Symmetry breaking in molecular artificial graphene

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Abstract

Symmetry breaking in graphene has profound impacts on its physical properties. Here we emulate symmetry breaking in artificial graphene systems by assembling coronene molecules on a Cu(111) surface. We apply two strategies: (1) differentiating the on-site energy of two sublattices of a honeycomb lattice and (2) uniaxially compressing a honeycomb lattice. The first one breaks the inversion symmetry while the second one merges the Dirac cones. The scanning tunneling spectroscopy shows that in both cases the local density of states undergo characteristic changes. Muffin-tin simulations reveal that the observed changes are associated with a band gap opened at the Dirac point. Furthermore, we propose that using larger molecules or molecules strongly scattering the surface state electrons can induce an indirect gap.

1. Introduction

The unique physics of Dirac quasiparticles can be mimicked in artificial graphene (AG) systems [1]. These AG systems include cold atom lattices [2–6], phononic crystals [7–10], photonic crystals [11–16], semiconductor nanopatterns [17–22] and molecular lattices assembled on metal surfaces, termed as molecular designers [23–34]. The tunability of the artificial systems makes them ideal playgrounds to exploit phenomena that are extremely challenging to access in real materials. For example, Kekulé structure, graphene pn junctions, deformed graphene, graphene nanoribbons, point and line defects, topological domain wall states, Lieb lattice, quasicrystalline structure, and fractal electronics have been realized in molecular designers [23–30]. These systems exhibit exciting physics such as Gauge field, edge states and flat band [35–38], to name a few.

In this work, we report the creation of molecular AG lattices with tunable band structures by assembling coronene molecules on a Cu(111) surface. Specifically, we focus on lattice symmetry breaking which is central to many phenomena such as massive Dirac fermions and topological phase transitions. We break the lattice symmetry by means of (1) breaking the inversion symmetry and (2) uniaxially compressing the honeycomb lattice. The sublattice-resolved local density of states (DOS) are probed using scanning tunneling spectroscopy. The spectra evidence characteristic changes, which are associated with gap opening at the Dirac point (DP) as revealed by muffin-tin simulations. Our results exemplify that molecular artificial systems offer unique opportunities to explore physics hosted in Hamiltonians of complex two-dimensional lattice with tunable on-site energy and hopping interaction.

2. Experimental and theoretical methods

Single-crystal Cu(111) substrate was cleaned by cycles of Ar⁺ sputtering and subsequently annealing to 530 °C. The sample was characterized using an ultra-high vacuum (10⁻¹⁰ mbar base pressure) scanning tunneling microscope (STM) system (Omicron GmbH) at cryogenic temperature (5 K). Coronene molecules (Sigma Aldrich) were thermally deposited at 290 °C on the Cu(111) substrate held at room temperature and then
annealed to 120 °C. The STM tip-induced manipulation was conducted by approaching the molecule with a bias voltage of −2 V, and then laterally moving the molecules to their destinations. The STM topography data were acquired in constant current mode. The dI/dV spectra were measured using a lock-in amplifier with a sinusoidal modulation of 1.5 kHz and 15 mV amplitude. For each pattern, we collect the dI/dV spectra after at least a 5 × 5 unit cell is fabricated when the finite size effects can be roughly negligible [24, 25]. The dI/dV spectrum is normalized by the spatially averaged spectra measured on the clean Cu surface with the same tips (see figure S1 is available online at stacks.iop.org/NJP/21/083005/mmedia) [23–25, 28, 29]. In local density of states (LDOS) maps, each dI/dV spectrum was normalized by I/V spectra.

The artificial systems were simulated using muffin-tin models that host non-interacting two-dimensional electron gas (2DEG) in a periodic array of repulsive disc-shaped potentials of 0.8 eV and the radius of the disc is 0.5 nm except for the data in figure 6 where the values are specified. The effective mass of the 2DEG is 0.38 m_e.

