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Laboratory-based real and reciprocal space imaging of the electronic structure of few layer graphene on SiC(000$\bar{1}$) using photoelectron emission microscopy

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ABSTRACT

We present real and reciprocal space photoelectron emission microscopy (PEEM) results on few layer graphene using laboratory based He I and II radiation. The combination of a focused high-intensity source and high transmission PEEM electron optics provides good signal to noise ratios for the different modes of acquisition. We demonstrate work function mapping and secondary electron analysis, related to the graphene layer thickness, band structure imaging from micron scale regions by wave vector resolved PEEM (*k*-PEEM) and local secondary electron spectroscopy, giving information on the valence and conduction band states and the dispersion relations of the π bands. Dark field PEEM is done by selecting the Dirac cone corresponding to the specific rotation of each graphene layer and allows spatial mapping of the commensurate rotation angles. The use of He II radiation increases the volume of reciprocal space accessible to *k*-PEEM and improves signal to background. The preferential linear polarization of the light source is used to investigate aspects of the electronic chirality near the Dirac cone. Recent developments in sample manipulation and cooling are presented.

1. Introduction

Photoelectron emission microscopy (PEEM) has made considerable progress in recent years thanks to instrumental innovation [1–3] and the availability of high brightness vacuum ultraviolet (VUV) and x-ray sources. Advances in energy filtered PEEM [4] allow sample analysis by a combination of high lateral, energy and wave vector resolution. By use of suitable imaging energy filters, photoelectrons with defined kinetic energy are imaged, allowing accurate chemical state mapping [5]. Equipped with a suitable transfer optic the PEEM instruments can also map the angular distribution of the photoelectrons by imaging the back focal plane of the objective lens [6–8]. This reciprocal space spectromicroscopy in the valence band region (*k*-space PEEM or *k*-PEEM) can be performed over selected areas of a few microns thanks to the use of a suitable iris or field aperture in an intermediate image plane. However, it is mainly confined to instruments installed on high brilliance undulator beamlines at synchrotron radiation sources. Here we discuss different aspects of laboratory based PEEM using a focused, high-intensity laboratory vacuum ultra-violet source which allows data acquisition with a good signal to noise ratio in a reasonable time.

The main example used is few-layer graphene grown on the carbon face SiC(000$\bar{1}$). In contrast to graphene grown, e.g., on metals, large homogeneous areas of Graphene remain difficult to grow on C-face SiC. One of the challenges in developing graphene based electronics is the control of the graphene morphology. Epitaxial graphene grown on electronics-grade SiC substrates shows thickness variations which depend on the growth conditions and properties which can be modulated by the graphene/SiC interface. Indeed, deeper understanding of the local morphology, its interface chemistry and the underlying growth process is needed as the first step towards controlling the local properties of the films. A non-destructive tool for investigating micron-scale variations in chemical and electronic properties is therefore indispensable. Most work has focused on monolayer graphene grown on the SiC(0001) (Si face) [9], the ability to grow thin graphene films on the SiC(000$\bar{1}$) (C face) has been demonstrated only recently [10]. C-face films offer a particular interest due to their *c*-axis ordering, their rotational stacking that effectively decouples adjacent graphene layers [11,12]. We have already observed novel Bragg diffraction of the Dirac cones via the superlattice formed by the commensurately rotated graphene sheets [13]. The work function, as measured by energy filtered PEEM, is

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found to vary up to some 100 meV across the surface according to both thickness and the graphene-SiC interface chemical state and commensurate rotations of the grapheme sheets can be measured [13]. Therefore to understand the local properties of such heterogeneous samples requires the capability to gain spectroscopic information from a small area in real space and k-space. We present results on work function mapping, spatially resolved band structure and dark field PEEM on few layer graphene. We introduce the use of He II radiation to obtain the spatially resolved band structure at higher excitation energies in the laboratory. Finally, we introduce a technically advanced sample stage which is used to explore polarization effects on the Dirac cone intensity and allows sample cooling down to 30 K and eucentric rotation.

2. Instrumental

For the work function analysis and parallel momentum $k_{x,y}$-resolved photoemission intensity distributions, we used the NanoESCA [1]. The setup includes an electrostatic photoelectron emission microscope and an aberration compensated double-pass hemispherical analyzer. In k-imaging mode, the NanoESCA resolves the complete hemisphere of the emitted photoelectrons with a k resolution of about 0.05 $Å^{-1}$. The analysis area for k-space can be precisely defined when the instrument is operated in real space and vice versa. Both a contrast aperture (CA) in the back focal plane and a field aperture (FA) in the intermediate plane of the instrument are operated independently from each other. The CA defines the angular acceptance of the instrument. A large CA is chosen for a maximum k acceptance, a small CA for dark field imaging [14]. In normal k-space mode a large contrast aperture is selected to allow a maximum of k-space transmission parallel to the surface plane. The instrument has been adjusted in such a way that the 2D k-space acceptance was about ± 2.5 $Å^{-1}$ around the Γ point. Alternatively, the instrument allows the selection of a small circle in k-space by positioning the contrast aperture around a distinct feature, e.g., for spectroscopy from a specific wave vector. While maintaining the contrast aperture positioned at a distinct point in k-space the instrument can then be switched back to real space without altering the analyzed electron energy to record dark field PEEM images. In this way a direct map of the surface as a function of the local electronic structure as observed in k-PEEM is obtained.

