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Landau level splitting in nitrogen-seeded epitaxial graphene

S.L. Rothwell [a], F. Wang [b], G. Liu [c], C. Xu [c], L.C. Feldman [c], E.H. Conrad [b], N.P. Guisinger [d], P.I. Cohen [a, *]

[a] Department of Electrical and Computer Engineering, University of Minnesota, Minneapolis, MN, 55455, USA
[b] Department of Physics, Georgia Institute of Technology, Atlanta, GA, 30332, USA
[c] Institute for Advanced Materials, Devices, and Nanotechnology, Rutgers University, Piscataway, NJ, 08854, USA
[d] Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL, 60439, USA

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ABSTRACT

We report scanning tunneling microscopy and spectroscopy (STM and STS) studies of graphene formed from a nitrogen-seeded SiC(000$\bar{1}$) surface. STM indicates that much of the graphene consists of wide flat plateaus with hexagonal features bounded by pleats and regions with disordered character. Nitrogen impurities are not observed in the epitaxial graphene layers. STS measurements on this surface show peaks corresponding to Landau levels associated with pseudo-magnetic fields as high as 1000 T. The energy distribution of Landau levels is consistent with an electronic model employing a finite bandgap.

1. Introduction

Graphene grown epitaxially on silicon carbide presents the intriguing possibility of atomic scale graphene modification by first altering the substrate. Recently we showed that multilayer epitaxial graphene grown on C-face nitrogen-seeded SiC has a valence band offset of 0.3–0.7 eV [1] from the Fermi level. Here, we examine the morphology and electronic structure of this nitrogenated graphene (NG). Landau levels are clearly observed and subsequently interpreted in terms of a pseudo-magnetic field. We show that the sequence of observed levels can be fit with a model that includes a bandgap, consistent with the earlier indications of a gap in this unique material.

Conventional graphene from many fabrication methods, including mechanical exfoliation, SiC epitaxy, and CVD among others, has been characterized extensively reporting high mobilities and no bandgap. Fabricating a semiconducting form of this material may only be achieved by a radical departure from the ideal monolayer sheet. Induced bandgaps in graphene have been reported under a variety of conditions. For example, various dopants [2–6] have been reported to induce a gap, but these films are expected to have low mobility due to scattering from substitutional dopants. An ordered functionalized band gap has been produced in graphene grown on SiC(0001) but because it is due to an intrinsic surface reconstruction, there is no way to control the gap size [7]. Graphene ribbons have experimentally demonstrated confinement induced bandgaps, but continue to present lithographic challenges to large scale fabrication and device integration [8,9]. Graphene placed on a periodic array of topographic features displayed possible small, strain induced gaps of 0.14–0.19 eV, dependent on feature pitch [10].

It has been predicted [11–13] and observed [14,15] that a distortion or strain of the graphene lattice will create large pseudo-magnetic fields. However no semiconducting graphene has been reported in association with such strain induced fields. Scanning tunneling spectroscopy (STS) spectra showing several Landau levels induced by pseudo-magnetic fields have been reported for spectra taken across graphene nano bubbles [14,16], graphene on ridges [15,17], planar strained graphene on copper foil [18], and molecular graphene assembled from CO [19]. Graphene intercalated with potassium was also reported to have Landau levels which were attributed to varying electrostatic potentials rather than strain [20]. In most of these reports a Landau level at the Dirac point is clearly visible. Scanning tunneling microscopy (STM) and STS results are presented here to determine the Landau level variation over NG films. These results are interpreted in terms of pseudo-magnetic fields inducing a Landau level sequence consistent with a finite bandgap [21,22].

2. Nitrogenated graphene

As previously reported, nitrogenated graphene was prepared by growth on the carbon-face SiC (000$\bar{1}$) on which there were 0.3

* Corresponding author.
E-mail address: picohen@umn.edu (P.I. Cohen).

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monolayers (ML) of N [1]. These starting surfaces were prepared by oxidation of SiC, followed by annealing in NO, and then etching to leave the submonolayer of N on the surface [23]. Graphene is then grown on the nitrogen-seeded substrates via controlled silicon sublimation [1,24,25]. Between 1 and 8 layers of epitaxial graphene were grown by heating to about 1400 C in a Si flux [24]. After growth, variable energy X-ray photoelectron spectroscopy (XPS) showed that about 0.2 monolayers (ML) of nitrogen remain at the interface between the SiC and graphene, strongly bonded to the SiC substrate. About 25% of the nitrogen bonds with the graphene and the SiC in sp^3 bonds, indicating there are strong bonds between carbon atoms in the first layer of graphene and carbon atoms in the substrate. STM indicates that the graphene films are not flat but bend smoothly over nanoscale ripples [1,25].

Angle-resolved photoemission spectroscopy (ARPES) measurements on 50 μm size regions showed Dirac cones that were broadened and which were shifted from the Fermi level to higher binding energy. These ARPES results at the graphene *K*-point (rotated 30° from the SiC $\langle 10\bar{1}0 \rangle$ direction) show valence band offsets that depend on the number of layers in the epitaxial graphene films. The graphene band structure of a 3 layer film with 0.2 ML interfacial nitrogen content shows an offset from the Fermi level of 0.7 eV, while that of an 8 layer film has a smaller 0.45 eV shift. The effective Fermi velocity (v_F) is reduced compared to pristine graphene, consistent with the opening of a bandgap. Both the 3 and 8 layer samples have $v_F = 0.8 \pm 0.05 \times 10^6$ m/s.

