FAST TRACK COMMUNICATION

Direct graphene growth on MgO: origin of the band gap

To cite this article: Sneha Gaddam et al 2011 J. Phys.: Condens. Matter 23 072204

View the article online for updates and enhancements.

Related content

- Direct graphene growth on Co3O4(111) by molecular beam epitaxy
  Mi Zhou, Frank L Pasquale, Peter A Dowben et al.

- Electronic structure of a graphene/hexagonal-BN heterostructure grown on Ru(0001) by chemical vapor deposition and atomic layer deposition: extrinsically doped graphene
  Cameron Bjelkevig, Zhou Mi, Jie Xiao et al.

- Epitaxial growth of graphene on transition metal surfaces: chemical vapor deposition versus liquid phase deposition
  Samuel Grandthyll, Stefan Gsell, Michael Weinl et al.

Recent citations

- Review on mechanism of directly fabricating wafer-scale graphene on dielectric substrates by chemical vapor deposition
  Jing Ning et al

- Electronic and optical properties of strained graphene and other strained 2D materials: a review
  Gerardo G Naumis et al

- First-principles study on bottom-up fabrication process of atomically precise graphene nanoribbons
  Tomoaki Kaneko et al
Direct graphene growth on MgO: origin of the band gap

Sneha Gaddam\textsuperscript{1}, Cameron Bjelkevig\textsuperscript{1,3}, Siping Ge\textsuperscript{1,4}, Keisuke Fukutani\textsuperscript{2}, Peter A Dowben\textsuperscript{2} and Jeffry A Kelber\textsuperscript{1,5}

\textsuperscript{1} Department of Chemistry and Center for Electronic Materials Processing and Integration, University of North Texas, Denton, TX 76203-5017, USA
\textsuperscript{2} Department of Physics and Astronomy, Nebraska Center for Nanostructures and Materials, University of Nebraska-Lincoln, Lincoln, Theodore Jorgensen Hall, 855 North 16th Street, NE 68588-0111, USA
\textsuperscript{3} Permanent address: Intel Corporation, 4100 Sara Road SE, Rio Rancho, NM 87124, USA.
\textsuperscript{4} Permanent address: Department of Physics, China Agricultural University, Beijing, People’s Republic of China.
\textsuperscript{5} Author to whom any correspondence should be addressed.

Received 17 December 2010, in final form 28 December 2010
Published 1 February 2011
Online at stacks.iop.org/JPhysCM/23/072204

Abstract

A 2.5 monolayer (ML) thick graphene film grown by chemical vapor deposition of thermally dissociated C\textsubscript{2}H\textsubscript{4} on MgO(111), displays a significant band gap. The apparent six-fold low energy electron diffraction (LEED) pattern actually consists of two three-fold patterns with different ‘A’ and ‘B’ site diffraction intensities. Similar effects are observed for the LEED patterns of a 1 ML carbon film derived from annealing adventitious carbon on MgO(111), and for a 1.5 ML thick graphene film grown by sputter deposition on the 1 ML film. The LEED data indicate different electron densities at the A and B sites of the graphene lattice, suggesting that the observed band gap results from lifting the graphene HOMO/LUMO degeneracy at the Dirac point. The data also indicate that disparities in A site/B site LEED intensities decrease with increasing carbon overlayer thickness, suggesting that the graphene band gap size decreases with increasing number of graphene layers on MgO(111).

(Some figures in this article are in colour only in the electronic version)
Figure 1. Intensity analysis of the previously reported [2] LEED pattern (75 eV beam energy) of graphene film, formed by free radical assisted CVD on MgO(111), which displays a band gap of 0.5–1.0 eV. The XPS-determined average carbon layer thickness is 2.5 ML. The average background-subtracted intensity (arbitrary units) of the A sites is 9.9 (±3), and that of the B sites is 7.5 (±0.9). Uncertainties in the average intensities correspond to the standard deviations.

