Tunable crystal symmetry in graphene–boron nitride heterostructures with coexisting moiré superlattices

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In van der Waals (vdW) heterostructures consisting of atomically thin crystals layered on top of one another, lattice mismatch and rotation between the layers can result in long-wavelength moiré superlattices. These moiré patterns can drive notable band structure reconstruction of the composite material, leading to a wide range of emergent phenomena including superconductivity1–3, magnetism4, fractional Chern insulating states5 and moiré excitons6–9. Here, we investigate devices consisting of monolayer graphene encapsulated between two crystals of boron nitride (BN), in which the rotational alignment of all three components is controlled. We find that bandgaps in the graphene arising from perfect rotational alignment with both BN layers can be modified considerably depending on whether the relative orientation of the two BN layers is 0° or 60°, suggesting a tunable transition between the absence or presence of inversion symmetry in the heterostructure. Small deviations (<1°) from perfect alignment of all three layers leads to coexisting long-wavelength moiré potentials, resulting in a highly reconstructed graphene band structure featuring multiple secondary Dirac points. Our results demonstrate that the interplay between multiple moiré patterns can be utilized to controllably modify the symmetry and electronic properties of the composite heterostructure.

The moiré pattern in lattice-mismatched vdW heterostructures acts as a synthetic superlattice potential with a periodicity larger than the atomic lattice. This can substantially alter the electronic response of the heterostructure, leading to device properties that can be fundamentally distinct from those of the constituent layers10. The moiré superlattice is highly tunable, with wavelength set by the interlayer twist angle11,12 and amplitude controlled by applying pressure11. Additionally, in contrast to simple electrostatically patterned superlattice potentials14, the atomic-scale registry of the neighbouring crystals determines the lattice symmetry of the composite heterostructure15. Moiré superlattices therefore provide a powerful opportunity to engineer novel, tunable electronic properties in devices fabricated from the assembly of two-dimensional (2D) crystals.

In multilayered vdW heterostructures, several recent studies have shown that multiple moiré superlattices can be present simultaneously owing to numerous mismatched crystal interfaces, and can together lead to dramatic consequences. For example, topological order was recently found in twisted bilayer graphene when rotationally aligned to BN1. This is presumed to arise from the combined effects of the twisted bilayer graphene superlattice (which results in low-energy flat bands15) and the graphene–BN superlattice (which breaks $C_6$ lattice symmetry of the graphene bilayer, defined as a 180° degree rotation combined with time reversal). In BN–graphene–BN heterostructures, new transport features have been identified at low density when all three layers are nearly aligned, indicative of a second-order moiré pattern resulting from interference between the two slightly rotated BN layers16. The interplay between multiple moiré patterns will therefore play a crucial role in future device design of vdW heterostructures. However, understanding these interactions in detail and developing a controllable means to exploit them has so far received little attention.

A notable challenge in the study of vdW heterostructures is controlling the orientation of the multiple interfaces. Here, we investigate encapsulated graphene devices in which the graphene layer maintains fixed zero-angle alignment to the bottom BN ($\theta_0 = 0° \pm 0.15°$), but with the top BN layer rotatable to arbitrary angle, $0° < \theta_1 < 360°$, using an atomic force microscope (AFM) tip17,18 (Fig. 1a,b). We find that the superlattice effects are additive when all three layers are perfectly aligned (that is, $\theta_0 = \theta_1 = 0°$), nearly doubling the moiré-induced bandgap in graphene that arises owing to broken inversion symmetry of the lattice15. Moreover, there are a number of qualitatively distinct stacking orders that can be realized as a function of the alignment of the top and bottom BN layers. In particular, for $\theta_1 = 60°$ the moiré potential is also enhanced, but restored inversion symmetry results in a large suppression of the graphene bandgap. Here, we report a system in which the moiré superlattice and crystal symmetry can be tuned independently, revealing a new degree of freedom in these structures. Finally, we investigate the case of small misalignment of the top layer (that is, small but non-zero values of $\theta_1$) such that the two interfaces give rise to separate and incommensurate moiré patterns with similar wavelengths.

Figure 1c shows spectra of the graphene 2D Raman peak at different values of $\theta_1$. In Fig. 1d we plot the full-width at half-maximum of the 2D peak (FWHM$_{2D}$) versus $\theta_1$ over a 60° range. Over most of this range the FWHM$_{2D}$ exhibits a constant value that is ~20 cm$^{-1}$ larger than isolated graphene. This behaviour is consistent with the presence of a single long-wavelength moiré pattern resulting from the fixed zero-angle alignment between the graphene and bottom BN11,19. When $\theta_1$ approaches 0° or 60°, the linewidth is broadened by an additional ~20 cm$^{-1}$, with FWHM$_{2D}$ near 55 cm$^{-1}$. We interpret this additional broadening to result from rotational alignment of the top BN layer to the graphene–BN bottom layer, and therefore
provides an absolute measure of the top BN layer orientation. In previous studies, the broadening of the 2D mode was understood to arise from moiré-scale relaxations of the graphene lattice. Our observation of an approximate doubling of this broadening signifies that the graphene couples similarly to the moiré patterns from both the top and bottom encapsulating BN layers.

