論文の内容の要旨

Scanning Tunneling Microscopy and Spectroscopy Studies of Graphene Zigzag Edges Fabricated by Hydrogen Plasma Etching

（水素プラズマエッチングで作成したグラフェンジグザグ端の走査トンネル顕微法および分光法による研究）

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Introduction

The two-dimensional carbon crystal graphene has attracted attention from scientists, industry and public due to its unique physical properties that may lead to the development of novel technologies in various fields. In addition to its atomic thinness, these include ballistic electronic charge transport, the half-integer quantum hall effect, a higher tensile strength than steel and long spin coherence lengths [1, 2]. Furthermore, graphene hosts a peculiar electronic state localized at the zigzag-type edge, the so-called edge state [3, 4]. The edge state is predicted to become magnetically ordered, making it a promising material for novel spintronic devices that may enhance computer performance. Such spin-polarization on narrow graphene nanoribbons with zigzag-type edges (zGNR) is well established theoretically [5, 6] but experimental confirmation remains controversial [7, 8]. This work aims to clarify the existence of magnetized edge states in zGNRs with high quality zigzag edges by use of scanning tunneling microscopy and spectroscopy (STM/STS) techniques at low temperatures. By this the necessary conditions for graphene zigzag edge states to become spin-polarized, as well as substrate effects, can be understood, which is important for device applications.

Hexagonal nanopits and high-purity zigzag edges created by hydrogen plasma etching

We utilized hydrogen (H-) plasma etching to produce hexagonal nanopits with monatomic depth on the surface of graphite (Fig. 1(a)) [9, 10], and on epitaxial graphene on the C-face and Si-face of SiC [11] with high yield (etching parameters: T = 600°C, P = 110-220 Pa, W_{RF} = 20 W, t = 10-50 min). These edges are aligned to the atomic zigzag directions (Fig. 1(b)), thus zGNRs are obtained between the nanopits. Different from previous studies, this technique gives us the advantage of obtaining zGNRs with clean edges, different shapes and widths, and well-known substrate interactions with graphite. For the main results, we probed the sample topography and electronic properties by

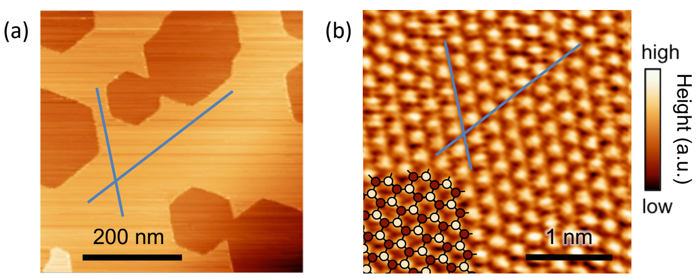

Figure 1: (a) STM image at T = 78 K on graphite with hexagonal nanopits created by H-plasma etching. (b) Atomic STM image on the same terrace as (a) and, in the bottom left corner, schematic lattice with A-sublattice (brown) and B-sublattice (white). Zigzag directions are indicated by blue lines. STM parameters: V = (a) 500 mV, (b) 300 mV, I = (a) 0.03 nA, (b) 0.04 nA.

STM/STS at low temperatures (60 mK ≤ T ≤ 78 K) in ultra-high vacuum ($P < 10^{-8}$ Pa, UHV), allowing for high spatial and energy resolutions.

At nanopit edges on the surface of graphite, we observed a single prominent local density of states (LDOS) peak (about 50 meV wide) near the Dirac point at T = 78 K and 4.7 K, that decays exponentially into the bulk (decay length $0.9 < \xi < 3.1$ nm). For the first time, we found LDOS suppressions accompanying the peak, indicating a large sublattice imbalance. We conclude that the edges of the hexagonal nanopits created on graphite by H-plasma etching are high-purity zigzag edges.

Observation of the spin-split edge states in zGNRs fabricated on graphite surface

We probed the zGNRs (width $4 \leq W \leq 42$ nm) between hexagonal nanopits at 60 mK ≤ T ≤ 4.7 K (Figs. 2(a)-(e)). Tunnel spectra across the parallel ribbon ((b)(c)), show two peaks close to the Dirac point near the edges with exponential decay into the ribbon center, forming a split with peak-to-peak separation $\Delta_{p\text{-}p}$ (≈ 45-55 meV). Importantly, the spectral structures depend on the edge sublattice, with $\Delta_{p\text{-}p}$ larger on the B-edge, above underlayer hollow sites, than on the A-edge, above atoms. This different substrate interaction is caused by the AB stacking on graphite and breaks the sublattice symmetry on the zGNR.

