Direct Observation of Electron Confinement in Epitaxial Graphene Nanoislands

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The peculiar electronic properties of graphene (G) come from the π-band and result from the overlap of π^* orbitals on neighboring carbon atoms. A simple tight-binding (TB) model of G shows that energy dispersion of the π-band is described by \( E = \pm v_F |p| \), where the carrier momentum \( p = \hbar k \) and the Fermi velocity \( v_F \approx 10^6 \) m/s.\(^1^–^3\) When carriers in G are confined, their properties depend on the confinement geometry. Previous studies showed how confinement of carriers in a G nanostructure affects the physical properties such as an electrical conductivity,\(^5^–^7\) a size-dependent energy gap opening near the Dirac energy \( E_D \),\(^8^–^10\) and electronic edge states dependent on the edge atomic orientations.\(^1^1\)

Surface inhomogeneities, such as defects or step edges, scatter the electrons and result in standing waves, so-called Friedel oscillations,\(^1^2\) which provide crucial information, such as screening effects and electron–electron interaction, of an electron system. Experimental observation of such wave patterns in the metallic surface states has been done by scanning tunneling spectroscopy (STS)\(^4^,^1^3,^1^4\) since the technique measures the differential conductance \( dI/dV \) signal, which is proportional to the local density of states (LDOS) of the sample surface, with the spatial resolution down to the atomic scale.

The pseudospins and chirality of the G honeycomb structure are known to give rise to different scattering behaviors from those of two-dimensional (2D) Fermi electron gases.\(^1^5^–^1^7\) In this short report, we discuss the spatial resolution of the LDOS of a nanometer-size G nanoisland using STS. The STS measurements were performed using a low-background, constant-current lock-in microscope with a modulation frequency of \( 100 \) kHz. The distance between the sample and the tip was maintained at \( 1 \) nm by feedback control. The STM tip was fabricated using a positive electron beam lithography and an inductively coupled plasma (ICP) etching process. The sample was prepared by mechanically exfoliating highly disordered graphite to G (250–500 nm) flakes on a copper foil, and then, the flakes were transferred onto a 4% Ir(111) surface. The energy dispersions of the Fermi level were measured in the range of \(-2 \) to \(+2 \) eV in steps of \( 0.1 \) eV at room temperature. The LDOS maps were obtained by the Fourier filtering method of the differential conductance spectra with a modulation frequency of \( 100 \) kHz.

**ABSTRACT** One leading question for the application of graphene in nanoelectronics is how electronic properties depend on the size at the nanoscale. Direct observation of the quantized electronic states is central to conveying the relationship between electronic structures and local geometry. Scanning tunneling spectroscopy was used to measure differential conductance \( dI/dV \) patterns of nanometer-size graphene islands on an Ir(111) surface. Energy-resolved \( dI/dV \) maps clearly show a spatial modulation, indicating a modulated local density of states due to quantum confinement, which is unaffected by the edge configuration. We establish the energy dispersion relation with the quantized electron wave vector obtained from a Fourier analysis of \( dI/dV \) maps. The nanoislands preserve the Dirac Fermion properties with a reduced Fermi velocity.

**KEYWORDS:** scanning tunneling spectroscopy (STS) · quantum confinement · standing wave · epitaxial graphene · Dirac Fermion · electron dispersion relation

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corresponding spatial modulation of LDOS.26,27

The energy dispersion relation is described by the equation $E = E_D \pm h\nu_f|k|$ with $E_D = -0.09 \pm 0.02$ eV and $v_F = (6.0 \pm 0.4) \times 10^5$ m/s.

**RESULTS AND DISCUSSION**

Figure 1A shows G islands grown on an Ir(111) surface. Constant current scanning tunneling microscopy (STM) images reveal that all islands have a uniform apparent height of $\sim 0.2$ nm. The surface of the islands shows a pattern with a periodicity of $2.52 \pm 0.03$ nm, regardless of size and shape of the G islands (see Supporting Information I). This pattern is known as moiré structure. It is ascribed to a spatial pattern of the electronic properties due to the G–Ir(111) lattices.25 The periodicity of the modulation arises from the superposition of the G and Ir(111) lattices.25 The monatomic apparent height and the moiré patterns, which induce a decrease in the border of the islands. For larger negative $V_b$ we identify four more distinct modulation patterns (Figure 3B–E). The patterns at lower $V_b$ show an increasing number of modulations over the area of the island. The modulation can be understood as a standing wave pattern resulting from the interference of electron waves. Our findings suggest a decrease in the electron wavelength (increase in the electron wave vector) toward larger negative energy, as shown in Figure 4. For the island in Figure 1C, we also observed a similar tendency in both $dI/dV$ and FT maps, as shown in Figure 3K–T. To compare the observed $dI/dV$ maps to the LDOS of confined electrons, we employ the multiple-scattering method.28,29 We extract the geometry from the STM images and use it for the calculation. The calculation reproduced very similar LDOS patterns with the same sequence of $dI/dV$ modulation patterns (see Supporting Information II).