While the 2D Raman peak is 60° periodic, the BN–graphene–BN trilayer lattice structure is not precisely equivalent upon 60° rotations of the top BN crystal. As illustrated schematically in Fig. 2a,b, for \( \theta_t = 0° \) the moiré pattern is three-fold rotationally symmetric, whereas for \( \theta_t = 60° \) the moiré pattern is six-fold rotationally symmetric. The lattice structures at the high-symmetry points of the moiré patterns (outer schematics in Fig. 2a,b) highlight the important difference between these two cases. For \( \theta_t = 0° \) the top-layer B (N) atoms sit atop the bottom-layer B (N) atoms and the overall structure breaks inversion symmetry. In contrast, for \( \theta_t = 60° \) the top-layer B (N) atoms sit atop bottom-layer N (B) atoms and the structure hosts inversion symmetry. The nature of inversion symmetry in graphene–BN heterostructures has previously been tied to band structure reconstruction of the graphene\(^{13,20}\), suggesting that the electronic properties of our devices may vary considerably with \( \theta_t \).

We first investigate room-temperature electrical transport of our device, and observe notable differences between \( \theta_t = 0° \) and 60°. Figure 2c–f shows the device resistivity, \( \rho \), as a function of charge carrier density, \( n \), for various values of \( \theta_t \). When the top BN is far from alignment (Fig. 2e), we observe both a sharp resistance peak at the primary Dirac point (PDP) and broad resistance peaks at finite density corresponding to the moiré-induced secondary Dirac points (SDPs). We note that the resistivity of the hole-band SDP is larger than the electron-band SDP but smaller than the PDP, consistent with previous room-temperature studies of graphene aligned to a single BN layer\(^{21}\). As \( \theta_t \) approaches zero (Fig. 2c,d), both the PDP and SDP grow, but their relationship inverts with \( \rho_{SDP} \) exceeding \( \rho_{PDP} \) very near \( \theta_t = 0° \). By contrast, near \( \theta_t = 60° \) (Fig. 2f), the SDP again grows, but less so, and the PDP appears slightly suppressed. The angle dependence of the PDP and hole-band SDP peaks are shown in more detail in Fig. 2g,h, where the peak resistance values are plotted over a full 360° rotation. In particular, we note that both the PDP and hole-band SDP are maximal at the angle we label \( \theta_t = 0° \). While translation of the top BN with respect to the bottom would change the overall stacking configuration, we observe nearly equivalent transport every \( \Delta \theta_t = 120° \). This suggests translation does not play a substantial role, and that the stacking configura-
transition with no translational offset is the structural ground state at the assigned positions.

In graphene aligned to a single BN layer, the staggered sublattice potential of the BN breaks inversion symmetry in the graphene layer for both 0° and 60° ‘aligned’ orientations, resulting in a bandgap at the PDP whose value is expected to scale with the magnitude of the effective superlattice potential \( \Delta PDP \). We conjecture that the asymmetry between \( \theta \) (Fig. 2a) in which the PDP gap is likely to be largest, and the inversion-symmetric structure at \( \theta = 60° \) (Fig. 2b), in which no PDP gap would be expected within a single-particle model. While lattice relaxations have been previously understood to enhance the breaking of inversion symmetry in graphene–BN devices\(^1\), similar lattice reconstruction is anticipated to retain the inversion symmetry at \( \theta = 60° \) (although we are not able to probe the microscopic lattice structure of our encapsulated samples, see Supplementary Section 8).

Figure 3a–d compares the temperature dependence of the PDP and SDP at \( \theta = 0° \) and 60°. Robustly insulating behaviour is observed at both the PDP and SDP at \( \theta = 0° \), whereas only weakly insulating behaviour is observed for \( \theta = 60° \). A linear fit to the thermally activated regime (black dashed lines in Fig. 3c,f) gives a measure of the activation gap, \( \Delta \). In Fig. 3g we plot the gaps for five different values of \( \theta \) (square markers). Both the PDP and SDP gaps are notably enhanced at \( \theta = 0° \), whereas at \( \theta = 60° \) both are notably reduced. The gaps have little dependence on \( \theta \) at all other angles. Our observation of \( \Delta PDP > 60 \text{ meV} \) observed in a pristine graphene device, may potentially be further enhanced under pressure\(^1\). Although the gaps extracted from an Arrhenius fit are not identically zero at \( \theta = 60° \), the device only exhibits activated behaviour over well less than a decade change in conductance, hence we expect our reported gaps to be an upper bound at this angle.

