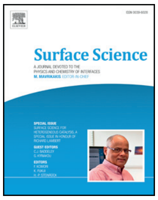
Surface Science xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc



Influence of surface defects on superlattice patterns in graphene on graphite

Maja Remskar *, Janez Jelenc

Solid State Physics Department, Jozef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia

A R T I C L E I N F O

Article history:
Received 29 October 2015
Received in revised form 29 January 2016
Accepted 6 March 2016
Available online xxxx

Keywords:
Graphene
Superstructure
Scanning tunnelling microscopy
Moiré pattern
Charge modulation

A B S T R A C T

Superstructures observed by scanning tunnelling microscopy on graphite have been reported several decades ago, but the interest in these superstructures recently intensified due to their occurrence in graphene grown on different substrates. Generally accepted explanation of origin of these superstructures is an overlap of disoriented top layer of graphite and the underlying graphite single crystal, which causes moiré pattern. Here we present experimental findings that the orientation of the superstructure is influenced by surface defects and edges of graphene. Superstructures in graphene put on graphite exist even if the graphene is not supported by graphite over its entire area. The modulation of the density of states influences the strength of intra-layer carbon bonds in such a way that the graphene breaks along the superstructure minima. The tunnelling conductance of the areas with superstructures is enhanced with regard to bulk graphite.

1. Introduction

The superstructures observed by scanning tunnelling microscopy (STM) on graphite have been reported already several decades ago [1]. The explanation of the origin of the superstructures has been proposed as the overlap between a disoriented top layer of graphite and the underlying graphite single crystal, which causes a moiré pattern. This model is based on three-dimensional tunnelling of electrons with Fermi energy of the same order as the work function of a typical layered material with weak interlayer interaction [2]. Strong corrugation amplitude of the tunnelling current from the superstructure in comparison with atomic corrugation was explained by zero decay of the nanoscale waves produced by scattering at the interface in the lattice-mismatched systems. Due to a low attenuation of the nanoscale waves, the superstructure in STM can be visible at heights around one monolayer above the top surface. Several other explanations of the superstructures were proposed by different authors and reviewed [3], such as network of dislocations, physical surface deformation, a multiple tip effect, adsorption of impurities, bond shortening, and nanoscale defects buried a few layers below the surface.

Intensified interest in the scientific community for these superstructures stems from their occurrence in graphene grown on different substrates, such as silicon carbide [4,5], rubidium [6], nickel [7], iridium [8], copper [9], and hexagonal boron nitride as an isostructural crystal to graphene. These Van der Waals heterostructures allow for the tuning of the electronic properties of two-dimensional atomic crystals, particularly of graphene, creation of unique systems for adsorption of clusters [10] as quantum dots arrays [11], and they represent a way of studying the fractal quantum Hall effect [12–14]. The brightest spots of the superstructure in the STM image with the maximum density of states can also represent adsorption sites for cationic atoms or molecules [10]. Moiré patterns of graphene on hexagonally packed surfaces were also studied theoretically [15]. Besides forming moiré superstructures, orientation mismatch of graphene flakes on graphite strongly reduces friction on atomic scale. Extremely low friction was observed for incommensurate relationship of two graphite layers [16]. Transition back to commensurate ground state is triggered by thermal fluctuations and performed with superlubric gliding or rotation [17]. Understanding of interaction between graphene flakes and substrate is of a great importance for their applications in nanomechanical systems.

Here we present experimental data obtained by STM studies of graphene flakes partially peeled off bulk graphite. We show that the superstructure lattice is influenced by surface and edge defects of graphene and vice versa, that the superstructure influences how graphene breaks. These findings represent a new insight into this old phenomenon with novel implications for graphene-based technology.