Interestingly, the energy intervals between any two neighboring patterns in Figure 3 are identical within our experimental accuracy, with an average separation of $0.16$ eV. This marks a distinct difference between the energy dependence of $dI/dV$ modulation patterns of G nanoslands as compared to those of metallic nanostructures.13,27,30

We obtain the wave vectors from the FT maps in Figure 3F–J (Figure 3P–T), which give rise to the modulation patterns of the $dI/dV$ maps in Figure 3A–E (Figure 3K–O). The patterns of Figure 3 are selected to show the largest intensity of the respective $k$-point. We observed that the intensity of a given $k$-point of the FT map varies with energy. Also, the position does not vary continuously with energy but changes in a discrete manner. In 2D electron systems, the radial average of the FT map has been used to determine the in-plane wave vector $k_r$ of a standing wave pattern.30–32 Under the same strategy, we take the average of the $k$ for the sixfold symmetric pattern in each FT map as the magnitude of wave vector for each modulation pattern in Figure 3A–E (Figure 3K–O). The obtained values

![Figure 1. (A) STM image (70 × 70 nm²) of G islands grown on Ir(111). (B,C) STM images of G nanoslands where electron confinement was investigated. See Figure 3. (D) Atomically resolved STM image in the edge region marked by the red rectangular box in C. G honeycomb lattice model is superimposed. Note that edges of the G nanoslands in our experiments showed zigzag-type arrangements of carbon atoms. Imaging parameters: $V_b = -0.05$ V, $I_{set} = 1$ nA (A,B); $V_b = -0.05$ V, $I_{set} = 2$ nA (C); $V_b = -0.03$ V, $I_{set} = 2$ nA (D).](Image 66x658 to 155x734)

![Figure 2. (A) $dI/dV$ curves measured from the center toward a corner of the island in Figure 1B. (B) $dI/dV$ curves measured from the center toward a side of the island in Figure 1C. The inset in each plot shows the STM image with the positions where the $dI/dV$ curves were taken. Measurement parameters: $V_{stab} = 0.5$ V, $I_{stab} = 1$ nA, $V_{mod} = 20$ mV (A,B); $V_b = -0.05$ V, $I_{set} = 1$ nA (insets of A and B).](Image 160x657 to 198x735)
clearly show a linear dependence of which is a signature of the conduction band. Also, expected from the electronic dispersion relation presented in Figure 3. The discrete nature of each island with the equation results in a linear fit with the equation results in $E_D = -0.088 \pm 0.022$ eV ($-0.086 \pm 0.021$ eV) and $v_F = (6.3 \pm 0.40) \times 10^5$ m/s ($6.0 \pm 0.38 \times 10^5$ m/s) for the island in Figure 1B (Figure 1C).

The $E_D$ offset of $\sim$0.1 eV with respect to the Fermi energy ($E_F$) reflects a small substrate-induced charge doping in our nanoislands, similar to the infinitely large G/Ir(111) systems. However, it is surprising that $v_F$ values extracted from the plots in Figure 4A are smaller by 30–40% than the Fermi velocity of free-standing G ($v_{F0}$).

The G–substrate interaction is known to affect the graphene band structure. Angle-resolved photo-emission spectroscopy (ARPES) has been employed to measure the band structure of G/Ir(111). Those experiments revealed the creation of minigaps in the G $\pi$-band due to the moiré interaction and the hybridization of Ir surface states with the G $\pi$-band at $E_F$. Nevertheless, the measured band structures showed the preservation of a linear $\pi$-band with the deviation of $v_F$ from $v_{F0}$ by only a few percent. Therefore, the G–substrate interaction itself appears to be not the only origin to explain the large reduction of $v_F$ in our experiment.

We suggest another mechanism for the $v_F$ reduction which could stem from the nanometer-size of the G islands in this study. In a TB model, $v_F$ is described by $h v_F = 3ta/2$, where $a$ is the nearest carbon–carbon atomic distance and $t$ is the nearest-neighbor hopping.
amplitude through the π orbitals of carbon atoms. This expression with \( v_F \) extracted from our study gives a hopping amplitude \( t \approx 1.7 \text{ eV} \approx 0.6 t_0 \), where \( t_0 = 2.8 \text{ eV} \) is the carbon–carbon hopping amplitude of freestanding G. It has been predicted that the modification in the hopping amplitude between carbon and impurity sites can locally reduce \( v_F \) due to the π orbital suppression at the defect sites. Recent STM and STS measurements near the defects in G corroborated this view and reported a considerable reduction of \( v_F \) down to \( \sim 0.3 v_F \). Furthermore, these studies showed that the reduction of \( v_F \) extends over several nanometers around the defect sites. The edge atoms of G grown on Ir(111) are known to have a much stronger interaction with the substrate than those in the central region of the island. The sharp decrease of the \( \frac{dI}{dV} \) signal near the island edge (see Supporting Information III) supports this view. This strongly suggests the suppression of the π-band in the near-edge regions. The edges of the islands, therefore, could act as extended lattice defects. Since the islands in this study have radii of 4–5 nm, one could expect a reduction of \( v_F \) over the whole area of the islands.

