Nanoscale studies of the oxidation and hydrogenation of graphite surface

Z. Klusek *, P.K. Datta, W. Kozlowski

Advanced Materials Research Institute, University of Northumbria, Ellison Building, Ellison Place, Newcastle upon Tyne, NE1 8ST, UK

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Abstract

Nanoscale studies of the thermal oxidation and hydrogenation of graphite surfaces have been investigated using scanning tunnelling microscopy and scanning tunnelling spectroscopy. These techniques have been used to study the electronic states of the islands located at the edges of thermally oxidized and hydrogen-etched graphite surface. Spectroscopy results have shown the presence of $Q_{2\pi}^{\pi}$, $Q_{2\nu}^{\pi}$, $Q_{2\nu}^{\pi'}$, $Q_{2\nu}^{\pi'}$, IS and negative differential resistance electronic states recorded over islands of such treated graphite. However, these states vanish on various regions on the thermally oxidized graphite islands. This is ascribed to the disappearance of $\pi/\pi'$ bands when the graphite surface oxidizes and indicates the presence of oxygenated groups on the graphite surface.

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1. Introduction

The thermal oxidation of graphite leads to the removal of monoatomic carbon layers from the surface and the formation of patches and circular pits on the exposed plane [1–8]. It has been shown that the mechanism of carbon–oxygen reaction depends strongly on the temperature. At temperatures below 700 °C the oxidation process is generally initiated at defects like steps [4,5], while above 700 °C oxygen reacts with carbon atoms in the basal plane [4,5].
An interesting question arises whether the oxidation of carbon leaves oxygen functionalities on the surface. The existence of oxygen heterogroups (C–OH, C–OOH) could provide protection against further oxidation of the surface particularly important when consisting of graphite in nuclear reactors. The analysis of thermally oxidized graphite surface by X-ray photoelectron spectroscopy (XPS) [2], Auger electron spectroscopy (AES) [2] and Raman spectroscopy [9] showed no traces of oxygen. However, the sensitivity of these techniques is not high enough to detect very small amounts of oxygen functionalities likely to appear on the surface. Unlike XPS, AES and IR, the other surface sensitive methods such as surface-enhanced Raman spectroscopy [9] and Thermal desorption spectroscopy (TDS) [10] were able to detect covalently bonded surface oxygen heterogroups.

In our previous paper [11] we suggested the use of scanning tunnelling microscopy/spectroscopy (STM/STS) technique to clarify the presence of oxygen functionalities on the graphite surface. The advantage of STM/STS is that, it gives information on the electronic structure of the investigated surface with atomic spatial resolution. This is due to the fact that the first derivative of the tunnelling current with respect to voltage i.e. \(\frac{dI}{dV}\) gives the measure of local electron density of states (LDOS) of the sample [12]. Since, the \(\frac{dI}{dV}\) is related to the chemical composition of the surface and their crystallographic structure, thus can be used to indicate any difference in comparison with pure graphite. These differences are related to the surface defects like: step edges, pit edges or covalently bounded surface oxygen heterogroups. Our spectroscopic data led to the conclusion that the oxygenated groups appear only at the small islands located at the step/pit edges on the thermally oxidized graphite surface. The finding of energetic heterogeneity (considered in terms of LDOS changes) on the islands indicated that the oxidation process was not uniform even in very small areas [11]. However, the question on the origin of the islands and their chemical composition was not resolved.

The purpose of this study is to gain further knowledge on the early stages of oxidation of graphite by obtaining a detailed understanding of the tunnelling spectra on the islands located at the step/pit edges on the thermally oxidized graphite. To achieve this aim we used both thermally oxidized graphite and graphite treated by atomic hydrogen. The advantage of using graphite exposed to atomic hydrogen followed by heating is that this method also leads to the formation of circular pits and steps on the exposed plane [13] without creating the covalently bonded oxygenates groups at the step/pit edges. The atomic hydrogen treatment leads only to the appearance of hydrogen terminated carbon atoms at the edge. As the C–H bond is the \(\sigma^*/\sigma\) states and does not mix with \(\pi/\pi^*\) states of graphite [14,15], it will be possible to investigate the influence of surface defects (islands) related to oxidation and hydrogenation on the tunnelling spectra separately.

In this paper we present some results of tunnelling spectroscopy performed on the thermally oxidized graphite and on the hydrogenated graphite surface followed by heating. The influence of the surface defects on tunnelling current is described. Finally, the significance of our results for better understanding of the process of graphite oxidation is elaborated.
2. Experimental

The common form of graphite is a hexagonal graphite, which consists of layers with honeycomb arrangement of carbon atoms. Neighbouring layers are shifted relative to each other leading to the ABAB... stacking sequence. The rhombohedral form with an ABCABC... stacking sequence forms 5–15% of natural graphite, however this form cannot be isolated from the hexagonal form. Since the naturally occurring graphite crystals are small the widely studied form of graphite is the highly oriented pyrolytic graphite (HOPG) with a well defined (0001) basal plane i.e. HOPG(0001).

