Evidence for Superlattice Dirac Points and Space-dependent Fermi Velocity in Corrugated Graphene Monolayer

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Recent studies show that periodic potentials can generate superlattice Dirac points at energies $\pm \hbar v_F |\mathbf{G}|/2$ in graphene ($v_F$ is the Fermi velocity of graphene and $\mathbf{G}$ is the reciprocal superlattice vector). Here, we perform scanning tunneling microscopy and spectroscopy studies of a corrugated graphene monolayer on Rh foil. We show that the quasi-periodic ripples of nanometer wavelength in the corrugated graphene give rise to weak one-dimensional (1D) electronic potentials and thereby lead to the emergence of the superlattice Dirac points. The position of the superlattice Dirac point is space-dependent and shows a wide distribution of values. We demonstrated that the space-dependent superlattice Dirac points is closely related to the space-dependent Fermi velocity, which may arise from the effect of the local strain and the strong electron-electron interaction in the corrugated graphene.

Since the laboratory realization of graphene in 2004 [1], this two-dimensional honeycomb lattice of carbon atoms has motivated intense theoretical and experimental investigations of its properties [2-8]. It was demonstrated that the electronic chirality (the spinorlike structure of the wavefunction) is of central importance to many of graphene’s unique electronic properties [3,9-12]. Recently, a number of theoretical studies predicted that the chiral nature of charge carriers results in highly anisotropic behaviours of massless Dirac fermions in graphene under periodic potentials and generates new Dirac points at energies $E_{SD} = \pm \hbar v_F |\mathbf{G}|/2$ in graphene superlattice (here $v_F$ is the Fermi velocity of graphene and $\mathbf{G}$ is the reciprocal superlattice vector) [13-16]. Despite these suggestive findings [13-16] and many other interesting physics [17-22] in graphene superlattice, the experimental study of this system is scarce due to the difficulty in fabricating graphene under nano-scale periodic potentials [23]. Until recently, it was demonstrated that graphene superlattice (corrugated graphene or moiré pattern) induced between the top graphene layer and the substrate (or the underlayer graphene) acts as a weak periodic potential, which generates superlattice Dirac points at an energy determined by the period of the potential [24-26]. These seminal experiments provide a facile method to realize graphene superlattice and open opportunities for superlattice engineering of electronic properties in graphene.

In this Letter, we address the electronic structures of a corrugated graphene monolayer on Rh foil. We show that the quasi-periodic ripples of nanometer wavelength give rise to a weak one-dimensional (1D) electronic potential in graphene. This 1D potential leads to the emergence of the superlattice Dirac points $E_{SD}$, which are manifested by two dips in the density of states, symmetrically placed at energies flanking the pristine graphene Dirac point $E_D$. The position of $E_{SD}$ is space-dependent and shows a wide distribution of values. Our experimental result demonstrates that the space-dependent $E_{SD}$ is closely related to the space-dependent Fermi velocity, which is attributed to the effect of the local strain and the strong electron-electron interaction in the corrugated graphene.

The graphene monolayer was grown on a 25 micron thin polycrystalline Rh foil, which is mainly (111) oriented, via a traditional ambient pressure chemical vapor deposition (CVD) method, as reported in a previous paper [27]. The sample was synthesized at 1000 ºC and the growth time was varied from 3 to 15 min for controlling the thickness of graphene. The thickness of the as-grown graphene was further characterized by Raman spectra measurements [27] and in this paper we focus on the structure and electronic properties of graphene monolayer. The as-grown sample was cooled down to room temperature and then transferred into the ultrahigh vacuum condition for further scanning tunneling microscopy (STM) characterizations. The STM system was an ultrahigh vacuum four-probe scanning probe microscope from UNISOKU. All STM and scanning tunneling spectroscopy (STS) measurements were performed at liquid-nitrogen temperature and the images were taken in a constant-current scanning mode. The STM tips were obtained by chemical etching from a wire of Pt(80%)Ir(20%) alloys. Lateral dimensions observed in the STM images were calibrated using a standard graphene lattice. The STS spectrum, i.e., the $dI/dV$-V curve, was carried out with a standard lock-in technique using a 957 Hz alternating current modulation of the bias voltage.

Due to thermal expansion mismatch between graphene and the substrate (the Rh foil contracts, whereas the graphene layer expands during the cooling process), defect-like wrinkles and ripples tend to evolve along the boundaries of crystalline terraces for strain relief [28,29]. Very recently, this thermal strain engineering was used to generate (sub)nanometer-wavelength periodic ripples in
graphene [30] and it was demonstrated that the strained graphene structures modify the local electronic structures dramatically [30-34]. Theoretically, it was predicted that corrugated graphene could lead to an electronic superlattice with a period set by the corrugation wavelength [35]. Motivated by this proposal, we address the electronic structures in graphene with quasi-periodic ripples of nanometer wavelength by STM and STS.

