Edge structure of epitaxial graphene islands

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Graphene islands grown epitaxially on 6H-SiC(0001) were studied using scanning tunneling microscopy and spectroscopy. Under specific growth conditions, ≈ 10 nm single-layer graphene islands are observed on top of the SiC buffer layer and align with the SiC(0001)-1×1 lattice directions. Atomic-resolution images show that the edges of the island closely follow an armchair-edge configuration.

The study of graphene, a single sheet of carbon with a honeycomb lattice, has the potential to lead to future carbon-based nanoelectronics.[1,2] However, many experimental graphene studies are still in their infancy due to numerous challenges in the synthesis of graphene. One of the most promising methods of graphene synthesis is the graphitization of SiC substrates.[1,3] Graphene grown epitaxially by this method has been shown to yield the physics of single-layer graphene, such as a linear band dispersion and chirality characteristic of massless Dirac fermions.[4] The growth mechanisms for graphene formation on the SiC substrate are not fully understood, however, presenting challenges for the development of large-scale integrated graphene electronics. Therefore, detailed studies of the initial stages of graphene growth are vital.

Recent work has shown that the growth of epitaxial graphene is predominantly from step edges for 6H-SiC(0001) annealed in vacuum.[5] In this work we show via scanning tunneling microscopy (STM) that a low density of epitaxial graphene islands also form on the surface. Graphene islands are of extreme scientific interest as their small sizes are suspected to yield novel electronic properties such as quantum confinement.[6,7] In this initial work we emphasize structure and electronic properties, but note that the simple observation of island formation opens the possibility to derive surface kinetic parameters from detailed measurement of island sizes and areal densities.[8]

In order to study graphene islands, we needed to produce a sample with a small coverage of single-layer graphene, roughly 10% coverage of layer 1 graphene (we use layer 0 to denote the insulating buffer layer and layer 1 to refer to the first layer with ostensibly graphene electronic structure).[9] To achieve such a coverage, we resistively heated a hydrogen-etched 6H-SiC(0001) sample to 1200 °C very quickly (≈ 40 °C/s) and held it at this temperature for 30 s in ultra-high vacuum (UHV). This temperature has been shown to be on the cusp of epitaxial graphene formation.[10–12] The heating process was repeated five times to induce more growth on the surface. All measurements were performed at room temperature in a custom-built STM system, described in detail elsewhere.[13] Iridium probe tips, used in tunneling measurements, were cleaned with field evaporation. Differential conductance, dI/dV, was measured with a lock-in amplifier, using a root-mean-square voltage modulation of 20 mV, at a frequency of 1.4 kHz.

Under the above growth conditions, on large layer 0 terraces, there appear a very small number of layer 1 graphene islands, typically 10 nm in width. One such island is shown in Fig. 1(a). This island is approximately 11 nm wide and ≈ 0.3 nm high, the upper limit found previously for layer 1 to layer 0 step edges.[9] Over a total scanned area of ≈ 10 μm^2, only eight islands were identified. Clearly, the growth is dominated by graphene formation at SiC step edges, consistent with prior observations.[5] However, the observation of a low density of large and isolated islands provides evidence for a diffusing carbon species of relatively high surface mobility, and perhaps for a large critical nucleus, as observed for C deposition on Ru.[14] The inset of Fig. 1(a) displays the SiC(0001)-$6\sqrt{3} \times 6\sqrt{3}R30°$ reconstruction (layer 0). Red arrows of the inset indicate the SiC(0001)-1×1 lattice vector directions, since the arrows are aligned with the "tetramers" (white features) that form a SiC(0001)-6×6 periodicity.[9] Figure 1(b) illustrates that the edges of the graphene island are aligned with the underlying SiC reconstruction, as also observed for layer 1 graphene terraces.[15] This is highlighted in Fig. 1(b) by overlaying two blue arrows, 120° apart and comparing to the SiC lattice-vector directions indicated in the inset of Fig. 1(a).