The graphite patches and pits were created by the use of thermal oxidation etching [11] and atomic hydrogen treatment [16]. During the hydrogen etching of graphite the chamber was filled with purified molecular hydrogen to a base pressure of $10^{-2}$ mbar. Then the dissociation process of molecular hydrogen into atomic hydrogen was carried out by the use of a 100 µm diameter tungsten wire heated to 2500 °C. The samples were exposed to an atomic hydrogen flux of $5 \times 10^{13}$ atoms/cm$^2$ s for 30 min followed by thermal heating of the sample up to 1400 °C to estimate the amount of desorbed hydrogen. The oxidation process of the HOPG(0001) surface was carried out in an externally heated quartz tube in ambient air condition. The heating was initiated by direct insertion of the sample into the tube preheated to the desired temperature and was stopped by withdrawing it from the tube. The experiments were performed at 700 °C. The heating time was 5 min. After the treatment the sample was cooled in a natural way in ambient air.

The STM/STS experiments were performed at room temperature with a commercial VT-STM/AFM system in UHV condition (Omicron GmbH). During the measurements performed the base pressure was of $2 \times 10^{-10}$ mbar. The tips used were prepared by the mechanically cutting from Pt$_{90}$–Ir$_{10}$ alloy wires. In the spectroscopic mode, the $I/V$ curves were recorded simultaneously with a constant current image by the interrupted-feed-back-loop technique. The $I/V$ curves were then stored in a laboratory computer and their voltage derivatives were obtained. After each acquisition sequence the surface was scanned again in order to observe the influence of spectroscopy measurements. In the case of visible surface damages, the spectroscopy data were not taken into account.

3. Results

3.1. Scanning tunnelling microscopy results

The STM studies carried out on thermally oxidized and hydrogenated graphite surfaces revealed the formation of patches and pits (Fig. 1(a) and (b)). The pits had different shapes, and appeared at different levels of the basal plane of the graphite sample. The depths estimated from the height profiles were in average 0.38 nm, which is roughly the spacing between the graphite layers (0.335 nm). Multilayer pits were also observed.
In both cases (hydrogenation, oxidation) it was also possible to observe regions with additional bright contrast at some etch-pit edges. These regions had shapes of irregular islands and were separated by unaffected graphite edges—as presented in Fig. 1(c) and (d). Furthermore, Fig. 1(c) shows the height profile across the pit (white line). According to the generally accepted view these islands can be assigned to the presence of oxygenated groups embedded within the sp² graphite network, when the thermally oxidized graphite surface is considered. However, this is not true in the case of hydrogenated graphite. It means that the bright contrast on the islands is not always caused by oxygenated groups. Clearly another mechanism is in operation. A detailed analysis of the tunnelling spectra carried out in this work has allowed us to
determine the basic spectroscopic properties of the island created by atomic hydrogen, and answer the question whether similar properties exist on the island created on thermally oxidized graphite.

3.2. Scanning tunnelling spectroscopy of pure graphite

Fig. 2 presents the $I/V$ curve and their derivative $dI/dV$ recorded on the pure graphite surface. The $dI/dV$ spectrum corresponding to the occupied states (negative voltage) shows two easily visible features. The main feature is a maximum in the density of states at around $-3.6$ eV, which is attributed to the flat $\pi$ band near the $Q_{2g}^-(\pi)$ point in the Brillouin zone [17]. Another one appears at $-3$ eV and is associated with the flat $\pi$ band near the $Q_{2u}^-(\pi)$ point in the Brillouin zone [17]. On the unoccupied part of the graphite spectra (positive voltage) a characteristic feature appears at $+1.8$ eV, and it is attributed to the specific points of the Brillouin zone: $Q_{2u}^+(\pi^*)$ and $Q_{2g}^+(\pi^*)$. Furthermore, we see a peak located at $3.2$ eV above the Fermi level (IS). The peak is related to the interlayer surface state [17]. In our measurements we were not able to resolve the $Q_{2u}^-(\pi^*)$ and $Q_{2g}^-(\pi^*)$ states. This is because in the high-energy spectroscopy ($\pm 4$ eV) we observed that the slope of the $I/V$ curve shows a drastic increase along with the voltage bias. It can qualitatively be explained by an increase of the tunnelling probability at large voltages. To overcome this problem, tunnelling spectroscopy measurements were performed at a larger tip-sample distance, i.e. at a smaller tunnelling probability. Furthermore, it is known that the $Q_{2g}^-(\pi^*)$ state is less visible in tunnelling spectroscopy experiments since it decays

Fig. 2. The $I/V$ curve and their derivative $dI/dV$ recorded on the pure graphite. Arrows mark the observed features.
faster into vacuum [17]. Then the convolution of the both factors, i.e. large tip-sample distance and specific nature of the $Q_{2g}(\pi^+)$ state, can make the state not appear in high-energy spectra at all.

