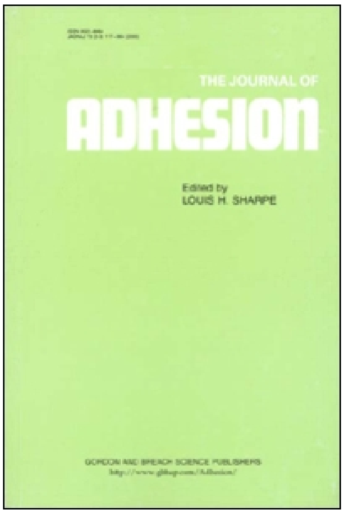

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A Study of the Effects of Low Power Plasma Treatment on Graphite and Highly Orientated Pyrolytic Graphite (HOPG) Surfaces*

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We have studied both the chemical and topographical changes induced on graphitic surfaces by low power plasmas using surface-sensitive X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and atomic force microscopy (AFM). Evidence is presented for two totally different reaction mechanisms for air plasma and nitrogen plasma interactions with these surfaces. Both plasmas chemically alter the first few atomic layers of the surface; however, air plasma treatment results in the formation of an oxidised layer, whereas nitrogen plasma treatment generates a much more open structure of loosely adhered material.

KEY WORDS: Graphite; highly oriented pyrolytic graphite (HOPG); contact mode atomic force microscopy (AFM); tapping mode AFM; X-ray photoelectron spectroscopy; plasma treatment

1. INTRODUCTION

Plasmas have been widely used to improve the adhesive properties of surfaces, e.g., Refs. 1–3. One such application is the treatment of carbon fibres in an attempt to improve their adhesion to epoxy resins[4]. Although such treatments are successful, the interaction of the plasma with the fibre surface is not yet fully understood. Carbon fibre surfaces consist of basal plane graphite, edge sites and defect sites. Instead of using carbon fibres, we have chosen two different graphitic surfaces for our experiments, namely graphite and highly orientated pyrolytic graphite (HOPG). This will allow us to understand how plasma interactions occur at the edge sites and on the basal planes.

Several research groups have investigated the effects that plasmas have on graphitic surfaces, e.g., Refs. 5–8. Evans and Kuwana[5] presented evidence to suggest that an oxygen plasma was capable of reacting with both the edge sites and basal planes.

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Scanning electron microscopy (SEM) did not reveal any change in the topography of these surfaces. Several years later similar results were obtained by Jones and Samman[9], by using a grazing angle XPS data collection technique. They showed that changes to the chemistry of the graphitic surfaces introduced by an air plasma remain at the first few atomic layers. Surprisingly, only one type of chemical group was introduced onto the graphitic basal plane which was thought to be of hydroquinone-like structure. Extending their study to carbon fibres revealed evidence for the introduction of carboxyl groups onto edge sites.

When a carbon surface is treated with a plasma it becomes "activated" and on exposure to air will adsorb contaminants from the environment, typically moisture. The reason for this activation has not yet been fully defined; however, it most likely results from a combination of increasing surface area, an increase in surface energy, and the introduction of metastable polar chemical functionalities which have a high affinity for moisture. This may overshadow the surface chemical changes induced by the plasma itself. For this reason, chemical characterisation of selected samples has been carried out *in situ* using XPS.

XPS is a technique with relatively low spatial resolution. To highlight whether reactions have occurred on basal planes or edge sites, field emission electron excited Auger spectroscopy has been used.

Any topographical changes to these surfaces are well below the resolution capability of the SEM. It is, therefore, necessary to use a scanning probe technique such as scanning tunnelling or atomic force microscopy to monitor the topographical changes occurring. Graphite has been extensively studied by scanning probe techniques, *e.g.*, Refs. 10–12. However, most have concentrated on scanning tunnelling microscopy (STM) due to the conducting nature of the substrate and the ease with which atomic resolution imaging can be obtained. We chose to use atomic force microscopy which lends itself more readily to larger scan area investigations. The features present are very loosely bound to the surface. In this paper, we will compare the images obtained from both contact and tapping mode AFM and highlight some of the pitfalls in collecting such images.

EXPERIMENTAL PROCEDURE

Materials

Samples of highly orientated pyrolytic graphite (HOPG) were supplied by Union Carbide, enabling analysis of an uninterrupted basal surface. Samples were prepared as 1 cm squares and freshly cleaved before each treatment and subsequent analysis. For the Auger chemical mapping, a step (~ 1 mm) was produced on a sample of HOPG so that both basal plane and edge sites could be analyzed. The graphite used was of ultra "F" purity, obtained from the Ultra Carbon Corporation, supplied as 1/2-inch, (1.27 cm) rods, allowing discs to be made for treatment and analysis.