Figure 1(a) shows a STM image of a flat area of graphene monolayer on polycrystalline Rh foil. No periodic moiré superstructures can be seen and almost identical feature has been observed in several tens flat areas of graphene monolayer on Rh foil. This feature differs quite from that of both the graphene bilayer on Rh foil and the graphene monolayer on a (111) surface of single-crystal Rh [27]. For the graphene bilayer, the misorientation between the bilayer usually results in moiré superstructures with different periods [27]. For the latter case, the strong C-Rh covalent bond and the lattice mismatch between graphene (0.246 nm) and Rh(111) (0.269 nm) could lead to hexagonal moiré superstructures with the periodicity of 2.9 nm [27,36-38]. The absence of moiré superstructures, as shown in Fig. 1(a), indicates that the coupling between graphene and the Rh foil is much weaker than that of monolayer graphene on a single-crystal Rh [27]. Fig. 1(b) shows an atomic resolution STM image of the graphene, where a clear honeycomb lattice is observed. Fig. 1(c) shows a typical STS spectrum of the sample. The tunnelling spectrum gives direct access to the local density of states (LDOS) of the surface at the position of the STM tip. The linear DOS around the Dirac point ED consists well with that of the pristine graphene. The inset is a Fourier transform showing the reciprocal-lattice of the graphene with quasi-periodic ripples of nanometer wavelength on Rh foil (V_{sample} = 440 mV and I = 10.31 pA). The inset is Fourier transform of the blue frame showing the reciprocal-lattice of the quasi-periodic ripples. The scale bar of the inset is 5 Gm^{-1}. (b) Zoom-in topography of the blue frame in (a) shows a 1D superlattice (V_{sample} = 393 mV and I = 10.31 pA). (c) Atomic-resolution image of the red frame in panel (b) shows a honeycomb lattice (V_{sample} = 393 mV and I = 10.31 pA). (d) Tunneling spectra, i.e., dI/dV-V curves, recorded at different positions, as marked by the stars with different colors, in panel (a). The spectra were vertically offset for clarity. The positions of the superlattice Dirac points, which contribute to the dips of the local density of states, are indicated by the arrows.

As mentioned above, a corrugated graphene monolayer with quasi-periodic ripples of nanometer wavelength is easy to be found along the boundaries of crystalline terraces of Rh foil. Fig. 2(a) shows a typical corrugated graphene with quasi-periodic ripples (see Fig. S1 in the supplemental material [42] for a line profile of the quasi-periodic ripples). The average width of these ripples is estimated to be about 3.5 nm and the height of these ripples is usually smaller than 1 nm. The inset is the Fourier transform showing the reciprocal-lattice of the ripples. Figure 2(b) and (c) show atomic-resolution images of the ripples and only a honeycomb lattice is observed, suggesting that the local curvature of the ripples does not break the six-fold symmetry of the graphene lattice. This result also implies that there is no gap opening at the Dirac point. In literature, a triangular lattice was observed on graphene wrinkle ~10 nm in width and ~ 3 nm in height [43]. The triangular lattice along the wrinkle may arise from its large local curvature (strain) that breaks the six-fold symmetry of the lattice. Figure 2(d) shows seven STS spectra recorded at different positions, as marked by the stars with different colors, in Fig. 2(a). Around the Dirac point, the DOS (the slope of the spectra) is linear in energy, which is similar to that of the pristine graphene. Besides the low-energy linear DOS, these spectra show two dips, which are generally of asymmetric strength, flanking the Dirac point. By taking into account the weak 1D electronic potential in the graphene induced by the quasi-periodic ripples [35], it is expected that the electronic chirality will result in highly...
The two dips in the tunneling spectra are due to the quasi-periodic ripples, which generate weak 1D periodicities along the x direction with spatial period L and barrier width W, as shown in Fig. 3(a). Here, we assume that L is much larger than the nearest-neighbor carbon-carbon distance. Therefore, the new Dirac points at energies $E_{SD} = \pm \hbar v_F |G|/2$ can be generated by the 1D potential at the boundary (MB) formed by the periodic potential [13]. The two solid curves are the theoretical dependence of Dirac points away from the Dirac point as a function of the potential period L. The two solid curves are the theoretical dependence of $E_{SD}(L)$ with $\eta = 0.95$ (blue) and 0.5 (red), respectively (here $\eta = W/L$). The solid circles are the positions of the superlattice Dirac points obtained from the tunneling spectra of Fig. 2(d).

The anisotropic behaviors of both the Fermi velocity of the charge carriers and the gap opening at the minizone boundary (MB) formed by the periodic potential [13]. Therefore, the new Dirac points at energies $E_{SD} = \pm \hbar v_F |G|/2$ can be generated by the 1D potential at the centre of the MB. Two dips in the tunneling spectra are attributed to the positions of the superlattice Dirac points in the DOS. The asymmetric strength of the two dips in the tunneling spectra, as shown in Fig. 2(d), was also observed in the superlattice Dirac points generated by 2D moiré potentials. The asymmetry was mainly attributed to the electron-hole asymmetry originating from next-nearest-neighbor hopping [25]. In strained graphene structures, such large electron-hole asymmetry is expected to observe because of the lattice deformation, which enhances the next-nearest-neighbour hopping [31-33]. Similar asymmetry of the STS spectra is also observed in other corrugated graphene (see Fig. S2 in the supplemental material [42] for STM and STS of another corrugated graphene with similar quasi-periodic ripples).

