Structural and electronic properties of grain boundaries in graphite: planes of periodically distributed point defects
Cervenka, J.; Flipse, C.F.J.

Published in:
Physical Review B

DOI:
10.1103/PhysRevB.79.195429

Published: 01/01/2009

Document Version
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

• A submitted manuscript is the author's version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

Citation for published version (APA):

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal?

Take down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Download date: 17. Nov. 2018
Structural and electronic properties of grain boundaries in graphite: Planes of periodically distributed point defects

J. Červenka and C. F. J. Flipse*

Department of Physics, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands

(Received 14 January 2009; revised manuscript received 6 April 2009; published 21 May 2009)

We report on scanning tunneling microscopy and spectroscopy of grain boundaries in highly oriented pyrolytic graphite. Grain boundaries showed a periodic structure and an enhanced charge density compared to the bare graphite surface. Two possible periodic structures have been observed along grain boundaries. A geometrical model producing periodically distributed point defects on the basal plane of graphite has been proposed to explain the structure of grain boundaries. Scanning tunneling spectroscopy on grain boundaries revealed two strong localized states at −0.3 and 0.4 V which extended up to a 4 nm distance from grain boundaries.

DOI: 10.1103/PhysRevB.79.195429

PACS number(s): 71.55.-i, 73.20.-r, 68.37.Ef

I. INTRODUCTION

Understanding the defect structures and their role on the electronic structure of graphite is a keystone for carbon nanosstructures and carbon materials in general. Defects are inevitable constituents of graphite which have profound influence on its electrical, chemical, and other physical properties. Recently, graphene (single layer of graphite) and few-layer graphene showed a number of unconventional properties1–3 and it seems to be of great importance to understand the influence of defects in this material for possible future applications.

Although graphite is one of the most extensively studied materials there are still new phenomena observed on the graphite surface with scanning tunneling microscope (STM) which are not well understood.4,5 In particular, defect structures in the sp2-bonded carbon lattice have many representations6,7 and have not been well characterized experimentally yet.

Grain boundaries are one of the most commonly occurring extended defects in highly oriented pyrolytic graphite (HOPG) because of its polycrystalline character. Observations of grain boundaries have been reported on the graphite surface with STM before8–11 and recently also on few graphene layers grown on C face of SiC.12 Periodic structures9–12 and disordered regions8 have been observed along grain boundaries. For a large-angle-tilt grain boundary evidence of possible presence of pentagon-heptagon pairs was shown.10 Although the structure of various grain boundaries in graphite has been examined with STM, there has not been established a proper model which can explain all the observed grain boundaries. Moreover, the electronic structure of grain boundaries has not been investigated so far.

Point defects and extended defects in graphene and graphite have been extensively studied theoretically in the last years.13–20 In general, defects in the carbon honeycomb lattice break the translation symmetry and give rise to quasilocated electronic states at the Fermi energy.14,15 These states extend over several nanometers around the defects forming characteristic (√3 × √3)R30° superstructures as has been observed with STM on graphite.21,22 In the absence of electron-hole symmetry these states induce a transfer of charge between the defects and the bulk.14 Moreover, it has been shown that point defects such as vacancies and hydrogen-terminated vacancies could be magnetic15–20 showing that electron-electron interactions play an important role in graphene systems because of low electron densities at the Fermi energy. These defects could be of the essential origin of ferromagnetism observed in different graphite samples.23,24

In this paper, we report on an experimental study of grain boundaries in HOPG. A systematic investigation of grain boundaries in graphite has been performed by atomic force microscopy (AFM), STM, and scanning tunneling spectroscopy (STS). Grain boundaries showed one-dimensional (1D) superlattices with localized states and enhanced charge density compared to the bare graphite surface. A crystallographic model producing periodically distributed point defects is introduced to reproduce all observed grain boundaries.

II. EXPERIMENTAL

Samples of HOPG of ZYH quality were purchased from NT-MDT. The ZYH quality of HOPG with the mosaic spread 3.5°–5° has been chosen because it provides a high population of grain boundaries on the graphite surface. HOPG samples were cleaved by an adhesive tape in air and transferred into a scanning tunneling microscope (Omicron RT and LT STM) working under ultrahigh-vacuum (UHV) condition. The HOPG samples have been heated to 500 °C in UHV before the STM experiments. STM measurements were performed in the constant current mode with either mechanically formed Pt/Ir tips or electrochemically etched W tips. STS spectra have been obtained by using lock-in amplifier technique. The same samples have been subsequently studied by AFM using multimode scanning probe microscope with Nanoscope IV controller from Veeco Instruments in air.