Plasma Treatment

Plasma treatments were carried out with a plasma cell built in-house. A half-wave helical resonator was formed from a 100-turn coil wound directly on the outside of a glass tube and centred within a shield made from 3" (7.6 cm) brass tubing. A simple self-excited, two-transistor oscillator delivered radio frequency energy to the centre of the helix at the resonant frequency (~ 13 MHz). Low power levels of less than 1 W were sufficient to sustain a plasma within the tube. This has been described in more detail elsewhere[13].

The carbon samples were mounted onto XPS sample stubs, held on the end of a transfer rod by means of a stainless steel frame. Treatments were performed at an operating pressure of 10^{-1} Torr, ambient temperature and a gas flow rate of 85 standard cubic centimetres per minute (sccm). Flow was controlled by means of an MKS mass flow controller with an operating range of 0–100 sccm. Treatment times varied in duration from one second up to a maximum of ten minutes, for both air and nitrogen plasmas.

X-ray Photoelectron Spectroscopy

Tests were performed by directly attaching the plasma treatment cell to the preparation chamber of the Scienta ESCA300 Spectrometer, which allowed us to study the immediate effects of the plasma on the carbon surfaces. Direct transfer from the plasma cell to the preparation chamber of the XPS was possible as the plasma system was fitted with the wide range turbomolecular pump, operating at pressures between 10^{-1} and 10^{-6} Torr. This enabled the transfer of samples, by means of the transfer rod and the existing ESCA300 transfer mechanism, for XPS analysis before exposure to the atmosphere. Analyses were performed using an aluminium Kα X-ray source (1486.6 eV), with all spectra obtained using a photoelectron take-off angle of 40°. Survey spectra were obtained using a pass energy = 300 eV and high resolution C1s, O1s and N1s spectra with a pass energy = 150 eV. All spectra were referenced to the C–C peak in the C1s spectra whose binding energy was taken as 285.0 eV. Relative atomic percentages were calculated using peak areas, with compensating sensitivity factors of C = 1.00, O = 2.80 and N = 1.73.

Atomic Force Microscopy (AFM)

Samples were analyzed on the the sub-nanometre scale using the Digital Instruments Nanoscope III Atomic Force Microscope, equipped with a 16 μm scanner and a multimode AFM head which may be used in either contact or tapping modes. Samples were analyzed in contact mode using a silicon nitride cantilever, with a tip apex-to-substrate distance of 200 μm, operating in constant force mode, giving variations in vertical displacement. For tapping mode AFM, 125 μm long silicon tips were used, which were resonant at approximately 300 KHz, also operated in constant force mode. Large scale spectra were obtained over 16 μm squares with smaller scale spectra taken at 595 nm x 595 nm. Tests were repeated over approximately five sample areas, to prove the reproducibility of the results.

Auger Electron Spectroscopy (AES)

Auger chemical mapping of the sample was performed using a VG Microlab II high spatial resolution Auger system operated at 30 kV. The field emission gun was capable of delivering a primary beam current of 10 nA into a 30 nm spot. The instrument was also used for some XPS analysis of samples after exposure to air. Samples, in this case, were analyzed using an Al Kα X-ray source (1486.6 eV), pass energy = 100 eV for the survey scan and pass energy = 10 eV for the high resolution spectra.

RESULTS AND DISCUSSION

Surface Chemical Changes

The Effect of a Nitrogen Plasma

A series of survey spectra taken from HOPG treated with a nitrogen plasma for different lengths of time is shown in Figure 1. The amount of nitrogen introduced onto the HOPG surface increases with time. On exposure to air the spectra from these surfaces change. The N1s signal disappeared and in its place an O1s signal of similar intensity appeared. The amount of oxygen adsorbed after exposure to air depended on the plasma treatment time. A plot of the O1s signal intensity with treatment time is shown in Figure 2a. This does not directly follow the introduction of nitrogen onto the basal planes which implies that nitrogen is not simply being replaced by oxygen on the surface. It has previously been suggested[9] that the basal planes of graphite become "activated" after plasma treatment and that this activated surface adsorbed moisture

