Scanning tunneling spectroscopy study of the edge surface states on oxygen-etched graphite surface with the presence of liquid crystal steps

Z. Klusek*

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

Abstract

Scanning tunnelling microscopy and spectroscopy are used to study electronic states at the edges of the monolayer graphite pits and liquid crystal steps. The graphite edge surface state exhibits a maximum in the local density of states in the energy range of 0.02 – 0.15 eV above the Fermi level. The edge state on the liquid crystal steps is not seen by tunnelling spectroscopy measurements. It is caused by the lack of the carbon zigzag regions leading to specific topology of the π electron networks.

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1. Introduction

The tight binding band calculations performed on the single-layer graphite ribbon with edges of two shapes such as zigzag and armchair, show specific localised states depending on the edge shape [1–4]. The ribbon with zigzag edge shows localisation of the electrons near the edge and peak in the density of states (DOS) near the Fermi level — localised edge state. The localised state stems from the topology of the π electrons networks with the zigzag edge and does not appear in the armchair edge [2–4]. The influence of the localised state on the global electronic properties considered in terms of DOS is rather small when the ribbon width is large. However, in this case the localised state can be observed on the local density of states (LDOS) measured in the vicinity of the zigzag ribbon edges. Furthermore, the predicted edge state in single-layer ribbon is well reproduced in the zigzag edges of the multi-layer AB stacking ribbons [5,6]. This suggests that the localised edge state can be observed on more realistic surface like AB stacked bulk graphite instead of single-layer graphite ribbon.

In previous papers we proposed the thermal oxidation [5,7] and atomic hydrogen etching [8] of the (0001) basal plane of highly oriented pyrolytic graphite surface (HOPG) in order to remove carbon layers from the surface and to form monolayer and multilayer circular pits on the exposed plane.

*Corresponding author. Tel.: +44 191 227 3838; fax: +44 191 227 3684.
E-mail address: zbigniew.klusek@unn.ac.uk (Z. Klusek).
The circular geometry of the pit makes it possible to find the proper zigzag orientation of the step edge (running around the pit, see Fig. 1) and to detect the localised state by use of the tunnelling spectroscopy technique (STS).

The aim of the present study is to obtain graphite monolayer circular pits and the 8OCB (4-n-octyloxy-4′cyanobiphenyl) liquid crystal steps on the same surface. In the liquid crystal steps the lack of the carbon zigzag regions leading to specific topology of the π electron networks is obvious. A detailed analysis of the tunnelling spectra will enable us to determine whether the localised states near the Fermi level exist on the graphite edges. Furthermore, the results obtained will make it possible to evaluate the role of different height steps on the STS data. It is because characteristic features on the tunnelling spectra can be caused by topographic effects. The results can be useful in interpreting the spectra obtained from the physically adsorbed molecules on the defective graphite substrate [9].

2. Experimental

The graphite circular pits are created by the use of thermal oxidation etching [5,7,10,11]. First a new surface of the HOPG (0001) sample is prepared by cleavage with adhesive tape. Then the oxidation process is carried out in an externally heated quartz tube in ambient air condition. The heating is started by direct insertion of the sample into the tube preheated to the desired temperature and is stopped by withdrawing it from the tube. The experiments are performed at a temperature of 800°C. The heating time is 3 min. After the treatment the sample is cooled in a natural way in ambient air.

The 8OCB steps are created by placing a few μg of 8OCB crystal on the HOPG surface with thermally etched circular pits. Then the heating of the 8OCB/HOPG (0001) sample above the 8OCB isotropic transition temperature (~ 84°C) is carried out. The details are presented elsewhere [12,13]. As it has been found during the experiments the best topographical results (well defined steps) are obtained at the temperature of 110°C and the heating time of 5 min. After the treatment the sample is cooled in a natural way in ambient air.

The STM/STS results are obtained using an apparatus with spectroscopic facilities [14]. The studies are performed in air, in a constant current mode with a typical tunnelling current set point of 0.2–1 nA and the sample bias of +1 V. The tips are obtained by the mechanical cut from the Pt90%–Ir10% alloy wires. The I/V characteristics are recorded simultaneously with a constant current image by the interrupted-feed-back-loop technique.