2. Methods

The STM studies have been performed at room temperature in ultra high vacuum (base pressure in the range of 10^{-10} mbar) using the AFM/STM microscope (VT-AFM, Omicron). Mechanically cut Pt/Ir tips have been used. The STM tip was biased, while the sample was grounded. The superstructures have appeared occasionally during use of graphite

---

* Corresponding author.
E-mail address: maja.remskar@ijs.si (M. Remskar).

http://dx.doi.org/10.1016/j.susc.2016.03.008
0039-6028/

Please cite this article as: M. Remskar, J. Jelenc, Influence of surface defects on superlattice patterns in graphene on graphite, Surf. Sci. (2016), http://dx.doi.org/10.1016/j.susc.2016.03.008

as a substrate for studies of different nanomaterials, such as MoS_2 based nanoflakes and nanotubes, WO_x nanowires and $Mo_6S_6I_2$ nanocrystals. The graphite single crystals were always freshly air cleaved using adhesive tape before ethanol suspension of the nanomaterials was drop casted. Then the samples were dried at 60 °C in air and inserted into the UHV chamber in standard way. The graphite single crystals HOPG SPI-1 Grade, 10 × 10 × 1 mm, Mosaic spread angle: $0.4^\circ \pm 0.1^\circ$, purity = 99.99, dimension: 10 mm × 10 mm × 1 mm, and the absolute ethanol, purity = 99.9, M = 46.07 g/mol, used in sample preparation were purchased at SPI supplies, West Chester, USA, and MERCK, respectively. All STM images taken in constant current mode are shown after applying line-by-line and planar background subtraction. No other image filtration or rotation was used. Scan direction corresponded to x-axis of an image.

3. Results and discussion

3.1. Graphene lying over surface imperfections

Fig. 1 shows a graphene flake lying over several surface ripples and a hole. The surface above the diagonal dotted line in the Fig. 1a reveals a trigonal superstructure with a period of 3.6 ± 0.2 nm (Fig. 1b). The deepness of the hole estimated from the line profile along the ripple is 0.4 ± 0.1 nm (Fig. 1c). This value approximately corresponds to the monolayer thickness of graphite (0.3354 nm). Line profile along the superstructure lattice (Fig. 1d) reveals a depletion of 0.35 to 0.4 nm at the valley of the ripple. The shape of the superstructure maxima is sinusoidal, while the minima are tip shaped. The corrugation was 500 pm ± 100 pm over the hole, 250 pm ± 50 pm over the valleys of the ripples, and 230 pm ± 50 pm over the convex areas of the ripples. At the left side of the image (Fig. 1a) the dotted boundary is attached to a corner (A) where two monolayers have been removed during cleavage of the graphite. The dotted line is boundary of the modulation. Corrugation of the dots is 1 nm ± 0.1 nm.

Shape of the hole's edge is blurred by a strong contribution from the density of states from the superstructure. Right edge of the hole (marked with B) is in line with serial features forming a 3 × 1 (or 6 × 1) giant superstructure (C) shown in the Fig. 1a. Origin of this giant superstructure is not known. Based on geometry, one can speculate that edge states of the hole interact with tunnelling current from moiré interface and trigger its periodic modulation. It is not clear where the hole is situated, but it is either in the second layer below the surface (I to III) or in the top layer (IV), schematically presented in the Fig. 2. The first three variants are more likely and II and III are of equal possibility due to blurred edges of the hole. The fact that the edges of the hole are parallel to the moiré superstructure, suggests that the layer with the hole is one of the layers of the interface creating the moiré superstructure and the model IV is less likely.

If the image is explained by the standard moiré model, which is based on mismatch and/or rotational disorder interface (moiré interface), then the interface would be buried three (I), two (II) or one (III) layers below the top surface. The defects in the topmost layer obviously affect the density of states at the moiré interface situated several monolayers below the surface. The corner (A) has an effect on the interface below the surface, and the edge of the hole (B) influences the orientation of the super structure lattice. The influence of surface

