The role of defects on the electronic structure of a graphite surface

J. Cervenka, C. F. J. Flipse
Department of Applied Physics, Eindhoven University of Technology, Den Dolech 2, 5612 AZ Eindhoven, The Netherlands
E-mail: j.cervenka@tue.nl

Abstract. We have observed one-dimensional (1D) superlattices at the grain boundary of highly ordered pyrolytic graphite (HOPG) with a scanning tunneling microscopy (STM). Observed 1D superlattices extend over micrometer length and have periodicities from 0.5 nm to 10 nm with a height corrugation up to 1.5 nm, due to electron density effects, which is 15 times larger than the graphite lattice corrugation observed with STM. Experimental observations are well explained by a simple model based on the complex electron interference at the grain boundary between two misoriented graphite layers.

1. Introduction
The role of defects on the electronic structure of graphite is an essential tool for understanding carbon nanostructures. Defects undoubtedly alter the electronic structure and therefore chemical, optical, and other properties. Understanding STM images of $sp^2$ bonded carbon is difficult and there is an unresolved debate over how defects manifest themselves. Recently, graphene (single layer of graphite) and few-layer graphene showed a number of unconventional properties [1, 2] and it seems to be of the great importance to understand the role of defects in these materials for possible future applications [3, 4].

Graphite is one of the most extensively studied materials in STM. However, there are still phenomena observed on graphite surfaces with STM, which are not well understood. Graphite shows superperiodical features often in STM experiments, which are not related to the topography of graphite. These features are called superlattices in literature [5]. Since graphite is commonly used for deposition of various molecules and biological species [6, 7], it is substantial to understand the origin of superlattices on graphite in order to properly distinguish between deposited material and superlattices on the graphite surface. Moreover, it was reported that superlattices on graphite could serve as the preferential adsorption sites for both atoms and clusters [8], which may present a way of preparing a template with any predetermined periodicity for adsorbing external atoms or molecules.

Graphite superlattices have been observed by many groups over the last two decades (for a review see [5]). Superperiodic hexagonal structures on a graphite surface arise during crystal growth or cleavage. Their formation is due to intrinsic defects of the substrate crystal. Superlattices may be observed if there is a misorientation of one or more of the graphite layers on or near the surface [9, 10, 11]. Most of them are widely believed to be the result of a Moiré rotation pattern, arising from the misorientation between two graphite layers. However, a simple
superposition of two rotated layers cannot explain fully the phenomena and it is believed that a superlattice is a direct consequence of interlayer electronic interactions of the topmost surface with the bulk [5]. Another type of superlattice has been observed on intercalated graphite compounds, for example with alkali-metals or electrolytic solutions, which show large-scale periodic superstructures, such as $2 \times 2$ and $\sqrt{3} \times \sqrt{3}$ superstructures [12, 13]. The last type of observed superstructures using STM is the $(\sqrt{3} \times \sqrt{3})R30^\circ$-superstructure. This superstructure is generated by perturbation of charge density by point defects, adsorbed species, steps and boundaries [14, 16]. It is effectively similar to the Friedel oscillations in the charge density around an impurity.

In this paper, we present results of STM measurements on grain boundaries of HOPG which are exhibited by 1D superlattices. 1D superlattices show enhanced charge density compared to the graphite surface. The experimental observation are compared to the simple model based on the interference of electron waves at the grain boundary.

2. Experimental

Samples of HOPG of ZYH quality were purchased from NT-MDT. The ZYH quality has mosaic spread $3.5^\circ \div 5.0^\circ$ which means that graphite grains have sizes around $30 \div 40$ nm [17]. This quality of HOPG provides a high population of step edges and grain boundaries on the surface. HOPG samples were cleaved by an adhesive tape in air and transferred into the scanning tunneling microscope (UHV AFM/STM, Omicron) working under ultra high vacuum condition at room temperature. STM measurements were performed in constant current mode with mechanically formed Pt/Ir tips.

3. Result and discussion

Figure 1 shows a typical STM image of 1D superlattice on graphite surface. Two periodicities within the superlattice are observed. The right image in the figure 1 represents cross section across the 1D superlattice from the left image in figure 1, going from point A over B to C. The periodicity along the line AB is 2.18 nm with a height corrugation 0.6 nm and the periodicity along the line BC is 3.83 nm with a height corrugation of 0.9 nm. These two periodicities are rotated towards each other by $30^\circ$, which is the angle between the line AB and BC. Different 1D superlattices with periodicities varying from 0.5 nm to 10 nm can be observed on the same sample. The superlattices are extending over length up to 10 $\mu$m and running over step edges of height up to 10 nm without changing their corrugation, direction and periodicity. We haven’t observed the superlattices with AFM on the same HOPG samples which means that the superlattices are not arising from topography but have purely an electronic origin. Since STM measures a tunneling current between tip and sample, it means that the superlattices have a higher charge density compared to the normal graphite surface.

