Epitaxial Graphene on SiC(0001): More than Just Honeycombs

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Using scanning tunneling microscopy with Fe-coated W tips and first-principles calculations, we show that the interface of epitaxial graphene/SiC(0001) is a warped graphene layer with hexagon-pentagon-heptagon ($H_{5,6,7}$) defects that break the honeycomb symmetry, thereby inducing a gap and states below $E_F$ near the K point. Although the next graphene layer assumes the perfect honeycomb lattice, its interaction with the warped layer modifies the dispersion about the Dirac point. These results explain recent angle-resolved photoemission and carbon core-level shift data and solve the long-standing problem of the interfacial structure of epitaxial graphene on SiC(0001).

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Graphene, a one-atom-thick planar sheet of $sp^2$-bonded carbon atoms in a honeycomb lattice, is the building block of many carbon allotropes. The strong in-plane $\sigma$ bonds form the backbone of the honeycomb, while the half-filled $\pi$ bonds exhibit linear band dispersion near the K points [1]. This unique structure leads to graphene’s novel physical and electronic properties such as room temperature (RT) quantum Hall effects, Klein tunneling, and high carrier mobility [2–4]. Recently, uniform wafer-sized graphene has been grown epitaxially on hexagonal SiC [5] and transition metal substrates [6,7], a critical step towards the development of graphene electronics [8,9].

Nevertheless, the mismatch with the SiC substrate can have profound effects on the physical and electronic properties of epitaxial graphene. On the (0001) C face, the formation of a “twisted” interface leads to the decoupling between different layers of multilayer graphene, each having as a single layer with a carrier mobility of 250 000 cm$^2$/V s [10,11], comparable to that of exfoliated graphene [4]. On the (0001) Si face, however, the picture remains controversial [12]. Structurally, graphitization has been known since 1975 to start with a $(6\sqrt{3} \times 6\sqrt{3})$ structure [13], which remains at the interface during subsequent layer growth. While earlier studies suggested that it consisted of graphene layers weakly bonded to either the $(1 \times 1)$ SiC(0001) surface [13,14] or Si-rich interface layers [15–17], recent work indicates a carbon layer covalently bonded to the SiC [18–23]. Another hotly debated issue is the origin of the gap near the K points observed by angle-resolved photoemission spectroscopy (ARPES)—a property crucial for its use in electronic devices [24–26]—but found only for the Si face, and absent for the C face and exfoliated graphene.

In this Letter, we show that these unique properties of epitaxial graphene on the Si face arise from a warped interfacial graphene layer, resulting from the periodic inclusion of hexagon-pentagon-heptagon ($H_{5,6,7}$) defects in the honeycomb to relieve the mismatch with the SiC substrate. The $H_{5,6,7}$ defects break the symmetry of the honeycomb, thereby inducing a gap: the calculated band structure of the proposed model along $\Gamma$–K is semiconducting with two localized states near K points below $E_F$, correctly reproducing the published photoemission and C 1s core-level spectra [22,23]. Furthermore, the next graphene layer assumes the defect-free honeycomb lattice, though its interaction with the warped layer leads to deviations from the linear dispersion at the Dirac point, shedding light on the origin of the observed anomalies in ARPES [25,26].

Experiments were carried out on epitaxial graphene grown on N-doped 6H-SiC(0001), which was first etched in a H$_2$/Ar atmosphere at 1500 °C. After annealing at $\sim$950 °C for 15 min in a Si flux to produce a $(3 \times 3)$ reconstructed surface, the SiC substrate was heated to $\sim$1300 °C to grow graphene in ultrahigh vacuum [27]. Scanning tunneling microscopy (STM) images were taken using W and functionalized W tips, where the latter are made by coating W tips with Fe at RT and followed by annealing at 500–700 °C in ultrahigh vacuum.

