Local Electronic Properties of Graphene on a BN Substrate via Scanning Tunneling Microscopy

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ABSTRACT: The use of boron nitride (BN) as a substrate for graphene nanodevices has attracted much interest since the recent report that BN greatly improves the mobility of charge carriers in graphene compared to standard SiO2 substrates. We have explored the local microscopic properties of graphene on a BN substrate using scanning tunneling microscopy. We find that BN substrates result in extraordinarily flat graphene layers that display microscopic Moiré patterns arising from the relative orientation of the graphene and BN lattices. Gate-dependent dI/dV spectra of graphene on BN exhibit spectroscopic features that are sharper than those obtained for graphene on SiO2. We observe a significant reduction in local microscopic charge inhomogeneity for graphene on BN compared to graphene on SiO2.

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allow a gate voltage to be applied between the graphene layer and the Si electrode, thus enabling tuning of the charge carrier density of graphene. All STM measurements were performed in UHV conditions (p < \(10^{-11}\) Torr) at 4.2 K in an Omicron LT-STM. Completed devices were annealed several hours at \(-500^\circ\text{C}\) in UHV before being transferred in situ to the STM for measurement. Before all STM measurements, the PtIr STM tip was calibrated by measuring the Shockley surface state of an independent \(\text{Au}(111)\) crystal. STM topographs were acquired in the current induced by a wiggle voltage (5 \(V\) applied to the sample with respect to the STM tip. STM topographs were calibrated by measuring the Shockley surface state of an independent \(\text{Au}(111)\) crystal. STM topographs were acquired in the constant current mode with the bias voltage, \(V_b\), defined as the voltage applied to the sample with respect to the STM tip. STM dl/dV spectra were obtained by lock-in detection of the ac tunnel current induced by a wiggle voltage (5–6 mV rms, 350–500 Hz) added to \(V_b\).

**Figure 1.** Optical image of graphene/BN device integrated into STM. A CVD-grown graphene layer is mechanically placed over a BN flake set upon a SiO\(_2\) substrate. The graphene is grounded via a gold/titanium electrode. A back-gate voltage \(V_G\) is applied to the doped Si electrode.

**Figure 2.** Graphene/BN surface topography. (a–d) The 20 nm \(\times\) 20 nm constant current STM topographs at four different graphene/BN locations show how the graphene/BN Moiré pattern changes depending on the rotational orientation (\(\theta\)) between graphene and the BN lattices (see text). (a) \(I_T = 0.1 \text{ nA}, V_b = 0.15 \text{ V}, V_G = -25 \text{ V}, \theta = 21 \pm 1^\circ\). (b) \(I_T = 0.2 \text{ nA}, V_b = 0.15 \text{ V}, V_G = 0 \text{ V}, \theta = 7 \pm 1^\circ\). (c) \(I_T = 0.2 \text{ nA}, V_b = 0.15 \text{ V}, V_G = -6 \text{ V}, \theta = 4 \pm 1^\circ\). (d) \(I_T = 0.15 \text{ nA}, V_b = 0.15 \text{ V}, V_G = -3 \text{ V}, \theta = 0 \pm 1^\circ\). (e–h) Fourier transforms of the topographs (a–d). The outer spots show the graphene reciprocal lattice, the inner spots show the graphene/BN Moiré pattern reciprocal lattice.

Atomically resolved STM topographs of graphene/BN are shown in Figure 2. Graphene/BN is more locally stable than graphene/SiO\(_2\) as evidenced by the fact that it can be imaged with tunnel currents higher than 2 nA in contrast to graphene/ SiO\(_2\) devices which typically become unstable due to tip–surface interactions for \(I_T > 1 \text{ nA}\). This higher stability for graphene/BN indicates more homogeneous bonding between graphene and BN and an absence of small suspended graphene areas that vibrate under the STM tip (as has been reported for graphene/SiO\(_2\)). The homogeneity of graphene/BN can also be seen by the extremely flat graphene/BN images shown in Figure 2. The four STM topographs of Figure 2 display different Moiré patterns arising from a lattice mismatch between the graphene layer and the underlying BN surface. The Moiré patterns differ in their lattice size and orientation with respect to the resolved graphene lattice. This difference is attributed to different twisting angles between the graphene and the underlying BN arising from differently rotated graphene grains and/or different BN crystallographic orientations within a single flake. Even though the BN lattice is not visible, its twisting angle with respect to graphene can be determined by considering the Fourier transforms of the Moiré pattern as shown in Figure 2e–h. Here the outer spots show the graphene reciprocal lattice and the inner spots indicate the Moiré pattern reciprocal lattice (arrows in Figure 2e). The relative orientation of the BN lattice can be extracted from the relation between reciprocal vectors \(k_{\text{BN}} = k_{\text{graphene}} - k_{\text{Moiré}}\) and by assuming a 1.7% difference between the lattice constants of graphene and BN. For a given \(k_{\text{graphene}}\) there is a unique relative orientation between the vectors \(k_{\text{graphene}}\) and \(k_{\text{Moiré}}\) which provides the vector modulus expected for \(k_{\text{BN}}\). The relationship between these vectors is shown in Figure 2e. The images in Figure 2 exhibit graphene–BN twisting angles of \(\theta = 21 \pm 1^\circ\) (Figure 2a), \(\theta = 7 \pm 1^\circ\) (Figure 2b), \(\theta = 4 \pm 1^\circ\) (Figure 2c), and \(\theta = 0 \pm 1^\circ\) (Figure 2d).