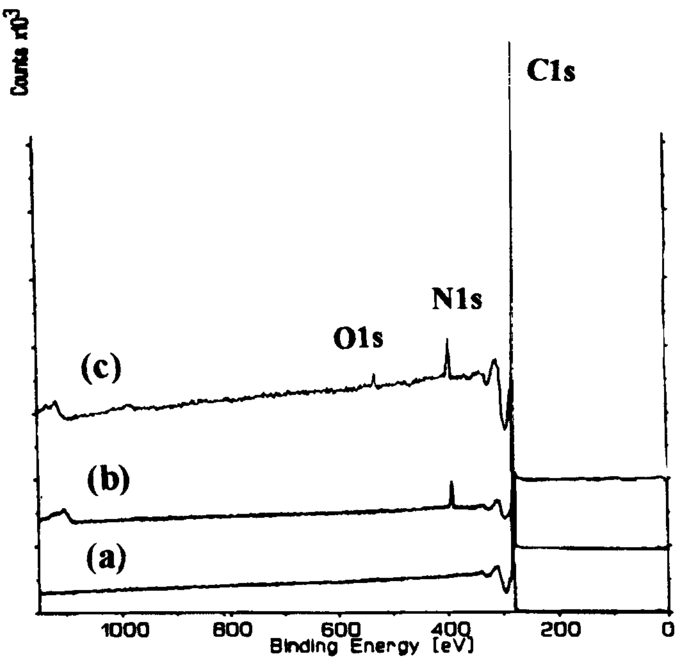


FIGURE 1 Survey spectra of HOPG: a) Untreated, b) after 20 seconds and c) after one minute of nitrogen plasma treatment, before exposure to air.

on exposure to air. However, in those experiments the nitrogen plasma did not chemically alter the HOPG surface, *i.e.* nitrogen was not detected on the sample surface immediately after treatment. The data in this latter case were collected on a Perkin Elmer 5400 using an unmonochromatised X-ray source. The XPS data obtained from our current experiments were collected at a surface-sensitive angle on a Scienta 300. The X-ray flux is much more intense than that of the PHI5400 and the instrument almost certainly has a greater sensitivity.

The treated *graphite* sample retained some of its nitrogen on exposure to air. Figure 2b shows how the level of both oxygen and nitrogen changes with treatment time. Once again, the level of oxygen present shows a maximum at shorter treatment times. The reason for this is as yet unexplained but it implies that the activation of the surface is greatest at these short treatment times. These results, however, give strong evidence that the nitrogen introduced onto the basal planes is not strongly bound, yet nitrogen-containing groups introduced onto the edge sites of graphite are stable. To confirm these results, an HOPG sample was prepared containing a scratch which exposed a large number of edge sites. Figure 3 shows three (AES) elemental maps (C, O, N) and a secondary electron image from this sample treated with nitrogen plasma after exposure to air. The edge sites of the HOPG are clearly visible in the secondary electron image. It is clearly evident that the N KLL signal is much more intense on the edge sites than on the basal planes. The O KLL signal, however, is uniformly intense over the whole of the sample region.

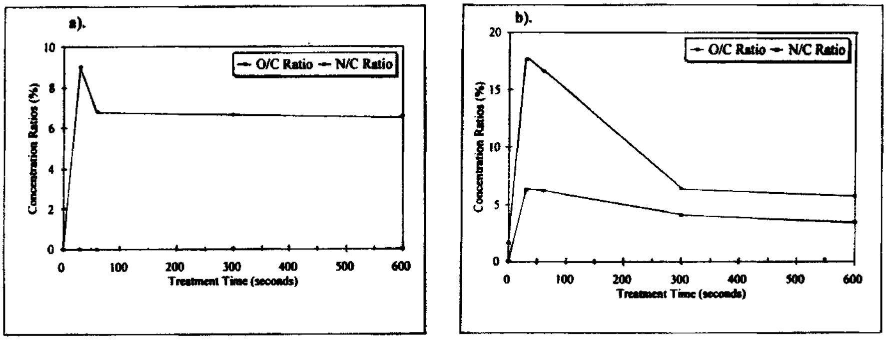


FIGURE 2 The effects of nitrogen plasma treatment time on the surface chemistry of a) HOPG and b) Graphite, *after* exposure to air.

TABLE I
Surface oxygen concentrations after various treatment times using an air plasma

Treatment Time	HOPG O1s (atomic %)	Graphite O1s (atomic %)
Untreated	0	2
30 seconds	13	22
1 minute	12	17
10 minutes	12	18