III. RESULTS AND DISCUSSIONS

A. Structural properties of grain boundaries

Figure 1 shows typical examples of grain boundaries observed on the HOPG surface with AFM and STM. In AFM, grain boundaries appear as lines protruding above a graphite
Grain boundaries form a continuous network over graphite surfaces. They interconnect each other as can be seen in STM images of a grain boundary continuing as a step edge. They interconnect each other as can be seen in STM images of a grain boundary continuing as a step edge.

Grain boundaries exhibit 1D superlattices with periodicities \( D_1 = 1.25 \text{ nm} \) in.

Figs. 1(a) and 1(d). AFM and STM images display only the surface signatures of grain boundaries propagating through bulk HOPG crystals. This is demonstrated in Figs. 1(a) and 1(c) where grain boundaries over run step edges of an arbitrary height without altering their direction, periodicity and, corrugation. During the cleavage of the HOPG substrate grain boundaries pose as weak points, therefore step edges are created out of them on a new formed graphite surface. Figure 1(b) displays a grain boundary at the bottom left part of the image, which transforms itself into a step edge in the right part of the image. Region I is separated by a monatomic step (0.35 nm height) from region II and by a double step (0.7 nm height) from region III.

Grain boundaries set bounds to so-called two-dimensional (2D) superlattices, which are frequently observed on graphite surfaces in STM. Two examples of 2D superlattices enclosed by grain boundaries are shown in Figs. 1(c) and 1(d). The most accepted origin of 2D superlattices discussed in the literature is a rotation of the topmost graphite layer with respect to the other layers which produces moiré pattern. Although moiré pattern cannot explain all the superlattices reported in literature, because it does not take into account the interaction between the graphene layers, it has been in good agreement with all periodicities of 2D superlattices observed in our STM measurements.

One of the most intriguing properties of grain boundaries is their well-defined 1D superlattice periodicity. We have analyzed various grain boundaries on HOPG surfaces. Their superlattice periodicities have been found in the range from 0.5 to 10 nm. In principle, two periodicities \( D_1 \) and \( D_2 \) are observed within a grain boundary as it is demonstrated in Fig. 2(a). The second periodicity occurs as the direction of a grain boundary changes by 30° or 90°. Figure 2(b) represents a cross section over the top of the grain boundary from Fig. 2(a) going over a polyline ABC with a 30° bend in the point B. The periodicity along the line AB is \( D_1 = 2.18 \text{ nm} \) with a height corrugation 0.6 nm and the periodicity along the line BC is \( D_2 = 3.83 \text{ nm} \) with a height corrugation of 0.9 nm. The value of the periodicity \( D_2 \) is approximately \( \sqrt{3} D_1 \). The \( \sqrt{3} \) relation between two periodicities in one grain boundary has been found to hold for all observed grain boundaries on HOPG.

In Fig. 3, atomically resolved current STM images of three different grain boundaries and their fast-Fourier-transform (FFT) images are shown. The grain boundaries exhibit 1D superlattices with periodicities \( D_1 = 1.25 \text{ nm} \) in.
STRUCTURAL AND ELECTRONIC PROPERTIES OF GRAIN...  PHYSICAL REVIEW B 79, 195429 (2009)

FIG. 3. (Color online) Current STM images of three different grain boundaries on HOPG (a), (c), and (e) and their corresponding FFT images (b), (d), and (f), respectively. Grain boundaries show 1D superlattices with periodicities (a) $D_1=1.25$ nm, (c) $D_2=1.4$ nm, and (e) $D_2=0.83$ nm. The angle between two graphite grains is (a) $\alpha = 12^\circ$, (c) $\alpha = 18^\circ$, and (e) $\alpha = 29.5^\circ$ and the angle between the grain boundary and the graphite lattice is (a) $\beta_{D1}=25^\circ$, (c) $\beta_{D2}=9^\circ$, and (e) $\beta_{D2}=13.5^\circ$. Scanning parameters: $10\times 10$ nm$^2$, $U=0.5$ V, and $I_z=0.3$ nA.

Fig. 3(a), $D_2=1.4$ nm in Fig. 3(c), and $D_2=0.83$ nm in Fig. 3(e). It is apparent from these images that grain boundaries in graphite are tilt grain boundaries which are produced between two rotated graphite grains. No preferential orientation of grains has been found in our measurements. Angles between grains have been determined to be in the interval from $1^\circ$ to $29.5^\circ$. Graphite grains are rotated by angles $12^\circ$, $18^\circ$, and $29.5^\circ$ in Figs. 3(a), 3(c), and 3(e), respectively. The rotation of the graphite grains can be seen as well in the FFT images in Figs. 3(b), 3(d), and 3(f) where points labeled as A and A$^*$ are forming apexes of two rotated hexagons representing the graphite lattices in the reciprocal space. Six points marked as B demonstrate $(\sqrt{3} \times \sqrt{3})R30^\circ$ superstructure which has been observed around point defects and step edges of graphite previously. 21,22 The $(\sqrt{3} \times \sqrt{3})R30^\circ$ superstructure is produced by scattering of the free electrons off defects, which generates standing-wave patterns in the electron density similar to Friedel oscillations in metals. 21 The center part of the FFT image marked as C represents the large real-space periodicities of the 1D superlattices.

