STS Studies of Zigzag Graphene Edges Produced by Hydrogen-Plasma Etching

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Graphene is a two-dimensional carbon crystal with remarkable electronic and mechanical properties, such as the half-integer quantum hall effect, and being stable at atmospheric conditions despite consisting of only a single atomic layer [1–3]. Reflecting its hexagonal lattice, graphene possesses two equivalent sublattices, and its electronic properties can be described by a bipartite Hamiltonian at low energies. One of the peculiar characteristics of graphene occurs at its edges. There are two stable edge types, armchair and zigzag, and only the zigzag edge can host a localized electronic state, named the zigzag edge-state (zz-ES). This is the localized state which originates from an imbalance between the two equivalent sublattices, and results in a flat band at the Dirac point [4]. The zz-ES was confirmed experimentally at naturally existing step-edges on graphite surfaces by scanning tunneling microscopy and spectroscopy [5–7] as a peak in the dI/dV spectra around the Fermi energy. It was found that the zz-ES decays exponentially with distance away from the edge [6]. More interestingly, the zz-ESs can be spin polarized in graphene nanoribbons between two zigzag edges which are necessarily of different sublattices [4, 8]. The zz-ESs are expected to be ferromagnetically spin polarized along the same edge, and anti-ferromagnetically between opposite edges. However, the experimental study of the zz-ES is limited and so is the study of the spin polarized state [9–11]. This is because it is not easy to obtain atomically precise zigzag edges. One promising method to fabricate zigzag edges is by use of chemical reactions. In this paper, we focus on edges on graphite surfaces obtained by chemical etching with hydrogen plasma (H-plasma) [12–14].

I. INTRODUCTION

STM/S measurements were done in ultra-high vacuum ($P \leq 10^{-8}$ Pa) [15] at temperatures of either 4.7 K or 78 K. To confirm the local electronic density of states (LDOS) around the edges, dI/dV spectra were measured across each edge. The dI/dV values, which are approximately proportional to the LDOS, were acquired by the lock-in technique with modulation voltage ($V_{\text{mod}}$) of 2.5–10 mV and a modulation frequency of $f = 1.23$ kHz. STM images were obtained at a tunneling current $I_{t}$ and a bias voltage $U_{g}$ applied to the sample. The H-plasma etching of graphite can be either isotropic or anisotropic depending on the etching temperature ($T_{\text{max}}$) and H$_{2}$ pressure ($P_{\text{H}_{2}}$). At certain values for $T_{\text{max}}$ and $P_{\text{H}_{2}}$, hexagonal nanopits with a depth of $0.34 \pm 0.02$ nm were fabricated on graphite surfaces, as shown in Fig. 1(a) [16]. This depth is close to the interlayer distance of graphite (0.335 nm), thus the nanopits

FIG. 1. (a) STM image of a graphite surface with hexagonal nanopits fabricated by H-plasma etching ($U_{g}$ = 0.5 V, $I_{t}$ = 0.03 nA) [16]. (b) Atomically resolved STM image of the graphite surface near the scanning range of (a) ($U_{g}$ = 0.3 V, $I_{t}$ = 0.04 nA). A schematic drawing of the hexagonal lattice of graphite is overlaid in (b). Bright and dark filled circles correspond to the two different sublattice sites, and only the white sublattice is observed in STM image. The blue lines in both images show the same two zigzag directions of the graphite lattice.

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FIG. 2. (a) STM image of the zigzag-direction edges of a H-plasma etched hexagonal nanopit ($U_g = 0.5$ V, $I_t = 0.04$ nA). The green arrow indicates the STM/S measurement path (20 nm long) across the edge and corresponds with the horizontal axes of (c), (d), and (e). The edge position is indicated by the blue dashed line. (b) The $dI/dV$ spectra extracted from the marked positions in (d), i.e., close to the edge (open triangles), on the lower terrace (open circles), and an average on the bulk region of the upper terrace (filled circles). (c) Height profile ($U_g = 0.3$ V, $I_t = 0.04$ nA), and (d) $dI/dV$ spectra colormap ($V_{mod} = 3.3$ mV) along the green arrow in (a) at $T = 4.7$ K. The vertical lines and small symbols just above the panel (d) show the locations where the $dI/dV$ spectra shown in (b) are extracted. The arrow and bars in (b) and (d) indicate the edge-state peak and LDOS suppressions, respectively. (e) The spectral weight over $35.6$ to $11$ mV, where the low-energy peak is included, is plotted on a semi-log scale across the edge after subtraction of a constant background. The solid red line is the fitted exponential function with a decay length of $\xi = 3.1$ nm, and the dashed red curve indicates a $d^{-2}$ dependence which is expected for the localized state of a single vacancy [19].

have monatomic depth and the step-edges correspond to the edge of a graphene sheet that is bound by interlayer van der Waals coupling to the graphite surface underneath. Figure 1(b) shows an atomic image of graphite obtained close to the scanning range of Fig. 1(a). It should be noted here that by STM one can obtain a triangular lattice on graphite, rather than a honeycomb one, because only one of the two sublattices of graphite is observed by STM due to the interlayer coupling. Since almost all the nanopit step-edges in Fig. 1(a) are aligned in the same direction as the atomic rows of the triangular lattice in Fig. 1(b), one can confirm that the edges are aligned along the zigzag direction, even though it was not possible to clearly resolve the atomic configuration just on the edge due to the high LDOS of the zz-ESs. Since the edges are produced by a chemical reaction with H-plasma, they are most probably terminated by H. If so, the edge C atoms are expected to be terminated by one H atom rather than by two, because the formation energy of single H terminated edges is lower than that of two H and STM images of H-plasma etched edges were consistent with such an edge termination [14].

