Global Control of Stacking-Order Phase Transition by Doping and Electric Field in Few-Layer Graphene

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ABSTRACT: The layer stacking order has profound effects on the physical properties of two-dimensional van der Waals heterostructures. For example, graphene multilayers can have distinct electronic band structures and exhibit completely different behaviors depending on the stacking order. Fascinating physical phenomena, such as correlated insulators, superconductors, and ferromagnetism, can also emerge with a periodic variation of the layer stacking order, which is known as the moiré superlattice in van der Waals materials. In this work, we realize the global phase transition between different graphene layer stacking orders and elucidate its microscopic origin. We experimentally determine the energy difference between different stacking orders with the accuracy of μeV/atom. We reveal that both the carrier doping and the electric field can drive the layer-stacking phase transition through different mechanisms: carrier doping can change the energy difference because of a non-negligible work function difference between different stacking orders; the electric field, on the other hand, induces a band-gap opening in ABC-stacked graphene and hence changes the energy difference. Our findings provide a fundamental understanding of the electrically driven stacking-order phase transition in few-layer graphene and demonstrate a reversible and noninvasive method to globally control the stacking order.

KEYWORDS: Graphene, ABA/ABC stacking, Stacking phase transition, Low-dimensional materials

Structural phase transitions play an important role in both engineering and science. Many important physical phenomena are accompanied by structural phase transitions, such as metal–insulator transitions, and magnetism, and these effects can be utilized in memory and optoelectronic devices. A new structural phase emerging in van der Waals multilayers is the layer stacking order, which plays a key role in defining the physical properties of two-dimensional (2D) heterostructures. For example, ABA- and ABC-stacked trilayer graphene have quite different electronic and optical properties. ABC trilayer graphene has an electric-field-tunable band gap, and ABC trilayer graphene/hBN moiré heterostructures can exhibit tunable Mott insulator, superconductor, and ferromagnetic behaviors, while these phenomena have not been observed in ABA trilayer graphene. It is therefore highly desirable to achieve electrical control of the layer-stacking phase transition in van der Waals materials. Previously, scanning probes have been used to modify the local stacking order of few-layer graphene, where the local tip interacts strongly with the devices. However, reversible electrical control of the global layer-stacking phase transition has been challenging, and a fundamental understanding of the energetics and phase transition of layer stacking orders is lacking.

In this Letter, we combine dual-gate electrical control and a noninvasive near-field infrared probe to investigate the layer-stacking physics and demonstrate that global electrostatic gating can drive the stacking-order phase transition in few-layer graphene.
graphene. We systematically image the evolution of this gate-controlled stacking-order phase transition in dual-gated small-twist-angle few-layer graphene using infrared scanning near-field optical microscopy (IR-SNOM). We determine the energy difference between different stacking orders with high accuracy at the μeV/atom level and reveal that both carrier doping and the vertical electric field can reverse this energy difference, but through different mechanisms. Carrier doping can affect the energy difference because of a non-negligible work function difference between ABA and ABC graphene. The electric field changes the energy difference by opening a band gap in ABC graphene. However, the electric-field-induced effect works only when the graphene is close to the charge-neutral regime, which is hard to reach with only a single back gate as proposed in ref 15.