### 3.3. Scanning tunnelling spectroscopy of thermally oxidized and hydrogenated graphite

The $I/V$ curve and their derivative $dI/dV$ recorded on the thermally oxidized graphite island (denoted by 1 in Fig. 1(c)) is presented in Fig. 3. The $I/V$ curve shows some differences in comparison with the spectra recorded on a pure graphite surface (Fig. 2). Mainly, at a negative bias voltage the decreasing of tunnelling current is associated with an increase in the absolute value of the bias voltage, i.e. with the presence of a negative slope in the $I/V$ curves. This phenomenon is called negative differential resistance (NDR) [18,19]. On the $dI/dV$ curve it is easy to observe that the presence of a negative slope in the $I/V$ curve produces NDR region on the $dI/dV$ plot (NDR $= -2$ eV); in addition the local maxima of LDOS are well recognized ($Q_{2g}^-(\pi)$, $Q_{2u}^-(\pi)$, $Q_{2u}^+(\pi^+)$, $Q_{2g}^+(\pi^+)$, IS). However, the problem whether the peaks at the occupied part of the spectra can only be attributed to the graphite bands is not obvious. This is because we observed strong NDR, so the tunnelling current could reflect both the density of states of the graphite and other effects such resonant tunnelling. Similar spectra were recorded on the islands denoted by 2, 3 and 4 as presented in Fig. 4. Furthermore, in Fig. 5 we present an example of $dI/dV$, which indicates energetic heterogeneity on some islands. In this case there are some regions

![Graph showing $I/V$ curve and $dI/dV$]
on the island denoted by 5 in Fig. 1(c), where $Q_{2g}^{-}(\pi)$, $Q_{2u}^{-}(\pi)$, $Q_{2u}^{-}(\pi^*)$, $Q_{2g}^{-}(\pi^*)$, IS, and NDR states were not resolved at all.

Fig. 4. The $dI/dV$ curves recorded on the thermally oxidized graphite islands denoted by 2, 3 and 4 in Fig. 1(c). Arrows mark the observed features.

Fig. 5. The $I/V$ curve and their derivative $dI/dV$ recorded on the thermally oxidized graphite island denoted by 5 in Fig. 1(c).
Fig. 6 shows the $I/V$ curve and their derivative recorded on the hydrogenated graphite island denoted by 1 in Fig. 1(d).

In principle the tunnelling spectra do not vary much from the one recorded on the thermally oxidized graphite and presented in Figs. 3 and 4, i.e. we easily recognize $Q_{2g}(\pi)$, $Q_{2u}(\pi)$, $Q_{2u}(\pi^*)$, $Q_{2g}(\pi^*)$, IS and NDR states. The spectra recorded on other islands were similar.

### 4. Discussion

The main experimental results of the paper presented in the previous section include:

- the presence of islands with additional bright contrast at the etch-pit edges on the thermally oxidized and hydrogenated graphite.
- the occurrence of $Q_{2g}(\pi)$, $Q_{2u}(\pi)$, $Q_{2u}(\pi^*)$, $Q_{2g}(\pi^*)$, IS and NDR states on the tunnelling spectra recorded over islands on the thermally oxidized and hydrogenated graphite.
- The presence of energetic heterogeneity resulted in disappearance of $Q_{2g}(\pi)$, $Q_{2u}(\pi)$, $Q_{2u}(\pi^*)$, $Q_{2g}(\pi^*)$, IS and NDR states on some regions on the thermally oxidized graphite islands.

In this section we will discuss the possible influence of the surface defects and heterogroups (C–OH, C–OOH) within the sp² graphite networks on tunnelling current. Following this, we consider the question whether the oxygen heterogroups exist on the surface.
In order to see the effect of bonded oxygen functionalities on tunnelling spectroscopy measurements, the surface heterogroups (C–OH, C–OOH) were created with the use of nitric acid, which is a well-known and effective procedure to oxidize graphite surface [20]. Then the oxidized graphite surface was analysed by XPS and by STM/STS techniques. The details were presented elsewhere [20,21]. In the present paper the important conclusions are listed below.

The XPS analysis revealed a clearly visible O1s core level after the acid treatment of the graphite sample. The comparison of C1s photoelectron lines before and after oxidation showed additional structures on the oxidized sample. These structures were due to the functionality groups created on the graphite surface by acid oxidation [20,21]. Additionally, all structures on the high binding energy side of the C1s peak were less intense after the oxidation process. These structures were attributed to \( \pi^* \) shake-up satellites and involved the transitions between the occupied and the unoccupied bands of graphite. Their decrease was also a strong indication that both the valence and conduction bands were affected by oxidation.

