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STM study of a grain boundary in graphite

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Abstract

A grain boundary in highly oriented pyrolitic graphite has been investigated by scanning tunneling microscopy (STM). Along the boundary, a periodic structure has been observed. Crystallographic models have been constructed in order to explain the bonding between the two grains and STM theoretical simulations have been carried out. They conclude to the probable presence of pentagon–heptagon chains at the boundary. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Highly oriented pyrolitic graphite (HOPG) has been studied extensively by scanning tunneling microscopy (STM). A clean sample is indeed easily prepared by cleavage and remains stable for a long time under ambient conditions. Being polycrystalline in nature, HOPG is composed of misoriented grains of micrometer size. However, very few observations of these grain boundaries have been reported by STM, probably because the grain size is large in comparison to the average scan range. Daulan et al. have shown atomic resolution of a tilt grain sub-boundary in graphite [1]. The observed dislocations could be interpreted in the frame of geometrical models.

After cleavage, the HOPG surface exhibits lots of defects like graphite flakes, steps, as well as coiled structures that complicate the interpretation of the STM images. It is interesting to recall that such graphite defects have even been confused with DNA strands [2]. Recently, experimental [3] and theoretical [4] STM images on carbon cones showed that the apex pentagon and the superstructure induced in the neighbourhood could be resolved. Moreover, Yoon et al. [5] showed theoretically that the interface between two HOPG grains could contain squares and octagons.

In this paper, we focus on one superstructure imaged by STM on a HOPG surface. This superstructure is observed running along the junction

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between two graphite grains and parallel to their boundary. Starting from the crystallographic orientations of the two lattices joining at the boundary, we succeeded in constructing a geometrical model that links the two lattices by replacing pairs of hexagons with pentagons and heptagons. The STM images obtained experimentally were then compared to simulated images obtained from theoretical calculations based on the reconstructed model. We conclude that the periodic structure observed by STM at the grain boundary can be explained by a regular succession of pentagons–heptagons pairs.

2. Experimental results

The STM microscope used in these experiments is a ''pocket size'' Easyscan microscope (Schaefer) operating in air and under ambient conditions. The images were recorded in the constant current mode with an intensity of 1 nA and a bias voltage ranging from 50 to 110 mV. The tip was mechanically cut from a Pt 80%–Ir 20% wire, immediately before use. The images were taken at a frequency of 3.6 Hz.

The HOPG was of ZYH grade (Advanced Ceramics). It was freshly cleaved before the experiments. The scan range available with the STM scanner (maximum 500×500 nm^2) is small in comparison to the graphite grains dimensions (several μm), and therefore it is usually difficult to observe the grain boundaries. The quality of the tip was confirmed by checking the atomic resolution on a flat terrace. The tip radius was evaluated to about 13 nm by performing a scan of a terrace edge. The STM images presented here are raw data. They are only corrected for the tilt, by subtracting a plane from the image.

Fig. 1 shows the STM image of a superstructure observed on HOPG. It appears like a left-handed double helix. This structure is more than 500 nm long and has a width of about 5 nm. On the left-hand side, the image is similar the ones published by Heckl and Binnig who attributed them to a grain boundary in graphite [6].

Usually, the connection between two grains of different orientations is made up of a series of defects surrounded by the almost undeformed hexagonal lattice. Stress and elastic deformations are induced during the joining. When the stress is released, it can create defects which are revealed as a superperiodic pattern. This is actually what we observe on this image. Indeed, the coiled structure can be interpreted as the result of elastic deformations on the boundary and the emergence of defects.

Fig. 2 displays a magnification of a lower part of the double helix, corresponding to a dark grey level, and delimited by the square drawn on Fig. 1.