Figure 2. C(1s) XPS and LEED spectra for formation of an ordered carbon monolayer on MgO(111): (a) XPS C(1s) spectrum of a multilayer adventitious carbon film observed immediately after insertion of the MgO crystal into UHV at room temperature (no LEED pattern is observed); (b) XPS C(1s) spectrum after annealing at 700 K in UHV in the presence of O2; the XPS-derived average carbon layer thickness is 1 ML; (c) the corresponding LEED pattern exhibits C3v symmetry; (d) XPS after anneal of the film in (b) to 1000 K in the presence of C2H4 (5 × 10^{-7} Torr, 25 min); the XPS-derived C thickness remains 1 ML; (e) corresponding complex LEED pattern; (f) close-up of the pattern in (e) with integrated, background-subtracted intensities (arbitrary units) for ‘A’ and ‘B’ spots (circled). The A spots have an average intensity of 18.7 ± 3, while the B spots have an average intensity of 12.9 ± 1. The uncertainties are the standard deviations. Other spots in the image are weaker and are attributed to multiple diffraction. The LEED patterns were acquired at 80 eV beam energy. The XPS spectra binding energies are referenced to a MgO lattice oxygen O(1s) binding energy of 530.0 eV ([11]).
presence of LEED scattering. Subsequent annealing to 1000 K in the a disordered carbon overlayer that does not contribute to the intensity is OH-terminated MgO(111) (1 × three-fold LEED pattern (figure 2(c)) is representative of an ∼ ordered carbon monolayer. The sputter deposition was at room temperature from a graphite target, followed by annealing to 1000 K in UHV.

Figure 3. (a) C(1s) XPS spectrum and (b) corresponding LEED pattern, acquired at 80 eV beam energy, for graphene formed by PVD on an ordered carbon film grown on MgO(111), as shown in figure 2. A multilayer adventitious carbon film is observed upon insertion of the MgO(111) single crystal into UHV (figure 2(a)), and extensive annealing in O2 at 700 K, 5 × 10−7 Torr removes all but ∼1 ML as determined by XPS (figure 2(b)). The corresponding three-fold LEED pattern (figure 2(c)) is representative of an OH-terminated MgO(111) (1 × 1) surface [11] and indicates a disordered carbon overlayer that does not contribute to the LEED scattering. Subsequent annealing to 1000 K in the presence of 5 × 10−6 Torr of C2H4 yields a C(1s) spectrum with unchanged average thickness, but with a feature near 288 eV binding energy (figure 2(d))—indicative of carbon in a higher oxidation state. The corresponding LEED pattern (figure 2(e)) displays apparent six-fold symmetry. Intensity analysis of this LEED pattern, however (figure 2(f)), indicates that this pattern actually consists of two C3v patterns. The A sites have an average, background-subtracted, intensity (arbitrary units) of 18.7 ± 3, compared to a corresponding value of 12.9 ± 1 for the B sites. These data indicate an experimentally significant difference in intensities on A and B sites, and thus indicate that the corresponding lattice sites in the real space graphene layer have different electron densities.

A similar pattern is observed for a partial graphene layer grown by exposing an ordered interfacial layer on MgO (similar to figure 2(c)) to PVD from a graphite sputter magnetron target in an Ar plasma at ambient sample temperature. Subsequent annealing in UHV yielded the XPS and LEED data shown in figures 3(a) and (b), respectively. The A site average intensity (figure 3(b)) is 4.7±0.4 and the average B site intensity is 1.5 ± 0.2. The average carbon thickness, determined from XPS, is 1.5 ML.

As summarized in table 1, the disparity between average A and B site diffraction intensities decreases as the carbon layer average thickness increases for graphene films grown on MgO(111). This disparity in intensities of adjacent LEED spots is also specific to graphene/MgO(111). Analyses of other LEED data for graphene films with 0 eV band gap, including graphene/Ru(0001) [2] and graphene/BN(0001)/Ru(0001) [1, 2], indicate no such disparities in average A site/B site diffraction intensities. The decrease in relative average A site/B site LEED intensity difference with increasing graphene thickness on MgO (table 1) is consistent with the primary cause for such differences being interactions between the MgO(111) surface and the first graphene overlayer so that with increasing graphene

### Table 1. LEED ‘A’ and ‘B’ site diffraction spot intensities as a function of carbon overlayer average thickness determined by XPS.