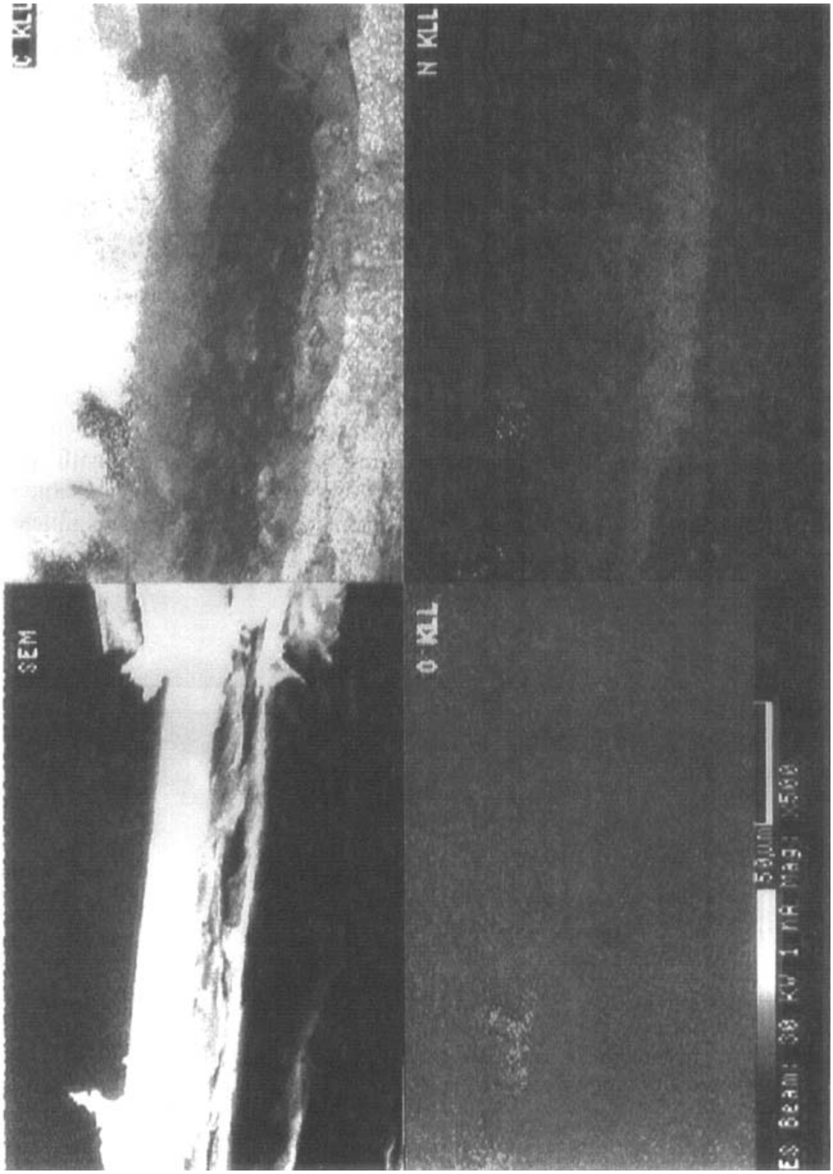
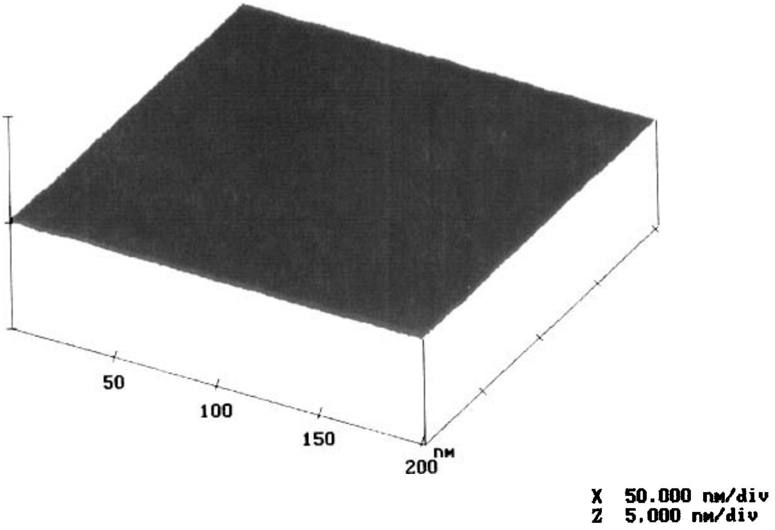