To further understand the experimental result, we compare our experimental data with the expected theoretical result quantitatively. For simplicity, we assume that the quasi-periodic ripples generate a weak 1D Kronig–Penney type of potential on graphene periodic along the x direction with spatial period L and barrier width W, as shown in Fig. 3(a). Here, we assume that L equals to the nominal width of the ripples. The intervalley scattering of such a system may be neglected because of that L is much larger than the nearest-neighbor carbon-carbon distance. Then, we can use the model developed in Ref. [13] to show the new Dirac points induced by the 1D potential and derive the period dependence of $E_{SD}$ (see the supplemental material [42] for details of calculation). Fig. 3(b) and (c) show energy dispersions of charge carriers at the minizone boundaries of a 1D graphene superlattice. The group velocity is not renormalized and the energy gap at the MB vanishes when $k_y$ is along the direction of the periodic potential, i.e., $k_y = 0$. Therefore, the 1D graphene superlattice generates four new Dirac points at energies $E_{SD} = \pm \hbar v_F |G|/2$, which contribute to the two dips in the tunneling DOS. Our analysis also indicates that the ratio of W/L only influences the position of the superlattice Dirac points slightly, as shown in Fig. 3(d).

The experimental $E_{SD}$ of different ripples of the corrugated graphene shows a wide distribution of values, as shown in Fig. 2(d). We carefully examined all the STS spectra and their measured positions. At a fixed measured position, the value of $E_{SD}$ is almost a constant irrespective of the STM tips and the measured times. However, at different positions, the value of $E_{SD}$ is space-dependent and shows a wide distribution of values. It suggests that the space-dependent of $E_{SD}$ is an intrinsical phenomenon in the corrugated graphene. Similar space-dependent superlattice Dirac points was also observed in each ripple of the corrugated graphene. This excludes the different width of the ripples as a dominating origin of the space-dependent $E_{SD}$. We attribute the observed space-dependent $E_{SD}$ mainly to the space-dependent Fermi velocity, which may originate from the local strain [44] and the strong electron-electron interaction [45,46], in the corrugated graphene according to $E_{SD} = \pm \hbar v_F |G|/2$. The model developed in Ref. [13] treated the ripples as the quasi-periodic electronic superlattice. The effects of both the strain and the electron-electron interaction were not taken into account in the model. However, recent studies pointed out that the strain and the electron-electron interaction influence the Fermi velocity of graphene dramatically [44-47]. For example, the Fermi velocity is only about $1.0 \times 10^6$ m/s for graphene without electron-electron interaction or with a very weak electron-electron interaction, whereas, it could reach as high as $3.0 \times 10^6$ m/s for graphene with strong electron-electron interaction [46]. Actually, the ripples of a corrugated graphene were predicted to lead to a strong electron-electron interaction [18,19,45]. Additionally, it was also predicted theoretically that the corrugated graphene will have a space-dependent Fermi velocity [44].

A best way to confirm the above analysis is to directly measure the space-dependent Fermi velocity in the corrugated graphene. However, this experimentally. Here, we propose a possible solution to explore the space-dependent Fermi velocity in the corrugated graphene. In the pristine graphene, the DOS per unit cell around the Dirac point is given by $\rho(E) \propto |E|^{1/2} [3]$, which indicates that the slope of the DOS reflects the magnitude of the Fermi velocity. Please
The value of \(\frac{1}{S}^{0.5}\) as a function of \(\frac{E_{SD}^{exp}}{E_{SD}^{th}}\). The linear dependence of \(\frac{1}{S}^{0.5}\) and \(\frac{E_{SD}^{exp}}{E_{SD}^{th}}\) indicates that the slope of the DOS of the corrugated graphene really reflects the magnitude of the Fermi velocity. The slope of the STS spectra recorded at different positions show a wide distribution of values, which is attributed to the effect of the local strain and the strong electron-electron interaction in the corrugated graphene. The right Y-axis of the Fig. 4(b) shows \(v_{F}^{\text{corr}} / v_{F}^{\text{flat}}\). Here \(v_{F}^{\text{corr}}\) is the local Fermi velocity in the corrugated graphene and \(v_{F}^{\text{flat}}\) is the Fermi velocity in the flat graphene monolayer (these values are obtained on the assumption that \(v_{F} \propto \left(\frac{1}{S}\right)^{0.5}\)).

The average Fermi velocity in the corrugated graphene is estimated as \(1.1v_{F}^{\text{flat}}\).

In summary, we address the electronic structures of corrugated graphene monolayer on Rh foil. We show that the quasi-periodic ripples of nanometer wavelength give rise to a weak 1D electronic potential in graphene, which leads to the emergence of the superlattice Dirac points. Our experimental results further demonstrate that the corrugated graphene has a space-dependent Fermi velocity originating from the strain and the electron-electron interaction. These results suggest that the strain and the electron-electron interaction play a vital role in the electronic properties of corrugated graphene and this system could provide an ideal platform to study strongly correlated phases in graphene with desirable properties.

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