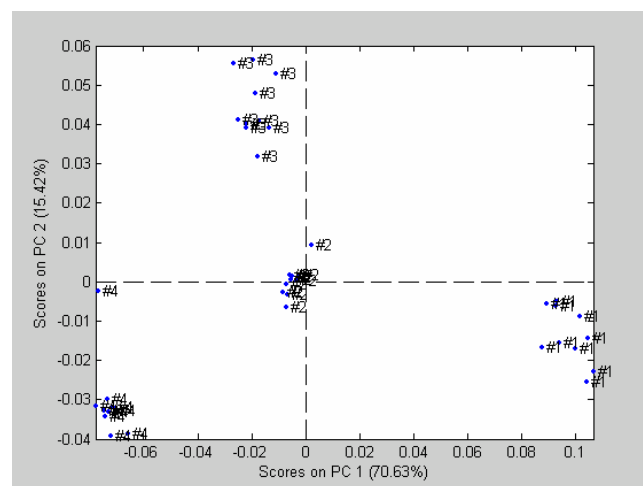


Figure 4. Principal Component Analysis of ToFSIMS spectra of an untreated HOPG surface (#1), HOPG treated with a hydrogen plasma for 1 minute exposure (#2), HOPG treated with a hydrogen plasma for 60 minutes exposure (#3), and HOPG treated with a methane plasma for 60 minutes exposure (#4).

The high coverage of hydrogen plasma-produced defects from our treatments has a profound effect when attempting to image small-scale regions of hydrogen plasma treated surfaces. When attempting to image these surfaces, the high coverage of defects means the image is dominated (i.e. totally covered) by indefinable, blurry features like those observed earlier in Fig. 3. Ruffieux et al. have previously shown images where a hydrogen plasma was observed to etch the surface of HOPG and produce atomic vacancies in the graphite lattice [4]. It is thought part of this etching process is hydrogen abstraction from the surface via atomic hydrogen [5,6]. Investigations into producing surfaces with minimal damage, to enable good atomic resolution images of hydrogen plasma treated surfaces are currently underway in our laboratory.

*C. ToFSIMS*

ToFSIMS results, shown in Fig. 6 (on the following page), show the average spectra (calculated from 10 repeated scans taken at different areas on each sample) for various HOPG samples treated with methane or hydrogen plasmas. The production of $C_xH_y$ groups, and in particular, the hydrogen content of these groups, gives an indication of the hydrogen content of the different surfaces.

The spectrum for the methane plasma treated sample has an obvious difference to the other samples, in that a relatively larger amount of higher-level hydrocarbons (i.e. above $C_6H_9$) were produced from the surface. Further analysis of the hydrogen content through observing these spectra is difficult, due to the large number of peaks.

Using Principle Component Analysis [7], the data contained in Fig. 6 can be analyzed by reducing the variables (i.e. the large number of peaks). Fig. 4 shows a plot of Principle Component 1 against Principle Component 2 for each of the individual spectra for each sample. In this plot, the repeated scans from each sample are observed to group together. This suggests each surface is quite different from the others, and also that each individual surface is quite homogeneous across the various areas scanned.

The loadings on Principal Component 1 can be observed in Fig. 5. Of particular interest are the high positive loadings given to hydrocarbon groups with low hydrogen contents (i.e. $C_2H_3$ and $C_3H_3$), and the large negative loading given to hydrogen ions. When correlated with the plot in Fig. 5, this indicates that the methane treated surface produces more hydrogen, and more groups with greater hydrogen contents in ToFSIMS spectra. This suggests that the methane plasma treated surface has higher hydrogen content than those treated with hydrogen plasmas.

These results can be correlated with the observed features in the STM images, which are therefore likely related to the hydrogen coverage of the carbon surface.
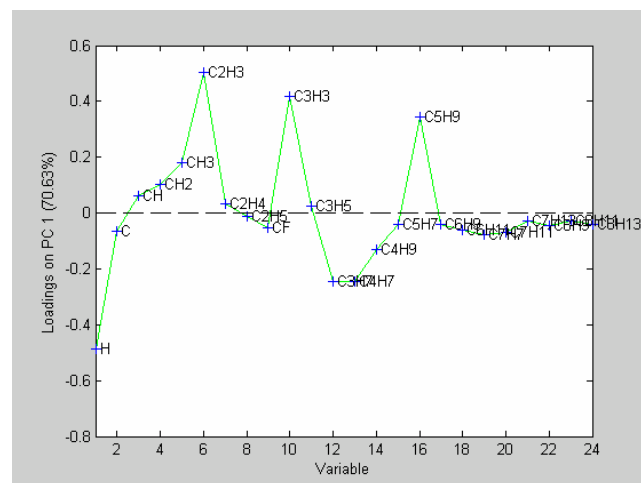