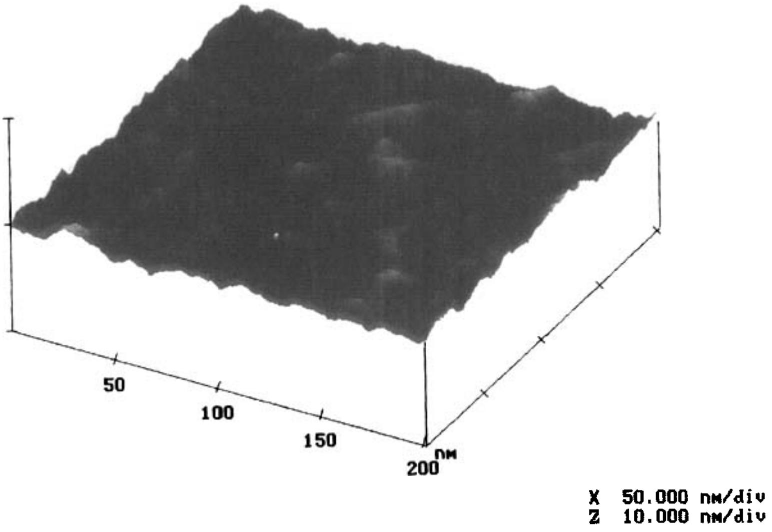
FIGURE 3 SEM image and C KLL, N KLL and O KLL AES maps of a step on HOPG.

The Effects of An Air Plasma

Both the HOPG and graphite samples are oxidised by an air plasma. Examination of the C1s spectra reveals that the treated HOPG surface contains mainly hydroquinone-

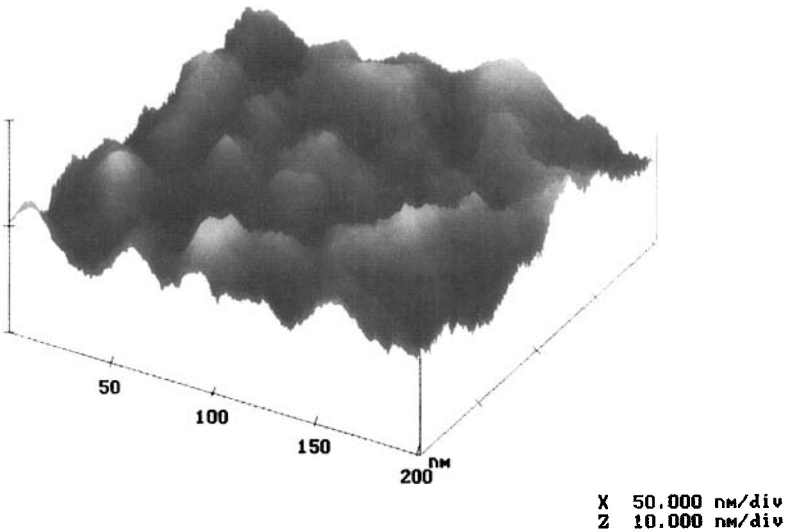


(a) Contact AFM: HOPG, untreated.



(b) Contact AFM: HOPG, 5 mins air.

FIGURE 4 Contact mode AFM scans of HOPG: a) Untreated, b) after 5 minutes of air and c) 5 minutes of nitrogen plasma treatment.



(c) Contact AFM: HOPG, 5mins nitrogen

FIGURE 4 *(Continued.)*

type functionality and the graphite sample contains keto-enol and carboxyl-type functionality. This agrees well with results previously obtained from HOPG and carbon fibre surfaces[9,10]. A nitrogen signal was not present in the XPS spectrum of the HOPG sample. This was expected since the nitrogen incorporated onto the basal planes is not strongly bound and can easily be replaced by oxygen as suggested in the previous section. Only a very small N1s signal was present in the spectrum from the graphite sample suggesting that the oxygen species in the air plasma preferentially react with the surface even at edge sites. Table I shows how the amount of oxygen present on the surfaces changes with treatment time. The level of oxidation seems to saturate out at 12% for HOPG and 18% for graphite. This has been seen by several other research groups using oxygen plasmas (see, *e.g.*, Ref. 7).