The edge state splitting is expected for spin-polarization. Along the B-edge in Fig. 2(e), the double-peak only appears on the parallel zGNR ($4 \leq l \leq 7$ nm), and not outside of it where only one peak appears ($l < 2$ nm). Thus, interaction of zigzag edge states on different sublattices stabilizes spin-splitting, which is the predicted condition for stable spin polarization. Cartoons of the spin-polarized interleaving edge states on a zGNR are shown in Figs. 3(a) and (b), where spins are aligned ferromagnetically on the same edge and antiferromagnetically on different edges.

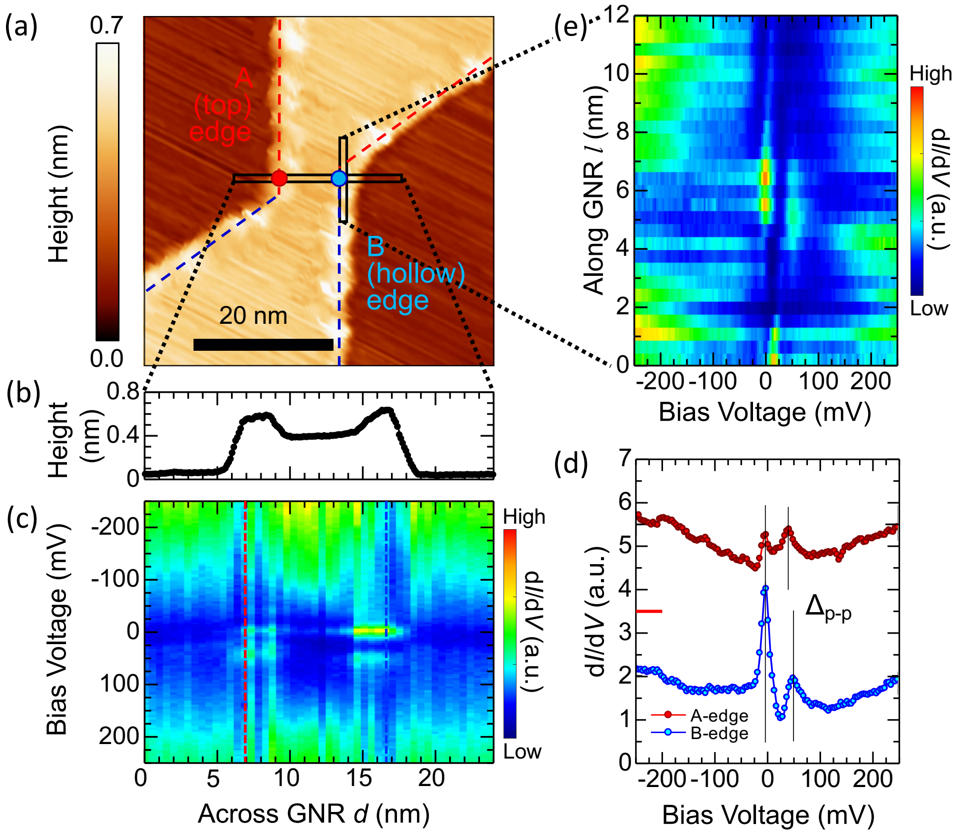

Figure 2: STM/STS measurements at T = 4.7 K on an etched zigzag graphene nanoribbon with $W = 9.9 \pm 0.6$ nm. (a) STM image showing A/B-edges by red/blue dotted lines. (b) STM height profile, (c) dI/dV colormap (indicating LDOS) *across* the GNR. (d) dI/dV edge spectra on the edges (positions marked in (a)), with $\Delta_{p\text{-}p}$ indicated. (d) dI/dV colormap *along* the B-edge. STM/STS parameters: V = 300 mV, I = (a)~0.04~nA, (b)-(e) 0.06 nA, V_{mod} = 4.0 mV.

