Tunable Electronic Properties of Twisted Graphene Layers in High Angles Regime

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Stacking two sheets of graphene on top of each other and then rotating one of them so that the sheets are slightly misaligned is one of the hot research directions in nanoelectronics. Here, using the density functional theory, we show that the electronic properties of the graphene nanoisland on the graphene substrate are modulated by changing the rotation angle. We observed that the mutual rotation in the range 0–60° contributes to the induction of the van Hove singularity and the quantum oscillation of the density of states at the Fermi level. Our results provide guidance for future experiments targeting the next generation of devices for nanoelectronics and twistronics.

topics: twistronics, electronic properties, graphene, van der Waals heterostructure

1. Introduction

The carbon-based family exhibits a variety of allotropes, from graphite to low-dimensional fullerenes, and from nanotubes to graphene. Two-dimensional graphene was extracted by mechanical exfoliation from bulk graphite [1] in 2004 and was quite surprising as it was previously believed to be thermodynamically unstable. For this discovery, Andre Geim and Konstantin Novoselov were awarded the Nobel Prize in 2010. The crystal structure of graphene consists of sp^2-hybridized carbon atoms. In a hexagonal lattice with two atoms per unit cell, each atom forms strong σ bonds with the three nearest neighbours.

The basic properties of graphene, such as the electron–hole symmetry of band structure, were well known by Wallace in 1947 [2], as well as band structure and Dirac points, but were discovered after Iijima's discovery of carbon nanotubes in 1991 [3]. This single-atom-thick two-dimensional material has been intensively studied for the last two decades because of its exceptional physical and electronics properties, chemical tunability, high crystal quality, high mechanical resistance, superconductivity after doping/intercalation, and large optical transparency [4–6]. In 2018, Cao et al. [7, 8] demonstrated that stacked graphene layers with relative rotations can have drastically different properties than their regularly aligned counterparts. Namely, it has been observed that a relative rotation of about 1.1° leads to superconductivity in pristine two-layer graphene [7, 8].
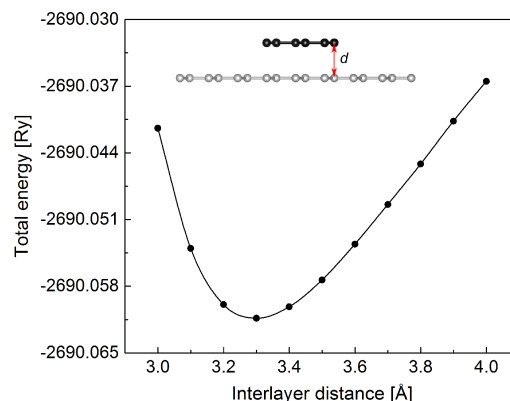

Fig. 1.   Total energy for initial AA stacking configuration (twist angle 0°) of two graphene sheets as a function of interlayer distance.

In this paper, we consider an AA stacking configuration where carbon atoms of the two layers (nanoisland and substrate) have exactly identical lateral positions. Using the first principle calculations, we examine the influence of the mutual rotation of these sheats on the electronic properties in the high angles regime from 0 to 60°.

2. Computational methods

To study the electronic properties of twisted graphene layers, first-principles calculations are performed within the framework of the density
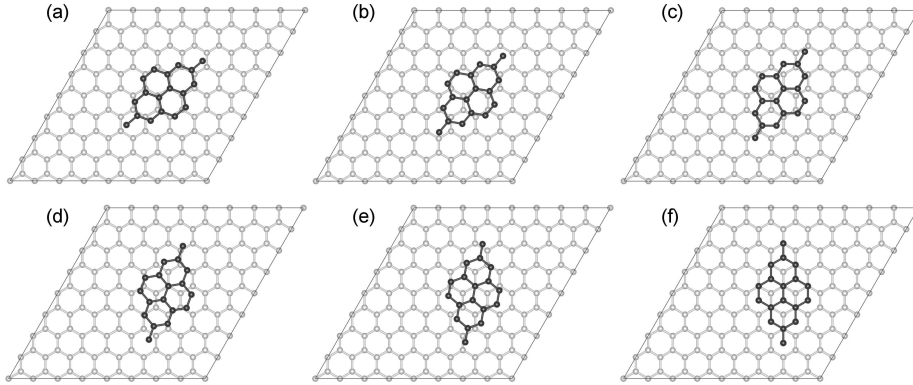
Fig. 2. Patterns of six graphene nanoislands on graphene substrate with the rotational angles of (a) $10°$, (b) $20°$, (c) $30°$, (d) $40°$, (e) $50°$, and (f) $60°$. The top and bottom graphene sheets are marked in black and grey, respectively.

TABLE I

Interlayer binding energy E_b [meV/atom] as a function of twist angle θ.

θ	$0°$	$10°$	$20°$	$30°$	$40°$	$50°$	$60°$
E_b	9.31	9.27	9.38	9.53	9.68	9.73	9.81

functional theory (DFT) [9] as implemented in the Quantum-Espresso package [10, 11]. Exchange–correlation potentials are treated within the generalized gradient approximation of Perdew–Burke–Ernzerhof theory (GGA-PBE). After conducting proper convergence tests, we obtained well-converged values for the kinetic energy cutoff of the wavefunction equal to 60 Ry and the kinetic energy cutoff for the charge density equal to 240 Ry.