A general evolution of LDOS i.e. \( \frac{dI}{dV} \) revealed by STS on the oxidized graphite was connected with the vanishing of the \( Q_{2g}(\pi) \), \( Q_{2u}(\pi) \), \( Q_{2u}(\pi^*) \), \( Q_{2g}(\pi^*) \) states and sporadic the appearance of the maximum of electron LDOS close to the Fermi level. The vanishing of the \( \pi/\pi^* \) bands for oxidized graphite was well correlated with the decrease of the \( \pi^* \) shake-up satellite from the C1s core level revealed by XPS. Obviously, the consequence of surface oxidation, which has also been demonstrated by XPS, is the creation of oxygen functionalities on the surface. In order to create functional groups, carbon–carbon bondings have to be broken before fixing oxygen. Then the sp\(^2\) hybridization that describes pure graphite was no longer valid and the sp\(^3\)-like bonds form. As a consequence \( \pi/\pi^* \) bands should disappear when the graphite surface oxidizes, which is seen on \( \frac{dI}{dV} \) curves [21].

In our present STS investigations we observed disappearance of \( Q_{2g}(\pi) \), \( Q_{2u}(\pi) \), \( Q_{2u}(\pi^*) \), \( Q_{2g}(\pi^*) \), IS, and NDR states on some regions on the thermally oxidized graphite islands (Fig. 5). These results were considerably different from the results recorded on unaffected graphite surface (Fig. 2) and hydrogenated graphite islands (Fig. 6). Therefore, the disappearance of graphite states is not the feature of pure graphite and hydrogenated graphite, but the feature associated with the change of the chemical composition of graphite due to the oxidation process. Furthermore, we observed distinct disappearance of \( \pi/\pi^* \) electronic states only on some islands (compare Figs. 3 and 4 with Fig. 5), which proves that the oxidation process was not uniform even in the atomic scale.

The important result of our work is the conclusion that the presence of islands at the pit edges cannot directly be associated with the existence of oxygenates groups. It is because similar islands exist on hydrogenated graphite surface, where the absence of covalently bonded oxygen heterogroups is obvious. Thus not only topographic measurements (STM) but also technique that provide local spectroscopic information (STS) at the atomic level is required to determine the chemical composition on the surface.

The presence of islands at the pit edges in the case of hydrogenated graphite can be explained by the formation of hydrogenated tetrahedral amorphous carbon...
clusters embedded within sp² graphite network during hydrogenation [22]. For the formation of such structures, carbon–carbon bonding has to be rearranged leading to a change from the to the hybridisation. Since, we have a mixture of the sp² and sp³ sites the π/π⁺ bands do not vanish completely. Furthermore, the presence of surface disorder (sp³ in sp²) may lead to the appearance of additional electronic defect states and localised surface states because of the presence of the highly strained atomic network structure. We believe that our spectroscopic results (Fig. 6) showing distinct NDR are caused by the localised defect states (resonant tunnelling) as a results of a sp³-type disorder in the perfect sp² graphite network [22].

In the case of the islands created by the thermal oxygenation of graphite the situation might be more complicated. It is because the islands may origin not only from oxygenated groups but also from oxygen the free tetrahedral amorphous carbon clusters created by the oxygen attack. This assumption can explain why we observe well-defined NDR features not only in the case of hydrogenated graphite but also in the case of thermally oxidized graphite surface. In the case of oxygenated graphite the disappearance of the π/π⁺ bands indicates a relatively large agglomeration of oxygen heterogroups embedded in the mixture of pure graphite and amorphous carbon clusters. As far as we know interaction effects related to the structure of such mixtures have not yet been addressed. More research needs to be done to understand the influence of the local surface defects on the obtained results.

5. Conclusions

By the use of STM we have observed islands with additional bright contrast at etch-pit edges on the thermally oxidized and hydrogenated graphite surface. The STS results recorded on the islands on the thermally oxidized and hydrogenated graphite have shown the presence of $Q_{2g}(\pi)$, $Q_{2u}(\pi)$, $Q_{2u}(\pi^+)$, $Q_{2g}(\pi^+)$, IS and NDR states. However, in some cases we observed energetic heterogeneity resulted in the disappearance of the mentioned states on various regions on thermally oxidized graphite islands. This is ascribed to the disappearance of π/π⁺ bands when the graphite surface oxidizes and indicates the presence of oxygenated groups on the graphite surface. Finally it is clear that STS has allowed to carry out a detailed study of the early of graphite oxidation.

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References