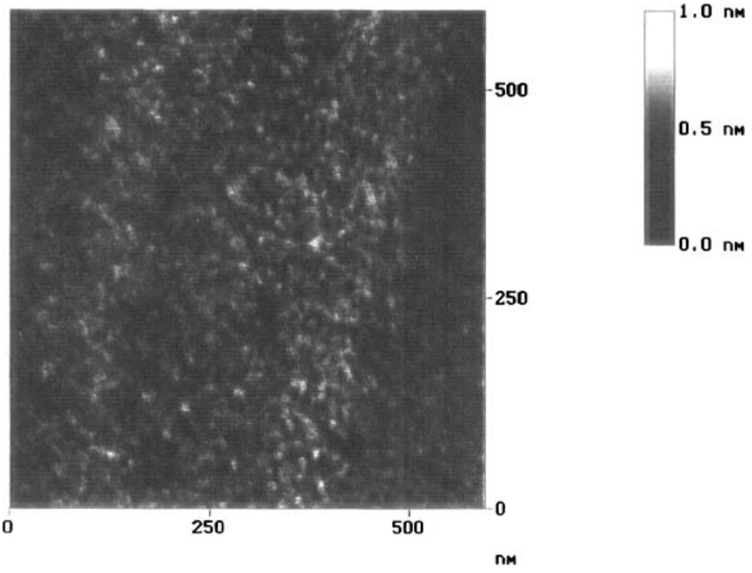
Changes in Surface Topography

It is known that chemical changes occur within the outermost layer of the substrate as such changes are not detected unless XPS data are collected at surface-sensitive angles. Such data are representative of the top 10–20 Å and any topographical changes on this scale would not be seen using scanning electron microscopy. We have, therefore, used atomic force microscopy to study these surfaces.

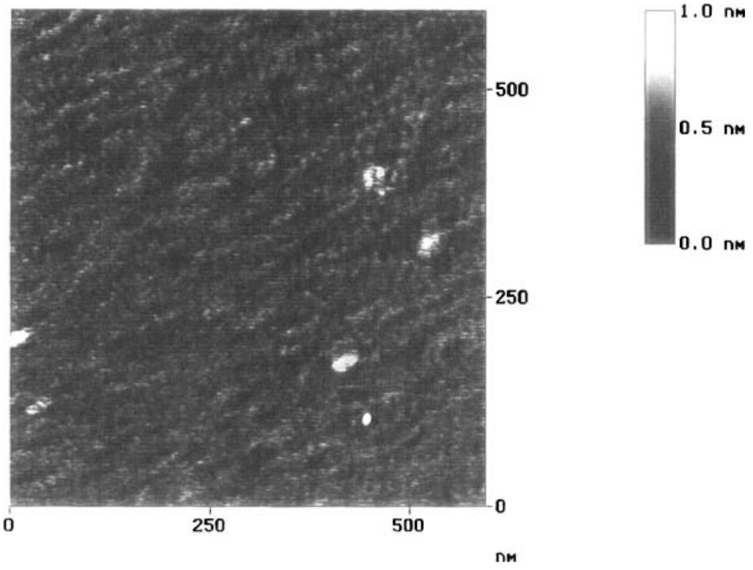
Contact Versus Tapping Mode AFM

Initially, plasma-treated HOPG samples were examined using contact mode AFM. As expected, the surface to freshly cleaved HOPG was atomically smooth. Both types of plasma treatment caused a roughening of the surface. The peak-to-trough distances were slightly higher than expected, especially for nitrogen plasma treatment (~ 7 nm).

This type of structure has been observed using STM on argon plasma treated surfaces[14]. They attributed this surface structure to a selective sputtering mechanism. However, in our system, where the power is over an order of magnitude less, ballistic sputtering is not thought to occur.

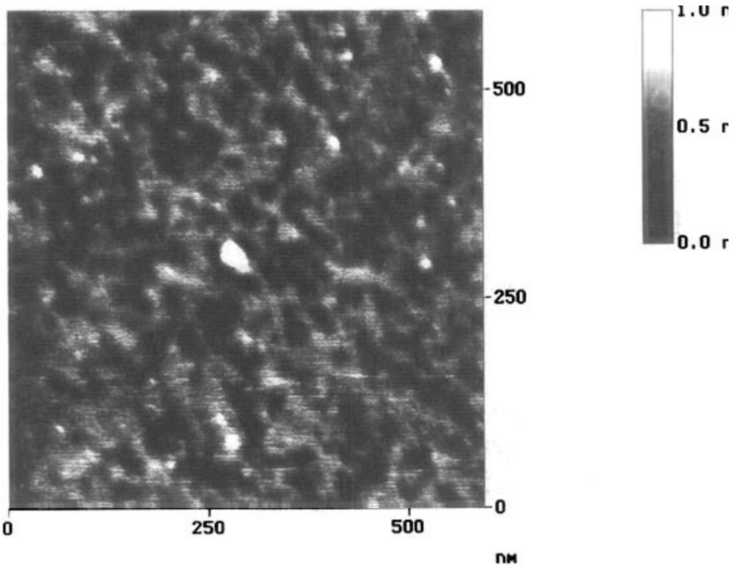


(a) Tapping AFM: HOPG, 20s air.



(b) Tapping AFM: HOPG, 1min air.

FIGURE 5 Tapping mode AFM scans of HOPG after a) 20 seconds, b) one minute and c) five minutes of air plasma treatment.