Atomic-resolution STM images of graphene islands can be used to determine whether graphene step edges are terminated in the "armchair" or "zigzag" configuration. This is illustrated in Fig. 1(c), where blue arrows are drawn to correspond to armchair edges and a yellow arrow indicates a zigzag edge. The data shown is from the middle of the island because electron scattering from the island edges significantly distorts the lattice imaging otherwise.[16] Combining the fact that a zigzag edge and an armchair edge are 30° apart and all the edges of the graphene islands are 120° or 60° apart, we conclude that a graphene island must be entirely surrounded by either zigzag or armchair step edges. By comparing the arrows of Fig. 1(c) and the island edges of Fig. 1(b), it is easy to see that the blue (armchair) arrows accurately align with the island edges. Therefore, this graphene island is bounded entirely by armchair edges.

All eight islands found on this surface were verified to have armchair edges (three by direct atomically resolved STM imaging and five by edge directions relative to the SiC lattice). This observation is at odds with a simple bond-breaking argument that would predict zigzag edges (4.1 broken bonds per nm) to have a lower energy than armchair
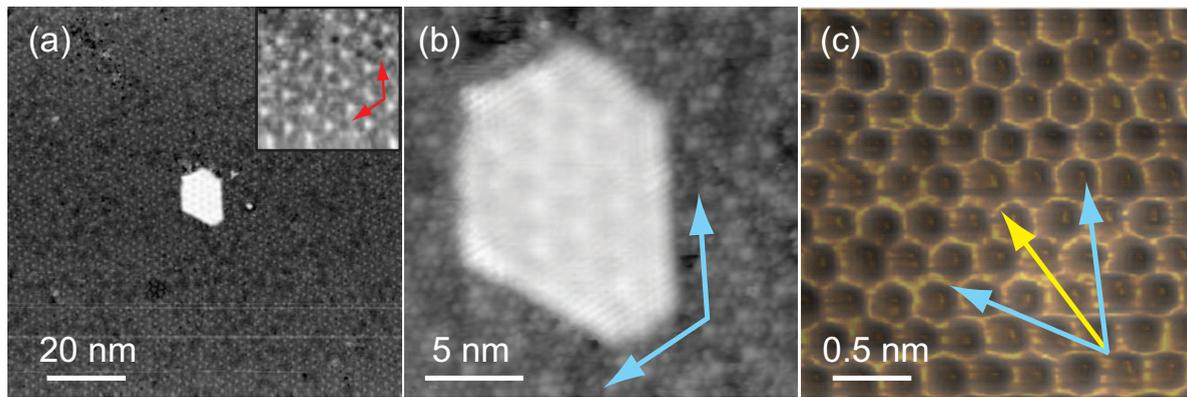
FIG. 1. (Color) Epitaxial graphene islands have preferred armchair edges. (a) 100×100 nm^2 STM topograph showing a small graphene island (white) surrounded by SiC reconstruction (tunneling conditions are 0.5 V and 0.1 nA). Inset: high-resolution STM topograph (12.5 $\times 12.5$ nm^2) of the SiC reconstruction. The red arrows indicate the directions of the SiC lattice vectors. (b) Higher resolution STM image (20×20 nm^2) of the same graphene island (tunneling conditions are 0.5 V and 0.1 nA). The 6-sided island has edges aligned with the SiC lattice vectors. (c) 2.5×2.5 nm^2 rendered STM topograph showing the graphene lattice of the island (tunneling conditions are 0.3 V and 0.1 nA). Overlaid on this image are the two lowest energy edge directions: zigzag (yellow arrow) or armchair (blue arrows). Blue arrows match the directions of the island edges, meaning the island is entirely made up of armchair edges.

edges (4.7 broken bonds per nanometer). However, recent density-functional calculations predict that clean graphene armchair edges have a formation energy approximately 1 eV per atom less than zigzag edges.[17] The larger formation energy for zigzag edges arises from the high density of states near the boundary, compared with absent boundary states for armchair termination.[17] Our results showing exclusively armchair edges on graphene islands are in agreement with these theoretical predictions.