Figure 1a shows the schematics of the IR-SNOM measurement and the dual-gated few-layer graphene device. A 10.6 μm continuous-wave laser is focused onto the apex of a metal-coated tip with radius of curvature (r) of ~25 nm, and the scattered radiation is collected and measured by an HgCdTe detector in the far field. The tip-enhanced infrared scattering can probe local infrared responses of the few-layer graphene sample with ~40 nm spatial resolution.\(^\text{16-18}\) Graphenes with different stacking orders have different electronic bands and optical conductivities, the difference between which is especially obvious in the infrared regime. Therefore, the different stacking orders can be distinguished by measuring their infrared absorption.\(^\text{19,20}\) Previous work has demonstrated that ABC graphene has a weaker optical response at a wavelength of 10.6 μm than ABA graphene in the IR-SNOM measurement.\(^\text{18,21}\) We use dual-gated few-layer graphene devices in our study. The few-layer graphene is encapsulated in hBN layers to achieve the highest flatness and homogeneity. We use monolayer graphene and thin hBN layers (~5 nm) as the top electrode and the top dielectric layer, respectively. Such thin top gate materials are crucial for high-quality near-field imaging of the encapsulated few-layer graphene. Dual-gated graphene devices allow us to differentiate the contributions from the carrier doping, \(n_D\), and the vertical displacement field, \(D\) (the \(D\) field). The doping level and \(D\) field are determined by \(n = (D_B - D_T)/\epsilon + n_0\) and \(D = \frac{1}{\epsilon}(D_B + D_T) + D_0\), respectively, where \(n_0\) and \(D_0\) are the environment-induced offsets in the carrier doping and \(D\) field, respectively, and \(D_T = \epsilon_T V_T/d_T\) and \(D_B = \epsilon_B V_B/d_B\), in which \(\epsilon_B = \epsilon_T = 4\epsilon_0\) are the dielectric constants of the hBN and SiO\(_2\) layers, \(d_T\) and \(d_B\) are the top hBN and bottom hBN + SiO\(_2\) layer thicknesses, and \(V_T\) and \(V_B\) are the top and bottom gate voltages, respectively. We can experimentally determine \(n_0\) by checking the gate voltage required to achieve the charge-neutral point (CNP) in electrical transport measurements (for more information, see the Supporting Information (SI)). However, there is no easy way to directly measure \(D_0\) and here we simply assume that it is equal to 0.

Figure 1b–d shows IR-SNOM images of a typical dual-gated pristine trilayer graphene under different gate voltages. Here \(d_T = 3.7\) nm and \(d_B = 350\) nm. We fix the bottom gate voltage \(V_B\) at ~100 V and vary the top gate voltage \(V_T\). At \(V_T = -1.5\) V, the trilayer graphene has the ABA stacking order, which shows a relatively bright contrast. When \(V_T\) is increased to 1.5 V, a dark area, corresponding to ABC stacking, emerges in the left part of the image. The ABC domain is prevented from further expansion by a wrinkle (labeled by the red solid line). When \(V_T\) is further increased to 2 V, all of the graphene within the image transits to ABC stacking. A complete set of data for this stacking-order phase transition of trilayer graphene at different

![Image](https://pubs.acs.org/doi/10.1021/acs.nanolett.9b05092)
top and bottom gate voltages is shown in the SI. This stacking transition is due to interlayer sliding, which takes place during the stacking domain wall movement process. We note that almost all of the stacking domain wall emerging in exfoliated and transferred multilayer graphene originates from atomic reconstruction that is movable. However, some line defects and/or point defects within graphene could pin the stacking domain wall (SDW) and increase the hysteresis of this phase transition.

To systematically investigate the stacking-order phase transition and the associated energy change, in the rest of this Letter we focus on small-angle (<0.1°) twisted few-layer graphene instead of pristine few-layer graphene. Figure 1e shows a typical IR-SNOM image of a twisted trilayer graphene (monolayer stacked on a bilayer), which exhibits networks of different stacking domains. The interlayer twist induces the formation of a moiré superlattice. However, with such a small twist angle, the moiré superlattice is relaxed into separated and alternating ABC (dark) and ABA (bright) stacking domains as a result of the atomic reconstruction, and they are separated by a network of SDWs. Three ABC and three ABA domains are connected to the same vertex. Unlike pristine trilayer graphene, such ABC and ABA domain configurations in twisted trilayer graphene are topologically protected, where the ABC and ABA domains can expand or contract depending on their relative energies, but they cannot disappear completely without a global change of the twist angle. The SDW is analogous to a 1D elastic membrane, while the ABC/ABA energy difference can serve as a 1D pressure that acts on the SDW to make it bend. Consequently, the bending direction and the curvature of the SDW can provide direct information on the phase type and the energy difference between the ABC and ABA stacking. The corresponding topography image (Figure 1f) shows no obvious topographic defects in the positions of the SDWs, which means that the SDWs will be free to move with minimal hysteresis.