3. STM results

In Fig. 2a typical image of etched monolayer pits on the HOPG (0001) sample treated at 800°C in air for 3 min is shown. A detailed structure of the pits can be seen by STM [5,7], while the depth of the etch pits can be estimated from the height profile. The average value is 0.35 nm, which is roughly the spacing between graphite layers and equals 0.335 nm. Double-layer pits are also observed.

In Fig. 2b STM images of the graphite sample with well visible monolayer pit edges accompanied with the 8OCB liquid crystal terraces and steps are shown. The liquid crystal region presents a number of well defined terraces whose width equals roughly 20 nm and its height 0.5–1 nm. In this case the microcrystallities of the 8OCB, that nucleate in the
form of a bulk rather than a two-dimensional molecular lattice, are observed. A detailed topographical analysis of the 8OCB liquid crystal structures on HOPG (0001) surface has been presented [12,13]. In the flat graphite regions a typical triangular structure with the spacing of about 0.25 nm between maxima in the image is resolved. We are dealing with pure graphite basal plane instead of adsorbed self-assembled monolayer of the 8OCB molecules, because the STM image of the two-dimensional 8OCB molecular lattice exhibits separated bright stripes with the spacing of about 5 nm between the maxima (Fig. 2c) [12,13].

The 2–4 nm region near the edges of the pit can be different from that in the smooth areas on the basal plane. In these regions a superstructure with the periodicity of $(\sqrt{3}x\sqrt{3})a$ ($a = 0.246$ nm) and rotated $30^\circ$ with respect to the underlying graphite lattice is often observed (Fig. 2d). This superstructure decays over a distance of a few nanometers from the edge of the pit. Similar structures can be seen on graphite near defects shaped like steps or adsorbed metal particles. It seems that the observed superstructures are electronic in nature, not a real surface reconstruction [15–17]. Apart from the well-known $(\sqrt{3}x\sqrt{3})R^{30^\circ}$ superstructure, a relatively unperturbed surface near the pit edges is also observed. In such regions a typical triangular structure of graphite with the spacing of about 0.25 nm between maxima in the image is resolved. In the case of pit edges showing triangular graphite structure, an extra contrast appears as small bright areas. This contrast can be assigned to the presence of the localised edge state.
4. STS results

The topographical results enable us to carry out STS measurements at different points over the graphite, graphite pit edges and liquid crystal step edges.

The $dI/dV$ versus bias voltage curve (measure of LDOS) recorded on the perfect graphite surface is presented elsewhere [18]. In this case it is possible to observe the state at about 0.65 eV below the Fermi level, which can be attributed to the point $P^+_1(\pi)$ in the graphite Brillouin zone. It is also possible to observe the $P^-_2(\pi^*)$ state located at about 0.80 eV above the Fermi level. The data are in good agreement with theoretical and other experimental results for unaffected graphite [19 and references therein].

In Fig. 3 the $dI/dV$ curves measured at different points at the graphite pit edges are presented. It is immediately seen that the strength of the observed $P^+_1(\pi)$ and $P^-_2(\pi^*)$ graphite states increases substantially. Furthermore, the $dI/dV$ curves show a distinct asymmetric form which is different from pure graphite. In this case instead of minimal increase of tunneling conductance at small bias voltages, we observe an abrupt increase of the $dI/dV$ quantity. In our interpretation the observed peaks located in the energy range 0.02–0.15 eV can be attributed to the localised edge state on the graphite pit edges. The observed features are well visible and cannot be mistaken with other graphite states.

Theoretical and experimental studies for a perfect graphite surface do not predict any states close to the Fermi level. This means that the interpretation of the peaks in the range 0.02–0.15 eV above the Fermi level as a localised edge state seems to be justified. The shift of the state energy can be explained by the influence of local surface defects on graphite band structure.

Additional studies show that the peaks attributed to the localised edge state decrease the distance from the pit edge. At about 1.5 nm from the pit the $dI/dV$ curves resemble the curves recorded over the unaffected graphite basal plane. The observations can be explained in terms of the decrease in the localised edge state magnitude with an increase in the distance from the pit edge [1]. Similar behaviour was reported previously [5,8].