The structure of the grain boundaries can be explained by a simple model where the superlattice periodicity is determined only by two parameters: $\alpha$ the angle between the grains and $\beta$ the orientation of a grain boundary in respect to the graphite lattice. The superlattice periodicity $D_1$ is given by a simple formula for a moiré pattern $D_1=d/2 \sin(\alpha/2)$, where $d=0.246$ nm is the graphite-lattice parameter. The second periodicity is defined as $D_2=\sqrt{3}D_1$. Periodicities $D_1$ and $D_2$ have different orientations toward the graphite lattice $\beta_{D1}=30^\circ \pm \alpha/2$ and $\beta_{D2}=\pm \alpha/2$, respectively. The sign depends on the chosen reference direction of the graphite lattice.

In Fig. 4, schematic illustrations of the crystallographical structures of two possible orientations of grain boundaries are shown. Periodically distributed point defects are created in this way. They are separated by superlattice periodicities $D_1$ in Fig. 4(a) and $D_2$ in Fig. 4(b). The periodicities of the grain boundaries and angles between the graphite grains have been chosen according to STM observations in Figs. 3(a) and 3(b). The combination of these two models within a grain boundary describes well all the possible internal structures and orientations of grain boundaries observed on the graphite surfaces. In addition, grain boundaries with a large-angle tilt such as shown in Fig. 3(e) would produce row of defects, which are resembling a structure with repeating pentagon-heptagon pairs similarly as was proposed by Simonis et al. 10

Grain boundaries, such as graphite edges, have two basic shapes which are rotated by $30^\circ$ toward each other. The orientation $\beta_{D1}$ in Fig. 3(a) has an armchair character at the axis of the grain boundary while the $\beta_{D1}$ orientation in Fig. 3(b) has a zigzag character. As it was mentioned before, grain boundaries are weak spots of graphite lattice, therefore step edges are produced out of them during the cleavage. If an edge would be created from the grain boundary by cutting it into half, the edges would have segments of zigzag or armchair edge of the maximum length as the superlattice period...
localized peaks are observed. The measured points have been extended up to a large distance 4 nm where no clear vibrations have found a short length of zigzag edges 

alternated by armchair segments, while the energetically optimized periodicity of the grain boundaries have been determined by fitting Gaussian curves after subtraction of a background signal. The error bar determines \( \sigma \), the width of the Gaussian peak. The points have been fitted by \( y = 0.88 \exp(-x/1.63) - 0.048 \).

DOS of grain boundaries an appropriate calculation has to be done, which is going to be difficult especially for grain boundaries with large periodicities. However, it cannot be concluded only from STM and STS measurements that grain boundaries are magnetic, and other technique such as spin-polarized STM has to be used in order to prove it.

Another origin of two split-localized states in the grain boundaries could be the internal structure of point defects within grain boundaries. Point defects in graphene can exist in several forms, such as single and multiple vacancies, interstitials, Stone-Wales defects, and other more complicated point defects. All of them can essentially occur in grain boundaries. Moreover, they can be saturated by different atoms such as hydrogen, oxygen, or nitrogen. Using only STM, it does not allow us to extract the exact atomic structure of defects. Nevertheless, the structure of defects is reflected in the shape and the symmetry of the charge modulation around the defects as it has been shown in a theoretical study of a single atomic and double atomic defects in graphene.18 The single atomic defect resulted in a simple trigonal symmetry in the charge modulation around the defect, while double atomic defect demonstrated twofold symmetry. From this point of view grain boundaries contain different point defects as seen in Fig. 3. In order to discern between the two proposed possibilities for diverse DOS of grain boundaries an appropriate calculation has to be done, which is going to be difficult especially for grain boundaries with large periodicities.
IV. CONCLUSIONS

In conclusion, a systematic scanning tunneling microscopy and spectroscopy study of grain boundaries in highly oriented pyrolytic graphite have been done. Different grain-boundary geometries have been characterized with a focus on their electronic structure. Grain boundaries showed a periodic structure and an enhanced charge density compared to the bare graphite surface. Two possible periodic structures have been observed along grain boundaries. A geometrical model producing periodically distributed point defects on the basal plane of graphite has been proposed to explain the structure of grain boundaries. Scanning tunneling spectroscopy on grain boundaries revealed two strong localized states at −0.3 and 0.4 V.

ACKNOWLEDGMENT

This research was financially supported by NanoNed.

---

9 Corresponding author; c.f.j.flipse@tue.nl