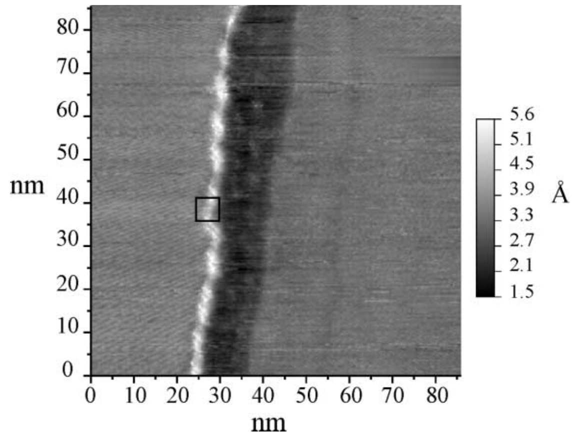

Fig. 1. STM image of HOPG with a coiled-like structure in the middle. This structure shows a double helix-like pattern and has a very small height. It is attributed to a grain boundary between two graphite grains of HOPG.

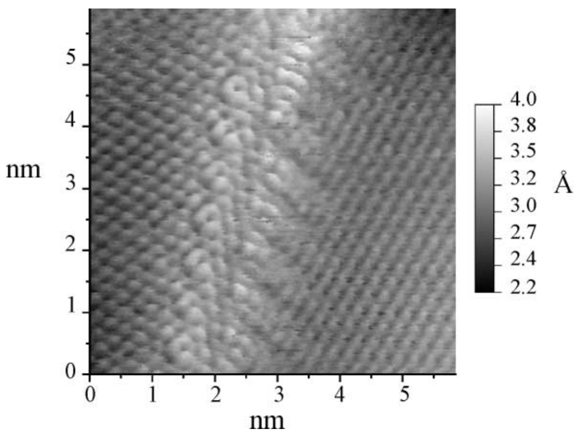

Fig. 2. Magnification of Fig. 1. One can see a superperiodic structure with the surrounding triangular pattern of graphite.

This magnified image was recorded with the same current intensity as for Fig. 1. From both sides of the imaged structure, we observe the typical arrangement of the hexagonal lattices of the two graphite grains. These two lattices are rotated by about 39° with respect to each other. Along the grain boundary periodically arranged protrusions appear as almost closed rings whose spatial separation is about 0.70 nm and whose shape is reminiscent of the one of 5-membered rings. Indeed, STM simulations performed on carbon nanotube junctions have previously shown that the STM signature of a pentagon–heptagon defect is roughly a ring of maximum intensity located around the pentagon [7].

3. Theoretical modelling

Taking into account the observed atomic structure of the two grains and their relative orientations, we looked for different possible models of joining the two lattices while keeping as low as possible the number of bonds affected by the process. The structure near the grain boundary was released by minimizing a molecular mechanics potential that incorporates quadratic dependences on bond-length and bond-angle variations. The structure, which consists of a single atomic sheet, was maintained flat during the process (no out-of-plane relaxation). We also tried to minimize the propagation of the distortions into the neighbouring lattices.

The best model obtained is represented in Fig. 3a. It makes use of a linear chain of abutting pentagons–heptagons separated by one row of hexagons. The orientation of the hexagons on both sides of the boundary is in agreement with the experimental STM image of Fig. 2. After allowing the model to relax, we see, on Fig. 3a that the pentagon is almost not affected, but that the heptagon is slightly deformed, as are the two hexagons separating the pentagon–heptagons pairs.

The STM images were computed as described elsewhere [8]: the STM tip is treated as a single atom with an s orbital, coupled to the π orbitals of the graphitic structure by hopping terms decreasing exponentially with the distance. The tunnelling current is derived from that tight-binding model by application of standard first-order time-dependent perturbation theory. The vertical position of the tip is adjusted to maintain the current constant like in real experiment. The voltage used in the simulation is the same as in the experiments.