### III. RESULTS AND DISCUSSION

Figure 2 displays the results of the measurements around one of the hexagonal nanopit edges. Figure 2(b) compares $dI/dV$ spectra close to the edge (open triangles) and on the bulk regions of the upper (filled circles) and lower (open circles) terraces away from the edge. Figures 2(c) and 2(d) show a line profile and a $dI/dV$ colormap, respectively, along the green line across the edge in Fig. 2(a). The colormap reveals that a low-energy peak at $U_g = -11$ mV appears locally at the edge. This peak does not appear in the bulk regions, i.e., on the upper terrace far away from the edge and on the lower terrace as shown in Fig. 2(b). The spectral weight integrated over $-35.6$ mV $\leq U_g \leq 1.0$ mV, where the low energy peak is included, is plotted as a function of distance from the edge in Fig. 2(e). This shows that the edge-localized state follows an exponential decay, rather than a power-law decay, away from the edge, which agrees with the theoretical expectation [4] and the previous experiment [6]. Therefore, it can be concluded that the edge-localized state is the zz-ES, and the step-edges of the hexagonal nanopits are indeed dominated by zigzag structure.
A. LDOS Suppression

The edge dI/dV spectra include not only the peak of the zz-ES, but also a suppression at both positive and negative bias voltage sides of the peak. This suppression becomes wider in bias voltage closer to the edge and forms a fan-like dispersion [Fig. 2(d)]. The dI/dV suppression can be seen clearly in Fig. 2(b). The edge spectrum is indeed characterized by the prominent low-energy peak, as well as by the suppressions of dI/dV on both sides of the peak. Although such a suppression had not been discussed previously [4–7], it was observed at most of the zigzag edges in this study. It should be noted that the LDOS suppression we observed is similar to that simulated for graphene with uncompensated single vacancies [17, 18]. The single vacancies in graphene also create a localized state, which features a LDOS peak at the Dirac point that decays as a power law, which is different from zigzag edges. This was theoretically expected [19] and experimentally confirmed by STM/S [20]. Moreover, it was simulated that an imbalance in the number of vacancies located on each sublattice creates LDOS suppressions at energies on both sides of the peak, where the peak intensity and the suppressed energy range are proportional to the degree of the sublattice imbalance [18]. Though it is not easy to create many uncompensated vacancies, the zigzag edge can be an ideal representative, because zigzag edge sites belong exclusively to one sublattice. Therefore, the present results suggest that the zigzag edges fabricated by our H-plasma etching feature a higher sublattice imbalance, and are thus closer to the atomic-scale zigzag edge structure than those studied in any previous experiments for natural step-edges [5–7].

Figure 2 is representative of the dI/dV features that were observed at most edges, however sometimes the suppression was less clear and in some cases it could only be observed on one energy side of the zz-ES peak. This may be due to a higher defect density that decreases the sublattice imbalance at those edges.

B. Decay Length

Figure 3 shows a histogram of the exponential decay length of the zz-ES (ξ) obtained for zigzag edges in this study (upper panel) and for naturally existing zigzag step-edges on graphite [6]. Note here that the statistics of ξ is improved compared to the previous study [6], because we could fabricate many zigzag edges on graphite surfaces.

At T = 78 K, the ξ values are distributed between 0.9 and 1.8 nm, and have an average of ξ78K = 1.2 ± 0.3 nm. It is somewhat surprising that ξ78K is similar to that obtained at naturally existing step-edges (1.2 ± 0.2 nm) because the zigzag edges prepared by H-plasma can have better atomic precision than the natural step-edges. It is theoretically expected in Ref. [6] that ξ is about 0.5 nm for a perfect zigzag edge, and that ξ becomes longer as armchair components are mixed with the dominantly zigzag edge. ξ ≈ 1.2 nm is also reported for a dominantly zigzag (8,1)-chiral edge of an unzipped carbon nanotube on Au(111), which agrees with the calculated value [9]. Therefore, ξ may become longer even with small amounts of defects on the zigzag edge. It is found that the ξ values obtained at the lower temperature (T = 4.7 K) tend to be longer than those at the higher temperature (T = 78 K). Such a temperature dependence has not been predicted before. This can be caused by the longer coherence length at lower temperatures, but further measurements are necessary to test whether the temperature dependence is consistently measured.

IV. CONCLUSION

We have investigated the step-edges of anisotropically etched hexagonal nanopits prepared by H-plasma on graphite surfaces by analyzing their electronic LDOS obtained by STM/S at low temperatures. Judging from the direction of the nanopit edges with respect to the atomic rows, they are considered as dominantly zigzag edges. A clear edge-localized state was found as a prominent low-energy peak in the LDOS that decays exponentially away from the edge. Most importantly, suppressions of the LDOS at energies on both sides of the peak were observed for the first time. These characteristics are similar to those simulated for highly uncompensated single vacancies on graphene which share the common feature of high sublattice imbalance with the zigzag edge. We concluded that our nanopit edges posses a much higher concentration of pure zigzag edge-structure than the edges studied in the previous measurements. Although we notice a possible temperature dependence of the decay length between T = 4.7 K and 78 K, further measurements are necessary to confirm it.
The present results indicate that the H-plasma etching is indeed a promising technique that can produce edges with exceptionally high-quality zigzag-edge structures. In the future, this can be used to investigate the expected spin-polarized zz-ESs at zigzag nanoribbons which can be obtained between two hexagonal nanopits.

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