To further investigate the properties of the islands, scanning tunneling spectroscopy (STS) was performed on the graphene islands and compared with STS spectra of graphene terraces. The results are summarized in Fig. 2. Figure 2(a) shows a large scale gradient STM topograph (0.25×0.25 μm^2 area) with both a single-layer graphene terrace (red arrow) and a graphene island (black square). Figure 2(b) is a magnified STM image of the graphene terrace [red arrow of Fig. 2(a)] showing the graphene lattice structure. The two-dimensional superstructure with period of ≈ 2 nm superimposed on the graphene lattice is a geometrical buckling of the graphene over the SiC reconstruction.[9] Figure 2(c) shows an STM image of an island [black square of Fig. 2(a)] similar in size to the one discussed in Fig. 1. This graphene island forms a triangle (≈ 10 nm on each side with a step height of ≈ 0.2 nm). The island is again bounded by armchair edges. Figure 2(c) shows that near the island edges there is significant scattering (blue arrows), which is evidence that graphene is discontinuous at this step edge.[18,19] The scattering periodicity, which arises from intervalley scattering due to the short-range disorder of the step edge, masks the atomic corrugation of the graphene lattice,[20] which is why the edge configuration must be determined from atomic-resolution STM images at the island interior.[16]

Figure 2(d) shows spatially averaged STS taken from the regions marked in Figs. 2(b) and 2(c). STS taken over the center of the graphene terrace [Fig. 2(d), red curve] is typical for single-layer graphene regions. The spectra from the terrace do not vary significantly at room temperature, unlike

what was recently observed for similar samples at low temperature,[21] and therefore we have averaged together spectra from a 100 nm^2 region of a single-layer graphene terrace [Fig. 2(d), red curve]. The plateau in the dI/dV curve near
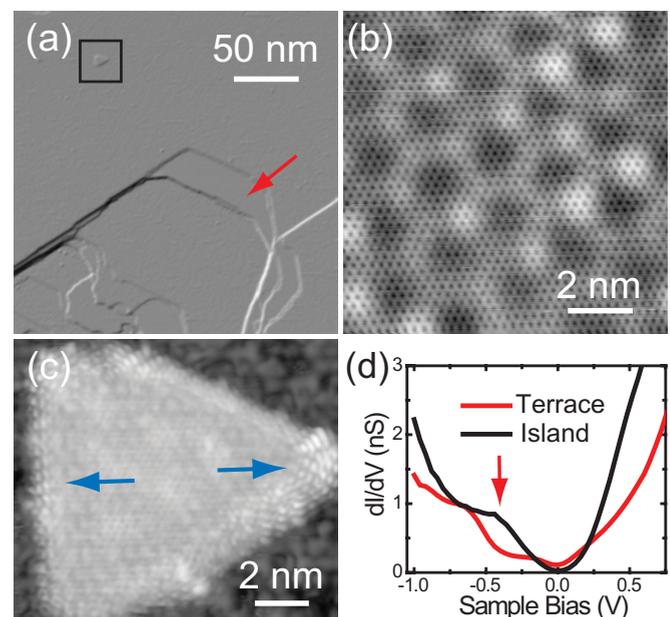
FIG. 2. (Color) STS measurements of graphene islands. (a) 0.25×0.25 μm^2 gradient STM topograph (tunneling conditions are 1.0 V and 0.1 nA) showing a graphene island (black square) and a graphene terrace (red arrow). (b) Atomic-resolution (10×10 nm^2) STM topograph clearly shows the graphene lattice structure of the terrace seen in (a) (tunneling conditions are 0.3 V and 0.1 nA). (c) STM topograph (10×8.7 nm^2) of the triangular armchair graphene island in (a) (tunneling conditions are 0.3 V and 0.1 nA). (d) Spatially averaged STS taken from the graphene island of (c) (black curve) and the graphene terrace of (b) (red curve). The conditions for spectra are 0.3 V and 0.1 nA. The local minimum observed on the terrace STS (indicated by the red arrow) is believed to be the location of the Dirac point.
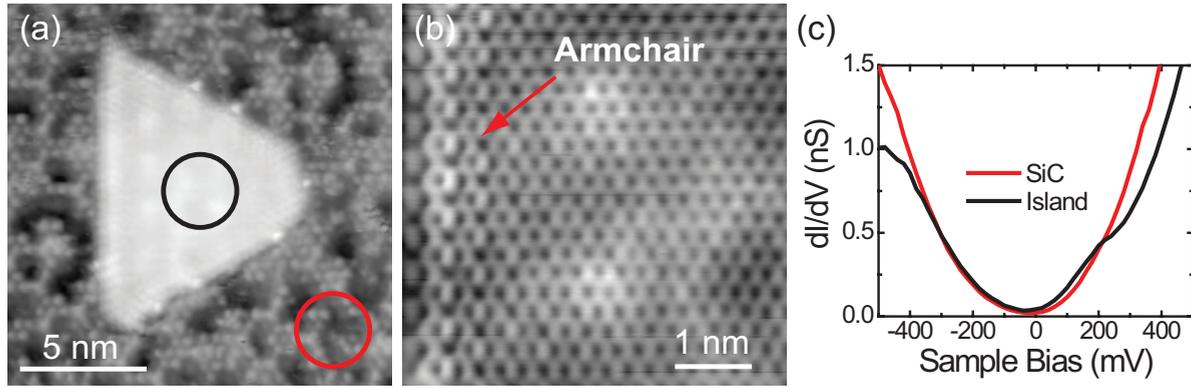
FIG. 3. (Color) Differences in STS between a graphene island and SiC reconstruction. (a) 15×15 nm^2 STM topograph (tunneling conditions are 0.3 V and 0.1 nA) showing another triangular armchair graphene island. (b) High-resolution STM image (5×5 nm^2) showing the armchair edge of the graphene island. (c) Spatially averaged STS from the center of the graphene island in (a) (black curve) and SiC reconstruction from the bottom right area of (a) (red curve). The two spectra are very similar at low bias. The conditions for spectra are 0.3 V and 0.1 nA.