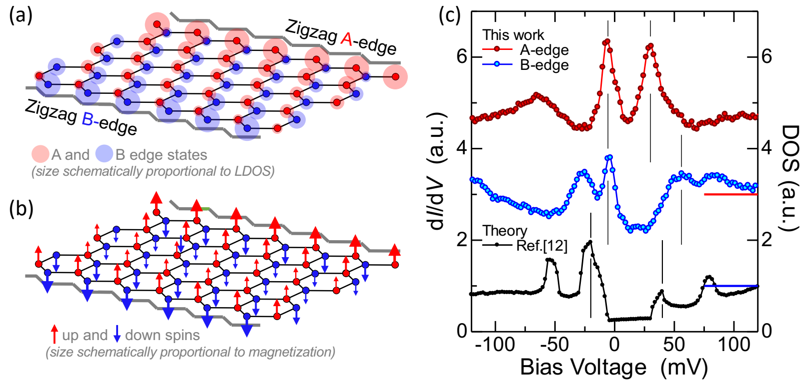

Figure 3: (a) Schematics of the edge state LDOS distribution, and (b) of the anti-ferromagnetic spin alignment on a zGNR. (c) Tunnel spectra measured at $T = 60$ mK on the A (red dots) and B (blue dots) edges of a zGNR with $W = 10.6 \pm 0.8$ nm on graphite and DOS of a spin-polarized zGNR on a graphene layer with $W = 6.7$ nm (black dots), extracted from the calculation of Ref. [12]. STS parameters: $V = 270$ mV, $I = 0.06$ nA, $V_{mod} = 2.1$ mV.

On some zGNRs, two peaks with additional LDOS structures were observed (Fig. 3 (c)). Such additional peaks are qualitatively consistent with the expected broken sublattice symmetry, as shown by the DOS extracted from band structures for a zGNR on monolayer graphene, based on density functional theory and tight-binding calculations by Chen and Weinert [8]. The observed finite in-gap DOS may be interpreted by the theoretically predicted spin-symmetry breaking semi-metallic state [12]. We examined 20 different zGNRs with various widths W and found that $\Delta_{p\text{-}p}$ inversely decreases with increasing W up to about 23 nm, beyond which no split edge states were observed. This inverse relationship between $\Delta_{p\text{-}p}$ and W is also predicted for zGNRs with spin-polarization.

STS observation of the edge states in zGNRs fabricated on graphene/SiC(000$\bar{1}$)

To better understand the effect of the substrate influence, we studied few-layer epitaxial graphene (2-10 layers) on SiC(000$\bar{1}$) (Fig.4(a)), whose electronic properties are modified by a stronger substrate influence and rotational disorder. We probed this sample by STM/STS at $T = 78$ K and 2 K after soft baking in UHV. H-plasma etching produced anisotropic nanopits as well, and completely removed the rotational disorder. The nanopits are larger and more numerous than on graphite, suggesting that more defects exist on this graphene sample. The interlayer distance is about 2% increased from graphite.

Before and after etching we found both n-type and p-type doping, depending on the terrace. At the etched nanopits, we found stronger doping on n-doped terraces, but no significant layer difference on p-doped terraces, indicating that n-doping stems from the substrate influence, and that p-doping is likely induced by surface adsorbates.

At the zigzag edges of the nanopits we observed localized LDOS peaks that are consistent with zigzag edge states. The doping shifts them farther away from the Fermi energy than on graphite, and wider LDOS peaks are observed, possibly resulting from more defects. On the zGNRs, several multi-peak edge states were observed which