Figure 5. The loadings on Principal Component 1 for the spectra from the four samples shown in Fig. 4.
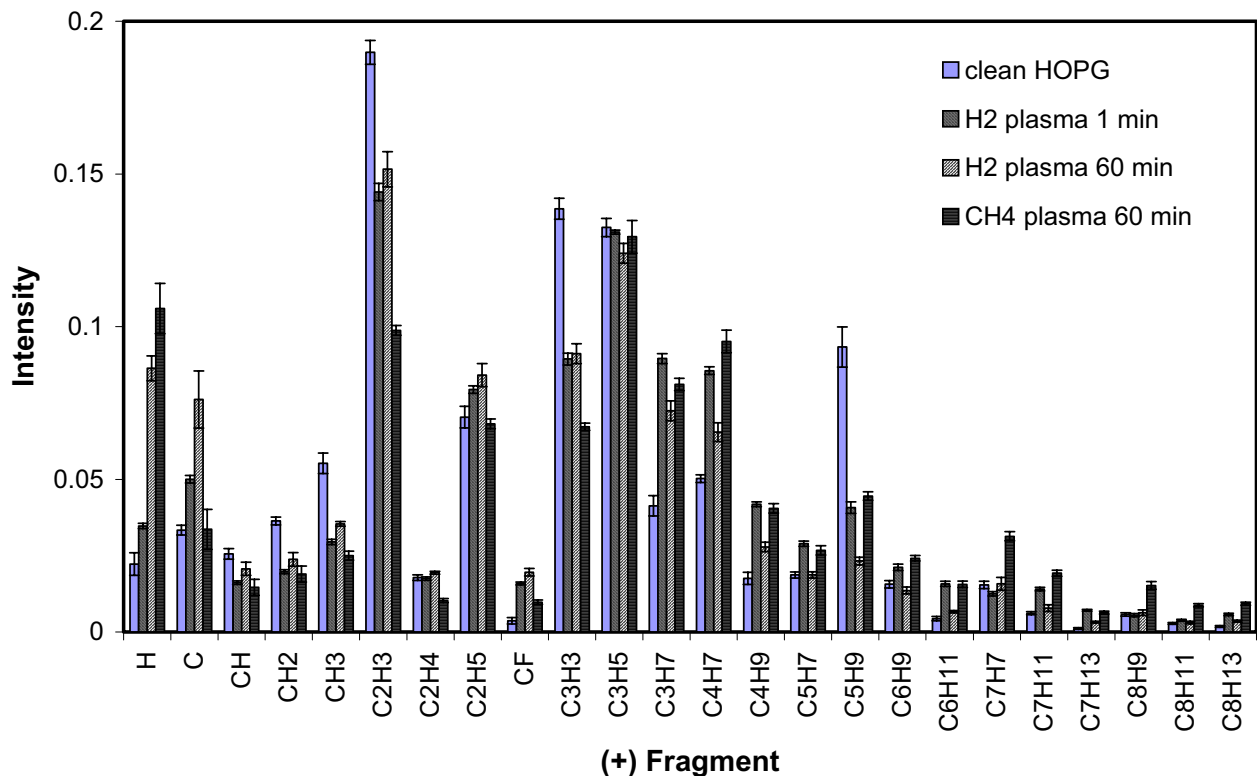
616

Figure 6. ToFSIMS spectra of an untreated HOPG surface, a HOPG sample treated with a hydrogen plasma (1 minute exposure), a HOPG sample treated with a hydrogen plasma (60 minutes exposure), and a methane plasma-treated HOPG sample (60 minutes exposure).

## IV. USE OF TREATED SURFACES FOR SENSORS

These results presented here elucidate how the initial step of plasma hydrogenation treatment will affect the performance of the final sensor. In particular, it is expected that maximizing the hydrogen coverage will aid further chemical modification, and hence be advantageous to final sensor performance. The variability in electrochemical reactivity of prepared sensors is also expected to be influenced by the homogeneity (i.e. distribution) and coverage of the bonded-hydrogen on the carbon surface. Etching and growth effects caused by the plasma hydrogenation lead to changes in surface roughness, which is also likely to affect surface suitability.

These preliminary investigations have highlighted the importance of the choice of gas for plasma hydrogenation (i.e. hydrogen or methane), as via STM measurement this has been observed to have an obvious effect on the treated surface morphology. ToFSIMS results have also indicated that surfaces treated with methane plasmas have quite different composition (in particular, with respect to hydrogen content) to those treated with hydrogen plasmas.

Ongoing investigations will enable optimizations of the plasma treatments used to prepare surfaces for carbon-based electrochemical sensors.

## REFERENCES

[1] M. H. Schoenfisch, and J.E. Pemberton, "Air stability of alkanethiol self-assembled monolayers on silver and gold surfaces," J. Am. Chem. Soc., vol. 120(18), pp. 4502-4513, May 1998.

[2] R. DeClements et al., "Electrochemical and surface structural characterization of hydrogen plasma treated glassy carbon electrodes," Langmuir, vol 12(26), pp. 6578-6586, Dec. 1996.

[3] J. C. Angus, P. Koidl, and S. Domitz, "Carbon Thin Films," in Plasma Deposited Thin Films, J. Mort and F. Jansen, Eds. CRC Press Inc.: Boca Raton, Florida, 2005, pp. 89-128.

[4] P. Ruffieux, O. Groning, P. Schwaller, L. Schlapbach, P. Groning, "Hydrogen atoms cause long-range electronic effects on graphite," Phys. Rev. Lett., vol. 84(21), pp. 4910-4913, May 2000.

[5] A. von Keudell, and W. Jacob, "Elementary processes in plasma-surface interaction: H-atom and ion-induced chemisorption of methyl on hydrocarbon film surfaces," Prog. Surf. Sci., vol 76(1-2), pp. 21-54, Sep. 2004.

[6] Y. Yamazaki, K. Ishikawa, N. Mizuochi, S. Yamasaki, "Structural change in diamond by hydrogen plasma treatment at room temperature," Diam. Relat. Mater., vol. 14(11-12) pp. 1939-1942, Nov. 2005.

[7] M. S. Wagner, and D.G. Castner, "Analysis of adsorbed proteins by static time-of-flight secondary ion mass spectrometry," Appl. Surf. Sci., vol. 231-2, pp. 366-376, Jun. 2004.