



Near-edge X-ray absorption spectroscopy signature of image potential states in multilayer epitaxial graphene



P.M. Coelho^a, D.D. dos Reis^a, M.J.S. Matos^a, T.G. Mendes-de-Sa^a, A.M.B. Goncalves^b, R.G. Lacerda^a, A. Malachias^a, R. Magalhaes-Paniago^{a,*}

^a Departamento de Física, Universidade Federal de Minas Gerais, Belo Horizonte, MG, CEP 30123-970, Brazil

^b Instituto de Física, Universidade Federal do Mato Grosso do Sul, Campo Grande, MS, CEP 79070-900, Brazil

ARTICLE INFO

Article history:

Received 7 August 2015

Accepted 9 October 2015

Available online 19 October 2015

Keywords:

Graphene
Graphite
Microscopy
Spectroscopy
Diffraction

ABSTRACT

Single layer behavior in multilayer epitaxial graphene has been a matter of intense investigation. This is due to the layer decoupling that occurs during growth of graphene on some types of substrates, such as carbon-terminated silicon carbide. We show here that near-edge X-ray absorption spectroscopy can be used to observe the signature of this decoupling. To this end, samples of multilayer graphene from silicon carbide sublimation were grown with different degrees of decoupling. Raman spectroscopy was used to infer the degree of structural decoupling. X-ray grazing-incidence diffraction and scanning tunneling microscopy showed that growth initiates with the presence of bilayer graphene commensurate structures, while layer decoupling is associated to the formation of incommensurate structures observed for longer sublimation time. Near-edge X-ray absorption spectroscopy was used to probe the electronic states above the Fermi energy. Besides the σ^* and π^* empty states, image potential states are observed and show a clear change of intensity as a function of incident angle. These image potential states evolve from a graphite- to graphene-like behavior as a function of growth time and can be used to infer the degree of structural coupling among layers.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Graphene is a novel material with electronic properties that are quite unique if compared to other condensed matter systems [1]. Its two-dimensional honeycomb structure composed of carbon hexagons makes it a semimetal where the electrons exhibit a linearly dispersing behavior. The case of an isolated sheet of graphene is easily understood, but once this sheet is in contact with a substrate or stacked on top of other graphene sheets, its behavior changes dramatically and has been a matter of intense investigation [2]. In special, the case of multilayer graphene (a pile of misoriented graphene sheets, where the stacking may or may not be well-defined) is extremely difficult to analyze.

It is well-known that multilayer epitaxial graphene can be grown by sublimation of silicon carbide substrates [3]. Such process takes place when the substrate is heated at a temperature where the silicon atoms desorb from the surface leaving a graphene layer behind. Once such graphene multilayer is formed an intricate stacking may be observed on the sample surface. If this desorption procedure is carried out while heating the carbon-terminated surface of silicon carbide [SiC(000-1)] in an environment of argon, the graphene layers exhibit an isolated graphene Raman signature [3].

One of the difficulties in working with epitaxial graphene is the correct identification of its behavior as two-dimensional (similar to graphene) or three-dimensional (graphite). The different behavior is a consequence of the stacking, which may result in distinct degrees of structural coupling. While graphite is formed by graphene layers which are AB stacked, multilayer graphene is composed of layers which do not show any specific type of stacking. If the layers do not form any type of defined structure [4], multilayer graphene exhibits a clear two-dimensional behavior, although being formed by several graphene layers. This can be observed using Raman scattering [5] or scanning tunneling microscopy (STM) [6], each technique with its advantages and drawbacks. While Raman spectroscopy lacks spatial resolution below ~500 nm, STM is a local technique (lacking statistical information) which only reveals the surface structure and is not completely reproducible due to tip preparation effects.