3. Results and discussion

3.1. Breaking of inversion symmetry

To break the inversion symmetry of a honeycomb lattice [39], we differentiate the on-site energy of the two sublattices using triangular shape potentials. Here, each triangular shape potential is composed of three disc potentials (coronene molecules). As illustrated in figures 1(a) and (b), these potentials are arranged as a triangular lattice on a Cu(111) surface which hosts 2DEG (blue background in figures 1(a) and (b)). The 2DEG is scattered by these triangular potentials and confined in the honeycomb channels (highlighted by the white frames in figures 1(a) and (b)) mimicking a honeycomb lattice model. The three-way junctions in the honeycomb channels represent artificial atoms, as indicated by the red (sublattice A) and green (sublattice B) circles. In figure 1(a), the sides of the triangular potentials are parallel to the honeycomb channels. With this configuration, the two sublattices are equivalent in the regard that the artificial atoms are surrounded by the same potentials. This structure mimics an AG lattice. In figure 1(b), the triangular potentials are rotated by 30°. The sublattice A atoms are surrounded by three discs, whereas the sublattice B atoms are surrounded by six discs at a larger distance. Consequently, the potential energy of the 2DEG at sublattice A is higher than that at sublattice B. The different on-site energy of the two sublattices mimics a hexagonal boron nitride lattice (AhBN).

The band structures of the two structures calculated using muffin-tin models are shown in figures 1(c) and (d), respectively. The AG structure features an intercepting DP at K point, while the AhBN structure has a band gap at K point. We calculate series of structures in which the triangular potentials are rotated gradually from 0° to 30°. Figure 1(e) shows that a gap is opened in all structures with a non-zero rotation angle and reaches a
maximum at 30°. This result suggests rotating the triangular potentials provides an effective way to breaks the sublattice symmetry and opens a gap at DP.

Figures 2(a) and (b) show the simulated sublattice-resolved DOS of the AG and the AhBN structures. Both sublattices of the AG structure feature a V-shape DOS which signifies the gapless linear dispersion of the massless Dirac fermions [23, 24, 40]. The DP is at the bottom of the V-shape. The peak below (above) the DP is associated with valence (conduction) band, thereafter termed as VB (CB) peak [23, 24]. Figures 2(c) and (d) show the spatial distribution of the LDOS map (LDOSM) obtained from the muffin-tin simulations. Figure 2(c) shows the LDOSMs of the AG lattice at the VB and the CB peak energy. The two sublattices appear similar intensity at both energies. Figure 2(d) shows the LDOSMs of the AhBN lattice at the VB and the CB peak energy. Both LDOSMs display a three-fold symmetry: at the VB peak energy, the sublattice B exhibits strong intensity, while at the CB peak energy, the sublattice A exhibits strong intensity. The two sublattices of the AG exhibit identical DOS with a V-shape, whereas the DOS of the two sublattices of the AhBN are nearly anti-symmetric with a gap of 52 meV.

To demonstrate the sublattice symmetry breaking experimentally, we manipulated disc-shaped coronene molecules on a Cu(1 1 1) surface to construct the triangular potentials [24]. An AG lattice and an AhBN lattice are shown in figures 3(a) and (b), respectively. Figures 3(c) and (d) show the sublattice-resolved normalized $dI/dV$ of the two structures, which reveal the LDOS of the two sublattices. The DP in AG is at $-0.34$ V, which is shifted by $-0.5$ V compared to our simulations due to the Cu(1 1 1) surface state onset energy. The AG doping level is modified by the lattice parameters which change the electron count per superlattice unit cell [23]. Note that the VB peak is higher than the CB peak due to a monotonically decaying background. The DOS intensity and lineshape differences of the two sublattices are caused by the imperfectness of the AG lattice. The real-space LDOSMs at the VB and CB peaks are shown in figure 3(e), showing the two sublattices display similar LDOS intensity.

In the AhBN structure, the sublattice symmetry is broken as manifested in figures 3(d) and (f). Figure 3(d) shows that the sublattice A features a two-peak DOS but the relative intensity of the two peaks is reversed as compared with the AG (figure 3(c)). Taking into account of the monotonically decaying background signal, the VB at $-0.38$ V is further weaker than the CB peak at $-0.32$ V. In sharp contrast, the DOS at the sublattice B features a pronounced VB peak at $-0.37$ V, while the CB peak is nearly absent. The sublattice asymmetry is displayed in LDOSMs (figure 3(f)). Both maps feature a three-fold symmetry: at $-0.38$ V, the sublattice B atoms exhibit stronger intensity than those of the sublattice A, while at $-0.32$ V, the intensity contrast is reversed. Experimental $dI/dV$ spectra do not resolve a band gap due to the limited energy resolution of $dI/dV$.
spectroscopy, life time of the 2DEG and bulk state contribution of Cu(111). Nevertheless, the sublattice symmetry breaking in the AhBN structure is evident, which is associated with gap opening [41].