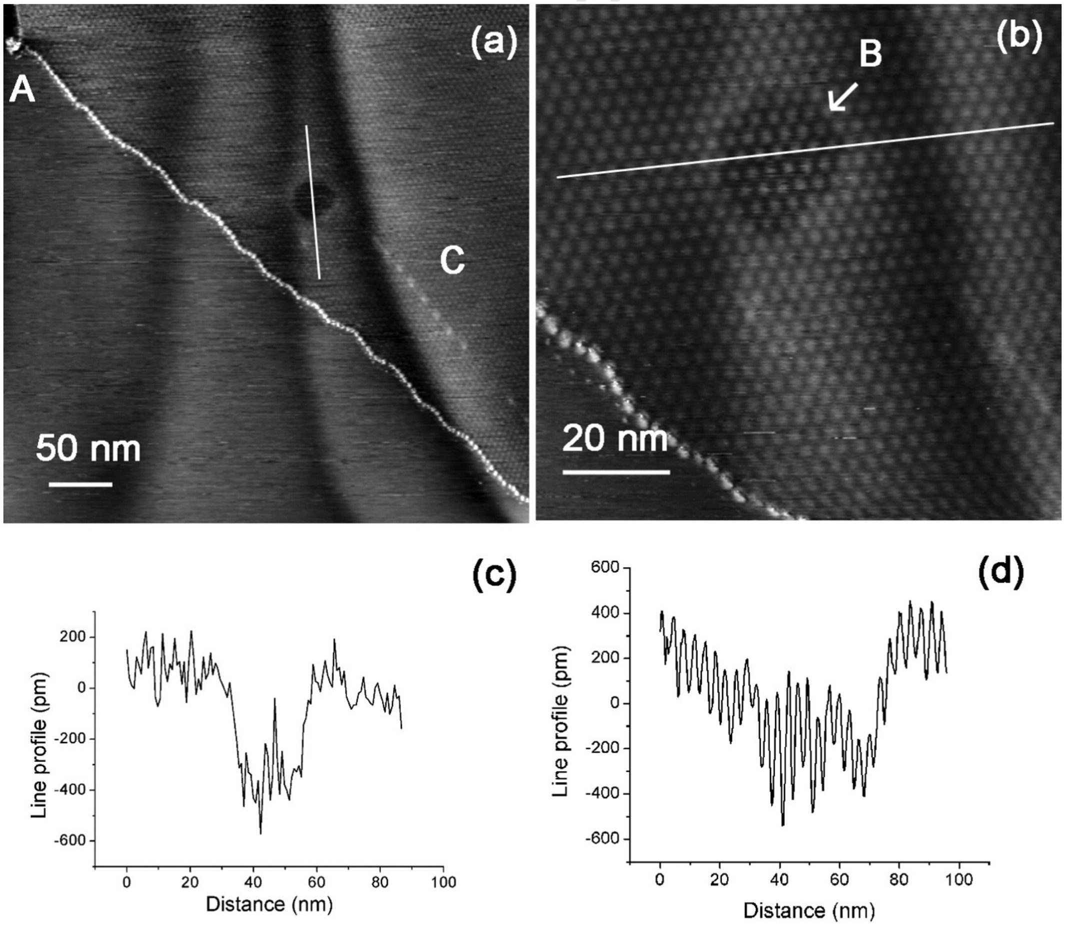


Fig. 1. a) Graphene flake lying over several surface ripples and over a hole ($U_T = 0.5$ V, $I_T = 0.5$ nA, Z-Range: 3.28 nm; speed: 300 nm/s); b) Trigonal distribution of superstructure maxima, 3.6 nm in period ($U_T = 0.5$ V, $I_T = 0.5$ nA; Z-Range: 2.27 nm; speed: 100 nm/s); c) Line profile along the ripples crossing the hole in direction along the ripples (shown in (a)); d) Line profile along the superstructure maxima (shown in (b)).

Please cite this article as: M. Remskar, J. Jelenc, Influence of surface defects on superlattice patterns in graphene on graphite, Surf. Sci. (2016), http://dx.doi.org/10.1016/j.susc.2016.03.008