The investigated bilayer systems consist of 146 C atoms (128 atoms in the first layer are substrate and 18 atoms in the second layer form nanoisland). To avoid interaction between neighbouring bilayers, a vacuum layer of 20 Å in the z-direction was introduced. The van der Waals interaction with a DFT-D correction of Grimme was considered [12]. Optimized atomic structures were obtained by fully relaxing both atomic positions as well as cell parameters using the Broyden–Fretcher–Goldfarb–Shanno (BFGS) quasi-Newton algorithm until all forces are smaller than 0.01 eV/Å. The Brillouin zone was sampled utilizing a $6 \times 6 \times 1$ $\boldsymbol{k}$-mesh in the Monkhorst–Pack scheme. To visualize the structures, we have used the Vesta software [13].

3. Results and discussion

After the initial structure had completely relaxed, the distance between the layers (d) for the AA-stacked configuration was calculated. This distance corresponds to the global energy minimum, which is found by calculating the dependences of the total energy relative to the distances between the nanoisland and the graphene substrate. As can be

see in Fig. 1, the interlayer distance is 3.3 Å, which is generally in agreement with the theoretical estimations and experimental observations of 3.1–3.5 Å for two identical graphene layers [14–17]. The average carbon–carbon bond length is about 1.42 Å.

Then, taking the calculated distance between the layers as a constant value, we studied how the twist angle between the layers can change their electronic properties. Previous calculations demonstrated that the electronic structure of the twisted bilayer graphene changes considerably with the change of the twist angle [18]. However, only the small twist angle regime ($\theta \lesssim 10°$) was investigated. Here, the electronic properties were investigated for the pure AA stacking ($\theta = 0°$) and six strongly twisted configurations ($\theta = 10°, 20°, 30°, 40°, 50°, 60°$) presented in Fig. 2.

Interlayer binding energy (E_b), defined as the energy required to separate two monolayers into isolated monolayers, is a relatively simple and quantitative measure of the strength of 2D materials with the van der Waals interlayer interaction [19]. For all investigated configurations, E_b was calculated from the total energy (E_{tot}), the energy of isolated nanoisland (E_{island}) and the graphene substrate $(E_{\text{substrate}})$, as follows

$$E_b = -\frac{1}{N}\left(E_{\text{tot}} - E_{\text{island}} - E_{\text{substrate}}\right), \qquad (1)$$

where N denotes the number of atoms in the unit cell. According to this definition (1), a larger value represents more favourable binding stability. As we can see in Table I, the binding energy is maximal for a twist angle equal to $60°$. This result denotes that the AB stacking configuration in which two adjacent layers are shifted in exactly the same way as in bulk graphite is energetically the most favourable.

The density of states (DOS) for the twisted graphene nanoisland above the graphene substrate, calculated as a function of θ, was plotted in Fig. 3. For comparison, we presented also DOS for the pristine graphene monolayer (substrate). We can notice that by creating a bilayer from nanoisland and
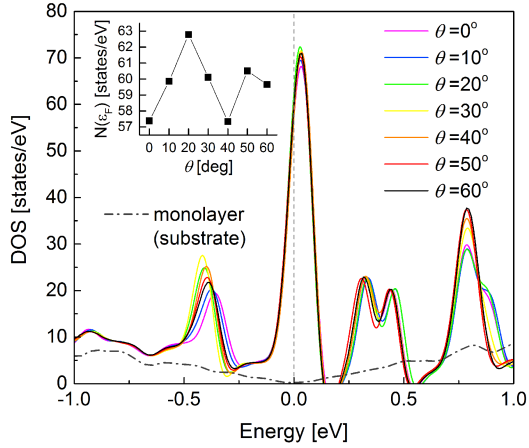
Fig. 3. Electronic density of states of graphene nanoislands on graphene substrate with rotational angles of 0–60°. For comparison the result for pristine graphene monolayer (substrate in this case) was also presented. The Fermi level depicted with the dashed vertical line is set to be zero. The inset presents the density of states at the Fermi level as a function of the twist angle.

graphene substrate, it is possible to induce a van Hove singularity (VHS) that is located close to the Fermi energy (ε_F). This is an interesting result in particular that pure graphene has linearly dispersing bands at the K point in the Brillouin zone, the so-called Dirac points and DOS, which is linear and vanishes at ε_F. Moreover, based on the inset in Fig. 3, we found oscillations in the electron density of states at the Fermi level $N(\varepsilon_F)$ as a function of the twist angle. This means that at a fixed interlayer distance, physical properties like e.g. conductance can be effectively controlled by tuning the twist angle, indicating the electrical properties tunable in nano-devices based on the twisted bilayer graphene system.

4. Conclusions

To conclude, we studied the electronic properties of twisted bilayer graphene in a wide range of twist angles. The obtained results demonstrate that in a system containing a nanoisland above the graphene substrate, it is possible to induce the van Hove singularities and modulate the value of electron density of states at the Fermi level by controlling the relative angle between the substrate and the nanoisland. These findings imply that twist angles could modify the electronic properties in the van der Waals materials and illuminate the way for the design of twist multilayer nanodevices.

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