<table>
<thead>
<tr>
<th>Average carbon thickness (ML)</th>
<th>Average A site LEED intensity (arb. units)</th>
<th>Average B site LEED intensity (arb. units)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>18.7(±3)</td>
<td>12.9(±1)</td>
<td>Interfacial layer</td>
</tr>
<tr>
<td>1.5</td>
<td>4.7(±0.4)</td>
<td>1.5(±0.2)</td>
<td>Interfacial layer + PVD</td>
</tr>
<tr>
<td>2.5 ([2])</td>
<td>9.9(±3)</td>
<td>7.5(±0.9)</td>
<td>Graphene-interfacial bilayer formed by FRA-CVD and annealing to 1000 K</td>
</tr>
</tbody>
</table>

* The uncertainties correspond to the standard deviations.
thickness, the overlayer becomes increasingly screened from these interface interactions. While a definite band gap has, to date, only been definitely observed [2] for the 2.5 ML graphene film on MgO(111) (table 1), the trends in LEED intensities summarized in table 1 suggest that band gaps also exist for the 1 and 1.5 ML graphene/MgO(111) films, and that the magnitude of the band gap decreases as increasing numbers of graphene layers progressively screen the MgO–C interactions at the interface, as demonstrated for single and few layer graphene films on SiC(0001) [3].

The ability to form graphene by PVD also suggests the potential for forming single or limited multilayer graphene on MgO. The recurring problem with CVD of two-dimensional systems is that the formation of a complete layer often renders the surface relatively inert towards subsequent deposition, as observed for CVD of hexagonal BN by thermal decomposition of borazine, or graphene formation by benzene decomposition on Ru(0001) [12]. PVD methods therefore offer an alternative route—although, of course, not self-limiting—towards the practical fabrication of single/few layer graphene on MgO substrates. It may also be that other (111) surfaces of oxides with the NaCl structure may similarly induce band gaps in graphene.

In summary, graphene layers can be formed by FRA-CVD or PVD on MgO(111). Substrate interactions result in different electron charge densities on graphene A and B sites (figures 1–3), as evidenced by different A site/B site LEED intensities. The disparity between average A and B site LEED intensities decreases with increasing carbon overlayer thickness (table 1). The observed A site/B site disparities in LEED intensities are specific to graphene films grown on MgO(111) and are not observed upon analysis of the LEED data for graphene films with 0 eV band gaps formed on Ru(0001) [2] or on BN(0001)/Ru(0001) [1, 2]. The data therefore strongly suggest that the previously observed [2] ∼0.5–1 eV bandgap for graphene/MgO(111) is due to graphene/substrate interfacial interactions, which remove the HOMO/LUMO degeneracy at the Dirac point, leading to formation of a band gap. Further, the data in table 1 suggest that such interfacial interactions are screened by successively deposited graphene layers, thus leading to the prediction of a decreasing band gap with increasing numbers of graphene overlayers grown on MgO(111).

A band gap of 0.5–1 eV may be suitable for FET applications [4, 5]. Although the effects of a band gap on graphene charge mobilities remain to be determined, the intimate contact of physically transferred graphene sheets with high dielectric constant liquid [13] or solid [14] substrates has been shown to yield electron mobilities >10^4 cm^2 V^-1 s^-1. Further, the ability to form few layer graphene by PVD, coupled with the apparent decrease in A site/B site intensity difference with increasing carbon layer thickness (table 1) suggests that both band gaps and mobilities may be tunable through the deposition of varying numbers of graphene layers on MgO. The graphene/MgO/Si system therefore has significant potential for practical FET device applications.

The work at UNT was supported by the Semiconductor Research Corporation, Division of Nanomanufacturing Sciences, under Task ID 1770.001 and Task ID 2123.001.

References