We show the evolution of the ABC and ABA domains in twisted trilayer graphene at different top (horizontal axis) and bottom (vertical axis) gate voltages in Figure 2a−l. Here \( d_T = 5.6 \text{ nm and } d_B = 350 \text{ nm}. \) The two diagonal axes therefore correspond to variations in the doping level and the displacement field, as illustrated by the inset in Figure 2d. The blue trace outlines a typical ABC domain, which exhibits striking changes controlled by both the carrier doping and the D field. The ABC domain is compressed in ungated trilayer graphene (\( V_B = V_T = 0 \text{ V} \)) because the ABA stacking order has a lower energy. However, the ABC domain becomes energetically more stable and expands dramatically at high p-doping and large displacement field.

### Figure 2.
Gate control of the stacking-order phase transition. (a–l) IR-SNOM images of the twisted trilayer graphene at different top and bottom gate voltages (labeled on the top and left sides). The inset in (d) shows the change in the doping level and the displacement field with the gate voltage. A typical ABC domain is outlined with a blue trace in each panel. The ABC domain is compressed in ungated trilayer graphene (\( V_B = V_T = 0 \text{ V} \)) because the ABA stacking order has a lower energy. However, the ABC domain becomes energetically more stable and expands dramatically at high p-doping and large displacement field. Scale bars: 1 \( \mu \text{m} \).
The local SDW curvature can be determined by the ellipselike curve to the difference. (a, b) IR-SNOM images of the SDWs with orientation-dependent local curvatures. Dark double arrows label the shear directions (i.e., the directions of the dislocation vector) of the corresponding SDWs. Blue curves were fitted to the theoretically predicted SDW shapes. The red dot and line in (a) label a point defect point and a line defect that pin the SDW. Scale bar: 1 μm. (c) Calculated SDW shapes with different $E_t/E_s$ ratios, among which $E_t/E_s = 1.6$ provides the best fit of the experimental data. The major and minor axes correspond to the shear and tensile directions, respectively. (d) Energy difference and phase diagram of the ABC and ABA stackings as a function of the doping and displacement field. Red and blue points correspond to the ABC and ABA phases, respectively. The green dashed line labels that phase boundary. The energy difference is evaluated from the measured SDW curvature (see the discussion in the text).

![Image](image_url)

Figure 3. Doping- and displacement-field-dependent ABC/ABA energy difference. (a, b) IR-SNOM images of the SDWs with orientation-dependent local curvatures. Dark double arrows label the shear directions (i.e., the directions of the dislocation vector) of the corresponding SDWs. Blue curves were fitted to the theoretically predicted SDW shapes. The red dot and line in (a) label a point defect point and a line defect that pin the SDW. Scale bar: 1 μm. (c) Calculated SDW shapes with different $E_t/E_s$ ratios, among which $E_t/E_s = 1.6$ provides the best fit of the experimental data. The major and minor axes correspond to the shear and tensile directions, respectively. (d) Energy difference and phase diagram of the ABC and ABA stackings as a function of the doping and displacement field. Red and blue points correspond to the ABC and ABA phases, respectively. The green dashed line labels that phase boundary. The energy difference is evaluated from the measured SDW curvature (see the discussion in the text).
Figure 4. Mechanism of the stacking-order phase transition. (a) Schematic of the electronic band structures of ABA and ABC graphene at zero D field. Only one gate is shown here. $E_{\text{CNP}}$ is the vacuum level, $\mu_i$ is the chemical potential, $E_{\text{CNP}}(i)$ is the position of the CNP, and $W_i$ is the work function measured at the CNP. The subscripts $i = 1$ and 2 represent ABC and ABA stacking, respectively. (b) IR-SNOM image of a trilayer graphene on a SiO$_2$ substrate with both ABC and ABA stacking and (c) the corresponding KPFM image. Scale bars: 2 $\mu$m. (d) Line profile of the surface potential averaged over the white box labeled in (c), which yields a work function difference of $\approx 18$ meV between the ABC and ABA phases. (e) Electronic band structures of ABA and ABC graphene with a nonzero D field. A band gap is opened in ABC graphene. (f) Calculated ABC/ABA energy difference at 300 K as a function of the carrier doping and the displacement field. The green dashed line denotes the phase boundary characterized by $\Delta E = 0$. The black dashed box indicates the phase space measured experimentally in Figure 3d. (g, h) Doping-dependent ABC/ABA energy difference at (g) zero and (h) nonzero D field. Blue curves are theoretically calculated values with (g) $D = 0$ and (h) $D = 1.47$ V/nm, corresponding to the solid and dashed line cuts in (f), respectively. Red points are experimental data for (g) $|D| < 0.3$ V/nm and (h) $|D| = 1.1-1.75$ V/nm, corresponding to the gray solid and dashed boxes in Figure 3d, respectively.