3. Experiment

The substrate used in these studies was a 6H conducting SiC(000$\bar{1}$) from Cree, Inc. Before graphene growth, the sample was first H_2 etched for 30 min at 1400 °C. The sample was then grown in an enclosed graphite RF furnace as previously described [10]. Before all measurements, the sample was annealed at 600 °C for 1 min in UHV to remove surface contamination. This gave a sample of mainly 2–4 graphene layers with thickness variations occurring on the few micron scale [13]. The PEEM experiments were done using both unmonochromatized He I and He II radiation from a focused laboratory VUV source. The photon beam was incident at 65° with respect to the sample normal and because of the focusing optics of the light source is 39% p-polarized. Dark images were recorded with the multi-channel plate (MCP) turned off in order to remove camera noise. Flat-field images were acquired to correct for MCP inhomogeneities. The parabolic non-isochromaticity of the instrument was corrected for all images [1,15]. Because of the high extraction voltage between the sample and the lens, the instrumental wave vector resolution and the dimensions of the reciprocal-space image are independent of the electron energy for the typical spectral ranges used in these experiments. If not stated explicitly the overall spectroscopic resolution was 0.2 eV which is sufficient for the investigated system and facilitates good transmission.

4. Results

The high crystallinity of the graphene sample is demonstrated by low energy electron diffraction (LEED), shown in Fig. 1. The SiC substrate and the graphene spots are clearly visible. There are low angle arcs around each graphene spot which is a clear signature of commensurately rotated graphene sheets [12].

4.1. Reciprocal space imaging with He I radiation

We first show results of bright field real and reciprocal space PEEM imaging using He I excitation. The threshold image series was acquired for $E-E_F$ from 3.5 to 8.0 eV in 25 meV steps, in a 62 micron of view (FoV) with an acquisition time of 2 s per image, repeated 10 times. The dynamic range had a S/N >3000. The work function map constructed from a pixel by pixel error function fit to the rising edge of the photoemission threshold is shown in Fig. 2a. The region marked by the small circle corresponds to three layer graphene [14]. This area has been selected by a 5.7 μm diameter iris for the reciprocal space imaging. A 3D representation of the raw data is shown in Fig. 2b in which the horizontal axes are k_x and k_y wave-vectors parallel to the surface and the vertical axis is energy. The characteristic Dirac cones are clearly visible. The 3D image expands with increasing energy due to the wave-vector horizon in k-space for $h\nu = 21.22$ eV. Fig. 2c is a constant energy cut in reciprocal space 0.2 eV below the Fermi level, showing the principal Dirac cones due to the top graphene layer and fainter cones due to the commensurately rotated layers. In Fig. 2d we show a cut perpendicular to ΓKM for the top graphene layer. From the characteristic linear dispersion the group velocity is estimated to be 0.96×10^6 ms^{-1}. The most intense band structure is observed for the topmost graphene

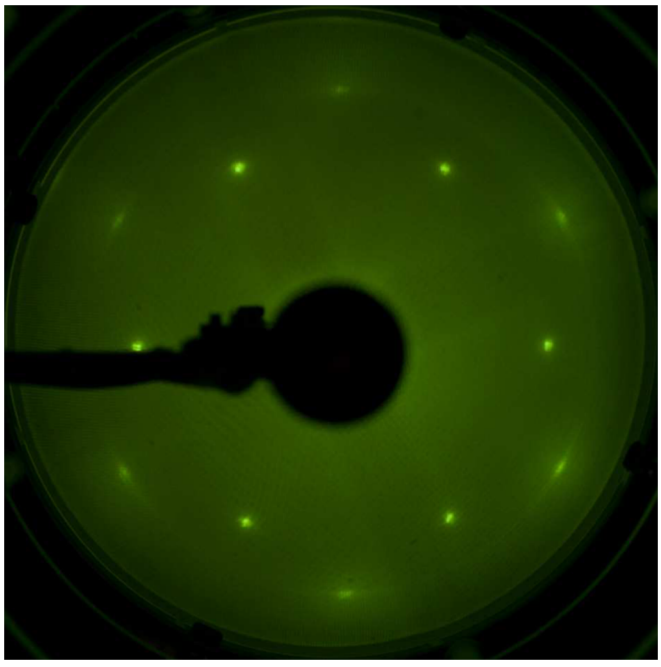

Fig. 1. LEED image of the FLG/SiC(000$\bar{1}$) at 70 eV.