First-principles calculations, using the full-potential linearized augmented plane wave method as implemented in flap [28], model the substrate using a $(6\sqrt{3} \times 6\sqrt{3})$ 6-bilayer supercell, with a vacuum region of $\sim$20–25 Å and a basis cutoff of $\sim$195 eV. Because of the usual density functional theory underestimation of the gap (1.6 vs 3.0 eV for 6H-SiC), comparisons of calculated density of states (DOS) and STM images are limited to biases within $E_F \pm 0.5$ eV.

Figure 1 presents an STM image of the $(6\sqrt{3} \times 6\sqrt{3})$ graphene/SiC(0001) interface, and closeups of the two main features observed: an up-pointing trimer marked by a triangle of sides $\sim$3.5 ± 0.2 Å, and a rosette marked by a hexagon of sides $\sim$3.2 ± 0.2 Å. While the appearance of the trimer is bias independent, the contrast of the rosette is slightly less in empty-state images. The ratio of trimer to rosette depends on growth conditions, but the former is always more populated. The image shown in Fig. 1(a), taken at an early stage of growth (the Si-rich $\sqrt{3}$ reconstruction still can be seen on part of the surface), shows a trimer-to-rosette ratio of $\sim$2:1. Higher ratios (e.g., 4:1) are
FIG. 1 (color online). (a) STM image of epitaxial graphene on 6H-SiC(0001) taken with an Fe-coated W tip at sample bias $V_s = -0.1$ V, tunneling current $I_t = 0.3$ nA. Expanded views of marked features taken at (b) $-0.1$ V and (c) $+0.1$ V. Image size: $4.5 \times 4.5$ nm$^2$. The arrow marks a common defect likely associated with Si vacancies in the substrate.

observed at later stages of growth, accompanied also by a greater number of defects. Close examination of images and line profiles (e.g., dashed line in Fig. 1) indicates: (1) neighboring features typically do not fall on the same line; (2) the spacing is nonuniform, averaging ~19 Å, i.e., about $6 \times$ the (1 x 1) lattice spacing of SiC(0001); and (3) the center of the rosettes consists of a downward pointing trimer, which can be better seen in 3D in Fig. 2(a).

STM images (not shown) of the $(6\sqrt{3} \times 6\sqrt{3})$ taken using W tips at larger bias (e.g., $E_F \pm 1.5$ eV) are similar to earlier studies [12,29–31]. Imaging at energies closer to $E_F$ (within $\pm 0.1$ eV) is challenging [29–31], but can be routinely achieved with Fe-coated W tips. Our modeling of the Fe/W tip indicates that the Fe minority spin channel has an especially sharp peak 0.5 eV below $E_F$, facilitating tunneling between the tip and graphene-specific states not accessible with conventional W tips. These images clearly reveal new details of the $(6\sqrt{3} \times 6\sqrt{3})$ structure that cannot be explained by existing models. For example, simulated STM images based on defect-free graphene covalently bonded to SiC(0001) (1 x 1) show features of only threefold or twofold symmetry [20,21]. In addition, most of these calculations indicate that $(6\sqrt{3} \times 6\sqrt{3})$ is metallic [18–20], rather than semiconducting around K as evident in ARPES [22,23]. A highly interacting graphene layer can yield a semiconducting gap [17], but requires complexes of Si tetramers and adatoms bonding to the SiC at the interface not seen in ARPES data at this stage of graphene growth [22].

Here, we propose a new interface model that accounts for STM, ARPES, and C core-level observations [22–25]. A $(13 \times 13)$ graphene layer is nearly commensurate to $(6\sqrt{3} \times 6\sqrt{3})$ SiC(0001) [12], which results in two high symmetry positions: a C atom or a graphene hexagon centered above a Si. Our calculations indicate that C atoms located directly above Si are pulled towards the SiC surface such that the Si-C bond is shortened to 2.0 Å from a nominal interplanar separation of 2.3 Å, consistent with other calculations [21].