We note that the relative resistivities of the \( \rho_{PDP} \) and \( \rho_{SDP} \) at room temperature (Fig. 2g,h) do not follow the same trends as the measured bandgaps (Fig. 3g), suggesting that the room-temperature transport is further complicated by additional details of the band structure and by various potential high-temperature scattering mechanisms (see Supplementary Sections 7 and 8, and Supplementary Fig. 8).

The band structure modification anticipated from symmetry considerations is illustrated schematically in Fig. 3h, where we anticipate the largest gaps for \( \theta = \theta = 0° \) owing to the doubled moiré potential, while at \( \theta = 60° \) inversion symmetry protects the Dirac crossings. Following this simple expectation, the measured gaps corroborate our previous assignments of \( \theta = 0° \) and 60°. We additionally measure the bandgaps in two ‘stationary’ devices (that is, without the ability to dynamically rotate the top BN, see Supplementary Section 5 and Supplementary Fig. 5). This is further complicated by additional details of the band structure (see Supplementary Section 2 and Supplementary Fig. 2), which also exhibit extended broadening of the FWHM. Raman peak. The gaps are similarly either enhanced or suppressed (diamond and triangle markers in Fig. 3g), suggesting this effect is generic for samples in which both BN layers are aligned to graphene.

Finally, we investigate the small-angle limit (0° < \( \theta < 1° \)) where the top and bottom BN yield moiré patterns with only slightly different periods. Figure 4b shows the hole-doped transport for three values of \( \theta \neq 0° \) in this regime. In addition to a peak in the resistivity at the PDP, we observe two sizeable peaks at finite hole-doped densities denoted \( n_{SDP,1} \) and \( n_{SDP,2} \). \( n_{SDP,2} \) is independent of \( \theta \) and corresponds to the SDP arising from the moiré potential of the perfectly aligned graphene and bottom BN (\( \theta_c \approx 0° \)), while the resistance peaks at \( n_{SDP,2} \) correspond to the moiré potential from the top BN. The position of \( n_{SDP} \) as a function of \( \theta \) is shown in the inset of Fig. 4b, and is in good quantitative agreement with the anticipated dispersion (see Supplementary Section 4 and Supplementary Fig. 4)\(^1\). We note that in the small-angle limit, thermally activated behaviour is observed at both \( n_{SDP,1} \) and \( n_{SDP,2} \), suggesting bandgaps associated with each SDP with typical values of ~20 meV and ~5 meV, respectively (see Supplementary Section 5 and Supplementary Fig. 5). This implies the reconstructed band structure shown schematically in Fig. 4c in which an isolated narrow band emerges between the two
superlattice gaps $\Delta_{\text{SDP}_1}$ and $\Delta_{\text{SDP}_2}$. Further theoretical and experimental effort is necessary to fully explore the consequence of this band reconstruction, however the appearance of a flat band whose width varies with rotation angle provides the intriguing possibility of hosting tunable correlated states at low temperature.$^{13,14}$

In a magnetic field, we observe sequences of quantum oscillations emerging from the Dirac points at $n = 0$, $n_{\text{SDP}_1}$, and $n_{\text{SDP}_2}$ (Fig. 4d,e, for $\theta_1 = 59.4^\circ$). We further observe weak signatures of resistive states adjacent to each of the three Dirac points, marked by orange arrows. To identify these resistive states more clearly, we plot $\rho / dT$ versus $T$ and $n$ in Fig. 4f. In addition to the insulating states previously discussed at the PDP and the two SDPs, we observe a negative temperature dependence at the same densities marked by orange arrows in Fig. 4d, suggesting the presence of new insulating-like states. The two coexisting moiré patterns may, in principle, interfere to produce a second-order moiré pattern with a very long period (Fig. 4a), inducing an additional resistive state at low density$^{15}$. However, the position of the low-density resistive feature does not agree precisely with quantitative theoretical estimates for all measured $\theta_1$ (see Supplementary Section 6 and Supplementary Figs. 6 and 7). The disagreement may arise due to unexpected structural reconstructions of the second-order moiré pattern, however at this point we are unable to understand these new resistive states in detail.

In conclusion, we demonstrate the ability to induce and control multiple moiré patterns within a BN–graphene–BN heterostructure. We are able to dynamically tune the crystal symmetry of the composite material by realizing distinct stacking configurations of the three layers, and further induce coexisting moiré patterns that combine to strongly modify the graphene band structure. Our techniques for engineering multiple moiré patterns within a single vdW heterostructure are quite general and can easily be extended to a wide variety of other device structures, motivating a new class of experiments in which the twist angle of multiple crystal interfaces can be tuned to realize novel material properties.