The next stage of our studies aims at measuring the tunnelling spectra in the regions in which liquid crystal terraces and step edges are observed. In Fig. 4, the typical $dI/dV$ data, which are recorded over the edges are shown. In the presented curves, the increase of the tunnelling conductance near zero bias voltage (which can suggest the existence of the localised edge state) is not observed. The lack of the edge state does not depend on the distance from the liquid crystal step. Furthermore, the general shape of these curves resemble the tunnelling spectroscopy data obtained for the flat liquid crystal terraces. Unfortunately, the identification of

![Fig. 3. The $dI/dV$ data for occupied and unoccupied electronic states recorded close to the graphite pit edge.](image1)

![Fig. 4. The $dI/dV$ data for occupied and unoccupied electronic states recorded close to the liquid crystal step edges.](image2)
other spectroscopic features, i.e. peaks near ± 0.6 eV (denoted as Π1 and Π2) and shoulders located at about ± 0.3 eV (denoted as S1 and S2) is not an easy task. Because, the electronic properties of the 8OCB molecular three-dimensional (3-D) crystal on HOPG differ essentially from those calculated for the isolated molecule. As a result, a model with adsorbed single molecule treated as a potential well with discrete energy levels and gap defined by the HOMO-LUMO region cannot be used to evaluate the energy of the molecular resonant states [20–23]. In our opinion, in such a dense structure the final image will not be a simple superposition of effects observed over a single molecule. Then we should consider both molecule–substrate and molecule–molecule interactions in the 3-D systems. As far as we know interaction effects related to dense molecular structure have not yet been addressed [24].

In addition to the point tunneling spectroscopy, it seems to be interesting to analyze the spatial maps of the $dI/dV$ quantity recorded at a given bias voltage. In Fig. 5(a) the constant current image of the graphite edge accompanied with 8OCB liquid crystal terraces is presented. In addition to the topography, the $dI/dV$ spectra over the entire area have simultaneously been recorded. In Fig. 5(b) the map of the quantity $dI/dV$ for the sample bias + 0.1 V is presented. In this picture the bright contrast indicates a large value of $dI/dV$. Since the $dI/dV$ quantity is a measure of electronic local density of states, the image of Fig. 5(b) corresponds to the map of the LDOS surface at the energy of 0.1 eV above the Fermi level. From the inspection of this figure it is easy to observe a high LDOS at the graphite step edges, which can indicate the localized state. The results clearly show that the edge state is only caused by the presence of the zigzag regions which form the graphite pit edges. In the liquid crystal step edges the lack of specific topology of the π electron networks makes no contribution to the increase of LDOS near the Fermi level. Furthermore, the sample preparation procedure enables us to minimise some topographic effects when the $I/V$ characteristics are recorded simultaneously with a constant current topography. These effects are due to variations of the vertical tip position (in order to maintain constant current) which exponentially affect the tunnelling barrier height. As a result some features on the $dI/dV$ spectra can be caused by complicated surface profile. Similar to the case of surface scanning, the influence of topographic effects on the tunnelling spectroscopy results strongly depends on the adjusted parameters and vary from sample to sample. Fortunately, in our experiments both graphite and liquid crystal step edges are investigated simultaneously at the same conditions. Even though the topographic effects are unknown, they can be treated as the background of the same order to the $dI/dV$ quantity measured at different points. As a result the observed features close to the Fermi

![Fig. 5.](image-url)
level are simply interpreted as a graphite edge surface state.

5. Conclusions

By the use of tunnelling spectroscopy we have detected the localised state near the Fermi level on the circular monolayer pit edges on the thermally etched graphite surface. In our opinion the state is caused by the carbon zigzag edge sites. The edge state appears as the maximum of the local density of states in the energy range of 0.02 – 0.15 eV above the Fermi level. The state magnitude decreases with distance from the pit edge as theoretically predicted. The shift of the state energy in the range of 0.02 – 0.15 eV can be explained by the influence of local surface defects on the graphite band structure. The presence of the edge state on the 8OCB liquid crystal step edges is not observed. It is because of the lack of the carbon zigzag regions leading to specific topology of the π electron networks in the 8OCB molecular crystal system.

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References