To better accommodate this bond distortion and retain the threefold coordination for each C atom, pentagons and heptagons—which cause positive and negative curvatures [32–34], respectively—can be inserted into the honeycomb lattice. Inclusion of three pairs of alternating pentagons and heptagons around a rotated hexagon ($H_{5,6,7}$) [Fig. 2(b)] significantly reduces the distortions of the C-C bonds, and preserves the long-range translational and rotational integrity of the graphene honeycomb. Placement of the $H_{5,6,7}$ defects at the two high symmetry positions leads to two variants. At the “top” site [Fig. 2(c)], three Si atoms sit directly below the corners of the central hexagon of the $H_{5,6,7}$, with this hexagon centered above a C of the SiC substrate. At the “hollow” sites [Fig. 2(d)], the central hexagon is centered over a Si, and three Si atoms are now bonded to C atoms at the edge of the $H_{5,6,7}$ defect. Overall, this transformation decreases interfacial Si-C bonds from 4 (6) to 3 at the hollow (top) sites, further reducing the mismatch with the SiC substrate. The result is a warped graphene layer covalently bonded to SiC(0001) (1 x 1), whose formation is favored by $\sim 0.1$ eV/C compared to a (relaxed) honeycomb structure, with the top site more stable than the hollow by 0.03 eV/C. (The calculated adhesion energy of the honeycomb layer, relative to isolated graphene, is slightly nonbinding by
entire graphene layer, as shown in Fig. 4(a), both the honeycomb and the interfacial structures (e.g., the trimers) can be clearly seen on the large terrace, while only a triangular lattice with a 2.5 Å spacing is observed on the smaller terrace in the lower right hand corner. This confirms that the warped graphene layer remains at the interface, and is still accessible by electron
tunneling up to the first layer [12,17]. Calculations indicate that the first layer graphene is quite flat, and the perfect honeycomb lattice spacing of 2.5 Å with an interlayer spacing of 3.2 Å relative to the warped interface layer. The k-projected band structure for the interface + first layer graphene [Fig. 4(b)] shows almost perfect graphene bands, with the Dirac point below $E_F$. The bottom of the $\alpha(\pi)$ band at $\Gamma$ is shifted upwards by about 1.3 (3.5) eV compared to the interface (Fig. 3), qualitatively consistent with the ARPES data [22,23].

The bands near the Dirac point are shown in more detail in Figs. 4(c)–4(e). The downward shift of $E_D = -0.4$ eV indicates that the layer is n-doped, consistent with experiment [25,26]. The calculated splitting of the Dirac states is only 33 meV. However, because of the interactions with the warped interface graphene layer, there are deviations from the linear dispersion of defect-free graphene, leading to parabolic dispersion above the gap, and an apparent gap of $-0.25$ eV [marked by the arrows in Fig. 4(c)], closely matching the $0.26$ eV gap reported in ARPES studies [25]. Comparison of Figs. 4(d) and 4(e) reveals subtle, but distinct differences in the dispersions, especially above the Dirac point, as a direct consequence of the different interactions between the first graphene layer and the two $H_{5,6,7}$ variants.

Closely related is the misalignment of the bands above and below $E_D$, illustrated by the dotted lines in Figs. 4(c)–4(e). The projections of the $\pi$ states below $E_D$ do not pass through the $\pi^*$ states above $E_D$, an observation previously attributed to electron-phonon or electron-plasmon interactions [26]. (Shifting the lines upward, the dispersion of the $\pi^*$ bands above $E_D$ can be fit, but then misaligns the $\pi$ states below $E_D$.)

In summary, the atomic structure of the graphene/SiC(0001) interface is found to be a warped graphene layer with the inclusion of $H_{5,6,7}$ defects in the honeycomb lattice, with the subsequent layer assuming the perfect honeycomb structure. Our results provide a consistent explanation of the available experimental data, and resolve a long-standing controversy regarding the interfacial structure of epitaxial graphene on SiC(0001), a material that may significantly impact the development of graphene electronics.

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