The noticeable difference between our work and the previous ARPES studies is the size of G. Thus, besides the G–substrate interaction, the small island sizes with the suppressed π-band near the edges provide one plausible scenario as a mechanism to induce the considerably small \( v_F \) in the nanometer-size G islands.

The survey of the effective size of the confinement \( L_{\text{eff}} \) would be an additional interesting aspect of the confinement phenomena in G as it is in the 2D Fermi electron confinement system. An effective way to obtain the confinement size along the symmetry axis of a threefold symmetric 2D structure by using a one-dimensional (1D) particle-in-a-box model has been introduced by Rodary et al.\(^{13}\) We applied the same analogy to the G islands in Figure 3. We take the magnitude of the wave vector \( k_n \) along one of the symmetric direction, as indicated in Figure 3HR, where \( n \) is the integer index determined from the sequence of \( \frac{dI}{dV} \) patterns shown in Figure 3A–E (Figure 3K–O).

## Conclusions

In conclusion, we perform STM and STS measurements of G islands on Ir(111). We observe a pronounced spatial modulation of the differential conductance \( \frac{dI}{dV} \) in nanosized monolayer G. We ascribe this to a spatial modulation of the LDOS, which is induced by electron confinement. The quantitative analysis of the modulation patterns using FT maps gives the electron dispersion, which is well described by Dirac-Fermion dispersion \( E = E_D - \hbar v_F k \) with \( E_D \approx -0.09 \text{ eV} \) and \( v_F \approx 6 \times 10^5 \text{ m/s} \). The π-band modification by the G-substrate interaction itself appears to be not the only origin to explain the large reduction of \( v_F \) in the nanosized G islands. The finite size effect, where the edge scattering contributes, may contribute as an other possible mechanism. Additionally, to derive the confinement size \( L_{\text{eff}} \), we apply the 1D particle-in-a-box model to the symmetry axis of the islands. The extracted \( L_{\text{eff}} \) is smaller by 2–3 G unit cells than the geometric size. This difference may stem from the strong carbon–substrate interaction at the island edges, giving rise to the depletion of G DOS in the near-edge regions. Our results show clear electron confinement effects in G nanostructures unperturbed by the zigzag edge configuration. G nanoislands on Ir(111) provide a new good platform to understand the pure quantum confinement effect in G.

## Methods

The experiments are performed in an ultrahigh vacuum (UHV) chamber equipped with a scanning tunneling microscope (STM) operating at 8 K and a chamber for sample preparation. The STM chamber is equipped with \( ^4 \text{He} \) bath cryostat operating at a base pressure \( P_b \) of \( 2 \times 10^{-11} \text{ mbar} \). The Ir(111) single crystal (MaTeck GmbH) was Ar \(^+\)-sputtered at room temperature (RT) (1 keV, 0.75 \( \mu \text{A}, 15 \text{ min} \)) and subsequently heated 10 times to 1200 K in an O\(_2\) pressure of \( 1 \times 10^{-8} \text{ mbar} \). Finally, it was annealed at 1370 K at \( P_b = 2 \times 10^{-10} \text{ mbar} \). In order to grow monolayer graphene, the cleaned Ir(111) surface was exposed to C\(_2\)H\(_4\) at RT and a pressure of \( 2 \times 10^{-9} \text{ mbar} \) for 2 min and subsequently heated to 1320 K for 2 min under the same partial pressure of C\(_2\)H\(_4\). The sample was then transferred to the STM chamber. STM images show that ~60% of the substrate surface is covered by G islands. Their sizes ranges from 6 to 50 nm in diameter. We perform STM and STS measurements on the G islands at 8 K and \( 2 \times 10^{-11} \text{ mbar} \). The STM images are obtained in constant-current mode. For STS, we employed a standard lock-in technique with modulation frequency \( v = 4 \text{ kHz} \) and root-mean-squared amplitude of 20 mV. Before each STS measurement, the tunneling condition was stabilized at \( V_{\text{stab}} = 0.5 \text{ V} \), \( I_{\text{stab}} = 1 \text{nA} \).

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References and Notes