$$\Delta E(n, D) - \Delta E_0 \approx \int_{-\infty}^{\infty} [\text{DOS}(\epsilon, D)f(\epsilon - \mu_2(n))] - [\text{DOS}(\epsilon, D)f(\epsilon - \mu_1(n))] d\epsilon$$

$$= \int_{-\infty}^{\infty} [\text{DOS}(\epsilon, 0)f(\epsilon - \mu_2(0))] - [\text{DOS}(\epsilon, 0)f(\epsilon - \mu_1(0))] d\epsilon$$

$$= n\Delta W$$

(2)

in which the energy $\epsilon$ is referenced to the CNP, $\mu_i(n)$ is the chemical potential at carrier density $n$, $\text{DOS}(\epsilon, D)$ is the density of states (DOS) at displacement field $D$, $f(\epsilon - \mu_i(n))$ is the Fermi–Dirac distribution, $\Delta W = W_2 - W_1$ is the work function difference, and $\Delta E_0$ is the energy difference when $D = 0$ and $n = 0$ (see the SI for details). The subscript $i$ can be 1 or 2, representing ABA and ABC, respectively. Here we neglect the carrier density difference between the ABC and ABA domains as an approximation. The work function difference gives rise to different quasiparticle energies in ABA and ABC graphene, resulting in the doping-dependent term $n\Delta W$. The $D$ field opens a band gap in ABC graphene but not in ABA graphene$^{2,27}$ (Figure 4e) and modifies the energy difference through the DOS in the first integral term.

Figure 4f shows the doping- and D-field-dependent $\Delta E$ calculated using eq 2 at 300 K. Here we assume the ABA/ABC work function difference to be 20 meV on the basis of the KPFM measurement. The energy difference between ABC and ABA stackings at zero doping and zero D field was set to $\Delta E_0 = 50 \mu$eV/atom to fit the experimental data. The black dashed box in Figure 4f outlines the phase space region that was measured experimentally, and the theoretically calculated phase diagram qualitatively reproduces the experimental data shown in Figure 3d. Figure 4g,h shows the carrier density dependence of $\Delta E$ near $D = 0$ and $D = 1.47$ V/nm, respectively. They correspond to the horizontal line cuts in Figure 4f and boxes in Figure 3d. Again, the experiment and theory show good overall agreement. Our results show that a very high accuracy of the energy difference, at the 10–100
In summary, we have demonstrated global electrostatic control of the layer-stacking-order phase transition in few-layer graphene and determined the energy difference between different stacking orders with unprecedented accuracy. These results provide a powerful tool for manipulating the layer stacking order and have the potential to be generalized in different van der Waals heterostructures. However, we note that this stacking-order transition is not expected to be realized in bilayer graphene since for bilayer graphene all of the stacking (AB/BA) owns the same electronic bands and properties.

**METHODS**

**Sample Fabrication.** Graphene and hBN were mechanically exfoliated onto the SiO$_2$/Si substrate using scotch tape. A poly(propylene carbonate) (PPC) stamp was used to perform the dry transfer procedure$^59$ from the bottom flake to the top flake. The PPC stamp together with the heterostructure was then peeled, flipped over, and placed on a SiO$_2$/Si substrate (SiO$_2$ thickness $\approx 285$ nm). The sample was annealed in vacuum for 5 h at 400 °C to remove the PPC stamp. Photolithography and electron-beam evaporation were performed to fabricate the electrodes (100 nm Au and 5 nm Cr). Finally, the top layer of graphene was cleaned by AFM tip scratching.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.9b05092.

Supplementary notes 1–8 and Figures S1–S6 (PDF)

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**Methods**

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