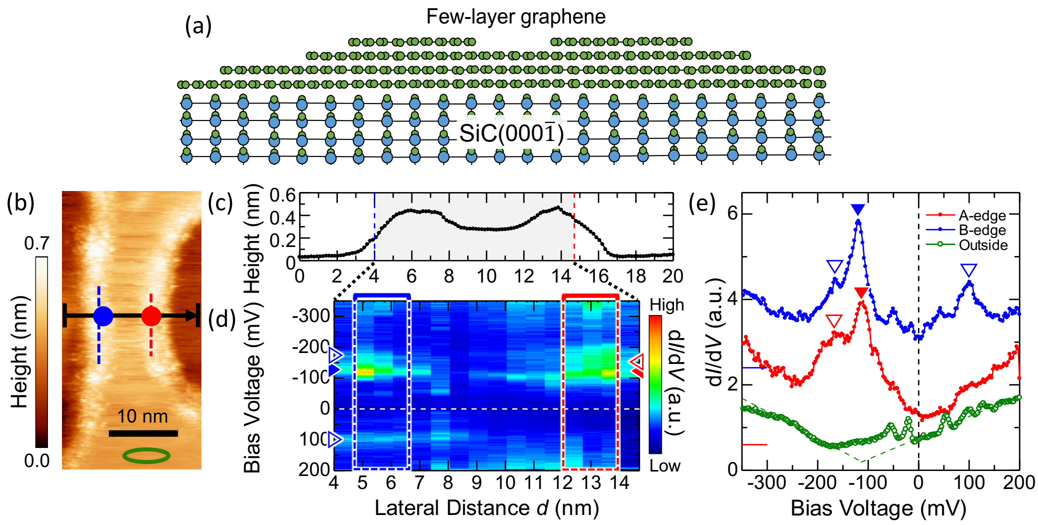

Figure 4: (a) Schematic of etched epitaxial graphene with different layers and nanopits on top of SiC(000$\bar{1}$). (b) STM image at $T = 2$ K of a zGNR on graphene/SiC(000$\bar{1}$). (c) STM height profile, (d) dI/dV colormap across the ribbon, (e) dI/dV spectra on the edges and outside the zGNR (positions are indicated in (b)(d)). The split edge peaks are indicated by triangles. Linear fits of data outside the zGNR (green dashed lines) estimate the Dirac point at about –113 mV. STM/STS parameters: $V = 200$ mV, $I = 0.03$ nA, $V_{mod} = 2.7$ mV.

are likely spin-splitted. A rather wide splitting of 220 meV was observed on the zGNR in Figs. 4(b)(c) on the B-edge (see (d)(e)). On both edges, a much smaller splitting appeared between overlapping peaks (triangles below –100 mV in (e)). Different characteristics appeared on other zGNRs, presumably due to more inhomogeneities and/or strong doping, that shifts the Dirac point by ±100 meV, in this system. Importantly, edge states appear prominently and the magnetic edge states seem to survive under such conditions. It is highly desirable to extend the calculations including AB stacked graphene layers [8] to the case of strong doping to compare with our experimental results from zGNRs on SiC(000$\bar{1}$).

Preliminary studies on hexagonal nanopit creation on graphene/SiC(0001)

Finally, we examined monolayer epitaxial graphene on the Si-face of SiC to test the robustness of the spin-split edge state under stronger substrate interactions. Anisotropic nanopits were also created with similar yield by H-plasma etching with the same parameters as for graphite, though the nanopit shape is less anisotropic (hexagonal). In addition, we found elevated surfaces with a height of 0.12 nm on more than half of the sample surface, where no substrate-induced 6×6 superlattice was observed by STM, but instead AB stacking was. Additionally, doping was weaker and a gap-like feature was obtained. All this suggests that the substrate was passivated by intercalated H-atoms during etching, releasing the buffer layer and forming quasi-free-standing (qFS) bilayer graphene. Therefore, hexagonal nanopits created on qFS graphene would be a hopeful candidate object for testing the robustness of the spin-split edge state in the near future.

Conclusions

In this work we obtained strong indications of spin-splitting of the edge states in zGNRs fabricated on graphite and on few-layer graphene/SiC(000$\bar{1}$) by H-plasma etching from high-resolution STS measurements at low temperatures. The predicted sublattice (pseudo-spin) symmetry breaking has been verified experimentally for the first time. The observed split or quasi-gap energy for zGNRs on graphite is in semi-quantitative agreement with the DFT calculation for a zGNR on graphene. For zGNRs on graphene/SiC(000$\bar{1}$), much wider splits were observed, possibly due to the weaker substrate interaction caused by a larger interlayer separation. In previous reports of spin-polarized edge states several limitations were always present, such as insufficient edge quality, unknown substrate interaction, inability to vary ribbon width, limited statistics of data, etc. Our measurements were able to avoid these problems successfully to show the strongest indication of the existence of the spin-polarized edge state achieved so far.

References

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