X-ray near-edge absorption spectroscopy (NEXAFS) performed at the carbon K-edge [7–15] could in principle be used, since it may yield a variable spatial resolution ranging from a few nanometers to millimeters. The differentiation of multilayer graphene from graphite is more difficult, since both have very similar NEXAFS spectra [9–11]. The NEXAFS spectra of graphene/graphite reveal σ^* and π^* empty states right above the Fermi energy [7], which have essentially the same energy signature. Besides these two very clear states, a number of additional peaks have been identified by Pacilé et al. [11] from few-layer graphene, such as a pre-peak right above the Fermi energy and an additional

* Corresponding author. Tel.: +55 31 34096625.

E-mail address: rogerio.paniago@gmail.com (R. Magalhaes-Paniago).

feature 4 eV above the Fermi energy, in between the σ^* and π^* peaks. The origin of this additional peak, first identified as an interlayer state [11,12,15,16], was clarified by Bose et al. [17]. It is associated with the presence of an intersheet hybridization of the first even image potential state which is an unoccupied electronic state with nearly free electronic properties. These states have a clear signature difference between monolayers and bilayers of graphene and also graphite [17–19]. Hybridization of graphene with the underlying substrate was also identified using NEXAFS [13,14]. In fact, Schultz et al. [14] have already used the signature of NEXAFS to obtain energy resolved micrographs of graphene deposited on copper and identify its interaction with the substrate atoms.

2. Materials and methods

In this work, three multilayer graphene samples were grown for 30, 45 and 60 min to observe the decoupling of graphene layers. The samples were grown by heating silicon carbide in a resistive furnace at 1780 °C under argon atmosphere. The first signature of coupling was obtained by a Raman spectroscopy analysis of the 2D band of all samples. X-ray grazing-incidence scattering was used to observe the orientational order of neighboring graphene layers, which is determined by the layer stacking. Starting from perfect order (AB stacking), the formation of bilayer commensurate structures with specific angles was observed. The stacking of the 30 min sample was studied by STM where most commensurate structures were measured, and the onset of the formation of incommensurate structure (a signature of graphene behavior) was also observed.

Our samples were grown by SiC sublimation at 1780 °C. The SiC(000-1) substrate was carbon terminated 4H-SiC purchased from Cree Incorporated (www.cree.com). The sample substrates were first annealed at 1700 °C for 10 min in a hydrogen atmosphere, to obtain atomically flat terraces, as confirmed by atomic force microscopy. The three samples were then obtained by annealing the substrate at $T = 1780$ °C in an argon atmosphere (pressure of 1 atm), with sublimation times of 30, 45 and 60 min. (for growth details see [4]). The measurements of Raman spectra were carried out using a Delta Nu Examiner 532 spectrometer with an Olympus BX51 microscope with a 100 \times objective lens and a visible laser of wavelength 532 nm. The X-ray Diffraction collection of data was carried out at the Brazilian National Laboratory of Synchrotron Light (LNLS) at beamline XRD2, a bending magnet X-ray source with a flux of 10^{10} photons/s and an X-ray wavelength of 0.1549 nm. STM measurements were done at room temperature using an Omicron Variable Temperature Microscope (VT-AFM) with an electrochemically etched tungsten tip and an ultra-high vacuum chamber with a base pressure better than 2.0×10^{-10} mBar. Prior to measurements all samples were degassed by a heat treatment of 200 °C for one hour to eliminate sample contamination. All samples were cooled down to room temperature before measurements.

Near-edge X-ray absorption spectroscopy was used to study the electronic states above the Fermi energy. Our NEXAFS measurements were performed for all samples under ultra-high vacuum conditions (better than 2×10^{-10} mBar) at the soft X-ray PGM beamline of LNLS. This variable line spacing grating undulator beamline (Apple II - type) delivers a photon flux of 10^{11} photons/s with an energy resolution $E/\Delta E = 6000$ [20]. Measurements were performed for a limited incident angle range of $\delta = 0^\circ$ to $\delta = 30^\circ$, (where 0° corresponds to normal incidence, see inset of Fig. 3). The absorption was detected by total electron yield. Besides the σ^* and π^* empty states, image potential states were observed and showed a clear change of intensity as a function of incident angle and structural coupling.