**Online content**

Any methods, additional references, Nature Research reporting summaries, source data, statements of code and data availability and associated accession codes are available at https://doi.org/10.1038/s41565-019-0547-2.

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Fig. 4 | Coexisting moiré structures in BN-graphene–BN heterostructures. a, Moiré pattern from graphene on BN (θ = 0°) (top left) and BN on graphene (θ ≠ 0°) (top right). A linear combination of these moiré patterns in a BN-encapsulated graphene heterostructure (bottom middle) yields two coexisting long-wavelength moiré patterns, as well as an additional second-order moiré pattern arising from their interference. b, ρ(n) at T = 1.7 K for device R1 with θ = 1° from perfect alignment. Arrowheads represent the carrier density corresponding to the PDP (nSDP), the SDP from the graphene and bottom BN (nSDP,2), and the SDP from the graphene and top BN (nSDP,1). Inset: nSDP versus θ measured from AFM topographs. Black dashed line shows the anticipated dispersion taking a lattice mismatch of δ ≈ 1.65%. Error bars are set by the uncertainty in measuring the top BN rotation angle from AFM scans. c, Illustration of the graphene band structure exhibiting two different SDP gaps in the valence band. Shaded red regions host electron-type carriers and blue regions host hole-type carriers. d, Landau fan diagram with θ = 59.4° at T = 1.7 K. Quantum oscillations with dominant sequence of filling factor ν = −2, −6, −10, ... emerge from the PDP, while quantum oscillations of ν = ±2 emerge from both nSDP,1 and nSDP,2. Orange arrows denote weak signatures of additional states. e, Schematic Landau level structure corresponding to the observations in d. f, dρ/dT as a function of T and n. Activated behaviour is observed at n = 0, nSDP,1, and nSDP,2. Orange arrows represent additional values of n that exhibit negative (but not activated) dρ/dT, and correspond to those in d.
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Author contributions
N.R.F. and L.M. fabricated the devices. N.R.F. and M.Y. performed the measurements and analysed the data. K.W. and T.T. grew the hBN crystals. C.R.D. and J.H. advised on the experiments. The manuscript was written with input from all authors.

Competing interests
The authors declare no competing interests.

Additional information
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Methods
The device fabrication of the rotatable devices essentially follows the techniques developed in refs. 12,18. All heterostructures were assembled using standard dry-transfer techniques with a polypropylene carbonate film on a polydimethylsiloxane stamp32, and rested atop a Si/SiO2 substrate. Device R1 consisted of a graphene Hall bar on an ~44-nm-thick BN layer resting on an ~11-nm-thick graphite gate. An ~56-nm-thick BN flake capped by ~40 nm of hydrogen silsesquioxane was subsequently transferred onto the graphene Hall bar. The hydrogen silsesquioxane cap acts as the etch mask to shape the rotating BN, and also provides additional durability during AFM pushes. ‘Stationary’ devices consisted of a graphene Hall bar fully encapsulated by BN, all atop a graphite gate. Electrical contact to all devices was made by Cr/Au (2 nm/100 nm). Supplementary Sections 1 and 2 and Supplementary Figs. 1 and 2 provide full details of the device fabrication.

Raman spectroscopy measurements were performed at room temperature in air. All measurements were acquired using a 532 nm wavelength laser with a power <1 mW. Measurements to extract the graphene–BN twist angle in stationary devices were performed before the addition of the graphite back-gate. In the rotatable device, the encapsulated graphene region sits atop the graphite gate. To isolate the Raman response from the graphene, we separately acquired a Raman spectrum from a nearby region of the graphite gate without the graphene and subtracted this background response. We extracted the FWHM_{2D} from a Lorentzian fit (see Supplementary Section 3 and Supplementary Fig. 3 for full details).

Transport measurements were conducted in a four-terminal geometry with a.c. current excitation of 10–100 nA using the standard lock-in technique at 17.7 Hz. The graphene contact regions (which extend beyond the graphite bottom gate) were gated to a high carrier density by applying a bias to the Si substrate (typically 5–50 V for SiO2 thickness of ~285 nm) to reduce the contact resistance. We extracted \( n(V_G) \), where \( V_G \) is the gate-voltage, by fitting the dispersion of the quantum Hall states in high magnetic field as \( n = \nu eB/\hbar \), where \( \nu \) is the filling factor, \( \hbar \) is Planck’s constant, \( e \) is the elementary charge and \( B \) is the magnetic field. The moiré wavelength, \( \lambda \), was calculated using the geometric relation \( \lambda^2 = \frac{8}{\sqrt[3]{n_{SDP}}} \), where \( n_{SDP} \) is the density at full filling of the moiré unit cell.

Data availability
The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

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