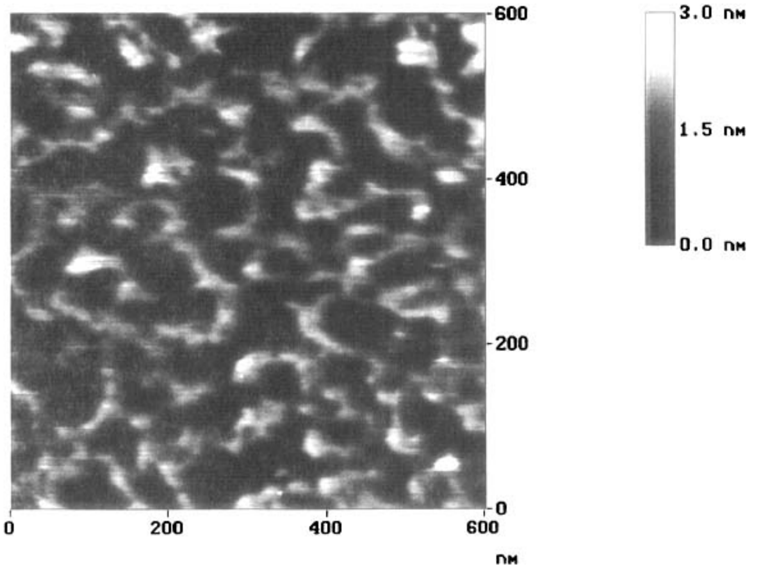
(c) Tapping AFM: HOPG, 5mins air.

FIGURE 5 *(Continued.)*

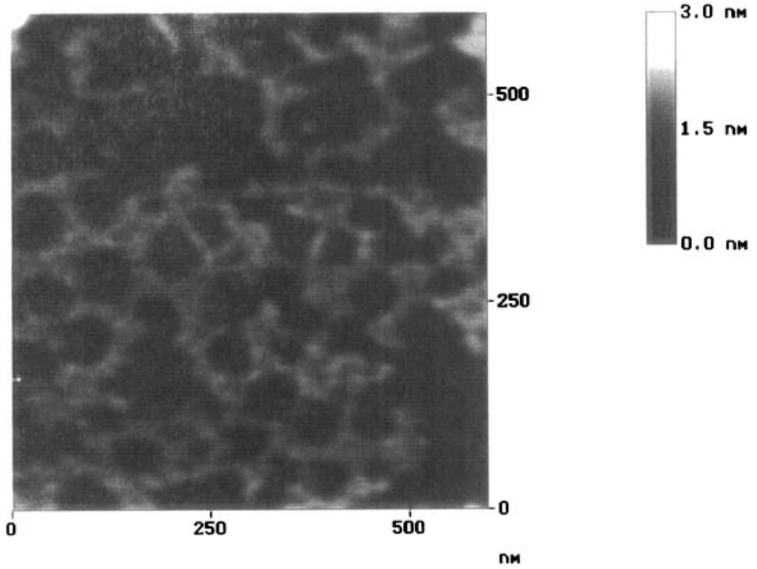
While collecting our images it was noticed that the first few scans were poor, in fact it appeared as if something was being dragged across the surface. However, after two or three scans the signal stabilised and good quality images were obtained. Reducing the force applied to the tip altered the peak-to-trough distance for these samples quite significantly. At the minimum force interaction required for contact AFM, average peak-to-trough distances of 3.6 nm and 1.0 nm were obtained for nitrogen and air plasma treated surfaces, respectively. The images obtained are shown in Figure 4. In the case of the nitrogen plasma treated sample there was still some evidence that some material was being dragged across the surface. With this in mind, we reverted to using tapping mode AFM.

Tapping mode AFM images taken from HOPG samples treated with an air plasma and a nitrogen plasma for several treatment times are shown in Figures 5 and 6, respectively. Clearly, the two plasmas alter the surface topography in totally different ways. The surface of the air plasma treated HOPG is roughened on a sub-nanometre scale. The average peak-to-trough distances is of the order of 0.3 nm. This is significantly less than that suggested by the contact mode data from similarly-treated samples. This distance is approximately equal to the interplane spacing for HOPG (0.336 nm) and does not change with treatment time. This adds support to the view that a saturation of surface sites occurs within 20 seconds of treatment time. However, as yet we have not determined whether this is a true saturation or a layer-by-layer etching mechanisms.

