



Surface structure of few layer graphene

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ABSTRACT

Understanding surface structure of graphene is important for its integration into composite materials. Here, we have used synchrotron X-ray reflectivity (XRR) to study the structure of commercially available graphene samples (prepared *via* chemical vapor deposition, and marketed as *graphene monolayers*) on SiO₂/Si at different temperatures. X-ray photoelectron spectroscopy, photoemission electron microscopy and atomic force microscopy (AFM) were employed to evaluate the composition and morphology of the graphene layer. Our results indicate that the samples we characterized consisted of 3–4 layers of graphene, which should thus be more accurately described as *few layer graphene* (FLG). Furthermore, a “contaminant” layer, comprising polymethylmethacrylate and graphene multilayers, was found present atop FLG. We also report tentative results on the effect of temperature on the graphene sample thickness. At 25 °C, the FLG thickness from XRR measurements was 13.0 ± 1.0 Å, in agreement with that obtained from AFM (13.9 ± 0.7 Å). Upon heating to 60 °C, the FLG thickness expanded to 13.8 Å, which further increased to 14.3 Å upon cooling to 25 °C. We attribute this temperature dependent thickness to the out-of-plane rippling of graphene as previously reported. These unprecedented results on the FLG surface structure are valuable to its potential bioanalytical applications.

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1. Introduction

Graphene is a one-atom thick, flat, carbon monolayer with a hexagonal carbon aromatic structure. As one of the basic carbon allotropes, it can be transformed into other carbon materials, such as carbon nanotubes and fullerenes. Since the 1970s, studies on growing graphene monolayers on crystals have been carried out, and the first graphene was successfully exfoliated in 2004 by Novoselov and Geim [1]. The unique 2D electronic properties of graphene have since stimulated numerous studies aiming to develop its use in applications such as supercapacitors, batteries, interconnects, transistors, phonon detectors, and sensors *etc.*[2]. Concurrently, advances in the production and modification of graphene sheets have continued to stimulate interest in its

potential application in biotechnology [3]. For instance, the surface charging of graphene due to ion adsorption has been exploited to monitor pH changes [4] and lipid membrane disruptions [5].

One of the most promising methods for producing high quality graphene on an industrial scale is chemical vapor deposition (CVD), which involves depositing graphitic layers atop another crystalline substrate, such as SiC [6], Ni [7], and Cu [8]. A polymethylmethacrylate (PMMA) coating is deposited atop *via* spin coating, and then the graphene can be transferred onto a desired substrate (*e.g.* SiO₂) after the original substrate is removed by chemical etching [9–12]. Graphene prepared by the CVD method has been reported to exhibit an electronic spectrum that can be described by a 2D analogue of the Dirac equation, similar to that of free-standing graphene [3]. Among all the substrates, Cu attracted particular attention. As confirmed by Raman spectroscopy, graphene deposited on Cu by the CVD method could yield over 93%

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coverage (with the rest consisting of 2–3 layer graphene), thanks to its weak interaction with graphene which benefits 2D crystal growth, thereby generating monolayer graphene on the Cu surface [13]. However, it is known that one of the issues with the transferred CVD graphene is the residues of PMMA and etching agents [9–12].

Previous studies have shown that the physical properties of graphene materials are determined by their structure, specifically the thickness and the defects or contaminants. For example, the thermal conductivity of graphene materials increases with the layer number, with monolayer, double-layer, and *few layer graphene* (FLG) (3–10 layers) showing different 2D electronic properties [14,15]; the transport properties in epitaxial graphene are influenced by its sp^2 aromatic lattice structure, which is in turn affected by its substrate and growth conditions [16,17]; and the presence of ripples and wrinkles on graphene is expected to have a negative effect on its electronic properties [13]. Thus, a precise determination of the thickness and morphology of graphene samples under different conditions is important.

Different techniques have been employed for the structural characterisation of graphene and its derivatives, as listed and compared in Table S1 in the Supporting Information (SI). For instance, graphene on silica was first revealed by optical microscopy, scanning electron microscopy (SEM), and atomic force microscopy (AFM) [1]. Non-destructive techniques such as electron microscopy (EM), Raman/Rayleigh scattering microscopy [10], ellipsometry [11,12], and near edge X-ray absorption spectroscopy (NEXAS) [18,19] have been used to study the graphene structure and/or its adsorbates. For the in-plane structural characterisation, scanning tunnelling microscopy (STM) and scanning tunnelling spectroscopy (STS) [8,13,16,25] have been used to image the graphene lattice. X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) [6,26,27] assisted by low energy electron microscopy (LEEM) and photoemission electron microscopy (PEEM) measurements [17,25,28–30] have also been employed for the compositional, structural and morphological characterisation of graphene on conductive substrates. AFM [20], total internal reflection fluorescence correlation spectroscopy (ITIR-FCS) [5], and quartz crystal microbalance with dissipation monitoring (QCM-D) [20] have been used to study lipid adsorption on graphene and related systems. However, these techniques have a limited capacity to probe the out-of-plane structure of the adsorbed layer.