Graphene/BN is characterized by a strong reduction in rms roughness compared to graphene/SiO\(_2\). The rms roughnesses
for the Moiré patterns exhibited in Figure 2, for example, are 0.02 Å (Figure 2a), 0.04 Å (Figure 2b), 0.06 Å (Figure 2c), and 0.17 Å (Figure 2d). These roughnesses are much smaller than the roughness typically measured for graphene/SiO₂, which is approximately 1.5–2.0 Å rms. The latter arises typically from the corrugation of the amorphous underlying SiO₂ substrate and is absent for the crystalline BN substrate. Figure 4a,b shows a side-by-side topographical comparison of typical graphene corrugations on a BN and SiO₂ substrate, respectively, and demonstrates the reduced roughness of graphene/BN over large areas.

Figure 3 shows STM dl/dV spectra obtained on a graphene/BN device using a set point of Iₜ = 0.2 nA and Vₖ = 0.5 V. No significant differences are observed in spectra obtained in this way from different devices or from graphene regions displaying different Moiré patterns. Each spectrum was taken at a different gate voltage, V₇, and thus corresponds to a different charge carrier density in graphene. Similar to previous reports for graphene on SiC, SiO₂, and Pt(111), we observe a gaplike feature of width ∼126 meV at the Fermi energy that does not depend on the charge carrier density. This feature is attributed to the opening of an inelastic tunneling channel via the excitation of out-of-plane phonons at the K/K’ points of the graphene reciprocal lattice.

The Dirac point energy for each spectrum was extracted from the local minimum in dI/dV (black dots in Figure 3a), as calculated from a polynomial fit to the data. The energy of the Dirac point versus the gate voltage is plotted in Figure 3b, where the energy of the inelastic phonon excitation (63 meV) has been subtracted. Points for E_D close to the Fermi energy are not shown due to the absence of a clear Dirac minimum in those spectra because of the influence of the phonon feature in

Figure 4. Comparing topography and charge density for graphene/BN vs graphene/SiO₂. (a,b) The 60 nm × 60 nm STM topographs of (a) graphene/BN (Iₜ = 0.2 nA, Vₖ = 0.25 V, V₇ = −6 V) and (b) graphene/SiO₂ (Iₜ = 0.02 nA, Vₖ = −0.225 V, V₇ = 15 V). Charge density maps obtained from conductance maps (see text) are shown for (c) graphene/BN (same area as in (a), acquired simultaneously) and (d) graphene/SiO₂ (same area as in (b), acquired simultaneously). The minima and maxima marked in the scales are the minima and maxima of the respective images.
this gate-voltage range. We fitted the Dirac point energy vs the
gate voltage with $E_D = \hbar v_F(|\pi t| V_G - V_d)\frac{1}{2}$ where $\epsilon$ is the
electron charge, $V_0$ is the gate-voltage offset of the neutral point ($V_0 = 14.1$ V for the data shown in Figure 3a), $v_F$ is the
Fermi velocity (taken as $1.1 \times 10^5$ m s$^{-1}$), and $\alpha$ is the
capacitance per area. From this fitting we deduce a smaller value for $\alpha$ ($3.0 \times 10^{10}$ cm$^{-2}$ V$^{-1}$) for the data shown in
Figure 3a than was previously seen for graphene/SiO$_2$ using similar Si wafers ($7.1 \times 10^{10}$ cm$^{-2}$ V$^{-1}$). This is consistent with the reduction of capacitance expected due to the larger
distance between the graphene layer and the Si electrode arising from the additional thickness of the BN flake. We find that $V_0$ and $\alpha$ vary for different measurements due to changes
in the work function of the STM tip$^{23}$ as well as differences in
the thickness of different BN flakes used for different devices.

Our graphene/BN spectra (including the case where the twist angle is $\theta \approx 0^\circ$) do not display any obvious feature indicating
the opening of a gap at $E_D$, as predicted to arise from the breaking of equivalence between graphene atoms when it is perfectly stacked on BN.$^{23}$ We observe an enhancement in the spectroscopic peak seen in the range $-0.25$ V $< V_i < -0.1$ V for low gate voltages ($-5$ V $< V_G < 20$ V) compared to graphene/SiO$_2$ devices.$^{16}$ This spectroscopic feature was explained previously as a result of many-body interactions in graphene/SiO$_2$. The fact that it is more pronounced for graphene/BN suggests a possible difference in electron–
electron interactions for graphene/BN compared to graphene/SiO$_2$ (such as might arise from variations in quasiparticle scattering rates$^{24}$).

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cantly reduced compared to what is observed for graphene/SiO$_2$. These authors contributed equally to this work.

**Author Contributions**

In conclusion, our results show direct microscopic evidence
that graphene/BN improves graphene stability, roughness, and
intrinsic local electronic properties compared to graphene/SiO$_2$.

The variable Moiré patterns observed here might be exploited as
periodic potential networks for patterning atomic or molecular adsorbates.$^{27}$ The smaller charge fluctuations and reduced
scattering seen for graphene/BN show that BN substrates provide
a promising route for investigating the intrinsic local behavior of graphene.

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**References**