The left image in a figure 2 shows a current STM image of 1D superlattice with an atomically resolved graphite surface having the lattice constant $d = 0.246$ nm. In fact, there are two graphite lattices separated by a boundary in the middle of the image. The 1D superlattice observed with STM represents the grain boundary of graphite. The upper graphite lattice is misoriented towards the bottom lattice by $7^\circ$. The 1D superlattice exhibits periodicity of 3.5 nm with the corrugation 1 nm, whereas the corrugation of graphite is only 0.1 nm. Making the fast Fourier transformation (FFT) of the current image allows to work in a two-dimensional reciprocal $k$-space (left image in the figure 2). In $k$-space, the honeycomb graphite lattice appears as a hexagon. Points labeled as A and A’ are forming apexes of two hexagons of two graphite lattices. The hexagons are rotated by $7^\circ$ towards each other. The center part of the FFT image marked as C represents the large periodicities from the STM current image, which has periodicity 3.5 nm in real space.
Figure 1. Left image: STM image of 1D superlattice on a flat HOPG surface with two periodicities ($50 \times 50 \text{nm}^2$, $U = 1\text{V}$ and $I = 0.12\text{nA}$). Right image: A line profile along the line ABC over the top of the superlattice. The periodicity between AB is 2.18 nm (height 0.6 nm) and the periodicity between BC is 3.83 nm (height 0.9 nm).

Figure 2. Left image: Current STM image of the grain boundary showing 1D superlattice on HOPG ($15 \times 15 \text{nm}^2$, $U = 1\text{V}$ and $I = 0.1\text{nA}$). Two grains are rotated towards each other by $7^\circ$. Right image: Fast Fourier transform (FFT) of the current image.

Points marked as B show periodicities $\sqrt{3}$ times larger than the graphite lattice periodicity. The points B construct apexes of the smaller hexagon rotated by $30^\circ$ towards the larger hexagon representing the graphite lattice. Actually, 4 B points are only visible in figure 1. Two points on the vertical axis do not appear because of the sharp cut-off of the current image which creates a cross going through the center of the FFT image. These $\sqrt{3}$ times larger periodicities create ($\sqrt{3} \times \sqrt{3}$)R30°-superstructure in the vicinity of the grain boundary. The ($\sqrt{3} \times \sqrt{3}$)R30°-superstructure is localized on the grain boundary where it has its maximum and decays from the grain boundary extending up to the distance $2 \div 4$ nm. This explains the reason why points B are less bold than A or A'.

Similar long-range oscillations with three-fold symmetry have been observed around point defects and around absorbed molecules on graphite before [14, 16]. The \((\sqrt{3} \times \sqrt{3})R30^\circ\)-superstructure is due to interference between normal and scattered electrons waves from the defect. The spots forming the small hexagon appear exactly at the same place where are the corners of the Brillouin zone (BZ) of graphite which are forming the Fermi surface of graphite consisting of small electron and hole pockets. The scattering process of electron at the grain boundary is due to the large momentum scattering between opposite corners of BZ corresponding to the momentum change \(q = 2k_F\). On metals large momentum scattering of surface states are responsible for the formation of Friedel oscillations.

In order to explain the different periodicities of observed superlattices we use a simple interference model of electron waves at the grain boundary. For simplicity, we model graphite lattice as lattice of the \(\beta\) sites only. This is allowed because STM images acquired at low bias shows predominantly every second carbon atom (\(\beta\) sites) of the graphite lattice. Since STM images are proportional to the local density of states at the Fermi energy and the Fermi surface of graphite collapses to the points at the corners of BZ then only a very limited set of \(k\) vectors contribute to the tunneling current. Hence, STM images of graphite acquired at low biases map the wave functions of the few electron states near Fermi surface. The electrons at the Fermi energy can be described by linear combination of the three plane waves that have the orientations and wavelength of the Fermi wave vector. The explicit form is given by

\[
\Psi(\mathbf{r}) = \sum_{j=1}^{3} A_j \exp(i\mathbf{k}_{Fj} \cdot \mathbf{r}),
\]

where the coefficients \(A_j\) are equal in amplitude and \(k_F = 4\pi/3d\) is Fermi wave vector where \(d = 0.246\) nm is the lattice constant of graphite. The electron density distribution \(|\Psi|^2\) associated with this wave function results in regions of equivalently high density at all \(\beta\) sites. A gray scale plot of calculated density of states of the interference between two plain electron waves given by expression 1 rotated by \(7^\circ\) is presented in figure 3. The misorientation angle is chosen the same as it was observed experimentally (figure 2).