Another powerful technique is X-ray reflectivity (XRR), which is widely used for probing buried interfaces and thin film monolayers [21], bilayers [22,23] and multilayers [24] structures. XRR has been used to study the structure of graphene coated with other popular materials in electronic devices (e.g. HfO_2 [25], Au [26], and perylene-tetracarboxylic dianhydride (PTCDA) [27]), and exposed and buried interfacial structures of graphene grown on SiC [28,29], showing its potential to be used on the structural characterization of graphene.

In this study, commercially available graphene samples on Si/SiO₂ widely used in the studies of graphene applications have been studied using synchrotron XRR. XPS, PEEM and AFM were also used to provide complementary information on the composition and morphology of the samples. Our findings are valuable to graphene research and applications, and also demonstrate the suitability of XRR as a sensitive method for characterising the graphene surface structure, paving the way for further investigations of biomolecular structures on graphene using XRR.¹

2. Experimental methods

2.1. Materials

Graphene samples prepared by an established CVD method were purchased from Graphenea Inc.² Briefly, the preparation process involves chemical vapor deposition of methane on a copper (Cu) foil to produce a graphene (mono)layer. Then a PMMA coating is deposited atop *via* spin coating, before the copper foil is etched away. Finally, the graphene is transferred onto a 1 cm × 1 cm Si wafer with a 300 nm SiO₂ top layer. Graphene produced is being marketed as “*monolayer graphene*”, and is widely used in the studies to evaluate potential application of graphene monolayers in electronic devices.

2.2. Experiment methods

The AFM investigation was conducted in ambient conditions using a MultiMode VIII microscope with a NanoScope V controller, utilizing PeakForce feedback control (Bruker, CA, USA). The cantilever employed was SCANASYST_FLUID+ with nominal spring constant and tip radius of 0.7 N m⁻¹ and 2 nm respectively.

XPS and PEEM measurements of the graphene samples were performed at the Bristol NanoESCA facility. XPS measurements of the FLG were performed with an Argus spectrometer before and after annealing at 450 °C at an ultra-high vacuum (UHV) base pressure of 4.0×10^{-11} mbar for 1 h. Core-level photoemission spectra were acquired at 45° w.r.t. the sample surface, using a monochromatic Al K α (1486.7 eV) X-ray source with a pass energy of 20 eV at room temperature and an estimate total energy resolution of 600 meV. The relative composition of C, O, and Si can be calculated from their corresponding photoemission line intensities.

The PEEM was performed using a NanoESCA II, and the measurements were carried out at room temperature under the UHV condition with a pass energy of 50 eV, a lateral resolution of 150 nm, and an overall energy resolution of 140 meV. The energy calibration was confirmed by fitting a Fermi edge of a clean metallic substrate at the same measurement condition. A He I (21.2 eV) discharge lamp was used as excitation source, and the absolute work function measurement for a particular sample area was obtained from electronic counting of the emitted photoelectrons [30]. The work function values in the maps were obtained by fitting the 600×600 camera pixels spectra with an “error function”. The low excitation photon energy makes PEEM extremely surface sensitive (to 2–3 atomic surface layers), and the PEEM images were acquired after cleaning by annealing to show the surface morphology.

Synchrotron XRR measurements were performed at beamline BM28-XMaS, European Synchrotron Radiation Facility (ESRF), Grenoble, France. A custom designed sample cell was used in all XRR experiments, as shown schematically in Fig. 1 [23,31]. The cell, originally designed to accommodate the “bending mica method” [21], consists of a chamber to house the sample stage for both curved and flat substrates. Temperature control in the range 10–90 °C is facilitated by two brass jackets sandwiching the chamber, one to house electrical heaters and the other connected to a water bath to provide cooling. Graphene samples were mounted on the sample stage in the XRR cell, which was sealed *via* two polyester (Mylar[®]) windows.

The X-ray beam energy was 14 keV (wavelength $\lambda = 0.8856 \text{ \AA}$), and the incident beam size defined by aperture slits was 100 μm (vertical FWHM) × 255 μm (horizontal FWHM). XRR scans were

¹ L. Zhou et al., “Evidence for air bubble formation on graphene surface in water”, in preparation.

² <https://eu.graphenea.com/>.

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