3.2. Uniaxial compression

When a honeycomb lattice is uniaxially-compressed, the Dirac cones are shifted away from the corners of the Brillouin zone and become elliptical instead of circular [42, 43]. Further compressed, the Dirac cones merge and an energy gap is opened. This causes a topological phase transition from a semimetal to an insulator [44]. Experimentally, however, the strain that could lead to such a topological phase transition is unrealistically too large to achieve in real graphene [42]. The merging of the DP in artificial systems was demonstrated experimentally in cold atom lattices [3] and microwave photonic crystals [14]. Recently, Feilhauer et al predicted that DP merging could also be realized in molecular AG [45].

We simulate the uniaxial compression by reducing the length of the AG lattice in the armchair direction. Here we use one coronene molecule to act as a disc-shaped potential. As illustrated in figure 4(a), the lattice vectors are defined as 

\[ \mathbf{a}_1 = \frac{L}{2} \mathbf{i} + \frac{\sqrt{3}L}{2\alpha} \mathbf{j}, \quad \mathbf{a}_2 = \frac{L}{2} \mathbf{i} - \frac{\sqrt{3}L}{2\alpha} \mathbf{j}, \]

where the parameter \( \alpha \) represents a uniaxial compression ratio in the \( y \) direction along the armchair edge. We carried out muffin-tin model simulations of the three compressed AG lattices (figure 4(b)). Figures 4(c)–(e) show the \( kx \) projections of the calculated band structures (see supplemental information) of the compressed lattices. With \( \alpha = 1.3 \) and \( \alpha = 1.5 \), the valence band and the conduction band touch at DP. With \( \alpha = 1.7 \), the Dirac points merge and a 50 meV gap opens around DP.

Figure 5(a) shows three experimentally-assembled AG lattices, as highlighted by the light blue frames, with compression factor \( \alpha = 1.3, 1.5 \) and 1.7 from bottom to top. The evolution of the DOS is shown in figure 5(b). When \( \alpha = 1.3 \), the DOS features a V shape with its bottom at \(-0.179 \) V and the VB (CB) peak at \(-0.252 \) V (\(-0.128 \) V). Compared with the uncompressed lattice [24], the uniaxial compression up shifts the DP by 50 mV and enlarges the separation between the VB peak and the CB peak from 100 to 124 mV. These effects are further enhanced in the structure with \( \alpha = 1.5 \): bottom of the V shape is up shifted to \(-0.170 \) V and the VB and CB peak separation is enlarged to 139 mV. When \( \alpha = 1.7 \), a shoulder feature appears at \(-0.034 \) V which is the band edge of CB. The separation between the VB peak and the CB peak enlarged to 168 mV.

The simulated DOS is plotted in figure 5(c), which captures the experimentally observed up-shifting of the V-shape bottom, widening of the separation between VB and CB peaks. The experiments and simulations fit fairly well. However, there is no gap found in the DOS even with \( \alpha = 1.7 \). This is consistent with the band structures in figure 4(e) as there is no real gap in the entire Brillouin zone. Although the DP merged and opened a gap around the DP, the bottom of CB and the top of VB overlap, resulting in the shoulder feature in the LDOS.

We further test the condition needed to realize a DP merging in molecular AG using muffin-tin simulations. When the potential energy of the molecule is increased from 0.8 to 1.6 eV, an indirect gap of 40 meV is opened, as shown in figure 6(a). Another way to open a gap is to use molecules with a larger radius to assemble the uniaxially-compressed AG. Figure 6(b) shows that using molecules with a radius of 0.7 nm can open an indirect gap.
Figure 4. (a) Uniaxially-compressed AG lattice. (b) Simulation models of the compressed lattices with $\alpha = 1.3, 1.5$ and $1.7$ from bottom to top. (c)–(e) The $k_x$ projections of the band structures of compressed lattices in (b).

Figure 5. (a) Experimentally-assembled AG lattices with $\alpha = 1.3, 1.5$ and $1.7$ from bottom to top. The scanning parameters are $-1$ V and $25$ pA. Scale bars: $3$ nm. (b) Normalized tunneling spectra acquired in the three lattices. (c) Simulation DOS of the compressed lattices with $\alpha = 1.3, 1.5$ and $1.7$ from bottom to top.
4. Conclusions

To conclude, we design artificial molecular lattices to mimic inversion symmetry breaking and uniaxial compression of graphene. The spatially-resolved DOS signifies the existence of a topological transition between a gapless phase and a gapped phase. We propose that an indirect gap can be opened under uniaxial compression of molecular AG using molecules that strongly scatter the surface state electrons or molecule with a large radius. We anticipate that the ability to tune on-site energy and hopping term of the molecular designers offers great potentials to emulate the physics of complex two-dimensional lattice systems.

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