The ARPES measurements [1,25] from nitrogen-seeded graphene π bands are broader in k than for pristine graphene, largely due to the corrugation of the graphene surface shown in Fig. 1. Small modulations in the local graphene height cause a local angular variation in the surface normal. Since the surface normal determines the orientation of the graphene Brillouin zone, the corrugated surface leads to local k_x and k_y shifts in the *K*-point. This leads to an ARPES image that is an area average of a distribution of parabolic cuts through Dirac cones from locally tilted graphene resulting in an *E*- and *k*-broadened spectra. Using STS we examine the spatial distribution of the local density of states (LDOS) corresponding to these results but in a way that senses the graphene bending differently.

Ultrafast time resolved terahertz spectroscopy also finds evidence of a bandgap in these NG films. Recently Mihnev et al. [26] showed an increase in the rate of carrier cooling and recombination by over two orders of magnitude. This was attributed to a distribution of finite bandgaps of which a subset was in a range to be bridged by optical phonon emission.

It is important to note that the single, linear Dirac cone in the ARPES measurement leads us to conclude that multilayer NG is not electrically coupled between the top layers. If the band structure was from multiple coupled layers, a second cone (or more) would be expected. Bernal stacking would produce a band shifted 0.5 eV from the observed cone to higher binding energy [27], however no other cones shifted in k_y are visible. Shifted cones would also be expected because of the rotational stacking of C-face graphene [28]. The lack of these cones means that the rotation angle between the top two layers of graphene captured in the 50 μm ARPES beam diameter must be rotated >10° with respect to each other (this angle is set by the detector slit window). Such a large relative rotation angle between the two layers is known to keep the layers electronically decoupled [29,30]. Thus these multilayer NG films act as electrically uncoupled, multiple, independent graphene layers [31]. Any STS data would be expected to similarly measure the LDOS and electronic features of monolayer graphene.

3. Results

STM and STS studies were primarily conducted at the Argonne National Laboratory (ANL) in a UHV variable temperature Omicron STM with an electrochemically etched tungsten tip at room temperature. Reported voltages are sample biases, and constant current mode was used for all images. STS was performed after cooling to 100 K. Images were also taken at Oak Ridge National Laboratory (ORNL) at room temperature. STS and images taken at Brookhaven National Laboratory (BNL) were at 4 K. As seen in Fig. 1, STM on NG

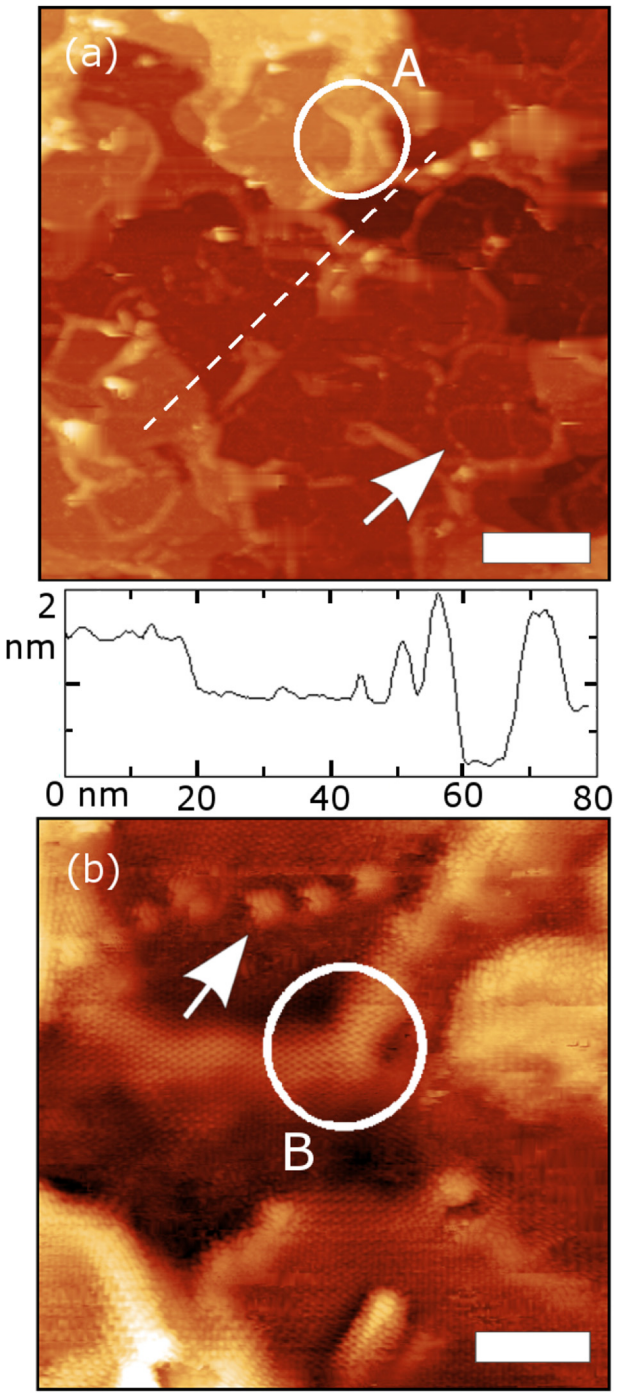

Fig. 1. Scanning tunneling microscopy of graphene grown on C-face nitrogenated SiC. (a) Overview of 4 layer NG showing plateaus and smooth pleats. Circle A highlights pleats at the edge of a plateau. 20 nm scale bar, 1 V, 0.03 nA. A topographic profile following the dotted line is plotted below. (b) Atomic resolution of a region with ripples and nanocaps from 0 to 1 nm in height. Circle B highlights a single ripple. 4 layer NG, 3 nm scale bar, 0.1 V, 1 nA. Images taken at ORNL (a) and ANL (b). (A colour version of this figure can be viewed online.)