The superposition of two lattices produces Moiré superlattice with periodicity \(D\). To describe the 1D superlattice a cross section of the 2D superlattice has to be taken in particular direction. Then two periodicities are created \(D\) and \(\sqrt{3}D\), where the Moiré superlattice \(D\) is given by

\[
D = \frac{d}{2 \sin(\alpha/2)},
\]

where \(d\) is the graphite lattice constant and \(\alpha\) is angle between two misoriented graphite layers. The orientation between the Moiré superlattices \(D\) and \(\sqrt{3}D\) with respect to the atomic orientation of graphite is expressed as

\[
\beta_D = 30 \pm \alpha/2
\]

\[
\beta_{\sqrt{3}D} = \pm \alpha/2
\]

Using the formula for the 1D Moiré superlattice with the experimentally measured angles \(\alpha = 7^\circ\) and \(\beta_{\sqrt{3}D} = 4^\circ\) we get periodicity \(\sqrt{3}D = 3.49\) nm. The measured superlattice periodicity is 3.5 nm (figure 2) which perfectly fits the calculated value.

In our simple model, the observed 1D superlattices are explained as the combination of two effects: in the first one, the superlattice periodicity arises from 1D Moiré pattern produced between two rotated electron waves, producing a large wave modulation depending on the angle of rotation. The second effect is due to a threefold symmetric electron scattering from the grain boundary which enhance the charge density of the 1D superlattice and giving rise to \((\sqrt{3} \times \sqrt{3})R30^\circ\)-superstructure. The combination of two effects explains well the periodicities and the height corrugations of the observed 1D superlattices.
4. Conclusion
We have shown that grain boundaries of HOPG exhibit 1D superlattices in STM measurements. The observed superlattices extend over micrometer length and have periodicities from 0.5 nm to 10 nm with height corrugations up to 1.5 nm due to electron density effects, which is 15 times larger than the graphite lattice corrugation observed with STM. Experimental observations have been explained by a simple model based on the complex electron interference at the grain boundary between two misoriented graphite layers.

5. References
[1] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V, Firsov A A 2004 Science 306 666
[2] Novoselov K S, Geim A K, Morozov S V, Jiang D, Katsnelson M I, Grigorieva I V, Dubonos S V and Firsov A A 2005 Nature 438 197
[3] Peres N M R, Guinea and Castro Neto A H 2006 Phys. Rev. B 73 125411
[4] Berger C, Song Z, Li T, Li X, Ogbazghi A Y, Feng R, Dai Z, Marchenkov A N, Conrad E H, First P N, and de Heer W A 2004 J. Phys. Chem. B 108 19912
[5] Pong W T and Durkan C 2005 J. Phys. D 38 R329
[6] Arscott P G, Lee G, Bloomfield V A and Evans D F 1989 Nature 339 484
[7] Clemmer C R and Beebe T P 1991 Science 251 640
[8] Xhie J, Sattler K, Ge M, Venkateswaran N 1993 Phys. Rev. B 47 15835
[9] Kuwabara M, Clarke D R and Smith D A 1990 Appl. Phys. Lett. 56 2396
[10] Osing J and Shvets I V 1998 Surf. Sci. 417 145
[11] Rong Z Y and Kuiper P 1993 Phys. Rev. B 48 17427
[12] Kelty S P and Lieber C M 1989 J. Phys. Chem. 93 5983
[13] Anselmetti D, Wiesendanger R, and Guntherodt H J 1989 Phys. Rev. B 39 11135
[14] Mizes H A and Foster J S 1989 Science 244 559
[15] Hahn J R and Kang H 1999 Phys. Rev. B 60 6007
[16] Kelly K F, Sarkar D, Hale G D, Oldenburg S J and Halas N J 1996 Science 273 1371
[17] http://www.ntmdt-tips.com/