The images obtained for nitrogen plasma treated surfaces shown a more open structure at short treatment times. The images for 20 seconds and 1 minute are quite different from that obtained after 5 minutes of plasma exposure. The peak-to-trough

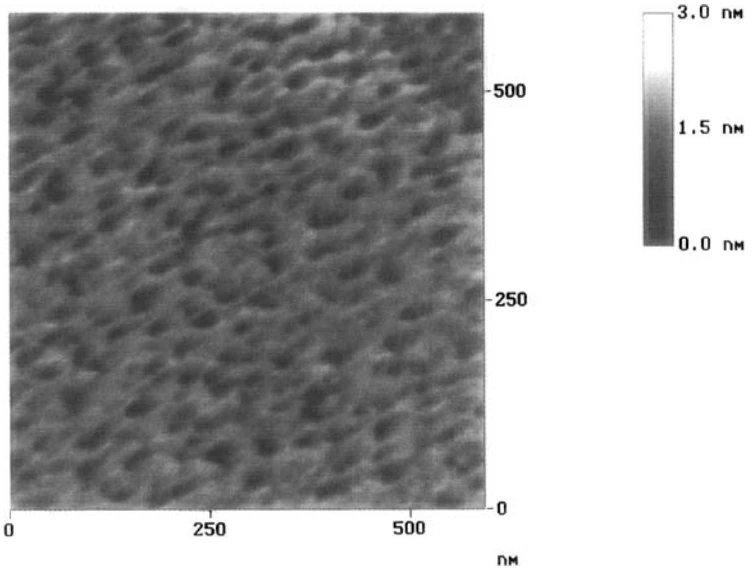


(a) Tapping AFM: HOPG, 20s nitrogen



(b) Tapping AFM: HOPG, 1min nitrogen.

FIGURE 6 Tapping mode AFM scans of HOPG after a) 2o seconds, b) one minute and c) five minutes of nitrogen plasma treatment.



(c) Tapping AFM: HOPG, 5mins nitrogen.

FIGURE 6 *(Continued.)*

distance for all samples is uniform across the sample, being of the order of 0.7 nm. For the shorter treatment times the bases of the troughs are atomically smooth. Their size is generally larger after one minute than for 20 seconds treatment time. After treating the samples for five minutes, the lateral dimensions of the troughs become much smaller and their concentration increases. Typical line profiles for samples treated in each plasma for 1 minute are shown in Figure 7.

The production of a weakly bound layer in the case of nitrogen plasma treatment is in keeping with the result obtained previously for the nitrogen plasma treatment of carbon fibres.[4] Fibres which had undergone nitrogen plasma treatment and had been immersed in resin before exposure to air adhered well to the epoxy resin; however, if the treated fibres were exposed to air before being immersed in resin the level of adhesion was low. At the time, these results were attributed to the adsorption of moisture onto

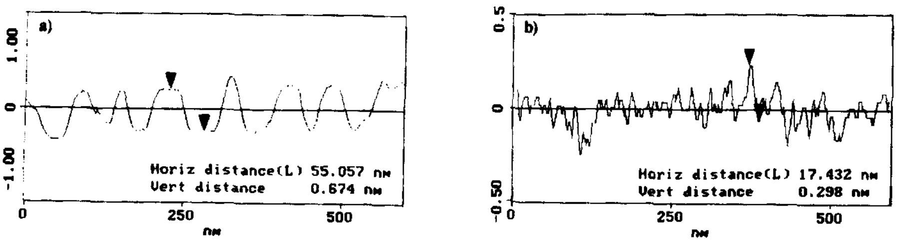


FIGURE 7 Line profiles showing peak-to-trough heights of treated HOPG surfaces after a) one minute of nitrogen and b) one minute of air plasma treatment.

the treated fibre which acted as a barrier layer inhibiting chemical bonding between epoxy resin and the functional groups introduced onto the fibre surface by the plasma treatment. The results presented in this paper confirm this conclusion and, in addition, show that the chemical functionalities introduced onto the basal planes of the carbon fibre are likely to be unstable and are removed when exposed to air. It is the combination of these two phenomena that results in the poor level of adhesion. In contrast, fibres treated with an air plasma showed good adhesion to epoxy resins. Full details of this fibre work are described elsewhere[15,16].

CONCLUSIONS

These results show that nitrogen and air plasmas interact with graphitic surfaces *via* totally different mechanisms. The oxygen species in an air plasma are much more reactive than the nitrogen species. Using a nitrogen plasma, only the functional groups introduced at the edge sites are stable on exposure to air. There is also evidence that activation of the basal planes occurs. Nitrogen plasma treatment introduced an open structure which was very weakly bound to the underlying graphite layers. In contrast, air plasma treatment apparently results in an oxidised surface layer being present on the surface. Both plasmas only affect the top 3–4 layers of the surface, at most.

We have also shown that it is essential to use tapping mode AFM to examine the true topography of these treated surfaces, as much of the chemically, altered layers are very weakly bound to the underlying substrate.

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