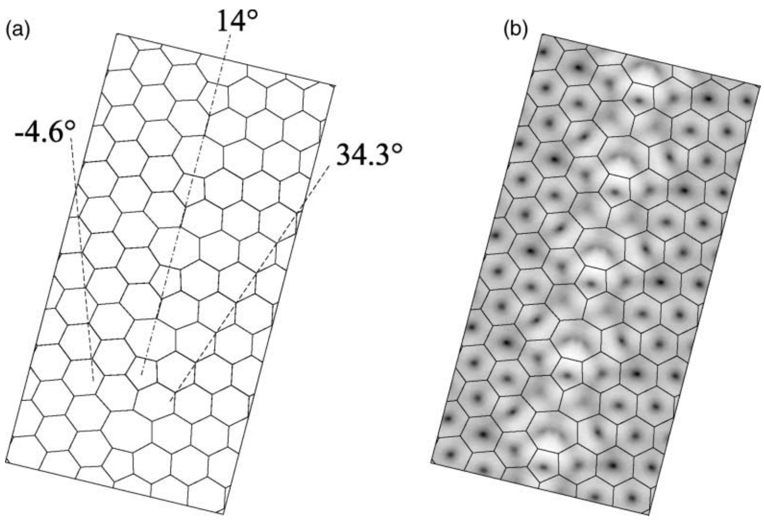

Fig. 3. (a) Relaxed atomic model of the grain boundary with a linear chain of abutting pentagons–heptagons separated by one row of hexagons. (b) Simulated STM image superimposed on the atomic model of (a).

The simulated STM image of the model 3a is displayed in Fig. 3b. One can clearly observe that from both sides of the boundary, the orientations of two grains are correctly reproduced as shown by two hexagonal patterns of black dots. The boundary appears as a regular succession of black dots centred at the pentagons, surrounded by broad white features extending in the direction of the heptagons and in the opposite direction. These structures indicate a higher density of states, which is indeed expected on the pentagons of the boundary. It is interesting to observe that these structures have approximately the shape of pentagons oriented opposite to the lattice pentagons. The separation between the black dots is measured as 0.67 nm in good agreement with the value measured on the STM image, for the separation between the protrusions of the superstructure. The comparison between the simulation and the experiments is better shown in Fig. 4, where the two images have been superimposed. Although the shape of the protrusions is not exactly reproduced by the simulation, there is sufficient similarity between the two images to confirm the existence of the pentagons. It is possible that more refined models could bring a better agreement, but the resolution of the STM pictures does not allow to proceed further.

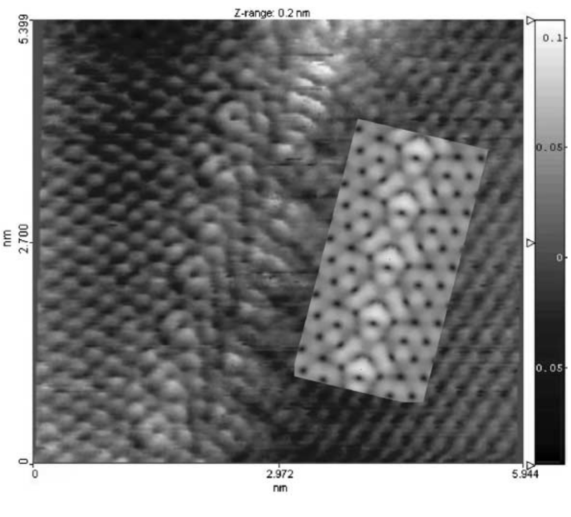

Fig. 4. Experimental STM image corrected according to the thermal drift. The STM simulation has been added on the right of the image in order to compare the periodicity and shape of the protrusion rings.

4. Conclusion

We have analysed by STM a grain boundary in HOPG. The good atomic resolution allowed us to observe a periodic superstructure. Models have been built in order to reproduce and understand the periodicity of this structure. STM simulations have been performed on these models. They are in good agreement with the experiments and show with clear evidence that presence of pentagons and shed some light on the way how the two grain lattices are joined.

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