−350 mV [Fig. 2(d), red arrow] could arise from the location of the Dirac point in graphene (E_D), as this location (i.e., doping level) is common for graphene on SiC.[21,22] The shift of the Fermi energy with respect to the Dirac point by 350–450 meV is understood as charge transfer from the SiC substrate to the graphene.[23,24] However, the exact location of the Dirac point is not clearly resolved in single-layer epitaxial graphene due to a lack of a sharp dip in the dI/dV, a feature observed for thicker graphene films.[22] Spatially averaged STS taken over the graphene island [Fig. 2(d), black curve] appears slightly different from the spectrum on the graphene terrace. Similar to the case of the graphene terrace, the spectra do not vary significantly over the whole area of the island, even near the edges, and therefore we average the spectra from across the entire island [Fig. 2(d), black curve]. The average spectrum from the island shows a slight reduction in dI/dV at the Fermi level compared to STS from the graphene terrace. It appears that over the island a gap opens at E_F, which would be expected for a graphene island of this size.[6,7] However, to fully understand the nature of the STS on the graphene island (compared with the terrace), the interactions of the graphene island and the SiC substrate need to be considered. Indeed, the tunneling to the SiC interface may dominate the differential conductance measurements, as evidenced in voltage-dependent imaging of the single-layer graphene terraces.[9]

In Fig. 3 we show that near E_F, STS spectra taken over graphene islands are similar to those from the surrounding SiC reconstruction. Figure 3(a) shows a third graphene island that is triangular, roughly 10 nm on a side, with a step height of 0.2 nm. This island, like the islands in Figs. 1 and 2, is comprised solely of armchair edges [Fig. 3(b)]. Figure 3(c)

displays a spatially averaged STS spectrum (black) from dI/dV data acquired near the center of the island (black circle) and a spatially averaged spectrum (red) from the SiC reconstruction (red circle). As seen in the plot, the spectra track one another fairly well, except for a feature in the island spectrum near 200 meV, which we speculate may be a discrete quantum state of the island. The spectral similarities may only be a consequence of similar size energy gaps at E_F. Alternatively, if there is a substantial gap in the island spectrum, in this energy range the density of states may be dominated by that of layer 0 beneath the island. More data is needed to fully explain the differential conductance of the graphene island, including more island sizes and possibly other substrates.

In this work we have shown that it is possible to grow epitaxial graphene islands on SiC(0001) under appropriate UHV preparation conditions. The graphene islands grow to roughly the same size (≈ 90 nm^2 in this work). It was determined that all of the edges of the graphene islands have the armchair-edge configuration, consistent with recent predictions.[17] STS measurements were performed on graphene islands and compared with nearby graphene terraces and the underlying SiC reconstruction. A significant difference is observed in the spectroscopy between the graphene terrace and the island. A more detailed study is needed to fully understand these differences.

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