3. Results

Raman spectra near the 2D peak of these 3 samples are shown in Fig. 1(a). The 2D peak exhibits a clear narrowing as growth time

increases, which is a signature of layer decoupling [3]. In the case of the sample grown for 30 min, the Raman spectrum is actually the composition of several Lorentzian peaks corresponding to different resonance processes from the band of graphite [6]. As time increases, it clearly becomes narrower with a linewidth of 27 cm^{-1} for 60 min, approximately the value for single layer graphene (25 cm^{-1}) [6]. This result essentially shows that the decoupling of the layers of carbon increases with growth time and the behavior for the topmost layers of the sample grown for 60 min is that of graphene with a single Raman scattering process.

A clearer structural picture of layer decoupling is achieved using grazing-incidence X-ray diffraction. In Fig. 1(b) we present the geometry of rotation scans that were used to identify the stacking between subsequent graphene layers. The incident X-ray beam (green) was positioned in a grazing angle $\alpha = 0.25^\circ$. In this geometry the diffraction is due to atomic planes lying perpendicularly to the surface, and the diffracted beam was collected by the detector (also in green) in a grazing exit angle $\beta = 0.25^\circ$ with respect to the sample surface, with a horizontal diffraction angle $2\theta = 42.628^\circ$, with respect to the incident beam, corresponding to the graphene (100) diffraction peak.

The sample was rotated around its azimuthal axis ω with the detector fixed to observe the angle of rotation between graphene layers. In Fig. 1(c–e) these rotation scans are shown. For the sample grown for 30 min (1(b)) there are peaks at very specific angles such as 3.89° , 6.01° , 7.34° and 9.43° . These peaks correspond to angles where commensurate structures are formed between two subsequent graphene layers [4]. They correspond to stacking configurations where the superstructure periodicity is a multiple of the graphene atomic period. One can notice that for the sample grown for 30 min the AB stacking (0° rotation angle) exhibits a very strong peak (off-scale), which corresponds to the initial formation of graphite. In the case of samples grown for longer time (45 min [1(c)] and 60 min [1(d)]), the AB stacking is much less pronounced and these specific commensurate angles are not clearly visible. Instead, a diffuse background is visible with no particular stacking. From the X-ray data, however, it is not possible to identify if more than one rotation between graphene layers occurs during the formation of multilayer graphene. The observation of different angles in these scans (for the 45 and 60 min samples) can be due to several rotations of commensurate structures or the presence of other types of stacking, leading to incommensurate structures.

To clarify this issue in detail, STM images of the sample grown for 30 min were taken. In Fig. 2(a–f) we show STM images of different regions of the same sample. Several Moiré patterns were observed, and the rotation angle ϕ from subsequent layers was inferred from the observed superstructure periodicity D following the relationship $D = a/[2\sin(\phi/2)]$ and $a = 0.246 \text{ nm}$ [5]. The values of D were precisely determined via Fast Fourier Transforms (FFTs) of each STM image. An analysis of over 20 STM images showed that about 80% of the rotation angles correspond to commensurate structures. A few incommensurate structures could be identified by STM. While Fig. 2(a–e) show images of commensurate configurations, Fig. 2(f) present an STM image corresponding to a rotation angle of $\phi = 6.4^\circ$, showing the formation of few incommensurate structures with layers with a lower degree of coupling.

A striking observation is the lack of atomic resolution in this particular image (2(f)), which was taken with exactly the same tunneling parameters as the others. This result was tested by changing from commensurate to incommensurate regions back and forth and observing the reproducibility of atomic resolution in commensurate regions and lack of it in incommensurate regions, excluding the possibility of a change in the tunneling condition. This is also a signature of loss of structural coupling of subsequent layers at the surface and an indication of the formation of multilayer graphene from incommensurate structures through the layer stack.

An electronic signature of layer decoupling of multilayer graphene may be obtained using near-edge X-ray absorption fine structure.

Download English Version:

<https://daneshyari.com/en/article/5421563>

Download Persian Version:

<https://daneshyari.com/article/5421563>

[Daneshyari.com](https://daneshyari.com)